A STRUCTURAL INVESTIGATION OF SOME COMPOUNDS SHOWING CHARGE-TRANSFER PROPERTIES

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LAYOUT OF THIS THESIS

The thesis is divided into chapters which deal, not with the individual compounds studied in sequence, but with some particular aspect of all of them. Thus Chapters I and II are an introduction to the chemistry of the compounds. Chapters III and IV deal solely with the X-ray crystallography (data collection, structure solution, and assessment of techniques), and can be read by themselves. Chapters V and VI describe independently the results and interpretation of structure determination of two sets of compounds; either relies only on I and II. (It has been impossible to separate the solving of the structure and discussion of results in Chapter V).

All the tables and diagrams, where not included in the body of the text, have been put in at the end of each chapter. I hope that this will make it easier to refer to them continually whilst keeping the text intact. In particular structure factors are contained in a separate chapter (VII).

Since the relation of molecules to each other is important, I I have tried to show this with clinographic drawings of the structures. These are to scale and are projections down the vector with direction cosines: -0.94, -0.193,-.290, in a right-handed system. The crystal axes are not arranged consistently, partly because of the differing shapes of unit cells, and partly to get the best view of the structure. The origin and axes are always labelled.

References are arranged on a chapter basis. The number refers to the table of references at the end of the chapter, unless otherwise indicated.

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SUMMARY

SUMMARY

The technique of X-ray diffraction has been used to investigate compounds which show charge-transfer properties in the solid state. It is shown how the results of structure determination can, under favourable conditions, give information about charge-transfer processes.

Two sets of compounds have been studied, both of which contain metal-chlorine bonds. The first is a series of mixed-valence cobalt hexammine chlorocuprates in which the average oxidation state of the copper can take any value between 1 and 2. The structure of the single-valence (copper (I)) compound, $[Co(NH_3)_6]_4Cu_5Cl_{17}$ was solved and data was also collected for a compound with Cu(I)/total Cu ~ 0.25. This was shown to have a structure to the single-valence copper (I) and copper (II) compounds and probable arrangements for the Cu(I) and Cu(II) ions are presented. It is shown that linear Cu-Cl-Cu bridges are almost certainly present and that these can account for the charge-transfer spectra. A new chlorocuprate anion, $[Cu_5Cl_{16}]^{11-}$ was discovered, which has 23(T) symmetry.

The second series contains a common cation, paraquat (pq^{2+}), which is N,N'-dimethyl-4,4'-bipyridylium. Four salts of this, $pqCoCl_4$, $pqPdCl_4$, $pqCu_2Cl_6$, and $pqCu_2Cl_4$ have been studied, and their structures are discussed in terms of charge-transfer. It appears that short N-Cl contacts, as little as 3.25 Å, are the main feature of the structures, and these are almost perpendicular to the plane of the aromatic ring. There is also some evidence for an attraction between the nitrogen and chlorine atoms.

The compound $pqFeCl_4$, which contains radicals, has been shown to be isostructural with $pqCoCl_4$, and the charge-transfer process is discussed in terms of pq^{2+} and $pq^{+\cdot}$. Electron density calculations for these species support the hypothesis that in these compounds the Nitrogen atom is necessary for charge-transfer. Another chlorocuprate ion, $(CuCl_2^-)_n$, was discovered, and the coordination of metal chloride anions is discussed.

Since the arguments used to relate X-ray results to electronic processes depend on knowing the accuracy of structural parameters, an analysis of the precision of these parameters was undertaken. It was shown that the estimated standard deviations are useful criteria of accuracy.

CHAPTER I.

CHARGE-TRANSFER and

ITS INVESTIGATION BY X-RAY STRUCTURE ANALYSIS OF CRYSTALS

INTRODUCTION

CRYSTAL STRUCTURE AND ELECTRONIC PROCESSES

The study of charge-transfer in a crystal has the advantage that the geometrical relationship of the entities involved is fixed and can be found, and that there is no variation with time. In contrast, the situation in a liquid fluctuates rapidly and at any moment is made up of many different configurations of unequal energies. Although for the complete description of charge-transfer in a solid the geometrical structurel must be known, X-ray analysis is of no direct benefit in the investigation of electronic processes. It can yield an average view of the electron density in a crystal, but this is as yet too inaccurate to be described meaningfully in terms of changes in valence electron structure. An alternative approach was adopted.

We assume that charge-transfer processes in a crystal will change the electronic structure in a way that will distort the geometry of the system. Since there is no way of predicting exactly what this geometry would be in the absence of charge-transfer, the identification of distortion must be partly subjective. The risk in this process is lessened by investigating a series of similar compounds to see if they all show the same effect, and if so, to interpret any variation. The variation of geometry of complexes with atomic number is a well-known method of investigating electronic properties (cf. Reference 1). Besides the possible weakness of argument in this process, there is the difficulty that it is usually impossible to analyse accurately enough the forces in any crystal structure. Only in an isomorphous series of compounds is the variation of intermolecular forces likely to be insignificant. The combination of other physical measurements, such as conductivity or absorption spectra, with X-ray structures is often very helpful.

Charge-transfer

i) Charge-transfer (C-T) can be loosely defined as the process:-

$$A + B \overset{h\nu}{\rightleftharpoons} A^{+} + B^{-}$$

where A and B (not necessarily neutral) may or may not be bonded. It is an oxidation-reduction process (usually reversible) where the energy is supplied by radiation, which when in the visible region results in the compound being coloured. (In this definition can also be included partial electron transfer, or a change in polarisation of a system. However, the crystals studied may involve complete transfer since A^{+} and B^{-} are known to be stable under moderate conditions. It is interesting that some charge-transfer compounds are thought to have a ground state where $A^{+} + B^{-}$ is the main configuration.)

Though oxidation-reduction must involve a change in electronic configuration, it is often more clearly visualised as involving something other than simple electron-transfer. Redox mechanisms have been widely studied in solution and, for transition metal compounds, appear to take place by two or three main mechanisms. The terminology of these is adopted for solid-state charge-transfer, although it is clear that the crystalline state imposes severe restrictions on atomic and possibly electronic movements.

i) (One) Electron-transfer is well-known in both inorganic and organic reactions, and most of the systems investigated later involve only unit changes in formal oxidation state. The Franck-Condon principle implies that reaction will be efficient only if the changes in geometry are small. This process is often called "outer-sphere"(2) as it uses the outer valence orbitals and must often take place over relatively large distances. It is basically independent of the co-ordination sphere, but can be helped in certain cases by electron delocalisation onto ligands. An example of this is the $IrCl_6^{3-}$ ... $IrCl_6^{2-}$ system, where delocalisation which helps electron-transfer has been shown by solid state e.s.r. (3). X-ray diffraction can give little direct evidence of "outer-sphere" mechanisms, but may help to deduce the orientation of orbitals which might be involved.

ii) Inner-sphere mechanism. If electron-transfer is so slow that ligand replacement is a faster process, oxidation is possible by atom-transfer, as in:-

$$\left[(NH_3)_5CoCl\right]^{2+} + \left[Cr(NH_3)_6\right]^{3+} \longrightarrow \left[Cl - Cr(NH_3)_5\right]^{2+} \qquad (4)$$

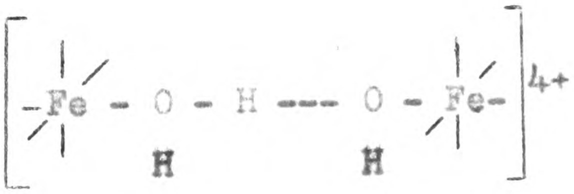
It is clear that only ligands capable of forming bridges can act, such as halogens (but not ammonia) and in charge-transfer, it is likely that intermediates involving bridges will be important.

The distinction between inner- and outer-sphere mechanisms is often not clear-cut. For example, although the equilibrium:

$$Mn^{18}O_4^- + MnO_4^{2-} \rightleftharpoons Mn^{18}O_4^{2-} + MnO_4^-$$

involves no atom transfer, it is greatly catalysed in solution by $Co(NH_3)_6^{3+}$ or Cs^+ (5). This implies that ion-pairs are important, and that polarisable species, such as Cs^+ or K^+ (see Chapter VI)(which are normally thought of as relatively "inert") can aid electron-transfer. In an ionic crystal where positive and negative charges alternate, this effect may well be significant. A reaction which occurs by both outer- and inner-sphere mechanisms simultaneously is the oxidation of $Co(CN)_5^{3-}$ by $\left[Co(NH_3)_5X\right]^{2+}$ to $\left[CoX(CN)_5\right]^{3-}$. The rate, above a certain value, depends on X, but otherwise is constant (6).

iii) Hydrogen-atom transfer. Inner-sphere reactions usually involve atoms linked directly to the metal. In the equilibrium between Fe^{2+} and Fe^{3+} in aqueous solution, the reaction is catalysed much more by hydroxyl than by chloride. This has led to the proposal (7) of the bridged state:



although this does not necessarily imply complete transfer. Where hydrogen bonds are formed in the crystal to ligands (e.g. NH_3, H_2O, or Cl) of transition metals, this mechanism is a possibility, especially as hydrogen atoms may be labile in the crystal.

Charge-transfer in crystals

Although the preceeding discussion has been of reactions in solution, the principles should apply in a limited degree to charge-transfer equilibrium in crystals. Electron transfer involving large changes in geometry is helped in solution by thermal excitation and this process is therefore rather unlikely in the crystal (unless excited states are involved). Similarly distinct atom transfer is not possible and a bridged intermediate will be more likely to involve electronic rather than atomic movement. An inner-sphere mechanism can be written:

$$A - X_{(i)} \text{---} B \rightleftharpoons A^{\delta+} \text{----}_{(ii)} X^{\delta-} \text{----} B \rightleftharpoons A^{\delta+} \text{--}_{(iii)} X - B^{\delta-}$$

which need not involve appreciable movement of X.

To investigate charge-transfer in crystals, we choose a system where (i) and (iii) are of roughly comparable energies. It can then be assumed that the geometry of B is not energetically too unfavourable for the formation of B^+ (or an excited state of B^+). It is possible also that state (ii) might be of lower energy than (i) or (iii) and that its existence would be suggested by bond length considerations. (In crystallographic terms, it is most unlikely that substantial amounts of (i) and (iii) exist in the same crystal, even in the presence of radiation.)

THE COMPOUNDS STUDIED

Metal-chlorine bonds were chosen as the common feature of all the compounds in which intermolecular (interionic) C-T was studied. The advantages of this are firstly that metal-chlorine systems (in the absence of C-T) have been well investigated and marked change in geometry is likely to be significant. Secondly, metal-chlorine-metal bridges are well-known and the ionisation potential of chloride is low enough to suggest that these could be important. Chloride is also roughly in the middle of the spectrochemical series suggesting that its crystal field demands on transition metal ions will not be too severe. (For example, both square planar and tetrahedral $NiCl_4^{2-}$ ions have been observed in crystals.) It is relatively small, and its very variable co-ordination number with (d^8), d^9 and d^{10} ions suggests that this geometry might be influenced by C-T effects.

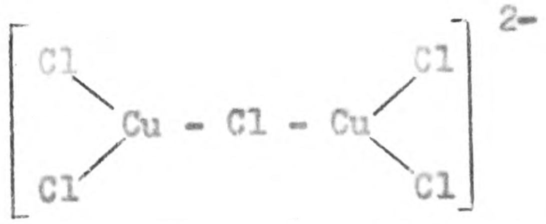
Mixed-valence compounds

If a crystal contains two adjacent valency states of a metal close to each other and in roughly similar environments, there is often a C-T equilibrium, which may lie close to centre. The whole crystal might approximate to a reaction intermediate and unusual geometrical features should be significant.

Most mixed-valence systems are either 1:1 (or similar simple formulae) or exist over only a small range of variable stoichiometry. There is an exception in the mixed-valence chlorocuprate(I,II) salts of cobalt(III)hexammine which appear to extend completely between the formulae $[Mam_6]_4Cu(I)_5Cl_{17}$ and $(4x)[Mam_6]Cu(II)Cl_5$ (where $Mam_6 = Co(NH_3)_6^{3+}$ or $Cr(NH_3)_6^{3+}$). There appear to be no intermediate compounds of fixed stoichiometry but well formed crystals showing charge-transfer appear to be formed with any desired ratios of valences.

The formulae of the end compounds appear to be definitely established (and are confirmed by X-ray analysis (8), (Chapter V). Analytical results for the intermediate compounds are indeterminate in deciding between two possible formulations for them. This is because, in going from the copper(II) compound to the copper(I) one, a fifth copper atom is introduced for each group of 4 original ones. Mori originally suggested that this was not introduced until the ratio $\{\mathrm{Cu(I)/total\ Cu}\} > 0.5$; Day and Culpin mentioned the alternative possibility that it was introduced in proportion to the $\{\mathrm{Cu(I)/total\ Cu}\}$ percentage. The intermediates can be described by the unwieldly formula; $[\mathrm{Mam}_6]_4(\mathrm{Cu(II)}_{1-x}\mathrm{Cu(I)}_x)_n\mathrm{Cl}_{12+2n-nx}$, where x is the mole fraction of $\{\mathrm{Cu(I)/total\ copper}\}$ (and is used to name the intermediates as "x% Cu(I)"). The parameter n, $4\{\mathrm{Co/total\ Cu}\}'$, is 4 for $x = 0$, 5 for $x = 1$, and is presumably a function of x, although this might depend on the method of preparation. The situation is depicted in Figure II.1., where Culpin's analyses are shown and the formulations of the intermediates are shown by lines (which need not be straight, and this is suggested in Chapter V). Mori suggested a compound $[\mathrm{Mam}_6]_2\mathrm{Cu}_2\mathrm{Cl}_9$ as an intermediate but there is no direct evidence for this.

Charge-transfer is very marked in these compounds as the compounds are dark-black except within about 10% of the end points. The dependence of the intensity of the charge-transfer absorption on mole fraction is shown in Figure I.1a. (9). The shape of the curve, which has no discontinuity of slope, suggests that there are no discrete phases (although points near the edges are ill-defined). This is also true for the single crystal and pellet conductivity, Figure I.1b. The curves are not accurate enough to relate intensity of absorption to the parameter n (see Chapter V). The crystals were made from the very dark mixture of CuCl and CuCl_2 in HCl (which has been studied by (10) $^{63}\mathrm{Cu}$ N.M.R. and absorption spectra (14, 11). This may contain a bridged intermediate of the type:



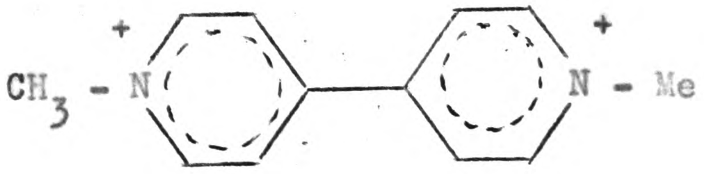
(although no evidence was given for the actual co-ordination of the copper).

The system is very suitable for X-ray analysis. The compounds crystallise in two space-groups (Fd3c for 0(+)% Cu(I) and Fd3 for 100(-)% Cu(I)), the latter being a sub-group of the first, (Part II work (12)). This means that there is no crystallographic necessity for any distinct phases and even the copper(II) and copper(I) compounds are very similar. The chlorocuprate(II) structure had been solved (8) and the positions of the corresponding heavy atoms in the chlorocuprate(I) were identical (Part II). Even though this had not been solved, its unusual stoichiometry could be explained satisfactorily in terms of space-group symmetry positions. The chlorocuprate(I) was therefore investigated more completely and data was also collected for an intermediate.

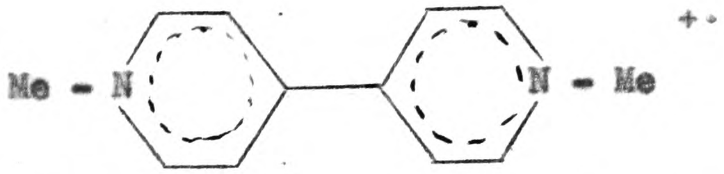
Since there is a possibility that a mixed valence compound might be sufficiently ordered to give a superlattice a similar compound for which this was likely was investigated as a parallel. Mixed lead(II) and (IV) chlorides in HCl solution give $\mathrm{Coam_6Pb(II)(IV)Cl_6}$, which is probably $\mathrm{[Coam_6]_2Pb(II)Cl_6.Pb(IV)Cl_6}$. The strong charge-transfer (although possibly aided by the cobalt(III)hexammine ions) is probably outer-sphere but X-ray analysis could still show if the two types of octahedra are different and regularly ordered.

Paraquat compounds

The combination of A and A^+ (as with the chlorocuprate(I,II)) is not the only method of trying to create a charge-transfer intermediate in a crystal. If A and B^- can be chosen so that their ionisation potentials are fairly similar, and if the change in lattice energy from AB to A^+B^- is small, then the equilibrium should be appreciable. Ionisation potentials (which are not usually available) can be crudely paralleled by electrode potentials and a particular suitable electron acceptor is paraquat, with an E.P. for reduction of 456 mV (13). Paraquat (pq^{2+}), or dimethyl viologen, is the N,N'-4,4' dipyridylium dication:-



which is easily reduced to the intense violet radical monocation:



($pq^{+\cdot}$)

Macfarlane (14) has made many salts of paraquat with metalchloride complex anions, of which the most interesting was $pqFeCl_4$, prepared from $pqCl_2$ and $FeCl_2$. This was blue and its absorption spectrum, Figure I.2, showed strong evidence of bands due both to pq^+ and charge-transfer. (This diagram also shows charge-transfer in other paraquat halides.) There was also an e.s.r. signal whose g-value could be interpreted as arising from a combination of pq^+ and $FeCl_4^{2-}$. Mossbaüer spectra, however, showed that the percentage of $FeCl_4^{2-}$ was probably small. This strongly suggested that X-ray analysis of the structure might give some indication of the charge-transfer path. A compound had also been prepared from Cu(I)Cl and $pqCl_2$ which appeared from e.s.r. evidence to contain Cu^{2+} ions and was very darkly coloured. This could have close connections with the other chlorocuprates.

There is obviously charge-transfer between paraquat and single halide ions as shown by the spectra of the crystalline halides, Figure I.3. This implies that MCl_4 anions would be worth investigating even when the central metal ion (e.g., Co^{2+}, Pd^{2+}) is not easily oxidisable. (The simple halides have been investigated elsewhere (17)).

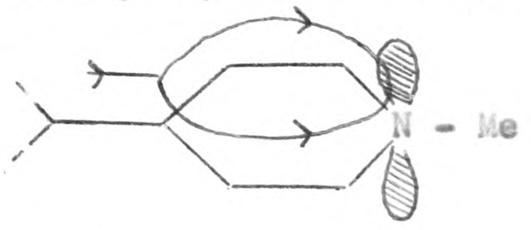
(Paraquat is, incidentally, a well-known weed killer which probably acts, in conjunction with chlorophyll, to produce radicals by a photochemical process. Paraquat chloride solution can be changed to radical monocation by irradiation.)

Charge-transfer involving organic systems

The movement of electrons has so far been considered as to and from definite sites, although delocalisation of (d-) electrons is certainly possible even in simple systems. When the electron accepting (or donating) power arises from no specific atom, but from a molecule as a whole, then a different mechanism must be postulated. The best known examples of charge-transfer involving delocalised (aromatic) systems are the benzene-iodine complex and the π - π complexes of flat aromatic molecules. The latter has been described by the principle of "maximum overlap" of π-orbitals (14) and is exemplified by the complex of copper oxinate and tetracyanobenzene (Chapter IV). X-ray structure analysis can give little information, except the extent of π-overlap. Since delocalised π-systems exist not only in paraquat but also in the metal anions (e.g., $PdCl_4^{2-}$), this sort of overlap might be possible and would be suggested by part of the anion lying close and parallel to the paraquat ion.

The benzene-iodine system and similar complexes have been shown (15) to involve a specific donor/acceptor associated with the middle of an aromatic system. The benzene-bromine and benzene-CCl_4 complexes are perhaps the most pertinent as they contain bonds with a terminal halogen directed nearly perpendicularly at the centre of the ring, and this can be called n-π charge-transfer. Its geometric requirements are due to a combination of suitable orbitals, but it is difficult to predict which these will be. Corresponding M - Cl --  π-system arrangements would be evidence for this type.

Organic molecules containing a donor atom (e.g., N, O) can form charge-transfer complexes which do not depend on delocalisation (15). An example is $(Me)_3N$ --- I_2, which can be written $(Me)_3 \rightarrow N^{\delta+}$ -- I -- $I^{\delta-}$, where stability is due to the donor power of the nitrogen and the polarisability of the iodine. A similar complex occurs with pyridine where no appreciable use of the π-electrons is made. (It is possible that by back-donation the lone-pair electrons on the iodine atom nearest to the nitrogen could interact with the ring π-system.) Hassel (15) notes several very short N --- Cl (2.31Å) and O --- Cl (2.50Å) distances although some were appreciably longer (~3.2Å). Paraquat cannot be directly fitted into this scheme as it has no lone-pair, but the π-electron density may be partially concentrated at the (positive) nitrogen atoms:



This would allow the electron accepting/donating power to act through the nitrogen atom even through originating from the whole system. (A more rigorous basis for this is described in Chapter VI from theoretical and experimental calculations of the π-electron density in pq^{2+} and $pq^{+\bullet}$.)

ASSESSMENT OF THE ACCURACRY OF X-RAY STRUCTURES

This geometrical method of investigating the electronic structure of compounds relies on the differences in bonds and angles of two structures being significant. The estimation of errors in parameters assumes that errors in F_{obs} are random, which is still valid for reproducible errors provided they do not affect the parameters systematically. This is reasonably true for most positional parameters derived from data of moderate accuracy. The use of these estimated standard deviations (e.s.d.'s) depends on their practical justification, which is rarely, if ever, undertaken as it involves repeated measurement of F_{obs} data and refinement of parameters. In particular it is interesting to know if different experimenters get results agreeing within their e.s.d.'s. This would involve the duplication of the measurement of complete three-dimensional data and is not usually attempted.

Duplicate data from a molecular complex

Because of a slight misunderstanding, Wright and I determined the structure of copper oxinate.2tetracyanobenzene independently and simultaneously. I have analysed the differences between the two structures and compared them with the e.s.d.'s (Chapter IV). The structure is included solely for the data comparison, etc. (though a paper on the chemistry is in the press (IV.8) and it is hoped to include a reprint in this thesis).

Methods of data collection

Photographic methods of data collection can only compare with counter measurements if much time and care is spent on them. The data compared above suggested that one-axis Weissenberg photographic data collection is a quick method whose error is accurately represented by its e.s.d.'s. Though very widely used (IV.1), little criticism of its merits and demerits has been made and I hope to have shown (Chapter III) that its use with heavy atom compounds is worthwhile. In particular, the time saved (which is valuable if a series of compounds is being investigated) outweighs the loss in accuracy.

Errors in bonds and angles

The systems studied provided a good basis for an empirical assessment of e.s.d.'s of bonds and angles. A series of compounds was taken (from the literature and this thesis) involving oxinate complexes in environments where their bond lengths and angles should be crystallographically indistinguishable. A statistical comparison was made on the basis that bonds and angles are independent.

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(*This review also describes Huckel calculation of π-electron densities and has a plot of bond order vs bond length. Both were used in Chapter VI).

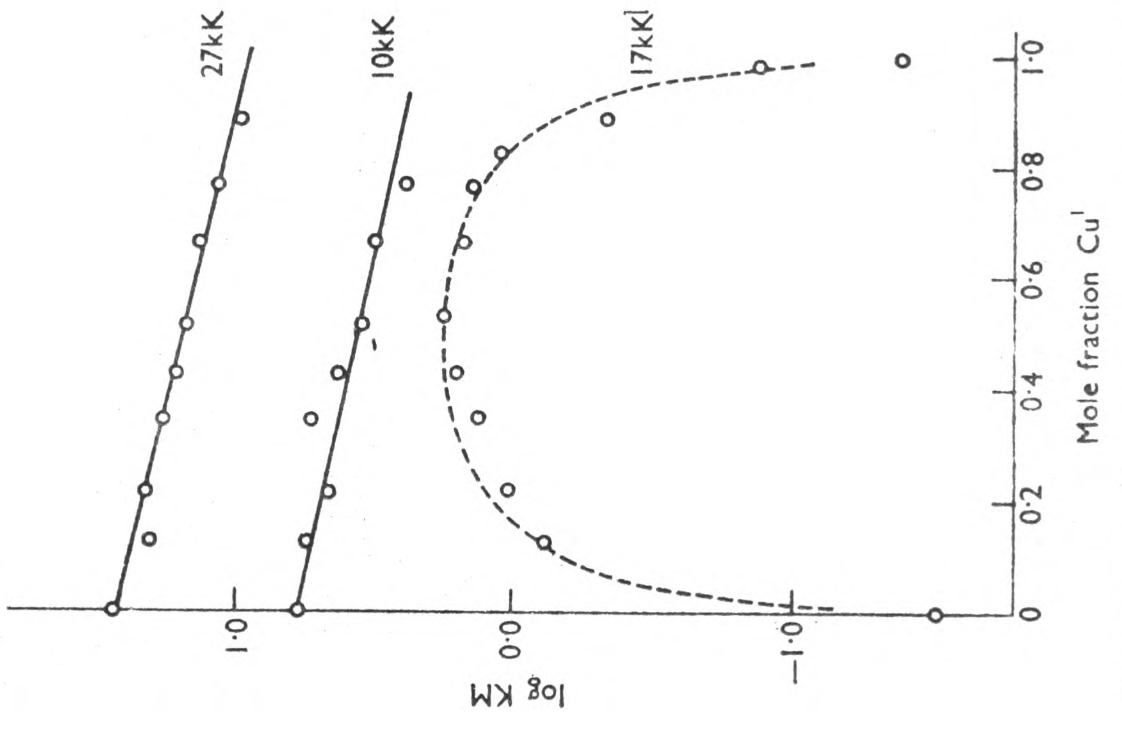


FIGURE 1. *Absorption intensity and composition of mixed-valence chlorocuprates.*

a

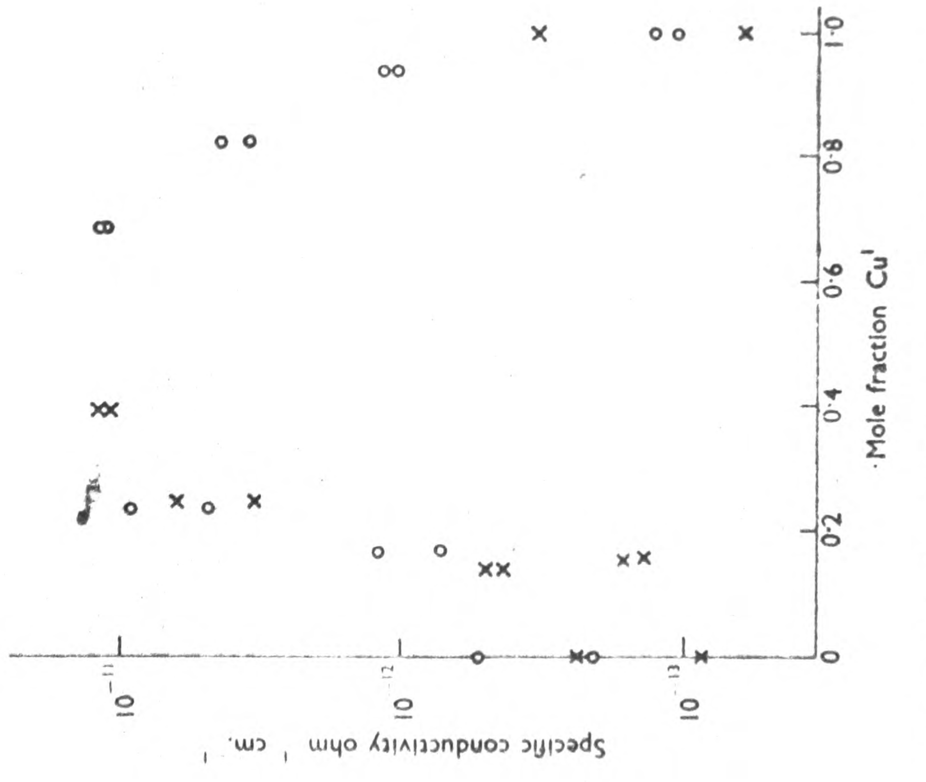
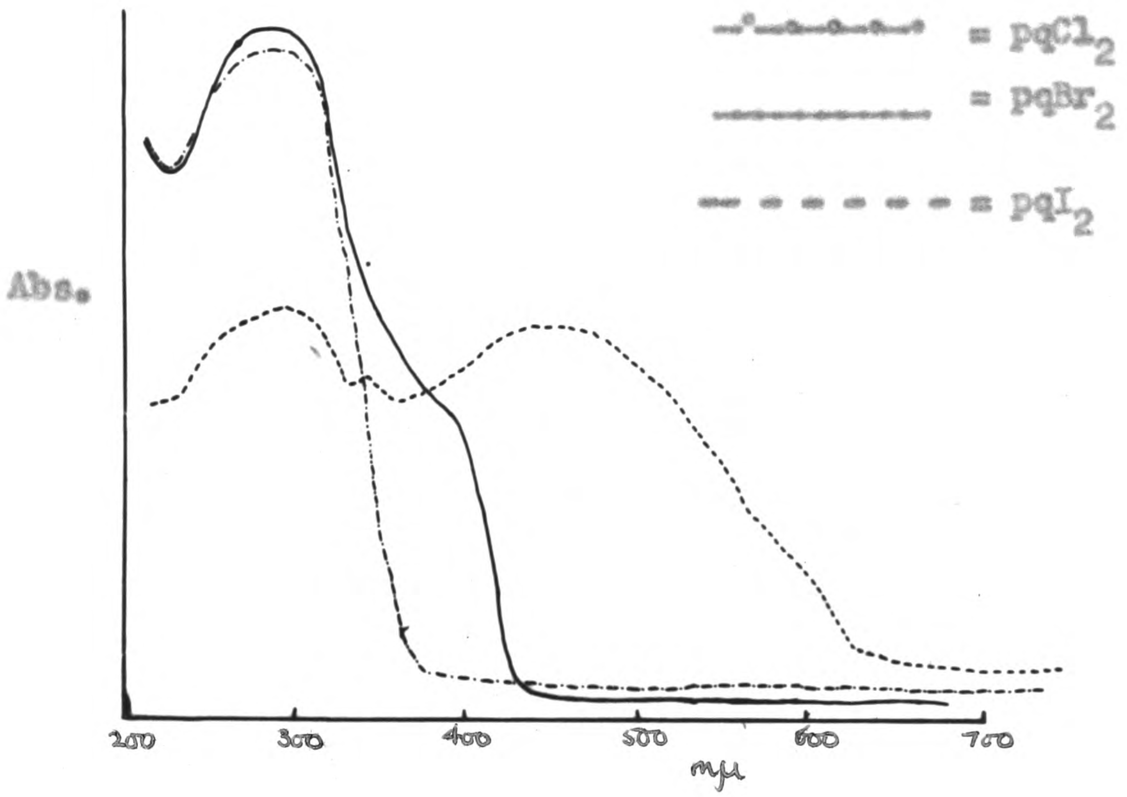


FIGURE 2. *Conductivities of mixed-valence chlorocuprates.* × = *single crystals;* ○ = *pellets.*

b

Figs. I. a. and b. Absorption and conductivities of mixed-valence Chlorocuprates(I,II)

Fig. I.3. Reflectance Spectra of solid pq halides



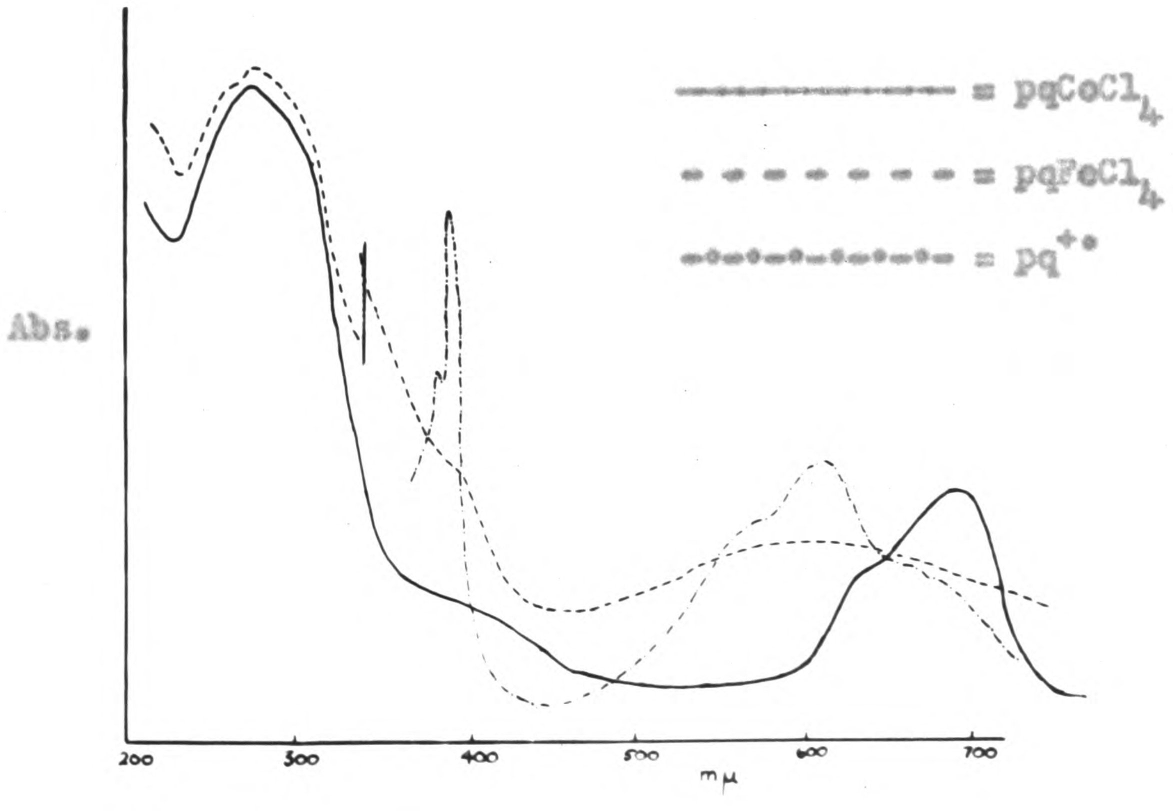


Fig. I.2. Reflectance Spectra of paraquat compounds

CHAPTER II.

PREPARATION AND PROPERTIES OF THE COMPOUNDS STUDIED

PREPARATION AND PROPERTIES OF THE COMPOUNDS

COBALT HEXAMMINE CHLOROCUPRATES(I,II)

(My Part II Thesis work is indicated where necessary.)

These compounds were originally prepared by Mori (1) who deduced the formulae of the end compounds. Day (2) and later Culpin (3) repeated the process and it was these crystals which were used in the structure analysis. They obtained the same end compounds as Mori but Culpin mentioned the possibility of the compounds lying on the lower line in Figure II.1 whereas Mori suggests the upper. The analytical results are clearly no use in differentiating these two cases and density measurements (Part II) are hampered by inhomogeneity of sample and the small variation of M.Wt. (1580 for $4Coam_6CuCl_5$ to 1537 for $[Coam_6]_4.Cu_5Cl_{17}$).

Cuplin also gave evidence that his method of preparation involving slow crystallisation from a hot solution, under N_2, gave a different analysis from Day's fast cooling. There is thus a possibility that the bulk sample produced is not homogeneous. It was clear however that individual crystals of the mixed-valence preparations contained copper(I) and copper(II) as they were all darkly coloured or black. Single crystal rotation photographs (Part II) showed that crystals taken from samples of 0 - 50% Cu(I) had space group Fd3c; crystals from samples over 80% Cu(I) belonged to Fd3(m). A crystal from a 67% Cu(I) sample showed marked streaking of high angle reflections implying some disorder.

Day and Smith (4) have recently stated that compounds with composition ~ 50% Cu(I) are in fact mixtures. They give no new evidence for this and do not indicate whether the mixture is macroscopic or a solid solution. This is hard to reconcile with the X-ray evidence of the high percentage intermediates, whose individual crystals are definitely not in Fd3c.

In the later X-ray analysis of a crystal from a 25% Cu(I) sample, no reliance was placed on this figure (Chapter V), but a substantial proportion of Cu(I) was assumed as the crystal was virtually black. The X-ray data suggest that this figure is, in fact, correct for the crystal studied.

PARAQUAT COMPOUNDS

Macfarlane (5) had prepared and kindly provided paraquat salts of several metal halide anions, but of the chlorides only $pqCoCl_4$ had been prepared as crystals. Powder photographs (on a Guinier de Wolff camera) showed that salts with anions $FeCl_4^{2-}$, $MnCl_4^{2-}$, $ZnCl_4^{2-}$ and $CuCl_4^{2-}$ were very similar to $pqCoCl_4$. Isomorphism appears to be good whilst probably allowing some latitude in bonds and angles.

The chloroferrate(II) was a dark blue hygroscopic powder unstable in air and giving small blue crystals when a methanolic solution was slowly evaporated. These were not single but oscillation and Weissenberg photographs had very similar patterns to $pqCoCl_4$. This was disappointing, especially as the compound contains radicals, but the chlorocobaltate(II) should have a very similar structure and this was undertaken.

Pure chlorocuprates. There was evidence from the e.s.r. signal of the complex $pqCl_2$ + CuCl that some copper(II) was present. However only a dark brown powder had been prepared and it looked as if some oxidation might have occurred and no good analysis was given. It was decided to try to prepare crystals of this compound, of the corresponding copper(II) compounds, and, in view of the e.s.r. evidence, to attempt the preparation of mixed valence compounds.

A suitable solvent was half concentrated hydrochloric acid (which had also been used in the preparation of the mixed-valence cobalt hexammine chlorocuprates). Paraquat dichloride recrystallised from ethanol was provided by I.C.I. Research Stateon, Jealots Hill, Berkshire. Analar copper(I) chloride was used but as it was green it was ground up with dil. HCl saturated with SO_2, and then filtered. This reducing atomoshere was used whenever it was desired to prevent oxidation.

Paraquat chlorocuprate(I) was prepared by dissolving 1 mmole of paraquat dichloride in a small amount of acid, heating and adding a hot saturated solution of copper(I)chloride (2 mmoles) in acid, all under nitrogen. The colour darkened immediately and the solution was left in a large amount of hot water to cool slowly. Beautiful thick black needles were formed which were relatively stable in air, but decomposed to copper(I) oxide when washed with water and appeared liable to surface oxidation. The crystals are prisms using the {110} faces and many have empty channels running down inside. The formula $(C_{12}N_2H_{14})Cu_2Cl_4$ was suggested by C,H,N analysis and confirmed by density measurements and X-ray analysis.

Paraquat chlorocuprate(II) was prepared by the same process, without the nitrogen, atomosphere using copper(II) chloride dihydrate. Large deep-red needles were produced which were green in reflected light (cf. $Me_2NH_2CuCl_3$, see Chapter VI). The formula $(C_{12}N_2H_{14})Cu_2Cl_6$ was proposed and confirmed as above. (N.B. The compound $pqCuCl_4$ (cf. Wallwork (6)) is formed only from non-aqueous solvents.)

Possible mixed-valence compounds

In an attempt to make a mixed-valence crystal, the above method was employed with a 1:1 mixture of copper(I) and copper(II) halides. Crystals were produced but appeared identical to the copper(II) compound and gave similar zero-layer Weissenberg photographs. It was observed that crystals of the copper(I) compound, if exposed to air in the presence of their mother liquor eventually oxidised to the chlorocuprate(II), and the supernatant liquid became green. An attempt to find an intermediate in this process was unsuccessful, and it is probable that it involves only dissolution, oxidation and crystallisation. The difference between the copper(I) and copper(II) compounds, as finally established by X-ray analysis (Chapter VI), is small but substantially larger than in the cobalt hexammine series and is the likely reason for the inability to crystallise an intermediate. Moreover, the e.s.r. signal from crystals of the copper(I) compound was repeated and found to be very weak indeed which suggests no appreciable amount of Cu^{2+} ions. (The original powder used may well have been substantially oxidised.) The single crystal conductivity along the needle axis was measured by M. Price and showed no photoconductivity, which might have been present, although the crystals were semiconducting.

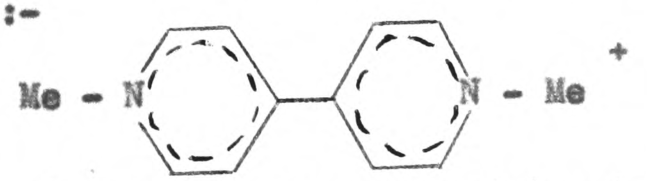
Other metal chloride salts

Crystals of other chlorides were made, including $pqPdCl_4$, $pqPtCl_4$ and $pqPbCl_4$, the last by the method above (using $PbCl_2$). Similar compounds with AgCl and AgBr could not be prepared but a hot solution of AgI in KI solution when added to pqI_2 solution gave dark red crystals on cooling which were not further investigated. The lead compound crystallised as long thin pale-yellow monoclinic needles whose cell dimensions were close to those of $pqCoCl_4$, and the density suggested $pqPbCl_4$. Further study was abandoned because the high absorption coefficient and heavy lead atom preclude accurate determination of the light atom positions.

Crystals of $pqPdCl_4$ and $pqPtCl_4$ were made by mixing equimolar amounts of hot solutions of $pqCl_2$ and K_2MCl_4 (M = Pd, Pt). Orange rhombs crystallised quickly from the solution and the colour suggests that not much charge transfer is occurring. The compounds had virtually identical cell dimensions and were assumed to be isomorphous. The formula was confirmed by density measurement and structure analysis (Chapter VI).

Paraquat radical cation

An attempt was made to prepare crystals containing the paraquat radical ion:-



or pq^+

In the hope of producing a compound isostructural with the two $pq^{2+}MX_4^{2-}$ types, singly charged tetrahedral and planar AX_4^- species were used. These were BF_4^- and $AuCl_4^-$, and charge-transfer should be strong in the second case as the electrode potentials are similar. The radical monocation was formed by reduction with magnesium metal of a degassed aqueous solution of paraquat dichloride under nitrogen. A very dark-blue viscous solution was obtained, and this was passed into an aqueous solution of potassium fluoroborate. Many white crystals of paraquat fluoroborate were obtained but there were some very thin ($\sim$.005 mm) dark-blue whiskers which might well contain pq^+ , but they were obviously too small for any X-ray work. A similar operation using potassium chloroaurate(III) solution produced a dark-brown intractable sludge which was not further investigated.

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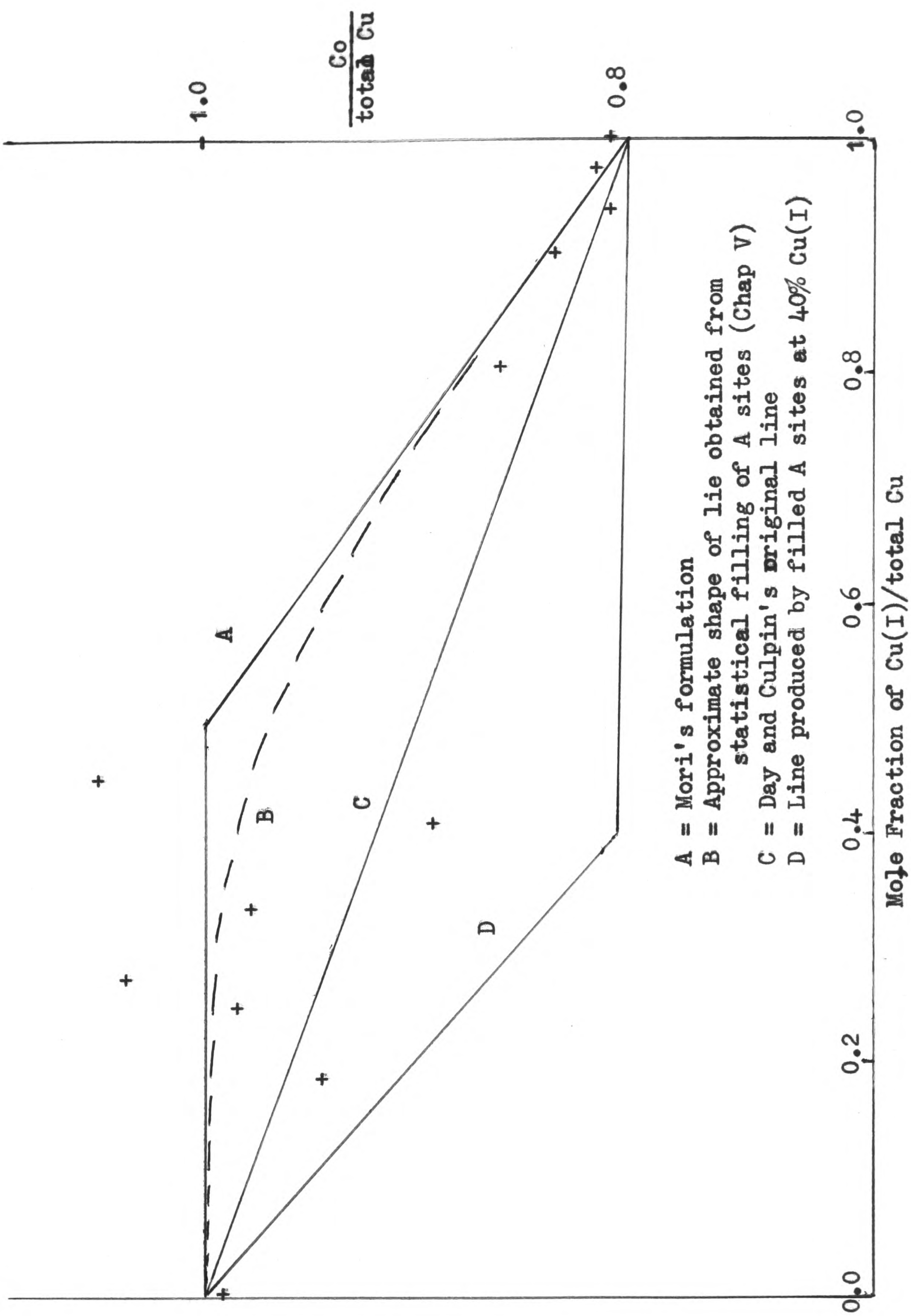

(Culpin's analytical results are not all shown, for the sake of clarity. However some lie above line A and some lie on line D.)

Fig. II.1. Possible Stoichiometries for the mixed valence chlorocuprates

(A plot of the Cobalt/Copper ratio with variation of the Cu(I)/Cu ratio)

CHAPTER III.

DATA COLLECTION AND STRUCTURE SOLUTION

COLLECTION OF X-RAY DATA

(Details of compounds are given in Table III.1.)

PHOTOGRAPHY

(a) Weissenberg

The accuracy of a structure determination is primarily dependent on the minimisation or corrections of errors in data collection and this is often limited by method and apparatus. The time spent on elimination of errors also increases rapidly with the precision obtained and is of doubtful value if there are appreciable approximations in the calculation of structure factors. For much of the following work only CuKα radiation (from rectifying but unstabilised generators) was available and was used with non integrating cameras with visual estimation of intensity. This usually leads to an 'R-factor' in the range 0.09 - 0.13 which imposes a severe restriction on the accuracy of light atom parameters ($\sigma \nless 0.07$Å). In addition no program for calculation of anisotropic temperature factors was easily available which also limits the final accuracy attained.

One-axis data

Because of this and the nature of the compounds studied, data are not required with great accuracy and were collected from one-axis only (usually the a-axis). This technique speeds data collection by at least twice and is widely used though little justification or criticism of it has been published. We therefore note the limitations of this method, particularly when compared to the use of data from two or more axes.

(i) Only $\sim 80\%$ of the copper sphere can be observed (if $\mu_{max} \sim 40^{\circ}$).

(ii) Reflections on or near the rotation axis are unobservable or inaccurate. If, however, reflections with $\xi < 0.15$ are excluded, less than 1% of the copper sphere is lost.

(iii) The shape of reciprocal space observed is not spherical, but only circularly symmetrical in the a-direction. Peaks which were originally spherical will be elongated along the a-axis.

(iv) Only one independent measurement of each reflection is made.

(v) The interlayer scalefactors are not usually available.

The first three effects are relatively unimportant as the main effect is to increase estimated standard deviations, particularly in the x-direction. An approximate formula (Cochran 12) gives $\sigma(r) \propto$ (R-factor)/(average Sin θ_{max}/λ for the three axes). For the compounds studied, this lack of data increases e.s.d.'s by $\sim$ 10%. It is noticeable that the e.s.d.'s along the x-axes are roughly this much greater than for the other two (e.g., Figure IV.2). The distortion in Fourier syntheses is small, and is unimportant unless subsequently used to predict anisotropic vibration. Twp-axis data have about 65% of the copper sphere in common, and two independent measurements of the same reflection will reduce its random error and some systematic error (e.g., spot shape), as well as checking the absence of large errors. But the time needed is at least doubled and lessens the fourth objection. It is more serious when data are very limited and need as much accuracy as possible.

The absence of layer scalefactors is more serious and although some scaling can be had from one or two second axis layers, the number of common reflections is small and a different method was used. Approximate layer scalefactors were obtained from exposure times, which are inaccurate because of generator fluctuations, developing conditions and varying spot shape. They were sufficiently good, however, to locate all the atoms in the structures, and after each least-squares cycle the function $\sum w(F_{obs}k_h - F_{calc})^2$ was minimised, where k_h are the scalefactors (1).

Measurement of intensities

The contrasted reflections were estimated visually, and no spot-shape corrections (e.g., 2) were made as the integrated density was measured as far as possible. Large spots close to the axis were omitted (3) and no correction for $\alpha_1 - \alpha_2$ splitting was made. Originally interfilm factors (in a 5-film pack) were determined experimentally giving for the four compound (Table III.1) zero-layer factors of 2.7, 2.6, 3.0, 2.9. As the value should be 2.93 (4) for CuKα there is a serious error in the first two which will give low values for large intensities. (This effect may well have been interpreted in many compounds as "extinction".) This is discussed in Chapter IV for the first compound. The error means that the intensity scale is effectively non-linear and is perhaps best minimised by making another or by using only a small portion of it and taking the published transmission factor (f). A term $f^{\sec\mu}$ must be used for higher layers. (This was done only for the last two compounds.)

Lorentz and polarisation corrections were applied (5) but not those for absorption. The crystals chosen were roughly cubical with $\mu a < 2$. There will be some errors because of this, but relative error between intensities is unlikely to average more than 10% and absolute error will be largely taken up by temperature factors.

(b) Precession method

This was only used, with molybdenum radiation, for the data from the 25% Cu(I) compound. This is face-centred cubic, a = 21.8Å, and 5 layers of data about the 011 axis, 3 about the 001 were collected, with up to three exposures of different times for each layer. Peak-heights were measured with a microdensitometer and assumed to be proportional to the integrated intensities. Lp corrections were applied and the many common reflections on different layers gave good layer scales. The final 'merging R-factor' for all common reflections (vide infra) was 0.14 for F^2.

COUNTER METHODS

(a) Linear Diffractometer

An early model of the Arndt-Phillips linear diffractometer (6) was available for short periods ($\sim$ 2 weeks). It had mainly been used for collecting data on protein crystals although some other data of rather low accuracy had been collected two years previously (13). Equi-inclination geometry was used which permits a Bragg angle of 30°

in any direction. However, there appeared to be inaccuracies in the ω-settings at $\mu = 30^{\circ}$, probably due to wear on the slides.

(i) Cobalt hexammine chlorocuprate(I)

For this molybdenum radiation with balanced Zr/Sr filters (7) was used, although there appeared to be little white radiation underneath the peak that was not proportional to the peak height. For systematic absences the count with the strontium filter was consistently larger ($\sim 20\%$) than that with Zr, and an empirical correction was made. Most reflections had an ω-spread of $\sim \frac{1}{2}^{\circ}$, but $1\frac{1}{2}^{\circ}$ was finally used to allow for slight drifts in ω, and the background was relatively low. The machine was easily set up to omit all systematic absences and, between layers, reference reflections on the zero layer were remeasured. These showed no statistically significant variation with time, implying stability of both crystal and equipment. Data processing included Lp corrections and rejection or remeasurement of reflections with significantly different backgrounds, or smaller than 3 s.d.'s of the total count.

As the system was cubic and 9 layers were collected, there was a useful check on the accuracy of measurement and also the layer scalefactors. The face-centering leads to two non-intersecting sets of data, one with all indices odd and the other with all indices even. Interlayer scalefactors can be compared within these sets but not between them, and the only solution would be data collection about a diagonal axis (as in the precession photography). Assuming that both sets are on the same scale, which is reasonable for counter data, scalefactors (k_h) from common reflections are as follows:-

Table III.2

Layer scalefactors for Cobalt hexammine chlorocuprate(I)

Layer (h)	0	1	2	3	4	5	6	7	8
Scale (k_h)	1.14	1.13	1.03	0.87	1.01	1.00	0.91	0.99	0.97

Table III.3 gives all "odd" reflections in the positive octant with more than one measurement of $|F^2_{hkl}C|$ (after scalefactor applications. Comparison with $|F^2_{khl}C|$ shows conclusively that in general $F^2_{hkl} \neq F^2_{khl}$ and the Lane group is m3 (as opposed to m3m). (It had been impossible to establish this from earlier photography, and is a demonstration of counter data for the determination of space group.) The "merging R-factor", defined as $R(a,b) = \sum|F^2_a - F^2_b| / \frac{1}{2}\sum|F^2_a + F^2_b|$ where a and b are equivalent reflections, was 0.098; this is significantly less than for the precession data and for the data compared in Chapter IV. The same function for a = hkl, b = khl was much higher, 0.36, although low enough to suggest that F_{hkl} and F_{khl} are not completely independent.

The crystal was a near-perfect octahedron, and axial reflections ($\xi = 0$) showed a four-fold intensity variation with 360° rotation of ω. This was not more than 15% which implies that absorption is small enough to be neglected or to allow calculations from crystal geometry. Because of the inadequacy of the final structure solution (Chapter V) absorption corrections were not worthwhile. Finally, in the application of scalefactors and merging of common reflections (1), reflections where $|F^2_a - F^2_b| > 0.2(F^2_a + F^2_b)$ were rejected.

(ii) Paraquat chlorocuprate(II)

This data was collected with CuKα radiation (filtered) which limits the resolution to $d_{min} \sim 1.5$Å. This was only done because molybdenum radiation was not available. Only a week could be taken and a crystal had previously been aligned photographically about a non-unique axis (a). There was no time to remount it and, as there are no reflections with $\xi = 0$, there may have been significant setting errors. Serious ω-errors were encountered on higher layers ($\mu > 25°$) though this may well have been due to mechanical errors. As the backgroup was small, this was partially overcome by increasing the ω-scan range to $4\frac{1}{2}°$ and using a larger counter aperture. Even so, most reflections on the highest layer (h = 4) had to be collected manually and some were obviously mis-set (compared with F_{calc}). The data is admittedly very poor but it was able to produce a rough structure, chemically plausible, whose gross features were interesting and where time and energy were insufficient for a full photographic determination.

(b) 3-circle diffractometer

Data for $CuOx_2$.2TCNB were obtained by Wright on a manually operated XRD-5 3-circle spectrogoniometer (14). It was his first experience of the machine and a few F_{obs} were very much less than F_{calc} or F_{obs} from photographs, and these reflections were excluded. Reflections at the edge of the data ($\theta \sim 50^{\circ}$) were also systematically weaker. CuKα radiation, with stationary-crystal technique (8), empirical conversion to integrated intensities (9) and a scintillation counter with pulse-height discrimination was used.

DETERMINATION OF STRUCTURES

The usual criteria for a structure solution being satisfactory are those of chemical reasonability and the agreement of observed and calculated intensities. Disagreement (a poor 'R-factor') may be due to errors in measurement of data and also approximation (e.g., the use of U_{iso}) in the calculation of structure factors. When the data may be inaccurate, chemical factors, such as interatomic distances or known geometry, are important.

The structures were all centrosymmetric and were solved by Patterson and heavy-atom techniques and also by postulating chemically reasonable structures. The heavy-atom method is particularly favourable if chlorine atoms can be located from the Patterson function as this usually removes any false symmetry. An indication of its power is shown in Figure III.1 which represents, for 4 structures, electron density in the plane of the paraquat ion phased on all the metal and chlorine atoms in each structure.

With at least the metal + chlorine atoms located, full-matrix least squares refinement was carried out. The program (10) allowed only for U_{iso} and a choice of 3 weighting schemes. Unit weights were used initially until refinement was nearly complete and then weights w, where $\sqrt{w} = F^*/F_{obs}$ unless $F^* > F_{obs}$ when $w = 1$. F^* was chosen so that $\sum w\Delta^2$ was approximately independent of F_{obs}, which worked well for photographic data so that systematic errors in Δ are minimised. Convergence was rapid and refinement was stopped when parameter shifts were less than their e.s.d.'s.

Determination of Individual Structures

There was a nice transition in the structure solutions from the mainly automatic Patterson and heavy atom methods to a chemical approach combined with the use of space-group positions. The outlines of the steps taken for each structure are described and summarised in Tables III, 4 - 7, as are final parameters. Diagrams of the structures, which may clarify their solution, are given in Chapter VI.

$CuOx_2.2TCNB$ was assumed to be in $P\bar{1}$ with the copper atom at the origin and structure factors dominated by its contribution. A map with all structure factors positive showed the 25 light atoms well resolved with only two spurious peaks. Only 90% of the final structure factors were negative which agrees well with theoretical predictions (e.g., Parthasarathy).

Paraquat $PdCl_4$, with only four molecules for the 16-fold general positions of the Patterson function showed all the necessary vectors for a square planar $PdCl_4^{2-}$ ion at (a) and evidence, from Pd to light atom vectors, for a twisted pq^{2+} ion at (b). This latter was verified by a Fourier synthesis, on Pd and Cl only, which gave the new electron density as in Figure III.1d. No evidence for the non-centrosymmetric space-group Iba2 was seen.

Paraquat $CoCl_4$, in Pnab (an alternative setting of Pbcn), must have both ions on either a centre of symmetry or two-fold axis. The latter is the only real chemical possibility for $CoCl_4^{2-}$ and the Patterson function was interpreted to give the orientation and position of these tetrahedral species. A subsequent Fourier synthesis is shown in part in Figure III.1a where the paraquat ion is on a two-fold axis and there are no significant spurious peaks.

Paraquat Cu_2Cl_6, in $P2_1/n$, was analysed with low resolution data (d_{min} = 1.5Å) which means that all peaks are poorly defined. Because of this there were two possible solutions for the position of the copper atom from the Patterson and vectors from chlorine atoms were not reliably identified. The first solution was chemically unlikely and Fourier syntheses based on it did not show reasonable chlorine atoms. A map on the second position, however, showed two well-resolved chlorine atoms and when these were introduced into the calculation, the third was clearly shown.

Calculated structure factors appeared encouraging at this stage and another Fourier synthesis gave Figure III.1c, clearly a paraquat ion at low resolution. Final structure factor agreement was not good

(R = 0.128) for counter data but there is little reason to doubt the structure and it is supported by chemical evidence (Chapter VI). Some of the outer reflections on higher layers appeared to be mis-set as F_{obs} was much lower than F_{calc} (these were removed). The temperature factors were ill-determined due to the lack of data and some were just negative, possibly due to absorption. No reliance is put on light atom bond lengths (and these are not listed) but the approximate planarity of the paraquat and the five-co-ordination of the copper atom are clear. It is most unlikely that a significantly different structure would be discovered by a more accurate determination.

Paraquat Cu_2Cl_4 crystallised in $P4_2/n$ (unique axis c) which has 8 general positions. As there are 4 formula units in the cell, the paraquat ion is likely to be at a centre of symmetry or possibly on one of the two diads. Figure III.2 shows the symmetry elements in $P4_2/n$ (and also some of the false symmetry, marked *, which is particular to this problem). The chlorine atoms probably lie in two sets of general positions.

The Patterson function had large peaks only at $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}\frac{1}{4}0$ (and symmetry-related positions) which strongly suggest that two or more special positions are occupied by the copper atoms. The cell dimensions (particularly the c-axis) and chemical considerations suggest a similarity with the last compound which has chains parallel to the short axis (Chapter VI). Two independent chains of $(CuCl_2^-)_n$ can be made by placing 2 atoms in each of $\frac{1}{4}\frac{1}{4}\frac{1}{4}$(a) etc. and $\frac{1}{4}\frac{1}{4}\frac{3}{4}$(b) etc. (both of symmetry $\bar{4}$) and the other 4 on the 4_2 screw at $\frac{1}{4}\frac{3}{4}z$(c) etc. Assuming that the largest Patterson peaks are copper-copper vectors, we have $z \sim \frac{1}{4}$. (N.B. The origin is taken at $\bar{1}$ and all calculations are done on this basis.)

Two infinite chains of edge-linked $CuCl_4$ tetrahedra can be made by putting the 16 chlorine atoms in two sets of general positions (incidentally leaving no space for the paraquat ion on the diad axis). The placing of the chlorine atoms was very difficult, for, although the orientation of both sets of tetrahedra could be clearly found from the Cu-Cl and intramolecular Cl-Cl vectors, there was no indication of their relative positions in the unit cell. In particular an isolated chain of edge linked (regular) tetrahedra involves both the symmetry elements 4_2 and $\bar{4}$ which creates further ambiguity. The only definite key at this stage, the identification and unravelling of the very large number of intermolecular Cl-Cl vectors, was quite impossible.

A Fourier synthesis on the copper atoms is useless as is shown by the false symmetry elements (*) in Figure III.2. Firstly there is a substructure with $c' = c/2$ so that copper atoms do not contribute to reflections with $l = 2n + 1$. This would be true even if the z co-ordinate of (c) were not $\frac{1}{4}$ but the fortuity of this introduces a second problem in false mirror planes (normally n-glides) at $z = 0$, $\frac{1}{4}$ etc. and also a false face centering for the sub cell $a' = b' = a/\sqrt{2}$. These three independent symmetry operators create an ambiguity of origin, at P or Q, but having made an arbitrary choice we automatically define the 4_2 and $\bar{4}$ (but not which tetrahedra lie on which).

The Patterson function showed two sets of chlorine atoms at translations of 0.093, 0.067, $\pm \frac{1}{4}$ etc. (denoted by (A)) and of 0.017, 0.111, $\pm \frac{1}{4}$(B) from copper atoms, making approximately regular tetrahedra, at undefined positions. There are 4 possible ways of arranging (A) and (B); two resulting from the ambiguity of which is on the 4_2 axis and this is doubled as there are two relative z-heights ($\pm \frac{1}{4}$) for the pair. A trial-and-error method of structure factors and least squares would be very time-consuming, very possibly unreliable and a different approach was adopted.

A Fourier synthesis was carried out with the B set attached to the copper atoms on the 4_2 screw. This axis was chosen because the chance value of z $\frac{1}{4}$ leaves the false mirror planes unbroken (Position X in Figure III.2). This map gave a clear indication of the absolute z-co-ordinate of the A set and x-, y- parameters consistent with the Patterson. Both sets were included in a least squares refinement of all the atoms and gave good agreement, $R < 0.3$. This solution, though seemingly correct, may not be the only one and the process was repeated with (A) used initially. This map showed not only the atoms put in but 'ghost' peaks closely related to the first solution.

Another Fourier synthesis, based on the first set of positions gave the electron density in Figure III.1b, a clearly resolved paraquat ion, which is additional indication of the correctness of the heavy atom positions. Refinement continued, but may be slightly meaningless for the z-parameters of the copper(c) and chlorine atoms because of the strong local supersymmetry of the heavy atoms. The correlation matrix (see Chapter IV) was calculated and showed no large covariances involving any positional parameters. The chlorine bridges appear to be fairly symmetric and this is quite acceptable. It had been hoped that the data, which appeared reasonably good, would have given better agreement ($R = 0.119$) but this might be due to errors in refinement.

This is the only compound solved from one-axis data that has a possible degeneracy of layer scales with heavy atom position, as the others have heavy atoms fixed in this direction (a-axis). The copper atoms make a contribution of $4_{f_{Cu}} (1 + \cos 2\pi l z)$ to even layers implying that small errors in the scale factors may be reflected in a slightly wrong value of z. This function can be rewritten as $8_{f_{Cu}} \cos^2 \pi l z$ (where $z \sim 0$) and errors are likely to be important only if they are roughly similar to $\cos^2 l$.

<u>The cobalt hexammine chlorocuprates (I) and (I,II)</u> cannot be discussed without detailed comparison of their structures and the chemical evidence. A separate Chapter (V) is devoted to this.

Results

The parameters of the paraquat compounds are listed in Tables III, 4, 5, 6, 7 which also give crystal data. The bond lengths and angles in the paraquat rings are given in Figure III.3a,b,c (without $pqCu_2Cl_6$)

and those of the anions in Chapter VI. Parameters, bonds and angles of $CuOx_2$.2TCNB are discussed in Chapter IV.

Scattering factors are those in INTERNATIONAL TABLES Vol. II (11) and anomalous dispersion corrections have been applied where necessary. Where necessary, ionic scattering factors have been used. Fourier syntheses in tetragonal space groups were calculated in monoclinic sub-groups (e.g., P2/n) with structure factors for $k\bar{h}l$ being included.

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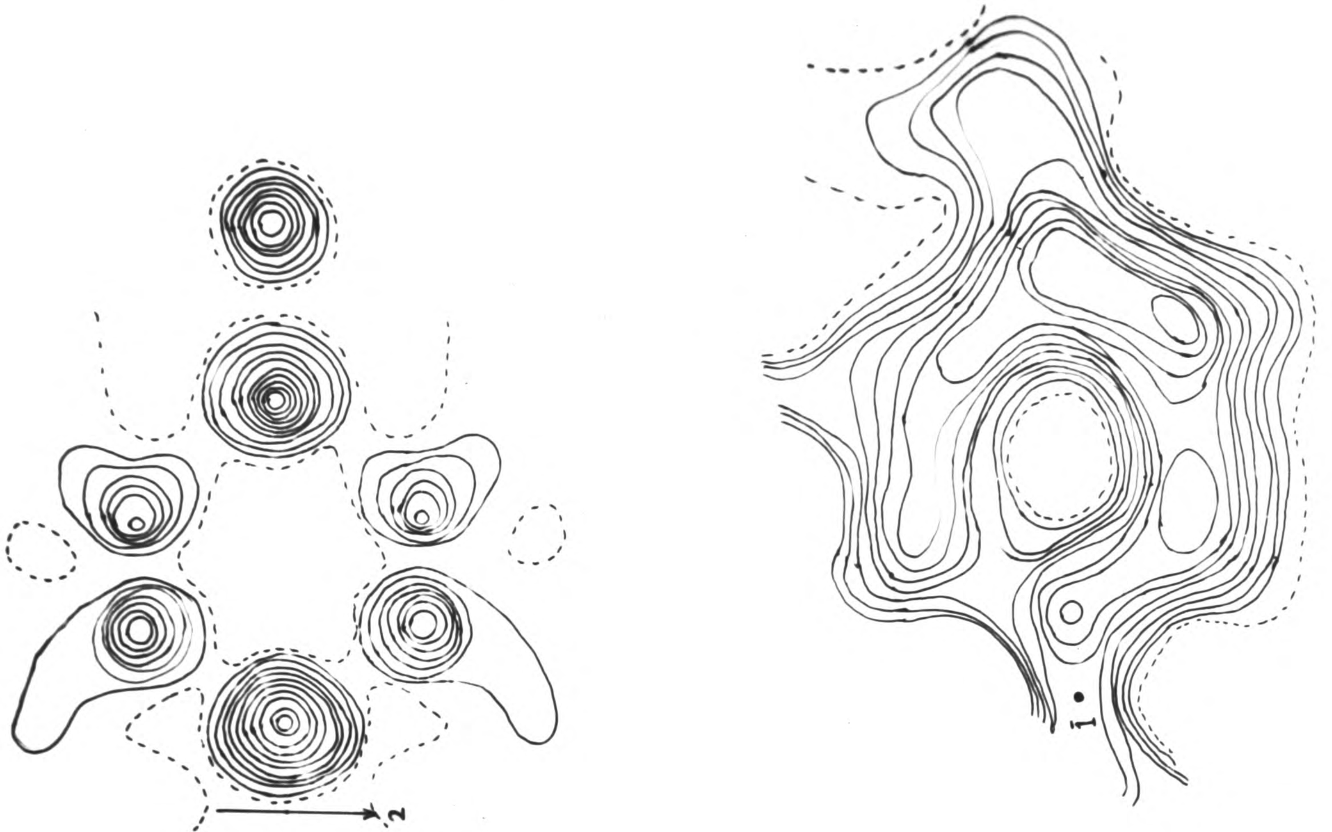
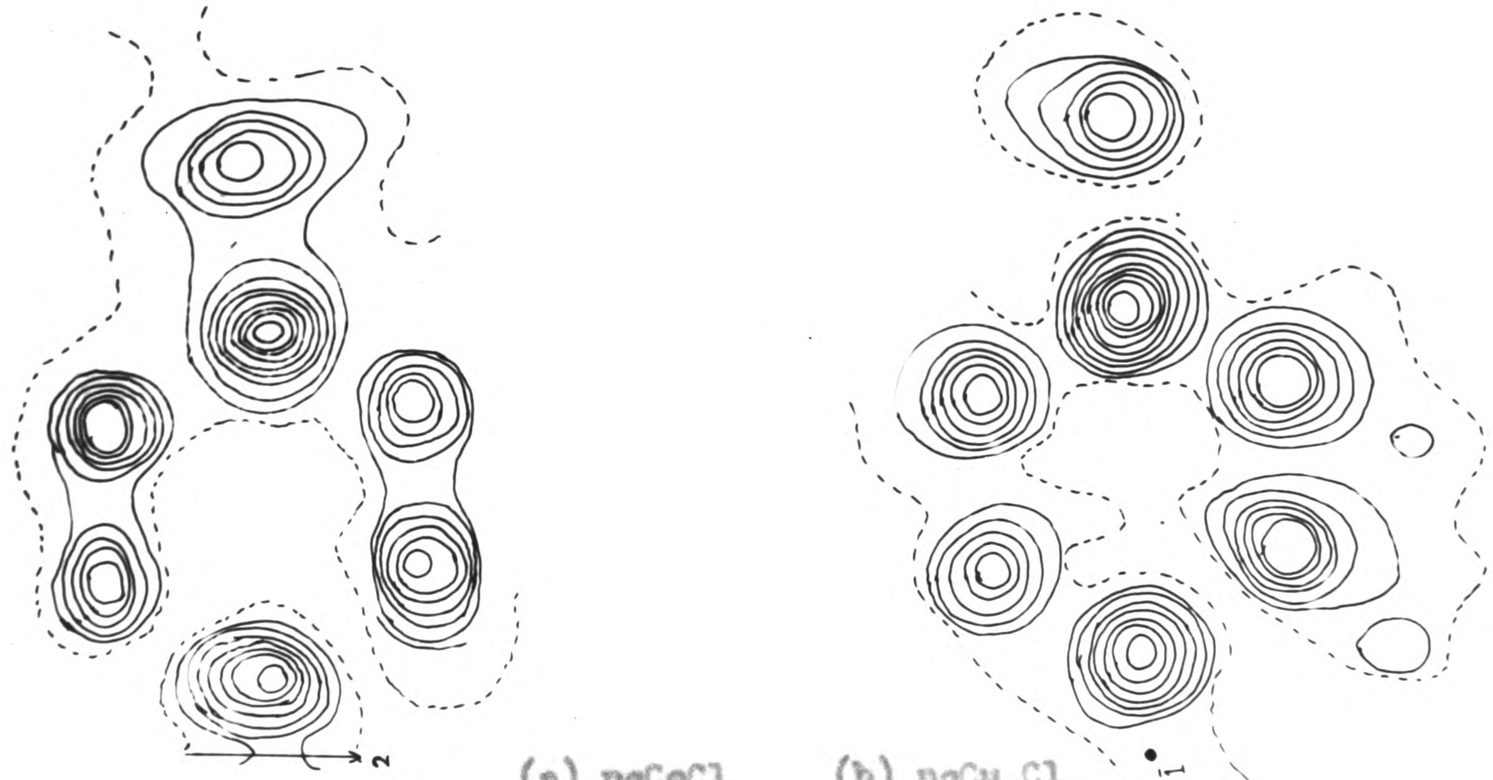


(d) pqPdCl$_4$ (c) pqCu$_2$Cl$_6$



(a) pqCoCl$_4$ (b) pqCu$_2$Cl$_4$

Fig. III.1. Electron Density (heavy atom-phased) in pq compounds

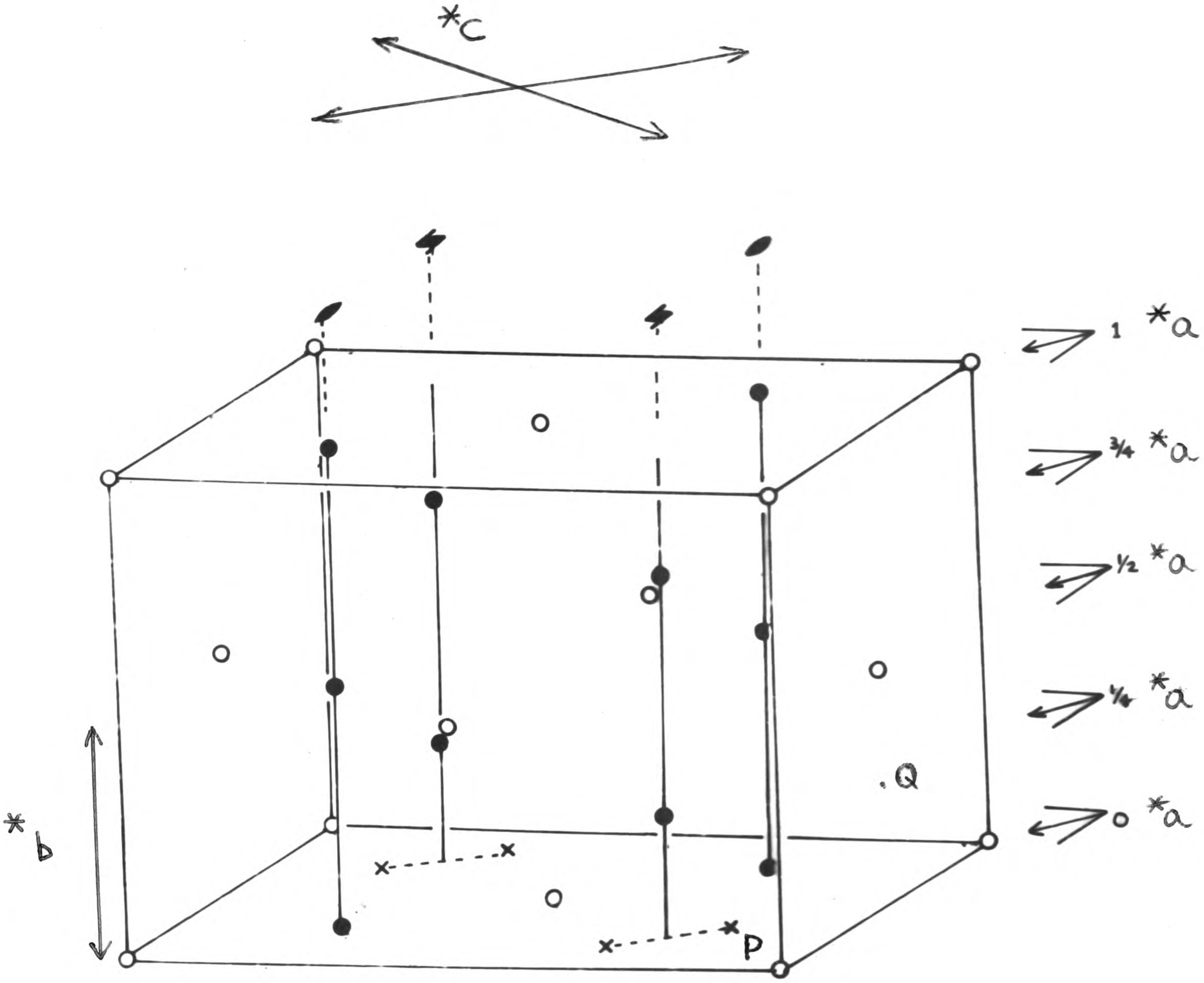


Fig. III.2. Symmetry Elements (and false symmetry) in $P4_2/n$.

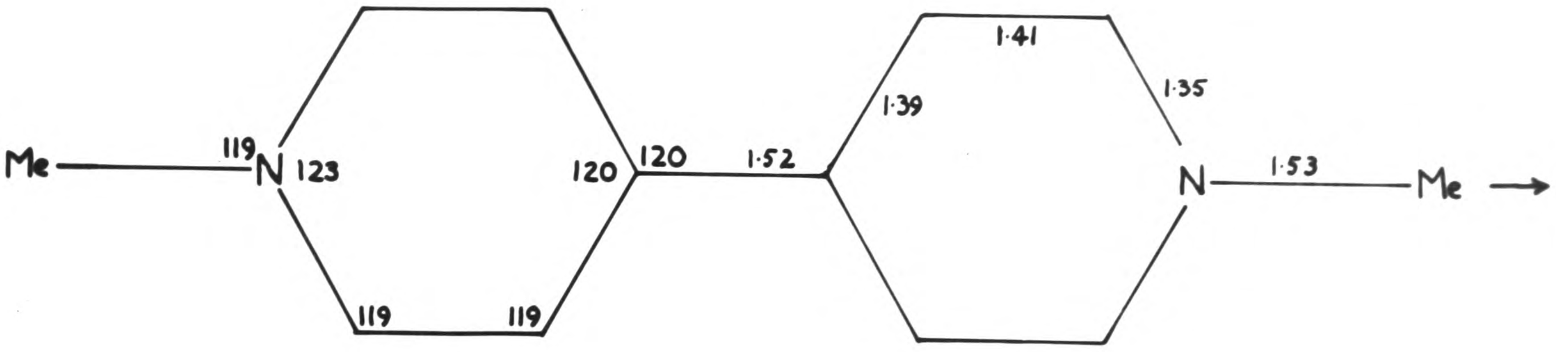
N.B. False symmetry is as follows:

*a, Mirror planes at nc/4
*b, Subcell along c-axis
*c, C-Face-centering
*d, Ambiguity of origin, P or Q? (P was finally chosen.)

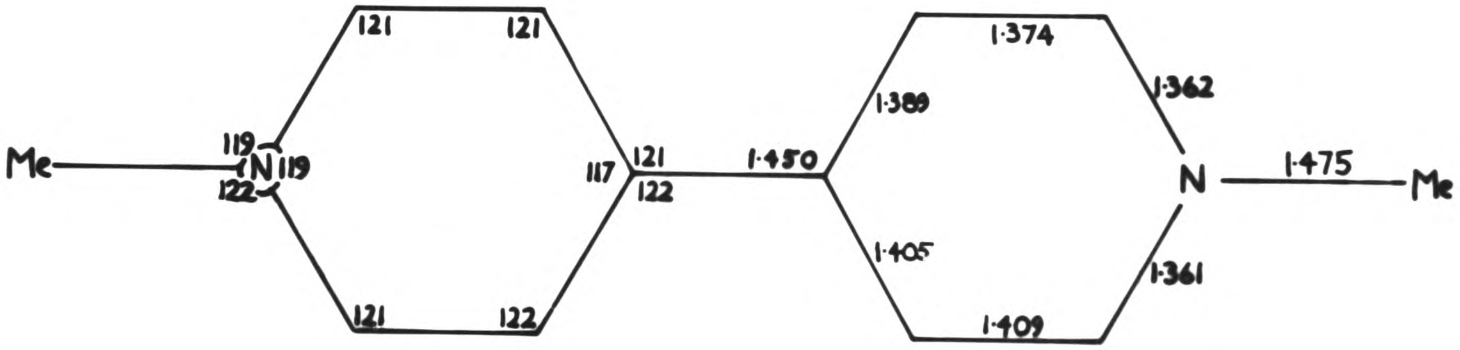
(B) tetrahedra lie round the ● on the 4_2 screw.

● Represents copper atoms
O " centres of symmetry, $\bar{1}$. There are a similar set, not shown, at a translation ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$).

Paraquat $PdCl_4$



Paraquat $CoCl_4$



Paraquat Cu_2Cl_4

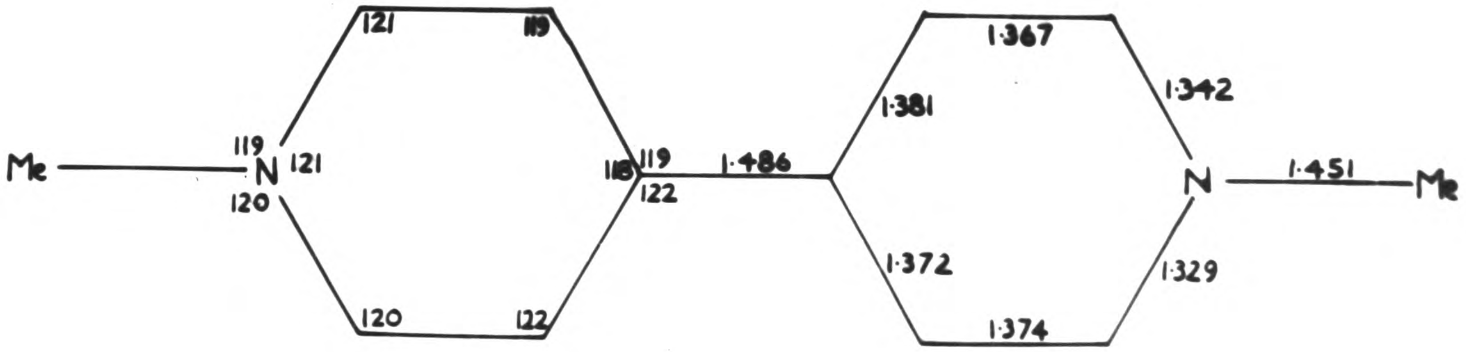


Fig. III.3. Bond lengths and angles in the paraquat rings.

Table III.1

Compounds on which data was collected

Compound	Method	Radiation	Resolution	R	Layer Scales
$[Co(NH_3)_6]_4Cu_5Cl_{17}$	L	MoKα	F	0.146	Poly-axis
$[Co(NH_3)_6]Cu^ICu^{II}Cl_n$ (25% Cu^I)	P	MoKα	F	0.087+	Poly-axis
$Cu(NOC_9H_6)_2.2C_{10}N_4H_2$	W	CuKα	OA	0.102	Refinement
$C_{12}N_2H_{14}CoCl_4$	W	CuKα	OA	0.117	Refinement
$C_{12}N_2H_{14}PdCl_4$	W	CuKα	OA	0.097	Refinement
$C_{12}N_2H_{14}Cu_2Cl_6$	L	CuKα	$\frac{1}{2}$F	0.126	Assumed Unity
$C_{12}N_2H_{14}Cu_2Cl_4$	W	CuKα	OA	0.119	Refinement

Method L = Linear diffractometer P = precession camera
W = equi-inclination Weissenberg camera

Resolution F = full CuKα sphere, $\frac{1}{2}F = d_{min}$ of 1.54 Å
OA = one-axis data

Layer Scales Poly-axis = use of reflections common to two data sets
Refinement = Minimisation of $\sum \omega \Delta^2$ by scale factors

Table III.3

Intensities(F^2) for $[Co(NH_3)_6]_4Cu_5Cl_{17}$, comparing F^2_{hkl} with F^2_{khl}

	h	k	h	k	h	k	h	k	h	k	h	k
Layer No.	1	3	1	5	1	7	3	5	3	7	5	7
hk 1							102				64	
kh 1							124				28	
hk 3	28	25	125		192	215					83	
kh 3			97		203							134
hk 5	97	102	69	75	32	32	230	221	141	134	2	
kh 5	125	124			64				84			
hk 7	203	190	64	65			84	83			6	4
kh 7	192		32	29			141					
hk 9	25	24	16	14	77	105	7	6	58	62		1
kh 9	15		6	6	147	172		10		27		
hk 11	20	16	55	52	44	68	93	87	34	35	24	24
kh 11	13	12	43	42	101	122	104	118	22	17	12	9
hk 13	52	50	14	13	33	31		18	12	10		
kh 13	57	56	9	6	28	25	15	12	16	18	3	
hk 15		53	7	10	3	7	52	52	20	23	2	2
kh 15	67	61	16	20	9	11	42	35	15	11	2	2
hk 17	9	7	10	13	26	30			3	3	11	13
kh 17	10	7	13	14	33	38			2	3	21	25
hk 19	6	9	5	5		5	39	39	17	20	10	9
kh 19	14	11	8	13	7	6	45	65	23	31	4	6
hk 21	7	8			18		18	18		9	6	6
kh 21	7				18	13	12	12		5	4	4

The values are (count x Lp^{-1} x 0.1 x k_h) where k_h are layer scales, given in the text.

The numbers at the head of each column indicate the layer on which data was collected.

Horizontally related numbers in each "box" should agree, but vertically related ones (corresponding to reflection about $\{110\}$) need not.

(Estimated Standard Deviations are mainly between 1 and 2)

Table III.4.

Details of Paraquat $CoCl_4$

Full Name: N,N'-dimethyl-4,4'-bipyridylium tetrachlorocobaltate(II)

Formula: $C_{12}N_2H_{14}CoCl_4$ Spacegroup: Pnab, No. 60. Z= 4

Dimensions of crystal (mm): 0.18 x 0.15 x 0.14 μ = 187 cm^{-1} (CuKα)

Cell parameters: a=7.70 b= 16.04 c=12.40 (Å)

Number of reflections: 926 (from a-axis) Final R= 0.117

Parameters refined, including scales: 38 + 7 scales.

Final parameters (x10^4)

	x/a	σ_x	y/b	σ_y	z/c	σ_z	Uiso	σ_U
Co	2500	-	2179	2	0	-	259	8
Cl(1)	747	6	1364	2	-990	2	398	10
Cl(2)	1091	5	3038	2	1146	2	296	9
N	78	16	895	7	2636	8	303	26
C(2a)	589	21	165	9	3091	11	390	33
C(2b)	503	20	1630	8	3108	11	373	32
C(3a)	1529	20	161	8	4016	10	367	31
C(3b)	1466	19	1650	8	4046	10	331	29
C(4)	2000	17	901	7	4517	9	288	27
C(Me)	-993	23	916	10	1675	12	476	38

Bond Distances and Angles in the Anion.

Co - Cl(1) = 2.26Å Co - Cl(2) = 2.28Å

Cl(1) - Co - Cl(1) = 109.4° Cl(2) - Co - Cl(2) = 105.6°

Cl(1) - Co - Cl(2) = 106.5, 115.8°

Cl(1) - N = 3.82Å

Shortest contact in the " molecular vice " is Cl(2) - C(2a) = 3.35Å

Table III.5.

Details of Paraquat $PdCl_4$

Full Name: N,N'-dimethyl-4,4'-bipyridylium tetrachloropalladate(II)

Formula: $C_{12}N_2H_{14}PdCl_4$ Spacegroup; Ibam, No.72. Z= 4

Dimensions of crystal (mm): 0.21 x 0.17 x 0.12 μ = 149 cm^{-1}

Cell parameters: a= 8.43 b= 13.50 c= 13.41 (Å)

Number of reflections: 595 (from a-axis) Final R= 0.097

Parameters refined including scales: 20 + 7 scales

Final Parameters ($\times 10^4$)

	x/a	σ_x	y/b	σ_y	z/c	σ_z	U_{iso}	σ_U
Pd	0	-	0	-	0	-	193	7
Cl(1)	-2376	6	850	3	0	-	340	12
Cl(2)	1351	5	1500	3	0	-	256	10
N	0	-	2398	12	2500	-	277	32
C(4)	0	-	4436	12	2500	-	378	36
C(3)	4378	17	1076	8	1693	9	274	25
C(2)	4404	17	2124	8	1701	9	310	26
C(Me)	0	-	1266	16	2500	-	378	46

Bonds and Angles in the Anion.

Cl(1) - Pd = 2.31 Å

Cl(2) - Pd = 2.32 Å

Cl(2) - N = 3.78 Å

Cl(1) - Pd - Cl(2) = 89.5°

Table III.6.

Details of Paraquat Cu_2Cl_4

Full Name: N,N'-dimethyl-4,4'-bipyridylium tetrachlorodicuprate(I)

Formula: $C_{12}N_2H_{14}Cu_2Cl_4$ Spacegroup: $P4_2/n$, No.86. Z= 4

Dimensions of crystal (mm.): 0.32 x 0.25 x 0.17 $\mu = 96\ cm^{-1}$ (CuKα)

Cell Parameters: a= b= 16.28 c= 5.90 (Å)

Number of reflections: 1199 (from c-axis) Final R = 0.119

Parameters refined, including scales: 40 + 6 scales.

Final Parameters ($x10^4$)

	x/a	σ_x	y/b	σ_y	z/c	σ_z	U_{iso}	σU
Cu(1)	2500	-	2500	-	2500	-	618	8
Cu(2)	2500	-	2500	-	7500	-	586	7
Cu(3)	2500	-	7500	-	-452	4	557	6
Cl(1)	3426	1	3164	1	5031	3	355	6
Cl(2)	8617	1	2335	1	-2102	3	363	6
N	9901	3	2007	3	2023	10	322	12
C(4)	-15	4	424	4	467	12	293	13
C(3a)	445	4	1035	4	-554	13	346	14
C(3b)	9467	5	637	5	2206	16	477	19
C(2a)	407	4	1815	4	303	13	365	15
C(2b)	6435	5	573	5	-2037	15	450	18
C(Me)	7849	5	138	5	-2195	15	423	16

Table III.7.

Details of Paraquat Cu_2Cl_6

Full Name:- N,N'-dimethyl-4,4'-bipyridylium hexachlorodicuprate(II)

Formula: $C_{12}N_2H_{14}Cu_2Cl_6$ Spacegroup: $P2_1/n$, No.14. Z=2

Dimensions of crystal(mm.): 0.27x0.20x0.15. μ = 101 cm^{-1} (CuKα)

Cell parameters: a= 6.29 b=10.74 c= 13.02 (Å) β = 98.65°

Number of reflections: 309 (from a-axis) Final R = 0.126

Parameters refined, including scales: 44 + 1 scale.

Final Parameters ($x10^4$)

	x/a	σx	y/b	σy	z/c	σz	Uiso	σU
Cu	2549	9	564	6	443	5	80	33
Cl(1)	4435	15	4478	11	3927	8	-140	42
Cl(2)	9473	16	3433	12	4621	9	-42	44
Cl(3)	3378	15	1455	11	1987	9	-110	41
N	263	50	3743	35	1306	28	-110	110
C(4)	4042	67	4710	45	280	38	88	154
C(3a)	2605	67	1144	45	4774	36	37	145
C(3b)	8584	77	40	51	3654	42	64	166
C(2a)	643	70	3456	46	237	38	-64	148
C(2b)	1713	73	4595	49	1759	36	-35	149
C(Me)	8328	57	3182	41	1846	30	-174	119

CHAPTER IV.

ANALYSIS OF THE ACCURACY OF STRUCTURES

(A comparison of various parameters and their estimated errors from identical or closely-related structures)

COMPARISON OF DATA AND PARAMETERS FROM SIMILAR STRUCTURES

Wright and I collected data, and solved the structure of, $CuOx_2$.2TCNB independently, and, as both of our methods of data collection are widely used, the data and parameters are compared in the light of their estimated standard deviations (e.s.d). This showed the use of one-axis data, still very widely used (1), to be a reasonable method in this case, even though layer scale factors were refined against the calculated structure. Very little has been published about the duplication of three-dimensional data collection for a particular compound and the comparison is usually not in terms of atomic parameters. The comparison appeared successful and was extended to an empirical investigation of the published e.s.d.'s for bonds and angles in similar structures. A short description of the statistical method used is given so that the notation is defined. It is clear that only the estimated precision is analysed and this cannot in any way appraise the accuracy of the answer.

Statistics of X-ray Analysis (cf 2, 3, 4)

Counting statistics (5) give a prediction of the uncertainty of an intensity measurement, but (although reasonable if F_{obs} is small) the actual disagreement with F_{calc} is usually several times greater (6). This is due to reproducible errors in F_{obs} and F_{calc} (although these often cause random errors in the parameters (p_i) if the problem is well-overdetermined; observations $(m) \gg$ parameters (n)). This consequence of the Central Limit Theorem allows us to calculate an s.d., $\sigma(p_i)$, for each parameter by assuming that the difference $(F_{obs} - F_{calc})$ is random. The $\sigma(p_i)$ will contain both truly random and reproducible errors (but not systematic errors which are absorbed by parameter shifts).

An estimate of $\sigma(p_i)$ is c^{-1}_{ii}, a diagonal term from the inverse matrix, but if absolute weights are not known, this is modified to $c^{-1}_{ii} \sum w \Delta^2/(m - n)$, which holds only for a full-matrix treatment. If the off-diagonal terms of this matrix are non-zero, the parameters are not independent, and statistical analysis is difficult; this was not the case in the present work as is shown later. The second formulation for $\sigma(p_i)$ was used and was determined from a full-matrix (4).

The probability of two measurements p_{i1} and p_{i2}, with s.d.'s $\sigma(p_{i1})$ and $\sigma(p_{i2})$, being different is related to $t_i = \Delta_i/\sigma(\Delta_i)$, where $\Delta_i = p_{i1} - p_{i2}$, and $\sigma(\Delta_i) = \{\sigma^2(p_{i1}) + \sigma^2(p_{i2})\}^{\frac{1}{2}}$. The probabilities that a randomly generated t_i exceeds 1.645, 2.33 or 3.00 are 5, 1, 0.1% respectively. This use of t_i is useful where only single parameters are to be compared, but for several independent t_i their overall distribution must be considered. In particular, for n random t_i, $\sum^n t_i^2 \sim n$; the probabilities that it is substantially higher or lower are those for χ^2 (with n degrees of freedom) exceeding a particular value (3).

If these probabilities are unallowably high or low, then $\sigma(\Delta_i)$ must be an under- or overestimate of the actual uncertainty or reproducibility. In particular, a low value of $\sum t_i^2$ suggests appreciable reproducible error common to both determinations (which might be due to absorption, extinction, and particularly errors in F_{calc}, as the same method was used for both sets of data). A high value is probably due to an error being absorbed in parameter shifts and not being reflected in $\sigma(\Delta_i)$. A reasonable value of $\sum t_i^2$ may, of course, be made up of equal amounts of these effects.

The duplicated structure determination of the complex copper oxinate 2TCNB

The structure was originally determined because it was hoped to study a series of similar compounds, and particularly to relate single-crystal spectra to the simple molecular geometry of the triclinic system. The chemistry of the compound is not uninteresting and is described in a paper to be published (8). If a preprint is available it is hoped to include this in the thesis, but the compound is included solely for the analysis of its X-ray data and parameters.

Data collection and treatment

The counter data collection (8) has already been described but some extra details of the photographic method are given. Seven layers, each consisting of two settings 180° different in ω were taken about the a-axis (nkl). The two settings on any one layer were exposed for equal times and assumed to be on the same scale as spots common to both appeared equal and this was confirmed by comparison with calculated structure factors. A zero layer photograph (h0l) was taken, but not used for layer scale factors, which were refined only after all atoms had been included and after every second round of least-squares.

Polarisation (and Lorentz), but not absorption, corrections were made. This is justifiable as an axial reflection ($\chi = 90^\circ$) on the diffractometer showed about 6% variation with ϕ. Wright's data (subscripted W) was refined to $R \sim .102$, subsequantly improved by calculation in Oxford where comparison with my data (M) suggested removal of some inaccurate reflections of high θ . Both sets of data were then treated identically, with a full normal matrix and isotropic temperature factors (except for assumed values for hydrogen atoms). Final difference maps showed nothing significant except marked anisotropic thermal motion for the copper atoms. The residuals were $R_W = .082$, $R_M = .102$, neither including unmeasured reflections. It was found that all the phases were identical for the two structures which is not surprising as the weakest $F_{obs\ M}$ were not measured and the refinement was similar in each case.

Comparison of the determinations

Comparisons are made of the parameters, with individual t_i, (Table IV.1) and some bonds and angles with individual t_i for the oxinate rings only (Table IV.2). Common structure factors are not listed, but $|F_{obs\ W}|$ and $|F_{calc\ W}|$ are published (8) and $|F_{obs\ M}|$ with $|F_{calc\ M}|$ are in Table VII .1.

Intensity data

The $|F_{obs}|$ data cannot be compared unless they are on correct relative scales, but neither set involved any absolute scale determination. Two possible methods to determine the relative scales (K) are to minimise a function of the sort $\sum w \{ |F_{obs}|_M k_h - K |F_{obs}|_W \}^2$, or to take $K = \frac{GM}{GW}$, where these are the scale factors obtained from refinement. In the first case, layer scales can be refined for F_M, and can be compared with those obtained from exposure times and the structure refinement.

The first method gives a merging R factor (Chapter III) for $|F_M|$ to $|F_W|$ of 0.079 (0.148 for F^2) and the second 0.09 (0.168 for F^2). The parameter K refined to 1.03 GM/GW (where 1/G is used to put F_{obs} on an absolute scale). This 3% difference between the structures is just compatible with the e.s.d.'s for GM (0.8%) and GW (0.6%), but it was found that the scales have high covariance with the temperature factors of the copper atom. This high value may also result from an effect shown in Figure IV.1, which shows plots of $\langle F_{obsM}/F_{obsW} \rangle$, $\langle F_{obsM}/F_{calcM} \rangle$ and $\langle F_{obsW}/F_{calcW} \rangle$ for various ranges of F. The first suggests strongly that $|F_{obs}|_M$ is systematically lower than $|F_{obs}|_W$ for high reflections, almost certainly due to the low film factors. Without the counter data, this might well have been ascribed to 'extinction', and it is surprising to what an extent the parameters are able to compensate for this effect (as the second curve shows). This compensation appears to lead to no systematic differences between the parameters obtained from both sets of data, with the possible exception of the temperature factor of the copper atom.

The layer scales determined for $(F_{obs})M$ by 3 different methods are listed in Table IV.3.

Table IV.3

Values of k_h to be applied to $(F_{obs})_M$

Layer	From Exposure Times$_M$	From $\|F_{calc}\|_M$	From $\|F_{obs}\|_W$
0	1.0	0.97	0.94
1	1.0	1.12	1.11
2	1.0	0.93	0.91
3	1.0	0.96	0.96
4	1.0	1.22	1.25
5	1.0	0.81	0.88

The layer scales obtained from exposure times are poor, but as they are not wildly wrong, they can be refined against F_{calc} to give surprisingly good agreement with the third column. If we assumed that no layer scaling is necessary for the 3-circle data, then the method employed for one-axis photographic data is within the limits of acceptable error. Certainly a large amount of second-axis data would be needed to better this agreement. This is not a general justification of the process used, but suggests that it is valid if there is a heavy atom whose position cannot affect layer scales. It may well result in an incorrect temperature factor for this atom, and precludes meaningful anisotropic refinement ( ). It is also likely to be invalid for more accurate determinations of parameters where vibration must be accurately analysed.

Parameters

$\sum^{25} t_i^2$ were calculated for the four sets of parameters: x-, y-, z- co-ordinates and isotropic temperature factors, U, and are given in Table IV.4.

Table IV.4

$\sum^{25} t_i^2$ for various parameters $= \sum^{25} \left\{(p_i)_M - (p_i)_W\right\}^2 / \left\{\sigma^2(p_i)_M + \sigma^2(p_i)_W\right\}$

Parameters	$\sum^{25} t_i^2$	Probability that $\chi^2_{25} > \sum^{25} t_i^2$
25 x-co-rdinates	10.0	0.99
25 y-co-ordinate	18.2	0.80
25 z-co-ordinates	30.9	0.20
25 U-parameters	32.3	0.15

(t_i for the copper atom was 8.8, which is very improbable, and may well be due to the high covariance between G and U_{Cu} or the lack of anisotropic refinement.)

It is clear that there is good correlation between the observed and estimated difference with the exception of x-co-ordinates. This is the axis for which 6 layer scales were refined and it is possible that the numbers of degrees of freedom should be reduced from 25 to 19. The probability that $\chi^2_{19} > 10.0$ is only 0.80 which is insignificant. Because of the slightly lower resolution in the x-direction, the e.s.d.'s of these parameters (M) are $\sim$ 10%.greater than for other axes. Overestimation of these might account for lower t_i values but even so $\sum^{25} t_i^2 \not> 12$ which is still significantly low. The good agreement of the temperature factors, depicted in Figure IV.3, implies that X-ray absorption in the two crystals is roughly equivalent.

It is interesting to compare the standard deviations of $(p_i)_M$ and $(p_i)_W$. There is very good correlation (Figure IV.2) and this is perhaps explained by Figure IV.4 where $\frac{1}{2}(\bar{\sigma}_M + \bar{\sigma}_W)$ for any atom (in Å) is plotted against $\frac{1}{2}(U_M + U_W)$. The positional s.d. of an atom, estimated from a Fourier synthesis (2), is proportional to the curvature of that atom, made up of experimental errors, form factor and temperature factor effects. Figure IV.4 suggests that $\sigma(r) \sim 0$ when $U \doteq -0.03$ and, if the scattering factors for light atoms can be written as (2):

$$f(s) \doteq Z \exp(-ps^2) \qquad \text{where } s = \sin\theta/\lambda$$

then $p \sim 2.5\text{Å}^{-2}$.

The validity of this analysis of e.s.d.'s has relied on neglect of any covariances, $cov(p_i p_j)$, which are estimated by the off-diagonal terms c_{ij}^{-1} of the inverted normal matrix. The correlation matrix (10), where $N_{ij} = c_{ij}^{-1} / \sqrt{c_{ii}^{-1} c_{ij}^{-1}}$ was calculated for (M) data. The leading diagonal must be unity but of the other 5151 terms, few had significant moduli. $N(G,U_{Cu}) = 0.83$, $N(G,U_i) \sim 0.2$, $N(U_{Cu},U_i) \sim 0.15$ and for the x - y - z - parameters of the same atom, $N(x_i y_i) \sim N(x,z_i) = 0.13$ and $N(y_i z_i) \sim 0.19$, possibly correlated with the deviations of the axes from orthogonality. The remaining $\sim$5000 terms contained only 16 terms $>$ 0.1 and their average was $\sim$ 0.02.

The analysis has supported the idea that e.s.d.'s for a well overdetermined structure (three-dimensional) are meaningful and that isotropic temperature factors have some significance. It would be risky to extrapolate this to analyses of much higher accuracy.

Previous comparisons of sets of data for a single compound

The above results are interesting mainly because of the lack of similar published comparisons. None of the few I shall mention are exactly similar.

The reproductivity of identical counter measurements from the same crystal (CaF_2) by different operators showed these could have "merging R's" on F^2 of 2 - 13%. Systematic errors in sin θ could lead to a ΔB of 0.3 (18). Previous experiments on NaCl showed that $|F^2|$ data came from the same population (19). No analysis of positional parameters could, of course, be done.

Photographs are also capable of high accuracy (20) but comparisons of good photographic data are rare. Two examples of relatively low accuracy are given.

Independent refinement of di-paraanthracene from two one-axis sets of photographic data about different axes showed that within the (high) e.s.d.'s for bond lengths (0.02Å) and B's (0.4Å^2) the two sets of data were consistent, although both were of limited resolution (21).

A comparison of two-axis CuKα photographic data and limited MoK data from one axis (collected on this linear diffractometer) can be made from an analysis of a bromoterpenoid (22). Two sets of parameters were independently refined but not compared (and both R-factors were very high). Taking these values, we get for 47 parameters:- $\sum^{47} t_i^2$ for x- y- z- and B-parameters = 62, 282, 75, 138. The temperature factors might agree better if absorption corrections had been made as B_{Cu} was usually greater than B_{Mo}. Values of 62 and 75 are just allowable, but the e.s.d's along the rotation axis (y) are underestimated by a factor of at least 2. The data were much more limited in that direction than for normal one-axis photographic data. It should be noted that the analysis was for a non-centrosymmetric space-group and did not use a full matrix approximation.

COMPARISON OF RELATED STRUCTURES

If the e.s.d.'s of a structure are reliable, it is interesting to compare its parameters with those of a related one, but this cannot be done directly except for isomorphous structures. However, a molecular entity of n atoms can be defined by 3n-5 co-ordinates, with a suitable choice of axes. These parameters are usually the reported bonds and angles, though these do not always have individual e.s.d.'s. An ideal set of structures for this is a series whose members each include a compound common to all, which is in an identical chemical state throughout. Two examples of this are molecular complexes with a common donor (metal oxinates) for which 8 reasonable structures are available and ionic compounds with a common cation (paraquat) - 6 structures. If we assume that the bond lengths and angles are unaffected by small changes in electronic configuration or molecular packing, then they should be identical within the estimated error. The absence of sizeable distortions in compounds with non-crystallographic symmetry suggests that packing forces can often be neglected.

It is often assumed that if in two structures no bond lengths differ by more than 3 e.s.d.'s, then these structures are identical. Although this argument can, with caution, be used for a single bond, for assessing two structures as a whole, the deviations must be taken together. It would be best to refer these to a common origin by minimising $\sum^{n\ \text{atoms}} W(\Delta\underline{r})^2$, where $\Delta\underline{r} = \underline{r}_a - \underline{r}_b$ and then to evaluate $\sum t_i^2$, where $t_i = (\Delta\underline{r})_i$/(e.s.d. along the line a → b). This is tedious and the simpler comparison of bonds and angles has been made. Although the atoms are assumed independent of one another, it is impossible to choose bonds and angles to satisfy this. The analysis should however show whether the e.s.d.'s of bonds and angles are of the correct order, or are useful for comparing structures.

Metal oxinates (MOx_2)

Apart from our determination(s) of $CuOx_2.2TCNB$, there are also reasonable ($0.08 \leqslant R \leqslant 0.14$) determinations of the α - and β - forms of

$CuOx_2$ (11,12), $CuOx_2$.picryl azide (13), $CuOx_2$.TCNQ (14) and three palladium compounds, $PdOx_2$ (15), $PdOx_2$.TCNB (16) and PdOx.Chloranil (17). It is assumed that all bonds and angles between light atoms will be unaffected by electronic effects even from Cu^{2+} to Pd^{2+}. As the compounds are planar (all published structures obey two-dimensional Euclidean geometry) they can be defined by $2n - 3$ parameters, (19 if $n = 1$).

Those chosen are shown, along with the tabulated values (p_{ij}), $i = 1 \rightarrow 19$, for each structure (j) in Table IV.5. Also tabulated are the respective weighted means, $\bar{p}_i$, with standard deviations, $\sigma(\bar{p}_i)$, for all copper structures, and similarly for palladium ones. These are calculated from individual $\sigma(p_{ij})$ if these are given, and $t^2_{ij} = \Delta^2_{ij}/(\sigma^2(p_{ij}) + \sigma^2(\bar{p}_i)$ where $\Delta_{ij} = \bar{p}_i - p_{ij}$; where only an average e.s.d., $\bar{\sigma}(p_j)$, was published, $\sum t^2_i$ was taken as $\sum \Delta^2_{ij}/(\bar{\sigma}(p_j))^2$. Although p_i are independent, an average $\sigma(p_i)$ was calculated as all the e.s.d.'s are of the same order. None of the $19p_i$ are linearly related to any combination of others, but are not independent in relation to movement of atoms.

We consider only the three questions:-

(a) Is any particular compound significantly different from the mean of the others with the same metal ($\sum^{i} t^2_{ij}$ for any j)?

(b) Are the mean parameters of the copper and palladium oxinates different?

(c) Are the mean bond lengths of all oxinate structures compatible with those calculated by Huckel theory (23)?

(a) Of the 8 compounds only $CuOx_2$.PA has large $\sum t^2_i$. This does not necessarily mean that the e.s.d.'s are too small and the effect may be due to the non-independence of parameters. (A large shift of C(9) alone could account for the two greaters deviations (in angles 18 and 19)). In general, however, the results imply that the published s.d.'s are likely to be wrong by less than a factor of two in either direction, and can be usefully employed to compare structural features within this accuracy.

(b) Palladium and copper oxinates have identical light-atom bond lengths angles, which agrees with their similar electronic structures. (Table IV.6.)

(c) The average deviation of r_{Cu} from r_{Huc} is $\sim 2\sigma(r_{Cu})$ which is good considering the approximations in the M.O. calculation. (Table IV.7.)

Paraquat structures (pq^{2+})

All the paraquat structures, including the first three (24) were planar (except $pqPdCl_4$) and have $\bar{1}$ or 2 symmetry. Two questions were:-

(a) Are all the ions compatible with the mean and does this have mmm symmetry? (It must be at least mm2 or 2/m)

(b) Can the bond lengths be interpreted in terms of valence theory?

The results are shown in Table IV.8, where mmm symmetry is assumed, and imply that all structures are compatible with this (as there are no extreme $\sum t_i^2$). The 4-4', 4-3 and 3-2 bonds differ significantly and the M-O bond orders are computed from them using an empirical curve (23). These can be compared with those calculated in Chapter VI and show reasonable agreement.

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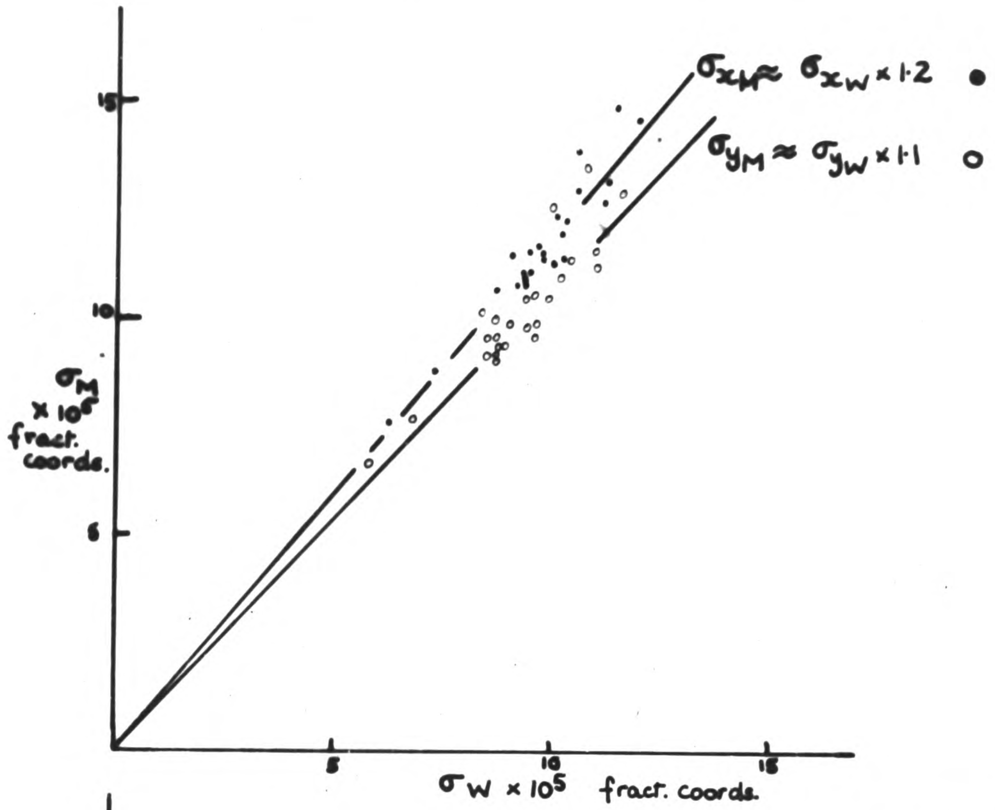
Fig. IV.2. Comparison of $(p_1)_M$ and $(p_1)_W$ for CuOx$_2$.2TCNB



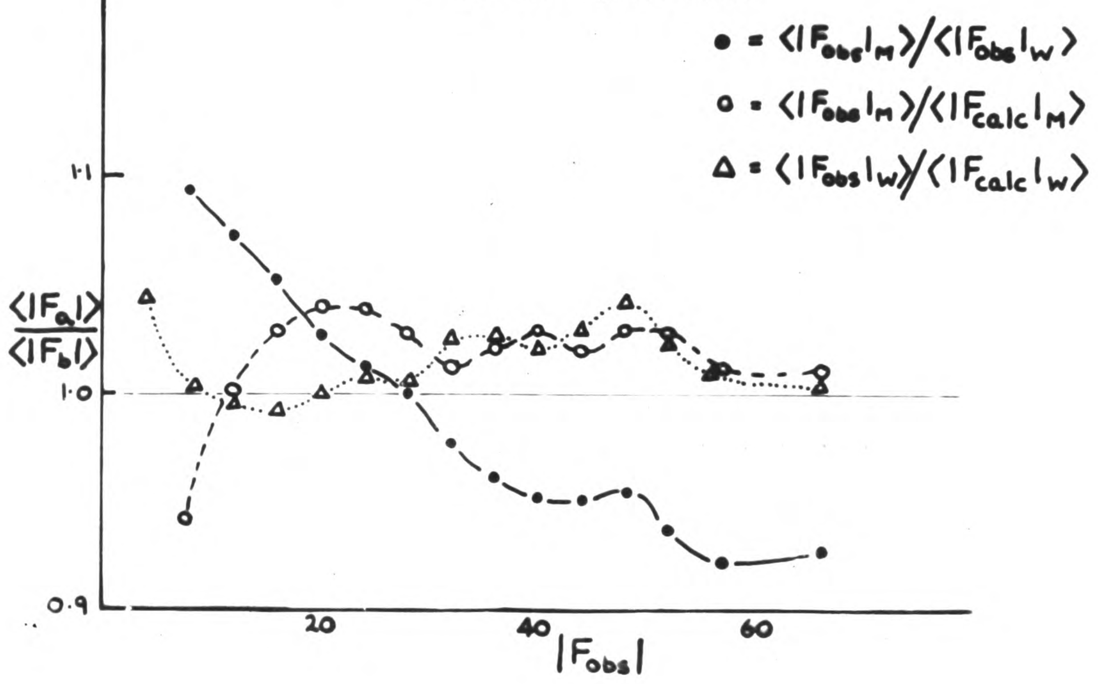


Fig. IV.1. Comparison of various F values from CuOx$_2$.2TCNB

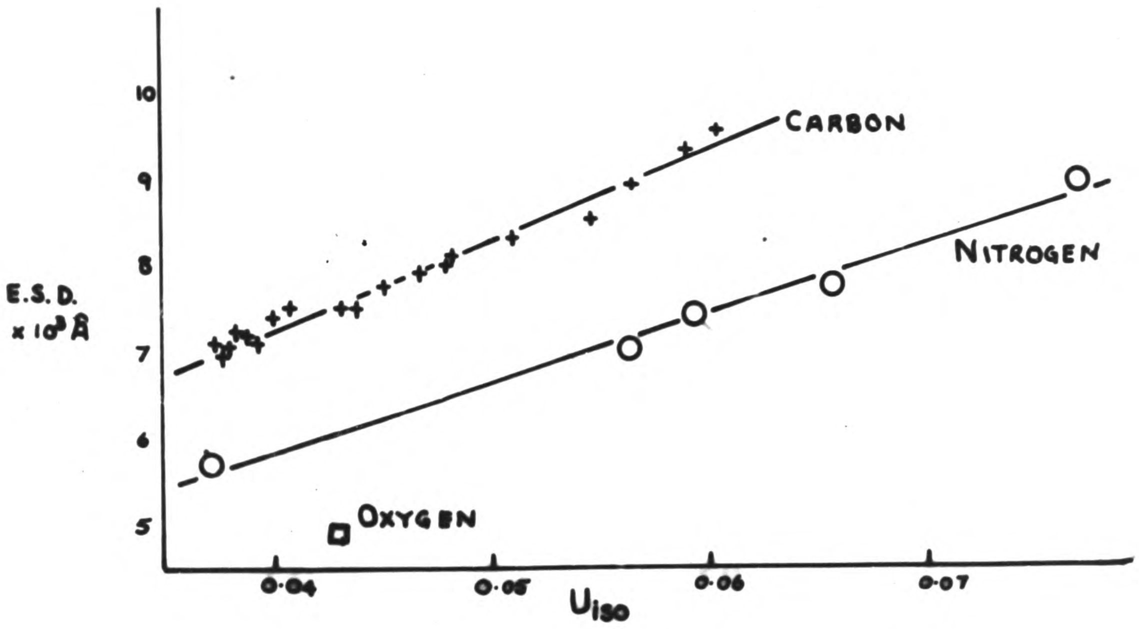


Fig. IV.4. Comparison of U_{iso} with the mean e.s.d. for that atom in Å. (for $CuOx_2.2TCNB$)

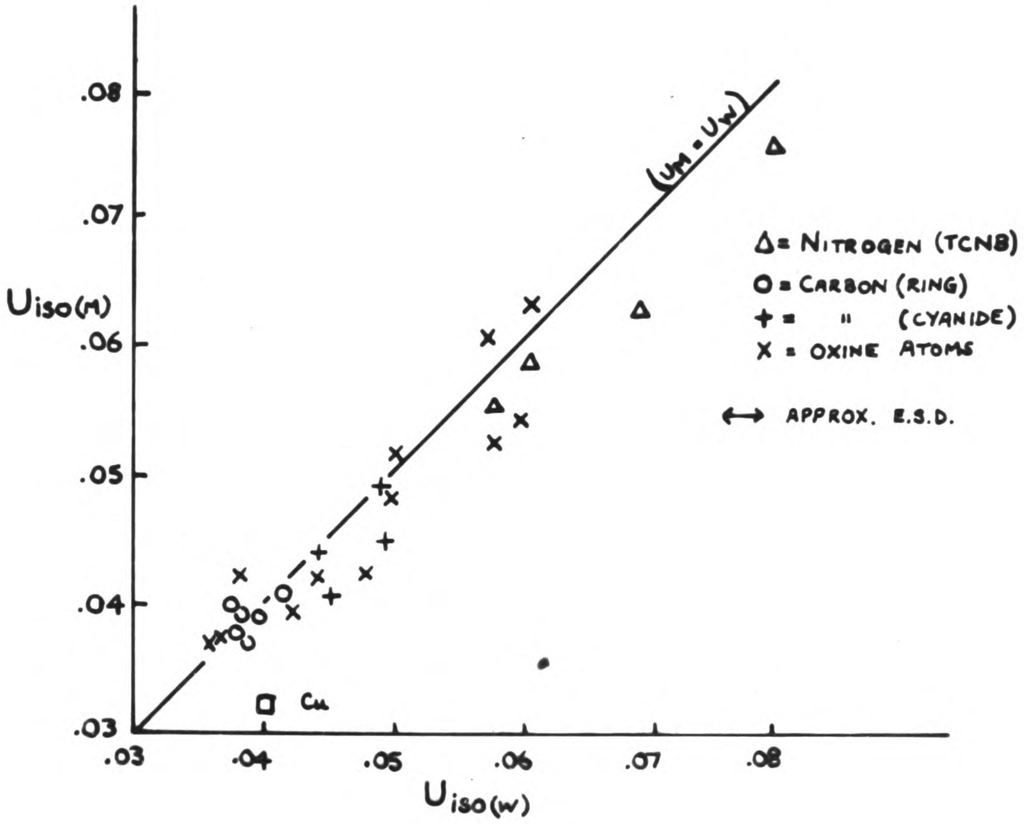


Fig. IV.3. Comparison of $U_{iso(M)}$ with $U_{iso(W)}$ for $CuOx_2.2TCNB$

Table IV.1

Atomic co-ordinates and thermal parameters (x 10^4) for $CuOx_2.2TCNB$ with estimated standard deviations

For each atom the upper value is $P_{i(W)}$, the lower $P_{i(M)}$ and hydrogen atoms are omitted.

The value of t_i^2 is tabulated for each parameter.

	x/a	$t^2_{(x)}$	y/b	$t^2_{(y)}$	z/c	$t^2_{(z)}$	U(iso)	$t^2_{(U)}$
Cu	0(0)		0(0)		0(0)		402(7)	77
	0(0)		0(0)		0(0)		323(5)	
O(1)	761(6)	0.1	-740(6)	0.5	1184(4)	1.7	439(13)	1.4
	758(8)		-746(7)		1178(4)		418(12)	
N(1)	-502(7)	0.2	2140(7)	1.0	822(4)	1.8	366(14)	0.2
	-506(9)		2150(8)		814(4)		375(13)	
N(2)	7054(11)	0.2	2417(10)	0.2	5536(5)	2.3	783(21)	0.6
	7046(14)		2410(13)		5549(7)		757(25)	
N(3)	7221(9)	0.1	-2065(8)	0.0	3788(4)	0.2	577(18)	1.2
	7216(11)		-2063(10)		3791(5)			
N(4)	3765(9)	0.4	1754(8)	0.7	-0015(5)	0.9	603(18)	0.6
	3756(11)		1743(10)		-0022(6)		583(19)	
N(5)	3836(10)	0.7	6136(9)	0.4	1714(5)	0.0	694(20)	7.4
	3823(12)		6127(10)		1713(6)		619(20)	
C(1)	-1144(10)	0.0	3584(10)	0.1	586(5)	0.3	477(19)	4.0
	-1144(11)		3579(10)		591(5)		425(17)	
C(2)	-1240(11)	0.0	5036(11)	0.7	1307(5)	3.5	574(21)	3.3
	-1242(13)		5049(11)		1292(6)		520(20)	
C(3)	-707(11)	0.0	4992(11)	1.0	2222(6)	1.6	596(22)	3.9
	-709(13)		4976(12)		2233(6)		537(21)	
C(4)	475(12)	1.1	3204(12)	0.7	3464(6)	0.0	579(23)	0.6
	456(15)		3189(13)		3463(7)		604(23)	
C(5)	1012(11)	1.0	1677(11)	0.7	3616(6)	1.4	603(22)	0.6
	1031(15)		1662(13)		3627(7)		627(24)	
C(6)	1122(11)	0.1	277(10)	0.1	2880(5)	0.8	501(19)	0.5
	1128(13)		283(11)		2887(6)		520(20)	
C(7)	652(9)	0.4	444(9)	0.5	1926(5)	0.3	381(17)	2.5
	662(12)		454(10)		1930(5)		419(17)	
C(8)	15(9)	1.1	2064(9)	0.0	1758(4)	0.0	370(17)	0.1
	0(11)		2061(9)		1759(5)		379(16)	

Table IV.1 (cont)

	x/a	$t^2_{(x)}$	y/b	$t^2_{(y)}$	z/c	$t^2_{(z)}$	U(iso)	$t^2_{(U)}$
C(9)	-72(10)	0.1	3452(10)	0.0	2514(5)	0.1	484(19)	0.1
	-78(12)		3453(11)		2516(6)		475(18)	
C(10)	5419(10)	0.0	2591(10)	0.3	3378(5)	0.7	415(18)	0.3
	5417(11)		2584(10)		3384(5)		401(16)	
C(11)	6028(9)	0.0	2143(9)	0.1	3721(4)	0.1	375(17)	0.7
	6028(11)		2147(10)		3718(5)		394(16)	
C(12)	6074(9)	0.1	581(8)	1.2	3093(4)	0.0	376(17)	0.0
	6077(11)		567(9)		3094(5)		379(16)	
C(13)	5575(9)	0.1	435(9)	0.2	2120(5)	1.6	384(17)	0.1
	5511(11)		440(9)		2111(5)		392(16)	
C(14)	4903(9)	0.6	1893(9)	0.2	1775(4)	0.1	384(17)	0.2
	4913(11)		1887(9)		1773(5)		373(16)	
C(15)	4855(9)	0.9	3454(9)	2.2	2407(4)	1.0	396(17)	0.1
	4841(11)		3473(9)		2400(5)		390(16)	
C(16)	6606(10)	0.0	2283(9)	0.2	4718(5)	6.2	481(19)	0.0
	6605(12)		2277(11)		4737(6)		483(18)	
C(17)	6709(10)	1.5	-890(9)	5.7	3472(5)	0.3	450(17)	2.2
	6727(11)		-922(10)		3475(5)		413(19)	
C(18)	4287(10)	0.9	1792(9)	0.0	786(5)	4.3	443(18)	0.2
	4302(11)		1782(10)		771(5)		432(17)	
C(19)	4268(10)	0.4	4940(10)	1.5	2036(5)	1.4	485(20)	1.6
	4258(12)		4957(10)		2027(6)		451(18)	

Table IV.2

Comparison of some bonds and angles from the two determinations (M,W) of $CuOx_2$.2TCNB

(E.s.ds and Δ_i of bonds are in units of 10^{-3}Å ; for angles, units of 0.1°)

BONDS	r_M	$10^3\sigma_M$	r_W	$10^3\sigma_W$	$10^3\Delta_i$	t_i^2
1	1.311	11	1.328	9	+17	1.4
2	1.405	13	1.412	11	+ 7	0.2
3	1.364	13	1.323	12	-41	5.4
4	1.405	13	1.423	11	+18	1.1
5	1.411	14	1.415	12	+ 4	0.0
6	1.336	15	1.321	12	-15	0.6
7	1.393	15	1.402	12	+ 9	0.2
8	1.397	13	1.392	11	- 5	0.1
9	1.423	12	1.424	10	+ 1	0.0
10	1.421	12	1.411	10	-10	0.4
11	1.319	10	1.304	8	-15	1.4
12	1.368	10	1.355	9	-13	0.9
						11.7

ANGLES						
1	123.6	7	123.7	6	+ 1	0.0
2	115.0	8	114.8	7	- 2	0.0
3	121.3	9	120.8	8	- 5	0.2
4	118.2	8	118.5	7	+ 3	0.1
5	121.6	8	121.9	6	+ 3	0.1
6	116.6	8	116.4	6	- 2	0.0
7	125.1	8	125.8	6	+ 7	0.5
						0.9
						12.6

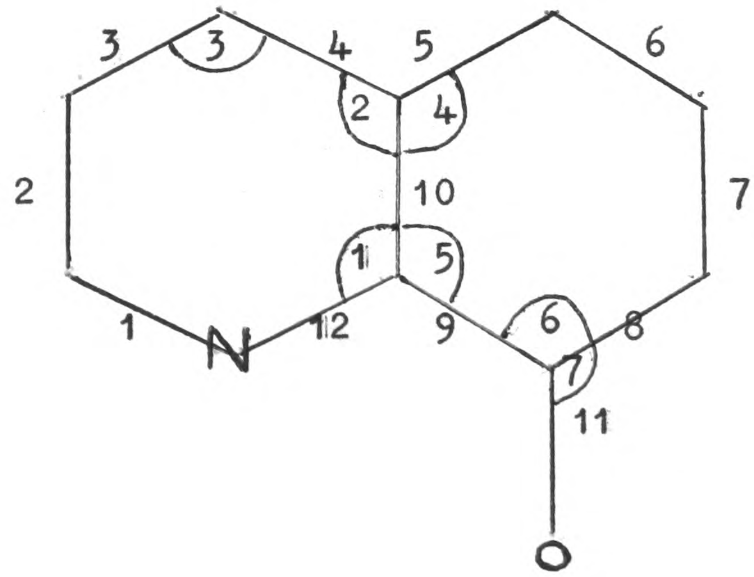


Table IV.5

Comparison of Bonds and Angles in Copper Oxinate and its complexes

(Δ_{ij} of Bonds is in units of 10^{-3} Å ; Δ_{ij} of Angles in units of 0.1°)

	α-$CuOx_2$	β-$CuOx_2$	$CuOx_2$.2TCNB(W)		$CuOx_2$.2TCNB(M)		$CuOx_2$PA		$CuOx_2$.TCNQ	Mean(Å)
BONDS	$10^3 \times \Delta$	$10^3 \times \Delta$	$10^3 \times \Delta$	t^2	$10^3 \times \Delta$	t^2	$10^3 \times \Delta$	t^2	$10^3 \times \Delta$	$\sigma \sim .006$
1	+ 2	+12	+ 6	0.4	-11	1.0	-12	1.4	+ 6	1.322
2	- 3	+12	+ 6	0.3	- 1	0.0	+34	2.9	-11	1.406
3	+ 3	+ 3	-29	5.8	+12	0.8	+18	0.8	+16	1.352
4	- 3	-18	+ 5	0.2	-14	1.2	+22	1.2	- 3	1.418
5	- 4	+ 2	+12	1.0	+ 8	0.3	-13	0.4	+10	1.403
6	+14	+ 6	-28	5.5	-13	0.7	+61	10.0	+23	1.349
7	+15	+29	-18	2.2	-27	3.5	0.0	0.0	-16	1.420
8	-15	+ 8	+ 2	0.0	+ 7	0.3	+10	0.2	- 2	1.390
9	+ 4	- 5	+ 1	0.0	0	0.0	-43	4.5	+ 1	1.423
10	- 3	+ 5	- 9	0.8	+ 1	0.0	+10	0.2	- 6	1.420
11	+ 2	+ 7	-14	2.5	+ 1	0.0	+32	2.6	+ 3	1.318
12	- 5	+12	+ 5	0.3	+ 8	0.6	+30	2.3	- 8	1.360
bond $\sum t_i^2$	13.4	7.4		19.0		8.4		26.2		
ANGLES										$\sigma \sim 0.4°$
1	+ 2	+ 4	+12	4.0	+11	2.4	+ 3			122.5
2	+ 3	+ 7	- 4	0.3	- 2	0.0	+ 1			115.2
3	- 2	+ 2	- 6	0.5	- 1	0.0	+ 1			121.4
4	- 9	-11	- 3	0.2	- 6	0.5	+18			118.8
5	- 5	+ 5	- 8	1.7	-11	1.9	+11			122.7
6	+ 6	+ 2	- 6	0.7	- 4	0 2	+67			117.0
7	- 7	- 9	+ 7	1.3	+ 6	0.5	-89			125.0
angle $\sum t_i^2$	6.0	5.4		8.7		5.5		>40		
$\sum^{b+a} t_i^2$	19.4	12.8		27.7		13.9		> 66.2		

Table IV.6

Comparison of Bonds and Angles in Palladium Oxinate and its complexes

(Δ_{ij} of bonds is in units of 10^{-2}Å ; Δ_{ij} of angles in units 0.1°)

	$PdOx_2$		$PdOx_2$.CA		$PdOx_2$.TCNB		
BONDS	$10^2 x \Delta$	t_i^2	$10^2 x \Delta$	t_i^2	$10^2 x \Delta$	t_i^2	Mean(Å) $\sigma \sim 0.02$
1	0	0.0	- 2	0.2	0	0.0	1.33
2	+ 2	0.4	+ 2	0.4	- 3	0.5	1.40
3	+ 6	4.0	- 3	1.0	- 4	1.8	1.36
4	- 3	1.0	+ 2	0.3	0	0.0	1.44
5	+ 4	1.8	- 7	5.5	+ 2	1.0	1.40
6	+ 5	2.8	- 2	0.1	- 2	0.4	1.41
7	- 1	0.1	+ 5	2.8	- 3	0.5	1.40
8	+ 4	1.8	- 2	0.4	- 2	0.4	1.40
9	+ 4	1.8	+ 1	0.1	- 5	2.7	1.44
10	+ 2	0.4	- 1	0.2	- 2	0.4	1.43
11	- 2	0.4	0	0.0	+ 2	0.4	1.31
12	- 1	0.1	+ 4	1.8	- 2	1.0	1.40
bond $\sum t_i^2$		14.6		12.8		9.1	

ANGLES	$10\Delta^\circ$		$10\Delta^\circ$		$10\Delta^\circ$		$\sigma \sim 1.0^\circ$
1	0	0.0	+2.0		-2.0	1.6	121.0
2	-1.0	0.3	-1.0		+2.0	1.6	116.0
3	+3.3	3.2	-2.7		-0.7	0.1	118.7
4	-0.7	0.1	+1.3		-0.7	0.1	118.7
5	-0.3	0.0	-0.3		-0.3	0.2	122.3
6	+0.3	0.0	-0.7		+0.3	0.0	116.7
7	+0.7	0.1	-1.3		+0.7	0.2	125.3
angle $\sum t_i^2$		3.7		5.0		3.8	
a + b $\sum t_i^2$		18.3		17.8		12.9	

Table IV.7

Comparison of Bonds and Angles in Copper Oxinates, Palladium Oxinates, and predictions from Hückel Theory

	CuOx$_2$(mean)	$t^2_{Cu/Pd}$	PdOx$_2$(mean)	Hückel calc^n
BONDS	$\bar{\sigma} \sim 0.007$Å		$\bar{\sigma} \sim 0.02$ Å	(Ref.)
1	1.322	0.1	1.33	1.32
2	1.406	0.0	1.40	1.40
3	1.352	0.1	1.36	1.38
4	1.418	0.8	1.44	1.41
5	1.403	0.0	1.40	1.41
6	1.349	6.3	1.41	1.38
7	1.420	0.7	1.40	1.41
8	1.390	0.2	1.40	1.38
9	1.423	0.5	1.44	1.41
10	1.420	0.2	1.43	1.42
11	1.318	0.1	1.31	
12	1.360	3.0	1.40	1.35
		12.0		
ANGLES	$\bar{\sigma} \sim 0.4°$		$\bar{\sigma} \sim 1.0°$	
1	122.5	0.2	121.0	
2	115.2	0.5	116.0	
3	121.4	6.0	118.7	
4	118.8	0.0	118.7	
5	122.7	0.1	122.3	
6	117.0	0.0	116.7	
7	125.0	0.0	125.3	
		6.8		
		====		
		18.8		

Table IV.8

Comparison of bonds and angles in paraquat ion from different structures (cf.Table IV.5)

	$pqCuCl_4$.		$pqBr_2$		pqI_2		$pqCoCl_4$		$pqCu_2Cl_4$		$pqPdCl_4$		Mean(Å
BONDS	$10^3\Delta$	$10^3\sigma$	$10^3\Delta$	$10^3\sigma$	$10^3\Delta$	$10^3\sigma$	$10^3\Delta$	$10^3\sigma$	$10^3\Delta$	$10^3\sigma$	$10^3\Delta$	$10^3\sigma$	$\sigma \sim 0.005$
N - Me	+2	6	-6	9	-19	14	0	18	-21	15	+58	30	1.472
N - C_2	-4 -7	6	+2 +5	9	- 4 +11	14	+21 +22	18	0 -13	15	+ 8	20	1.342
C_2 - C_3	+4 -6	6	+ 4 -19	9	+ 3 +19	14	+29 + 6	18	+ 1 - 6	15	+37	30	1.373
C_3 - C_4	-3 -3	6	- 5 +14	9	+ 2 + 8	14	+ 7 0	18	-15 -24	15	- 6	30	1.396
C_4 - C_4'	+4	9	-10	12	+16	20	-17	25	+22	22	+56	40	1.464
$\sum^{8} t^2$		4.3		9.4		6.1		6.1		7.5		7.2	
ANGLES	10Δ		10Δ		10Δ		10Δ		10Δ		10Δ		
Me-N-C_2	+7 +2	7?	+ 3 - 4	8	- 6 + 4	9	-10 +25	12	- 4 + 5	11	-10	14	
C_4'-C_4-C_3	+1 +6	7?	+ 5 - 5	8	-26 + 3	9	0 - 9	12	+ 6 -24	11	-18	14	
$\sum^{ang} t_i^2$		2 ===		3.8 ===		7.0 ===		6.7 ===		5.3 ===		3.2 ===	
$\sum^{12} t_i^2$		6.3		13.2		13.1		12.8		12.8	$\sum^{7} t_i^2$	10.4	

CHAPTER V.

STRUCTURE ANALYSIS AND DISCUSSION
of the
COBALTHEXAMMINE MIXED-VALENCE CHLOROCUPRATES(I,II)

MIXED VALENCE HALIDE COMPOUNDS

Several 1:1 mixed valence compounds containing metal halide anions have been investigated by X-rays. These have usually contained oxidation states differing by two units and among the best known are Rb_2SbCl_6 (Jensen) and $(NH_4)_2SbBr_6$ (Lawson). These both contain discrete SbX_6 octahedra and the second shows two distinct types with Sb-Br lengths of 2.56 Å and 2.80 Å, which implies $Sb(v)Br_6^{-}$ and $Sb(III)Br_6^{3-}$ ions. This difference leads to the existence of a superlattice of weak reflections, and to a very small distortion from cubic symmetry (a = b = 10.66 Å, C = 2 x 10.76 = 21.52 Å). The strong reflections, indexed as pseudo-cubic (Fm3m), have a final R of 0.078; the weak reflections, which lower the symmetry to I4 /amd, had R = 0.197. This shows that relatively small changes in geometry can lead to an interpretable X-ray superlattice.

Mixed valence Lead(II) and (IV) chlorides.

A similar compound is $Co(NH_3)_6PbCl_6$ (Mori 1951), produced from Pb(II) and Pb(IV) chlorides, which shows very strong C-T, presumably outer-sphere between $Pb(II)Cl_6^{4-}$ and $Pb(IV)Cl_6^{4-}$ ions. As the bond distances in these are significantly different, it should be possible to see if they exist in an ordered array. The gross structure of this compound is similar to $Co(NH_3)_6TlBr_6$ with a rock salt lattice, Pa3, (Wat 1950) but there are some extra powder lines (Day 1967) not belonging to this system.

Single crystals (provided by Dr. P. Day) were investigated with copper radiation, although the high absorption coefficient of ~ 600 precludes accurate work. Only zero level photographs, hol, okl and hko were taken which shows the symmetry of the reciprocal lattice to be m3 although there were several reflections which do not belong to Pa3. These had indices

$h = 2n-\frac{1}{2}$, $2n$, $2n+\frac{1}{2}$ (when related to the original lattice constants) and suggests strongly a superlattice. However further analysis was very difficult as there is evidence of twinning. Reflections of large θ are split, not into the usual $\alpha_1-\alpha_2$ doublet, but into 3 equal spaced spots, which can only mean the existence of two axes different by ~ 0.02 Å (in 11.5 Å). It is unlikely that the twinned crystals are tetragonal as the reciprocal lattice has no tetrads (although these could be obscured by the twinning), and might be of 3 orthorhombic pseudo-cubic crystals related by T symmetry (23). In spite of this accident it is probably safe to assume crystallographically different $PbCl_6$ groups with outer-sphere charge transfer.

MIXED VALENCE CHLOROCUPRATES(I) and (II)

The structure of $Cr(NH_3)_6CuCl_5$ (Wat 1961), and the cobalt analogue (Part II), contain a rock salt lattice containing regular $CuCl_5^{3-}$ trigonal bipyramids. The parameters, in Fd3c, which have not been fully refined, are given in Table V.1. The final R was 0.19 and no structure factors have been published but comparison with the other compounds suggests this is the correct structure, and it is shown in Fig.V.1a.

TABLE V.1.

Parameters of Chromium Hexammine(III) Pentachlorocuprate(II)

No/Cell	Atom	x/a	y/b	z/c	B	
32	Cu	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	2.0	
32	Cr	0	0	0	2.0	
64	Cl(axial)	0.175	0.175	0.175	2.0	assumed
96	Cl(equat.)	$\frac{1}{4}$	0.075	-0.075	2.0	
192	N	0.07	0.05	-0.03	2.0	

$a = 22.18$ Å

$Cu-Cl_{ax} = 2.32$ Å

$Cu-Cl_{eq} = 2.35$ Å

An attempt to solve the structure of $Co(NH_3)_6\ _4Cu_5Cl_{17}$ from rotation photographs had been made (Part II). The space-group appeared to be Fd3m (although this has been disproved in Chapter III) and only the copper and cobalt atoms could be located. These were in identical positions to those given above, with the addition of 8 copper atoms at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ etc, but the agreement was poor, R 0.43.

More orthodox data collection for $[Co(NH_3)_6]_4Cu_5Cl_{17}$ and "25%Cu(I)" has been described in Chapter III. The pure copper(I) compound is described first.

Structure Analysis of $[Co(NH_3)_6]_4Cu_5Cl_{17}$

The positioning of the heavy atoms as described above is unavoidable both from space-group symmetry and the similarity of the intensity data to the copper(II) compound. (The cobalt atoms are actually in two equivalent 16-fold sets at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$). Neither Patterson nor Fourier syntheses are useful at this point as there is too much symmetry, and cobalt and copper have nearly equal X-ray scattering powers. The positioning of the chlorine atoms must be on a trial and error basis, compatible with both the space-group and chemical criteria. These latter must preclude bunching of negative charge, and include a close similarity to the copper(II) structure. The 126 chlorine atoms in the cell can be split into 3 groups:- 32 in (d), xxx; 96 in general positions (f), xyz; and 8 in (b), $\frac{3}{8}\frac{3}{8}\frac{3}{8}$. The first group can be positioned tetrahedrally about the 8-fold copper atom (A) and bonded also to the 32-fold copper atoms (B). (See Fig. V 2). This is the only feasible coordination for copper atom (A) and it is most unlikely that this is an isolated ion. A linear Cu-Cl-Cu bridge has not otherwise been found, and the chlorine atom was placed roughly at the centre (x/a = 0.190). This is virtually identical with the position of one axial chlorine in the copper(II) compound. At this stage there should be enough scattering material placed to give a useful Fourier map. (The computation of these maps was impossible directly and was carried out in the non-centrosymmetric sub-group F222. Structure factors are referred to the non-centric origin in Fd3 (Table VII 7) but parameters (Table V 2) are given relative to the centric origin for ease of comparison with related structures).

The map showed acceptable peaks for all atoms introduced and two large peaks at 0·28, 0·07 , -0·08, and 0·28 , -0·08, 0·07, related in position by the plane 110. As the second was about half the height of the first, it is probably a "ghost" peak, produced by false symmetry. The first was used for position (f) and gave an acceptable tetrahedral coordination for copper (B). Three rounds of least-squares preceded another Fourier map which showed no ghost peak and two independent nitrogen positions giving excellent octahedral cobalt hexammine cations. These octahedra are in virtually the same orientation as those in $Cr(NH_3)_6CuCl_5$ (e.g. Tables V.2 and V.1. The chlorine atom at $\frac{3}{8}\,\frac{3}{8}\,\frac{3}{8}$ had been included as this is the only position allowed by symmetry, but there was little evidence for it from the Fourier syntheses and its U_{iso} had risen to 0.11, very high for an ionic structure. It is in a large hole, with a minimum radius of ~ 4 Å, and might be vibrating excessively. A model was investigated with it forming the fifth coordination position of the copper(B) atoms and with statistical occupancy of 4 positions. This showed no better agreement although it is chemically acceptable as it is very close to the Cu(II) structure and involves penta-coordination.

Although the refinement had converged at 0.146 and the structure is chemically very acceptable, the agreement of structure factors is poor. A detailed analysis of this was carried out, firstly by comparing F_{obs} and F_{calc} and secondly F_{hkl} and F_{khl}. For the first group, the reflections were split into those to which the heavy atoms had a large (in phase) contribution and those with none at all. The first set showed excellent agreement, $R = 0.066$, but the second set had $R = 0.22$. Although these latter are significantly weaker, this is still a serious disagreement, particularly when these weaker reflections can be measured experimentally to ±5% in F (Chapter III). This implies that the heavy atoms are definitely located, but the lighter atoms, particularly the chlorines, are not completely correct although they have a very close relation to the actual structure. The overall agreement is however very similar to that in the bromoantimonate discussed earlier.

The discrepancy is probably explained by a comparison of F_{hkl} and F_{khl} both for F_{obs} and F_{calc}. In effect this measures the closeness of the space group to Fd3m rather than Fd3, as for the former $F_{hkl} \equiv F_{hlk}$. For a random distribution of atoms in Fd3, the merging $R_{hkl \leftrightarrow khl}$ should be ~ 0.8, whereas it is very much lower (Chapter III). This is represented in Fig. V.3. where the maximum value of a F_{hkl}/F_{khl} pair is plotted against the minimum. The plot for F_{obs} suggests that F_{hkl} and F_{khl} always have the same sign, whereas there is no such constraint on F_{calc}. This implies very close mirror symmetry down $\{110\}$, which is not represented in the calculated model. There are two ways by which this symmetry can be approached. Either there is a disordered structure with approximately equal amounts of two mirror-related arrangements, or the crystal consists of twinned sections related by the $\{110\}$ plane.

For the first case we can write:

$$F_{hkl} = (F(hkl,xyz)) + (1-\lambda)(F(hkl,yxz))$$

which can be rewritten as:

$$F_{hkl} = (F(hkl,xyz)) + (1-\lambda)(F(khl,xyz))$$

A model was set up for calculation with a chlorine atom at xyz with occupancy λ and an identical atom at yxz with occupancy $1-\lambda$. A value of 0.7 was taken for λ, as this was implied by the first Fourier map, and λ was refined. It converged to a value of approximately unity, reverting to the same situation as before.

The second case can be represented by:

$$F^2_{hkl} = (F^2(hkl,xyz)) + (1-\mu)(F^2(hkl,yxz))$$

or

$$(F^2(hkl,xyz)) + (1-\mu)(F^2(hlk,xyz))$$

There is no way of evaluating μ except by writing a programme to minimise not $\sum w(F_{obs}-F_{calc})^2$ but $\sum w(F^2_{obs}-F^2_{calc})^2$ and introducing it as a parameter. There is no clear justification for this, especially as the present least-squares programme would need considerable modification. Data collection on several distinct crystals might also produce a crystal with better differentiation between $|F_{hkl}|$ and $|F_{khl}|$. There is no morphological evidence as all the crystals are beautifully formed octahedra with no $\{hkl\}$ faces.

In spite of this the structure would appear to be basically correct, as it is chemically reasonable and the cobalt hexammine octahedra, which are the only definitely known chemical species, are well defined on the Fourier maps. It consists (Fig. V.3, Table V.2) of discrete $Co(NH_3)_6^{3+}$ ions with $Cu_5Cl_{16}^{11-}$ ions and, presumably, single chloride ions, vibrating excessively. This complex chlorocuprate has a central copper atom exactly tetrahedrally coordinated by 4 chlorines at 2.26 Å. The four other copper atoms have a coordination number between 3 and 4, with one long bond of 2.49 Å and 3 shorter of 2.32 Å, with the angle between these 99° instead of tetrahedral. An inviting speculation is that $CuCl_4^{3-}$ and $CuCl_3^{2-}$ ions occur in solution and condense together in the ratio 1:4 to give the final complex. This has T (or 23) symmetry deviating only from $\bar{4}3m$ by a rotation of the terminal $CuCl_3$ groups by ~18°.

Structures of the Intermediate Compounds

We can see clearly how the copper(II) and copper(II) structures are related (Figs. V.1 and V.2) and how intermediate compounds could be formed over the whole range. The 32 Co and 32 Cu (B) remain in the same positions as do the ammine groups. We start with the copper(II) structure which has 4 apical Cu-Cl bonds "pointing" at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$. These would appear to remain in all the structures and at some stage the "hole" at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ is filled by a copper(I) ion (A), the exact point at which this starts depending on the stoichiometries of the intermediates. In the copper(I) structure the other apical chlorine has disappeared and the equatorial chlorines have moved about 0.6 Å. The formulation of the intermediates must involve fractional occupation numbers, and those between "0% Cu(I)" and "50% Cu(I)" must lie in Fd3c. This means that the symmetry of the copper atom is 32 and the overall occupancy, as seen by X-rays, of the apical positions must be equal. (The local situation may be of lower symmetry, randomly distributed). The total occupancy of these sites must decline regularly from 2 to 1 over the system as the average oxidation number of copper atoms (B) change similarly. The difference between the two stoichiometries depends only on the point of introduction of the fifth copper atom (A) and its attendant chloride ion.

The overall average electron distribution can be broken down in more than one way to local arrangements with less than space group symmetry. One such is where the $CuCl_5^{3-}$ bipyramid changes to $Cu(I)Cl_4^{3-}$ groups, which must be randomly oriented in two directions. These will be trigonal pyramids but it will be hard to determine if the 3 basal chlorines are coplanar with the copper atom. In the pure copper(I) phase, however, the orientation of these pyramids is ordered so we must assume a change at some stage to disorder. Assuming (as an example only) that the 50% copper(I) compound is totally disordered, then the average structure around the copper could be represented by two half occupied axial chlorine positions with either 3 fully occupied equatorial sites or 6 half-filled sites related by the diad axes.

An interesting possibility is that for compounds with small amounts of copper(I), the amount of "interstitial" copper (A) depends on the chance arrangement of the copper (B) units. For this (A) atom to be incorporated, a hole (X) (Fig. V.2) must be made for its attendant chlorine. This is impossible in the copper(II) structure and is only likely if copper(I) pyramids (B) replace copper(II) bipyramids. If enough of these are aligned correctly a large enough hole will be left at their bases. This number will be between 1 and 4 and this can be related to Fig. II.1. If it is 1, we follow a straight line to a limiting composition of $Cu(II)_3Cu(I)_2Cl_{20}^{12-}$ at 40% copper(I), whose structure is shown below, Fig. V.5.

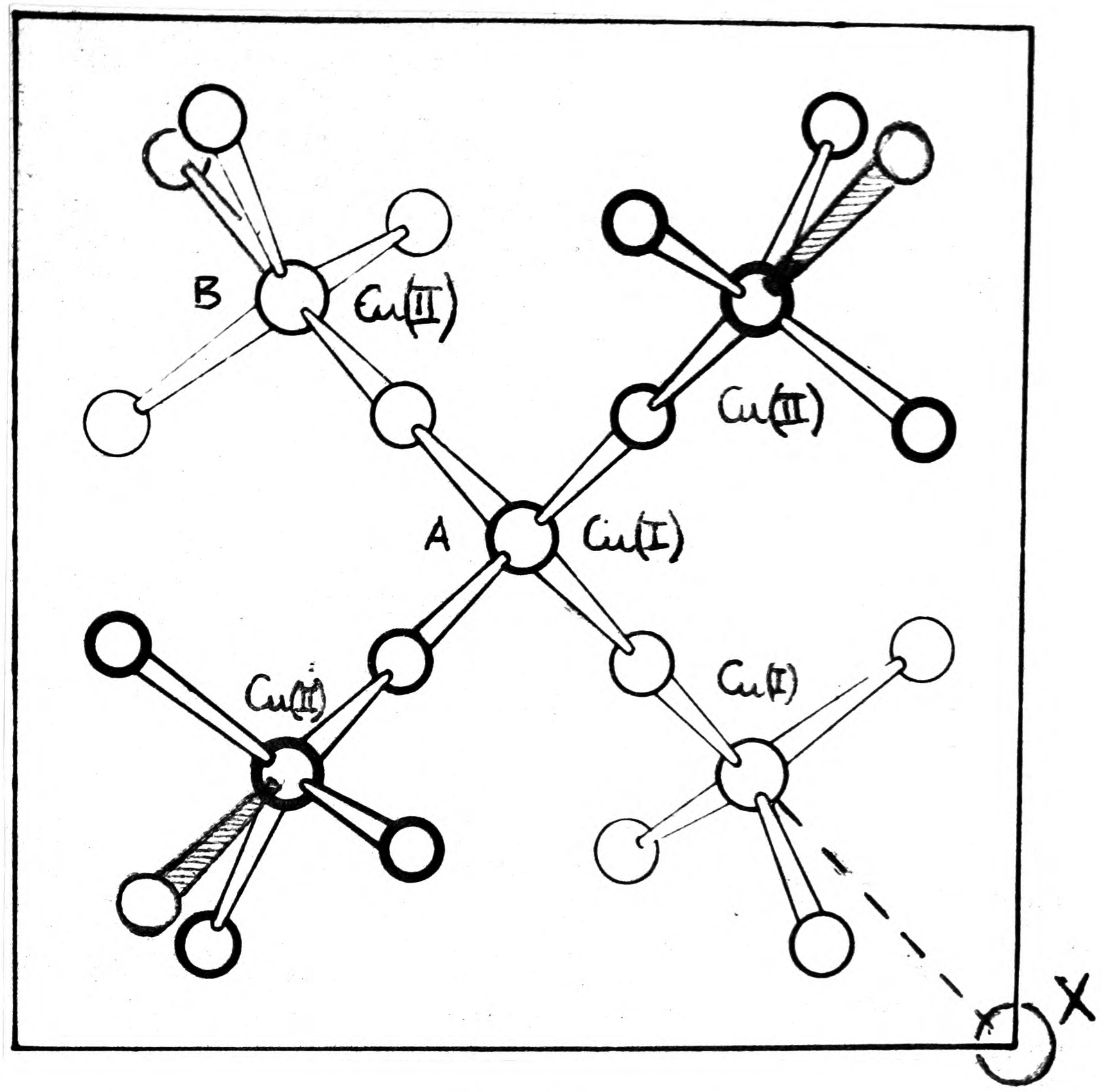


Fig. V.5.

This would be acceptable but for the chemical analyses, and the fact that the hole for the chloride ion is small and negatively charged. If however we require the absence of two apical chlorines to make a large enough hole for the introduction of the new chloride ion, and make the assumption that the arrangement of Copper(I)(B) ions is random (true if Cu(I)/Cu(II) is small), we can argue as follows: For a possible Cl^- site, the change of being surrounded by two Cu(I) ions is $4!\,x^2/2!2!$ where x is the fraction of copper(I). The chance that both will have their bases towards the site is $\frac{1}{4}$ of this, or $\frac{3}{2}x^2$. The corresponding formula for sites with 3 and 4 apical chlorines absent are $\frac{1}{2}x^3$ and $x^4/16$. If $x \sim 0.2$ these sites cannot be formed independently and the model becomes very involved. However we can now postulate that the sites will begin to be ordered (although no evidence for this exists). The exact arrangement of the intermediates is very comparable to the problem of hydrogen bonds in ice or ammonia.

It is much more difficult to guess at the structures of the compounds with little Cu(II), partly because the stoichiometry in that region is even less certain. The d^9 configuration of Cu^{2+} makes regular tetrahedral coordination of (B) unlikely and perhaps the best solution is a random arrangement of $[Cu(I)_4Cu(II)Cl_{17}]^{11-}$ ions with Cu(II) ions in (B) sites. This would require the shift of a chlorine atom (X) from a hole to the fifth coordination position of a (B) site.

Crystallographic Data for Intermediate Compounds

The main evidence for the absence of a superlattice in these compounds was from rotation photography (Part II) and it is possible that very weak reflections could have been obscured by the high fluorescent background. (It is significant that the reflections due to the superlattice in the chloroplumbates(II,IV) were only visible on Weissenberg films.) However the precession photographs of the 25% Cu(I) compound showed no spots not belonging to Fd3c, and this is not unreasonable for compounds which have no discrete stoichiometries.

This implies that intermediate compounds must be treated as statistically disordered and that the atomic positions will be occupied by fractional amounts of atoms. The data collected on the 25% Cu(I) compound appeared good since there was a relatively large percentage of measurable reflections to which only the light atoms contribute. Since the structures of the end compounds are very similar it is unlikely that the data from an intermediate can give much information but it may answer three questions:

(a) What is the occupancy of the (A) site at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$?

(b) What is the occupancy of the axial chlorine atoms?

(c) Can the equatorial chlorine atoms be distinguished as filling either a single set of positions or two unrelated sites (implying distinct Cu(I) and Cu(II) atoms statistically disordered)?

The data was analysed both by Fourier and least squares methods, and three approaches were followed.

(1) A least squares calculation was done using Watanabe's parameters for the pure copper(II) compound. Although it is impossible that these are correct, the structures must be very similar and refinement converged with R = 0.110. These parameters are given in Table V.3 and imply that Watanabe's structure is almost certainly correct. A difference map was calculated, on which two main features appeared. These are shown in Fig. V.5., and are peaks of $3e/\text{Å}^3$ about 0.3 Å from the copper (B) atom and large spherical peaks of $6e/\text{Å}^3$ just off the equatorial diads. The first implies very marked vibration of the copper atom or statistical disorder of these displaced from ½½½. The second peaks are in almost exactly the same relationship to the copper (B) atom as the 96 'equatorial' chlorine atoms in $[Cu_5Cl_{16}]^{11-}$, both $\sim$ 0.6 Å from the diad. As the latter atoms have final peak heights of $\sim 30e/\text{Å}^3$, it is likely that these peaks are a pair of chlorine sites with total statistical occupation $\sim$ 25% connected with the copper(I) atoms. There was no significant difference density either at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ or in the axial or equatorial chlorine atom positions, but this might be due to errors in temperature factors, or overall scale. The final nitrogen positions are very close to those in the copper(I) compound (and Watanabe's rough ones).

(2) In an attempt to formulate this more precisely, the following model was chosen:

(a) Co, Cu(A) and N in standard positions (cf. copper(I) compound)

(b) Axial and equatorial chlorines from copper(II) compound with 75% occupancy.

(c) Two $CuCl_4$ tetrahedra from copper(I) compound with <u>total</u> occupation 25%, related by equatorial diads.

(d) The copper atom at (A), $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, with
$0 < \text{occupancy} < 25\%$.

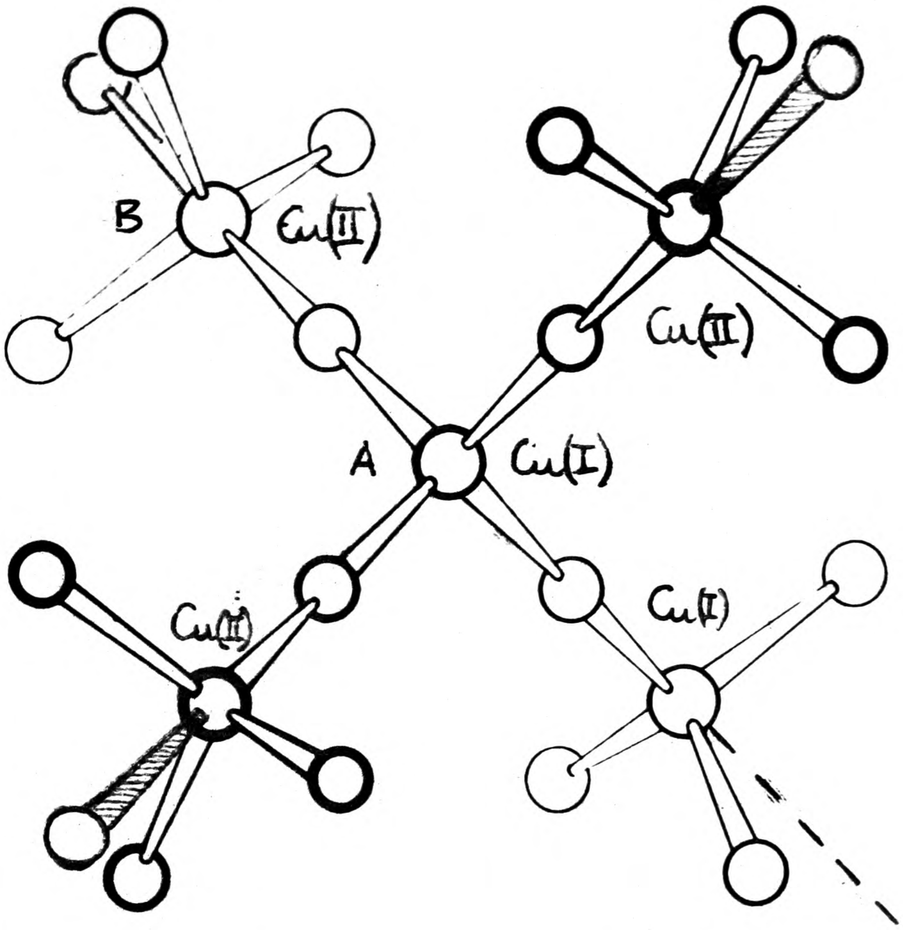
These positions were used to calculate structure factors and carry out least squares refinement. This was not successful and diverged catastrophically. It is clear that the problem has a number of near-singularities in the normal matrix and although the model is plausible, attempts to fix one or more parameters are unlikely to be useful.

(3) This model had complete chlorine atoms situated between the equatorial sites and the "copper(I) sites", 0.6 Å distant. The parameters of these atoms were refined without difficulty to R = 0.082. This approximation of two close disordered sites to a single atom is clearly good (although it is not impossible that, if the compounds are true C-T intermediates, the chlorine atoms occupy a position midway between the sites). The occupancy of site (A) dropped swiftly to zero.

These results suggest that the formula of the intermediate can be written $Co(NH_3)_6 . Cu(A)_0 Cu(B)Cl(eq)_3 Cl(ax)_{1.75}$ where Cu(B) has an average oxidation state of 1.75. The axial chlorine atoms occupy particular sites but there are two sets of half-occupied equatorial chlorine positions, corresponding to random orientation of the $CuCl_4$ tetrahedra. An adequate description is the combination of 75% $Co(NH_3)_6CuCl_5$ with 12½% of each of $Co(NH_3)_6(CuCl_4\uparrow)$ and $Co(NH_3)_6(CuCl_4\downarrow)$ where these are the two orientations.

Evidence from Physical Data

The structures of the intermediate compounds must satisfy the requirements of the absorption spectra andconductivity measurements. The spectra can be explained by intermediates of the type:-



The C-T can then take place by electron-transfer through the chlorine bridges, in a very similar fashion to the solution intermediate. Assuming that the mechanism is not affected by the Cu(I)/Cu(II) ratio, then this presumably determines the intensity of the absorption. At small ratios this should be roughly proportional to the concentration of (A) sites. The lead compound suggests that an outer sphere mechanism may be possible and electron transfer may occur between copper(I) and copper(II) in (B) sites. This might be favoured energetically as it avoids the use of the tetrahedral site (A); absorption would be proportional to x. Data from Fig. II.1. is inconclusive, but for small concentrations of copper(II) either argument leads to a linear dependence of absorption on x.

The conductivity data is more complicated as the end compounds use an ionic mechanism but the intermediates a semi-conductive one. It is possible to postulate outer sphere conductive methods which are presumably dependent solely on the random distribution of copper(I) and copper(II) units. There is a possibility however of chains being set up in the structure for which electron transfer can occur over reasonable distances. These would be the consequence of (A) sites occurring adjacently by chance and could give inner sphere conduction. Outer sphere mechanisms might operate over the short gaps between chains. In this system there is also a chance of atom transfer (Cl) over short distances from a 5 coordinate Cu(II) to an incompletely coordinated Cu(II). The final answer must rest on more physical measurements on the compounds.

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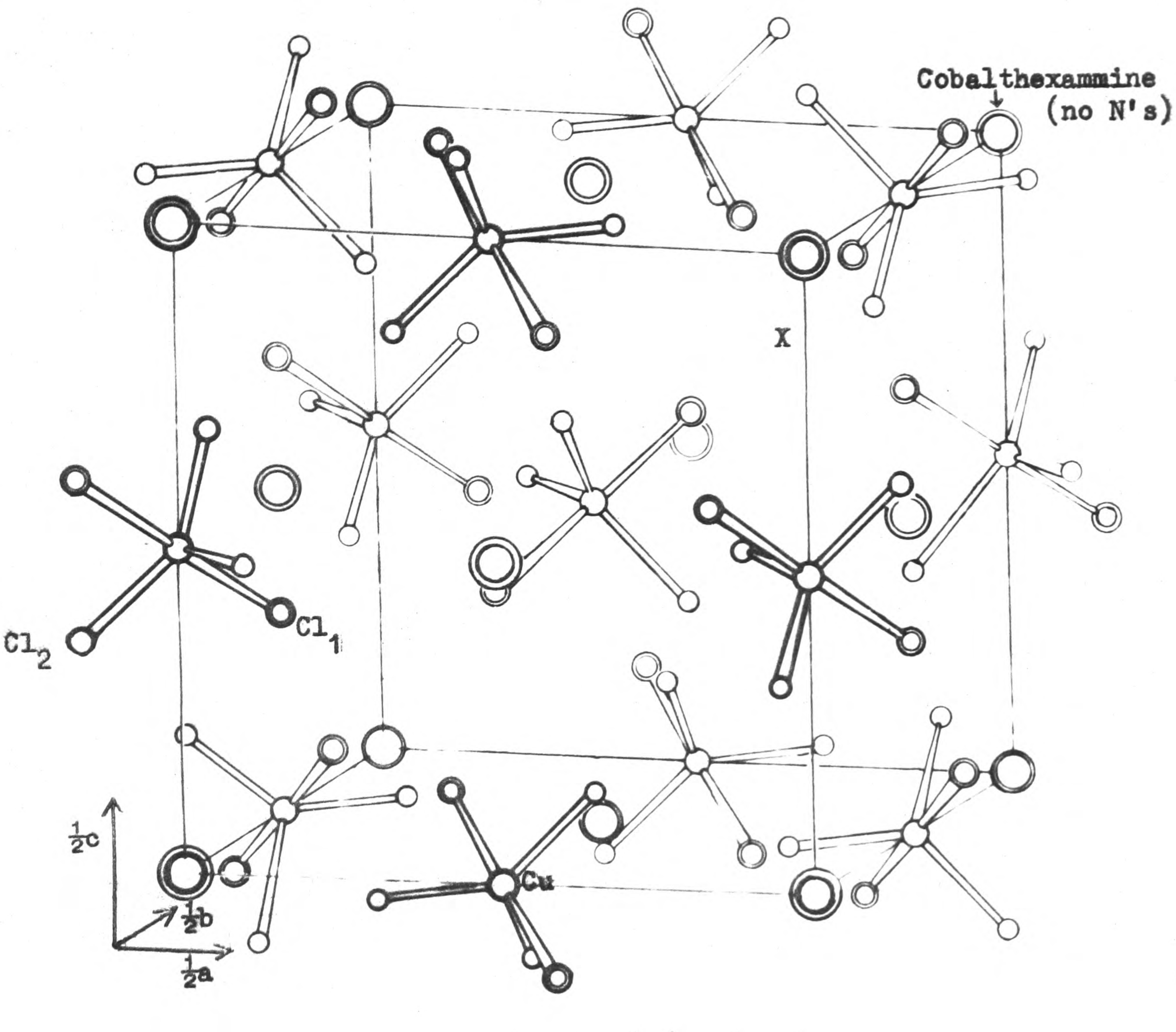


Fig. V.1. Clinographic view of Watanabe's structure

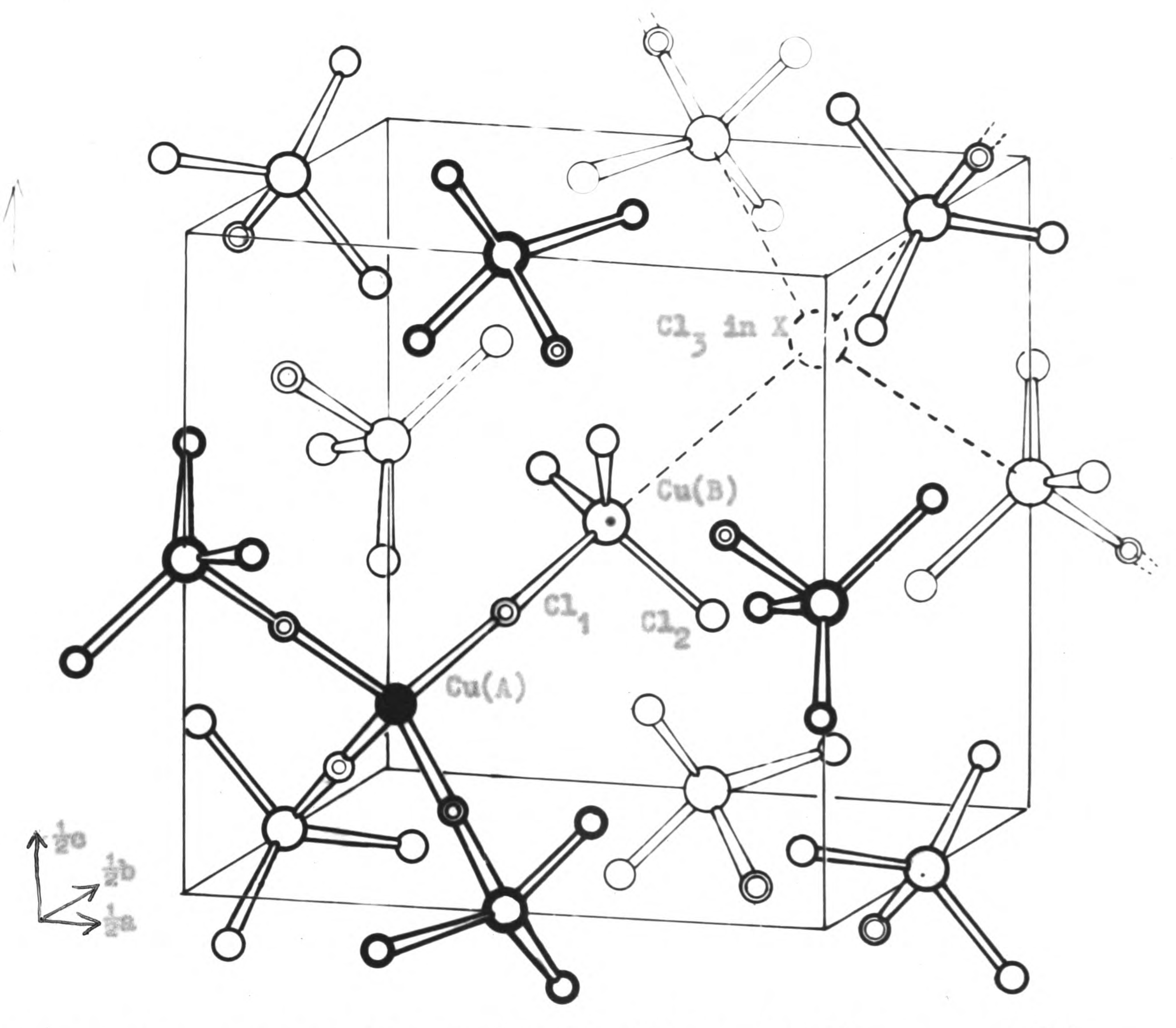
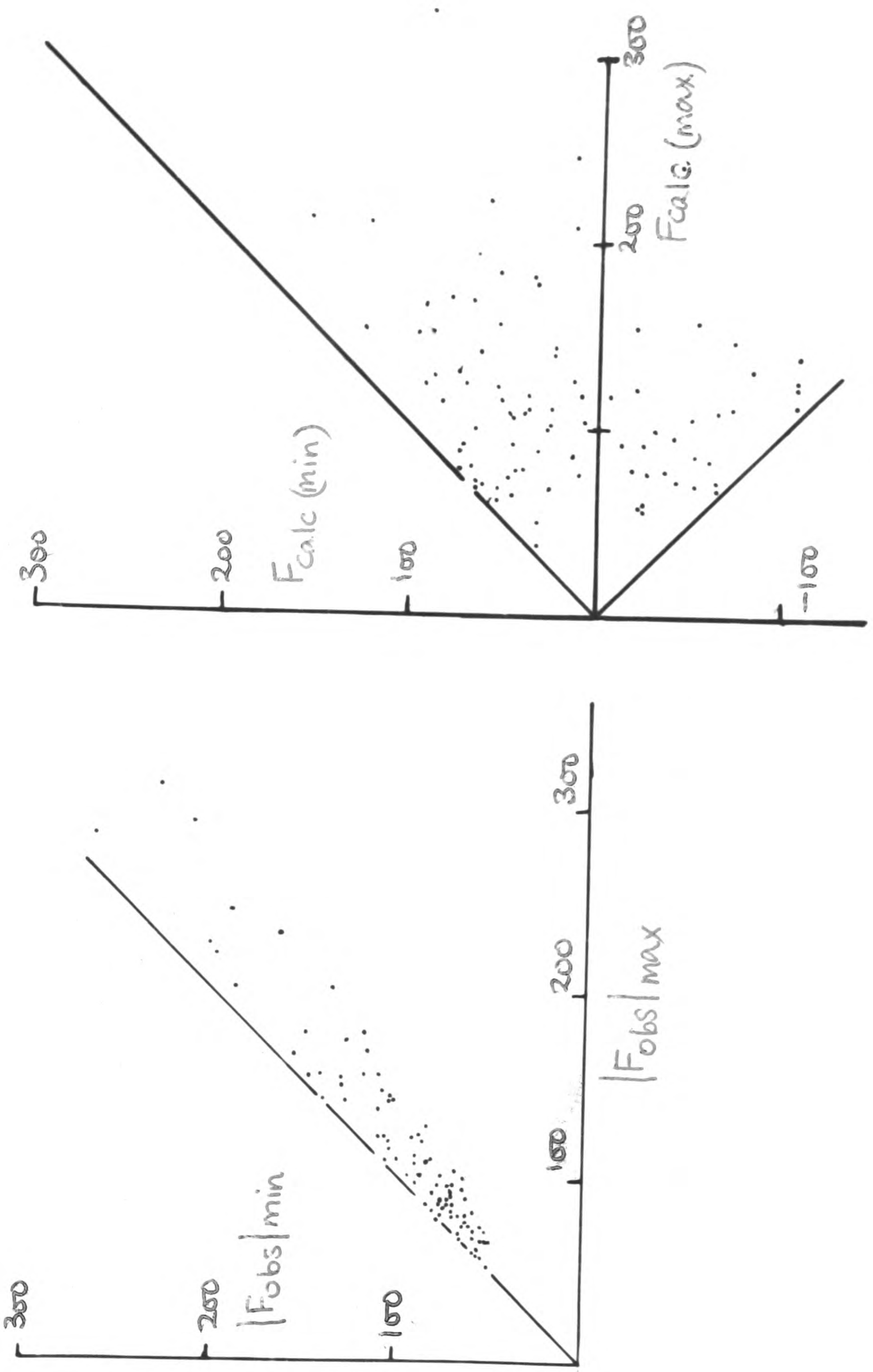


Fig. V.2. Clinographic view of Cobalthexammine Chlorocuprate(I)

(on the smame scale and from the same viewpoint as the preceeding diagram. The cobalthexammine ions have been omitted but are in identical positions.



Figs V.3.a and b. Plots of the maximum of a pair F_{hkl}, F_{khl}, against the minimum, for the chlorocuprate(I). Values in electrons.

Fig. V.4. Difference Electron Density in '25%Cu(I)' Chlorocuprate

Contours are at intervals of $2e/\text{Å}^3$, and the positions of the atoms, except nitrogen and cobalt, which contribute to F_{calc} are shown, (model (1)). The equatorial atoms in model (3) were placed at P and P'. The orientation and origin of the diagram are exactly as in Fig. V.1. but the scale has been enlarged x2.

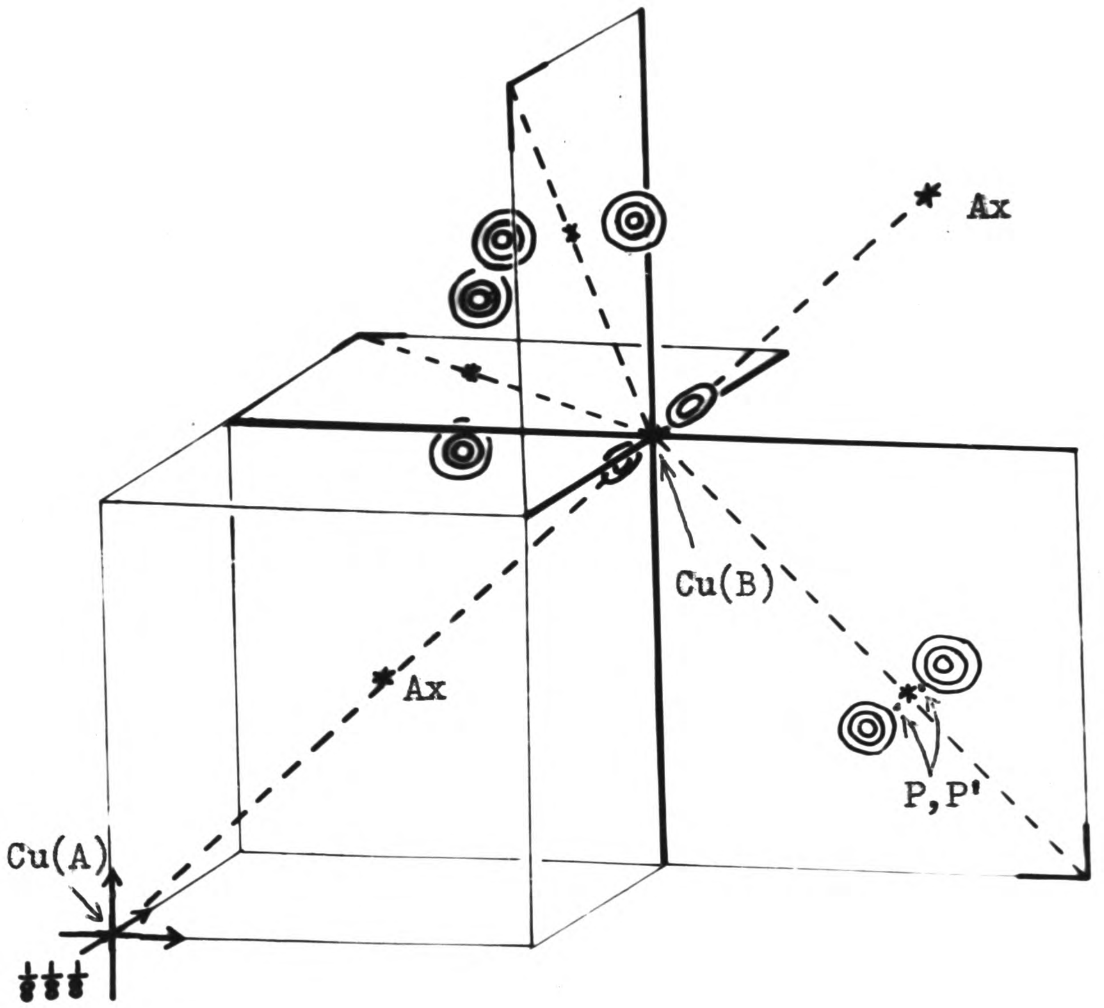


Table V.2.

Final Parameters ($\times 10^4$) for $[Co(NH_3)_6]_4Cu_5Cl_{17}$

(Referred to centrosymmetric origin)

	x/a	σ_x	y/b	σ_y	z/c	σ_z	U_{iso}	σ_U
Co(1)	0	-	0	-	0	-	105	27
Co(2)	5000	-	5000	-	5000	-	137	29
Cu(B)	2509	3	2509	3	2509	3	343	26
Cu(A)	1250	-	1250	-	1250	-	169	33
Cl(bridge)	1849	4	1849	4	1849	4	122	29
Cl(terminal)	2777	5	713	5	-748	5	343	25
Cl(interstitial)	3750	-	3750	-	3750	-	700	(constant)
N(1)	621	13	593	13	-306	13	151	67
N(2)	5350	16	811	16	-269	16	331	86

The temperature factor of the interstitial chlorine atom was kept constant and its ocupation number was refined. This converged to about 0.45 atom per site.

Other Details

Cell parameters; a= 21.80Å   Spacegroup; Fd3, No.203., origin at $\bar{3}$.

Z = 8 formula units   Number of asymmetric units = 96.

Dimensions of crystal; Regular octahedron, side = 0.40 mm $\mu = 45 cm^{-1}$ (Mo)

Number of reflections; 457   Final R = 0.146

Bonds and angles not mentioned in text;

Co(1)-N(1) = 1.98 Å   Co(2)-N(2) = 2.00 Å

N(1)-Co(1)-N(1) = 89.6, 90.4°   N(2)-Co(2)-N(2) = 89.1,90.6Å

Cu(A)-Cu(B) = 4.72Å   Cu(B)-Cu(B) = 7.70 Å

N.B. The structure factors calculated and tabulated in Chapter VII were based on the non-centrosymmetric origin at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$. Their magnitudes are unaltered but their phases are different.

Table V.3.

Parameters for $Co(NH_3)_6Cu(I)_xCu(II)_{(1-x)}Cl_n$ (x=25%)

No unique solution can be given and both sets of parameters, obtained from methods (1) and (3) in the text, are given.

Final Parameters from Method (1) ($\times 10^4$)

	x/a	y/b	z/c	U_{iso}
Co	0	0	0	173
Cu(B)	2500	2500	2500	487
Cl(axial)	1880	1880	1880	540
Cl(equatorial)	2500	760	-760	590
N	704	510	-299	216

From Method (3)

Co	0	0	0	170
Cu(B)	2550	2550	2550	346
Cl(axial)	1880	1880	1880	523
Cl(equatorial)	2621	768	-756	346
N	707	511	-298	292
Cu(A)	1250	1250	1250	300(assumed)

The ocupancy of the Cu(A) sites was refined and converged to a value of 0.12 per site. This is probably not significant.

Other Details

Cell parameter; a= 21.81Å Spacegroup; Fd3c, No.228. Z= 32 formula units.

Origin at $\bar{3}$ for parameters, at 23 for S.F.s.

Number of reflections; 171 Final R = 0.122 (method(1)), 0.087 (method(3))

Bonds and angles from method (1):

Cu-Cl(ax) = 2.34 Å Cu-Cl(eq) = 2.35Å Co-N = 2.01 Å

N-Co-N = 89.8, 90.2°

CHAPTER VI.

STRUCTURES OF THE PARAQUAT METAL CHLORIDES
AND
DISCUSSION OF THEIR CHARGE-TRANSFER

THE STRUCTURES OF THE PARAQUAT SALTS

Although the structures of the paraquat compounds are unequivocal, mere presentation of parameters and diagrams is not very useful as this gives no very clear idea of the arrangement of the ions in space. Accordingly I have tried to select any features which are interpretable in terms of the charge-transfer and in particular to try to systematize features common to one or more structures. The presentation is thus not necessarily structure by structure, but rather by parallel discussion of common points. In the diagrams I have emphasised the features I feel important, particularly the packing of the ions. Although the compounds have been mainly studied from the viewpoint of charge-transfer, the complex anions are also interesting and are discussed separately as coordination compounds.

Gross Aspects of the Structures

All the structures have isolated paraquat ions with the mmm symmetry demonstrated, (except for pqPdCl$_4$, with 222 only). The cobalt and palladium compounds have the expected tetrahedral $CoCl_4{}^{2-}$ and square planar $PdCl_4{}^{2-}$ anions but both copper anions are chain structures (along the needle axes). These can be formulated as $(Cu(I)Cl_2)_n^{n-}$ and $(Cu_2(II)Cl_6)_n^{2n-}$. It will be remembered that the latter compound is determined only at low resolution although the heavy atoms are moderately accurate.

Structural Interpretation of the Charge-Transfer

As described in the introduction, there is no particular feature of the paraquat ion which confers on it the property of electron acceptor and the ion must be considered as a whole. There are probably about four possible geometric effects we could look for in these complexes:-

(a) A reasonably large planar system in the anion which is parallel to and overlaps the aromatic cation.

(b) A short contact between a specific atom, probably the nitrogen, in paraquat and a chlorine of the anion.

(c) A direct "outer-sphere" interaction between the metal atom and the aromatic system, which would be difficult to observe unless there were some very short distances.

(d) A chlorine atom approaching the centre of the aromatic system, with the latter preferably in line with the metal-chlorine vector.

(e) There have been recent speculations that hydrogen atoms of phenyl groups, etc. can fill the coordination positions of a metal atom. On this unproven hypothesis it is just conceivable that a $M{-}{-}{-}H_3{\equiv}C{-}N$ system can be set up with hyperconjugation helping the "conduction" of electrons.

Features of the Structures

(All arguments involving distances or angles involve effects several times larger than 3e.s.d.s).

The main feature common to all structures is the proximity of one of the chlorine atoms to the nitrogen atom. The separation ranges from 3.23 to 3.84 Å, and the nitrogen-chlorine vector is approximately perpendicular to the paraquat ion in all four structures, although this is not too surprising. It is impossible to deny that this might be chance or that it is an accidental consequence of a more important structural feature that has not been noticed. Whether or not this close contact involves charge-transfer, however, there are two relatively convincing pieces of evidence for an attractive force between the nitrogen and chlorine.

Intermolecular Contact Distances

It is difficult and dangerous to attempt to show that any of the Cl-N distances are less than those predicted by Van der Waals radii, for these will vary significantly according to orientation and nature of hybridisation. Comparable contact distances are hard to find, but in π-π charge-transfer complexes of chloranil with palladium oxinate (1) and with the oxine dimer (1), the chloranil is tilted so that chlorine-ring distances are increased. This suggests that these contacts are not much less than 3.45 Å, whereas two of the chlorine-nitrogen (paraquat) distances are ~ 3.25 Å. (These occur in $pqCu_2Cl_4$, which shows the most intense charge-transfer of the compounds studied).

Distortion of the Anions

Much more convincing evidence of attraction is the apparent distortion of the chlorocobaltate and chlorocuprate(II) ions. Evidence from crystallographic distortion is often marginal since it is usually impossible to calculate intermolecular forces reliably enough to know how packing will affect the individual molecules.

The $CoCl_4^{2-}$ ion in Cs_3CoCl_5 was shown to be tetrahedral (2) and later (3) to be significantly distorted from $\bar{4}3m$ symmetry to $\bar{4}2m$. This corresponds to an elongation along the $\bar{4}$ axis, with two angles of 106° and four of 111°. It was explained in terms of an electronic effect, and would be expected to be present in $pqCoCl_4$. This has only (approximate) 222 symmetry (Pnab requires only 2) and the angles are shown in Table III.4. If it is assumed that the shape of the anion is not wholly dependent on electronic effects, then the distortion from $\bar{4}2m$ can be reasonably explained as a twisting of about 10° round the diad axis. Besides distorting the bond angles (a significantly endoergic process) this moves two of the chlorine atoms nearer the nitrogens (N-Cl = 3.82 Å) which implies these may create an attractive couple on the anion. The necessary reaction to this is provided by a molecular "vice" of two paraquat molecules "clamping" the other two chlorine atoms. Figs. VI.1 and VI.2 try to give some idea of this. The structure of the isomorphous $pqCuCl_4$ (4) has a distorted $CuCl_4^{2-}$ tetrahedron with contact distances of N-Cl = 3.50, 3.54 Å. The distortion is even larger than in the cobalt compound but is readily explained by the well-known Jahn-Teller effect. This is incidentally an interesting comparison of electronic and steric energies, suggesting that at 3.5 Å the repulsive and attractive forces of the N-Cl contact may be roughly equal, as the ion is virtually undistorted from $\bar{4}2m$ symmetry.

The case of N-Cl forces distorting the $(Cu_2Cl_6^{2-})_n$ anion in $pqCu_2Cl_6$ is strongly supported by the very similar structure of $(Me_2NH_2)_2Cu_2Cl_6$ (5). Both structures (Figs. VI.3. and VI.4. for $pqCu_2Cl_6$) have planar Cu_2Cl_6 dimers, with a long fifth Cu — Cl bond linking dimers. The 5-coordination of d^9 ions is unpredictable and, as chlorocuprate(II) anions form planar complexes (6) and 4 planar bonds with two long bonds (7), there might be a strong tendency for the dimer to remain substantially flat. In both structures there are short N-Cl contacts and the (very similar) dimers are significantly non-planar. In $(Me_2NH_2)_2Cu_2Cl_6$, although not stated, the bond must be a hydrogen bond, N^+-H ---Cl^- (3.25 Å). This is impossible for paraquat and implies that, regardless of the stable conformation of the anion, the energy of the N---Cl system (3.47 Å) must be similar to the hydrogen bond and implies a definite attractive force. The distortion of the anion from planarity is exactly as if the relevant Cu-Cl bond was bent by an N-Cl force and is about 1Å or 34° (24° only in the methylammonium salt).

The most convincing short contacts, however, occur in $pqCu_2Cl_4$, Figs. VI.5 and VI.6, and this has the most intense charge transfer, being jet-black. The nitrogen atom is surrounded on each side of the paraquat plane by chlorine atoms at 3.25 Å and 3.26 Å.

The Cl-N-Cl angle is 163°, and the N-Cl vectors are again nearly perpendicular to the paraquat plane. There cannot easily be distortion of the Cu-Cl bonds as the anion is a chain and each chlorine atom a bridge in it.

The planar $PdCl_4^{2-}$ should be an ideal anion for producing a short Cl-N bond as steric hindrance is small. The crystals showed little charge-transfer and hopes were further confounded when a long N-Cl distance (3.78 Å) and a non-planar paraquat were unexpectedly found (Figs. VI.7 and VI.8). This shows how dangerous it is to make generalisations from even half a dozen similar crystal structures. I have no explanation of this structure, particularly not what forces cause the internal rotation of the paraquat ion. This could perhaps be connected with the weak charge-transfer, but whether cause or effect is not clear; the hypothesis of charge-transfer I now present requires a planar paraquat.

This N-Cl interaction appears to be the main feature common to the structures. Besides this evidence (and the $CuCl_4^{2-}$ structure) N-I and N-Br distances of 3.84 and 3.68 are present in pqI_2 and $pqBr_2$ (4). Without knowing the detailed structures of these it is difficult to know whether these represent the closest approach, but if N-Cl is taken as 3.45 Å, these distances correlate well with ionic radii for the halide ions (III.11).

Electronic Interpretation of these Features

The existence of a N-Cl force does not *per se* suggest that anything but electrostatic interaction is involved. It is difficult to evaluate the partial charge on the Cl atoms but this should be high in $Cu_2Cl_4^{2-}$, as it should for N^+. Making the assumption that this close proximity is necessary to the charge-transfer, we can investigate the possibility of the set-up approximating to a reaction intermediate. Since there are probably radicals in $pqFeCl_4$, (and assuming that its structure is basically that of $pqCoCl_4$)

a model proposed for C-T in this structure must be compatible with the electron distributions in pq^{2+} and $pq^{+\cdot}$. The assumption is also made that all the structures (except possibly the palladium one) involve the same mechanism for this process.

Electronic Structure of Paraquat and its Radical

Only the ground states of the paraquat and its radical are discussed, partly because there is no evidence otherwise, and partly because the molecular orbital calculations have only been made for these. Moreover the electron spin resonance measurements quoted were taken on a solution of $pg^{+\cdot}$ (assumed to be in the ground state). The two common methods of investigating electron distribution in radicals are spin densities from e.s.r. splitting constants and direct M.O. calculation of π-electron coefficients. Splitting constants for $pg^{+\cdot}$ and related compounds have been used to calculate π-electron densities and corresponding calculations from M.O. approach have been made (8). These showed that $\alpha_N = \alpha_C + 0.6\beta_C$, where α is the coulomb integral and β is the resonance integral gave the best fit of observed and calculated densities. Calculations for pq^{2+} and bond orders had not been made.

A programme (11) was available for Mc calculations of -electron densities and bond orders (I.1). Calculations were set up for both paraquat and its radicals on three models: (a) an inductive one with all resonance integrals = 1 for neighbouring atoms, a modification (b) with this integral 0.8 for the central bond, and (c) a "pseudo-atom" model to attempt to account for the effect of the methyl group. (This in effect postulates hyperconjugation between the methyl hydrogen atoms and the ring). For the first two models $\alpha_N = \alpha_C + 0.6\beta$ and $\alpha_{C2} = \alpha_C + 0.09\beta$, whereas for the last, $\alpha_N = \alpha_C + 1.4\beta$, $\alpha_{C2} = \alpha_C + 0.45\beta$. The results, shown as π-densities and π-bond orders, are given in Fig. VI.9. The first two methods give similar results except for the centre bond; although the third has slightly different values, the qualitative picture of all three is similar. There is, of course, no account of π-densities or electron correlation in this method.

This suggests that if an electron is transferred to create a radical in the ground state, it will be most strongly involved with the nitrogen and C_4 atoms. The symmetry of the lowest available orbital for this electron is shown in Fig. VI.10. As the metal chlorine bond is always roughly parallel to the paraquat the proposed mechanism for C-T is as shown below (Fig. VI.11.)

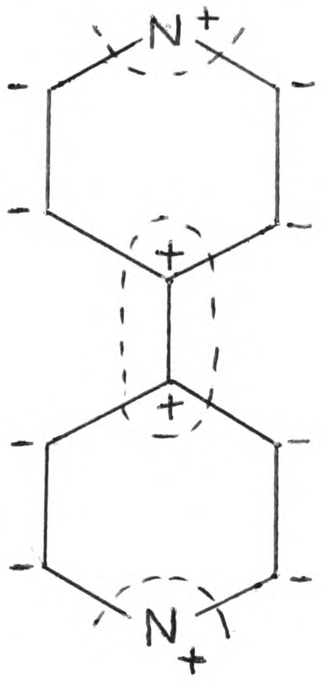


Fig. VI.10.

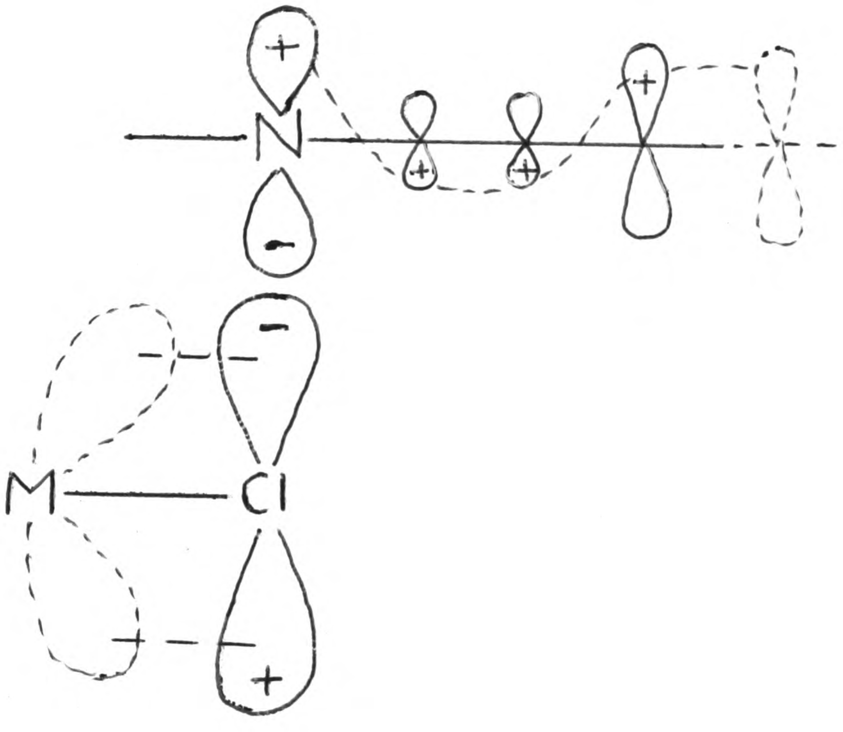
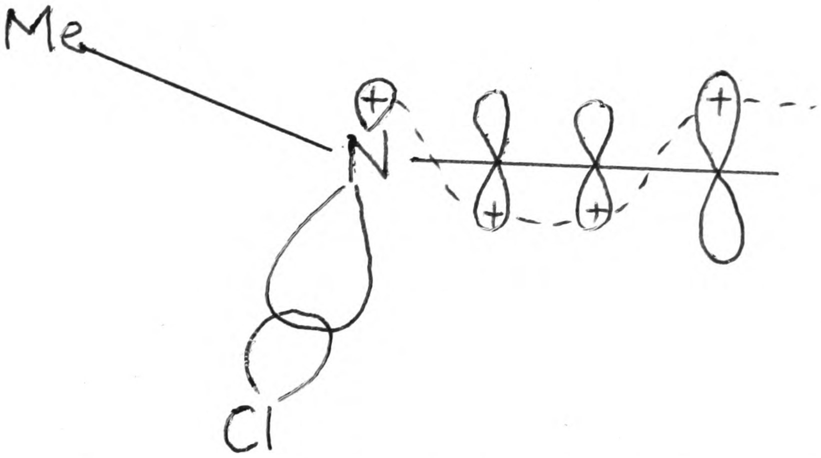


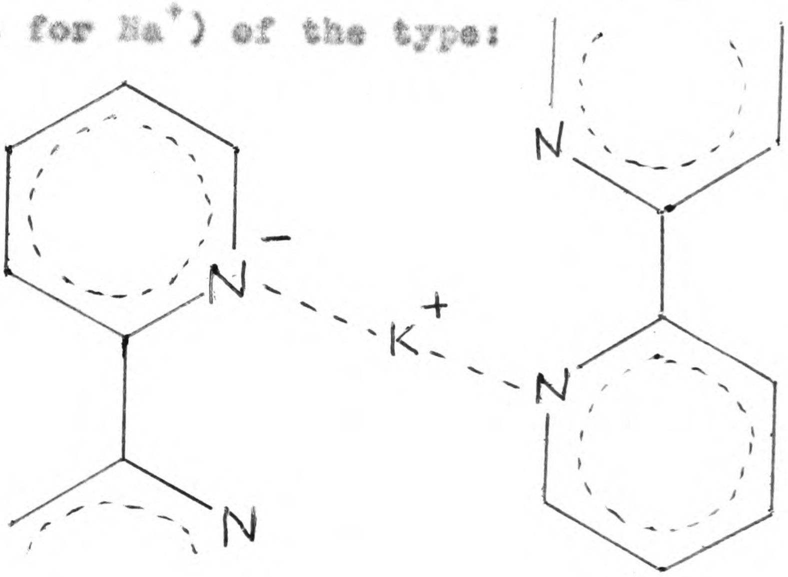
Fig. VI.11.

(This also accounts for C-T in the simple paraquat halides). The p orbital may be bonded to the metal which would facilitate electron transfer from a metal via the chlorine. If the unfilled orbital on the nitrogen were regarded as localised, then although C-T could take place, in a similar manner but reverse direction to that in the py-I_2 complex, radical formation is unlikely. It seems that the system is more similar to the benzene-I_2 complex, involving the whole π-system but a specific atom at the point of transfer. There is a possibility that if the Cl-N distance were very short the nitrogen might have some sp^3 hybridisation and the methyl group be distorted out of the paraquat plane:-



There is also the possibility that if similar compounds occur with the diacid of 4,4'-dipyridyl, then hydrogen bonded charge-transfer could be possible.

Electron transfer between 2,2'-dipyridyl and the ion-pair K^+2,2'dipyridyl$^-$ has been studied by line broadening of e.s.r. spectra (12). This may well involve a bridged intermediate (for K^+ but not for Na^+) of the type:



with $\Delta E_{act} \sim 10$ kcal/mole. The electron structures of the two species will be very similar to those of paraquat (although there is the possibility of the lone pair being used). If K^+---N interactions are possible, a N^+---Cl analogue appears very reasonable.

The changes in bond order (and length) from pq^{2+} to pq$^{+\cdot}$ are not very great and so the Franck-Condon principle should be reasonably obeyed. The crystallographically observed bond orders, Fig. VI.9 calculated from plots of bond order against bond length (I.1), give some confirmation that the paraquat ion in the compounds is in the dipositive (ground) state.

Conformation of the Paraquat Ion

The two main forces determining the conformation of bipyridyls (and biphenyls) are steric hindrance (repulsion) between the C_3 hydrogen atoms and the resonance stabilisation, which are in opposite directions. They predict a twist from planar (θ) of 90° and 0° and gaseous electron diffraction determinations of θ as 41.6° for biphenyl (13) and 37.2 for bipyridyl (14,15) suggest that they are of the same order. Crystallographic determinations show that these type of compounds are almost all planar in the solid (16)(17), biphenyl (18), triphenyl (19), although this has marked libration of the central ring (20), and seven of the paraquat compounds. Only pq$PdCl_4$(50°) and 4,4'-dinitrodiphenyl(33°) (21) appear to be twisted. The packing of biphenyl has been explained in terms of quadrupole moments (22) and it is likely that intermolecular forces are important in determining conformation, besides the two intramolecular effects above.

COORDINATION IN THE ANIONS

The bond lengths in $CoCl_4^{2-}$ (Table III.4) are in good agreement with those of Mason (2.25 Å); those in $PdCl_4^{2-}$ (Table III.5) with $(NH_4)_2PdCl_4$ (23), Pd-Cl = 2.30 Å in 4/mmm. The coordination of copper(I) and (II) has been extensively studied and even with halogens there are over twenty different coordinations. Copper(II) chloride anions form square planes (6), distorted octahedra (7), distorted tetrahedra (4), trigonal bipyramids, distorted square pyramids (5) and the coordination appears to be almost wholly related to the packing. For instance, it is difficult to visualise anything but a trigonal bipyramid if the large spherical tripositive $Co(NH_3)_6^{3+}$ is used as a cation.

For copper(I) the situation is as varied. Surprisingly no crystalline $CuCl_4^{3-}$ has been found (although $Cu(CN)_4^{3-}$ is known) but chains of tetrahedra exist:- vertex linked (25), edged linked (pqCu_2Cl_4), edge and vertex-linked in $Cu_2Cl_3^-$ (26) and vertex-linked ($Cu_5Cl_{16}^{11-}$). 3-coordination does not seem to occur with chloride ion although several with cyanide have been found. The compound Cu.CN.NH_3 (27) has 4 coordinate copper(I) with Cu-Cu distances of 2.14 Å, (cf. pqCu_2Cl_4). It seems that although electronic forces do play a part in copper(II) compounds with chlorine, to a large extent their stereochemistry, and that of copper(I), is dependent on the shape, size and charge of the positive ion.

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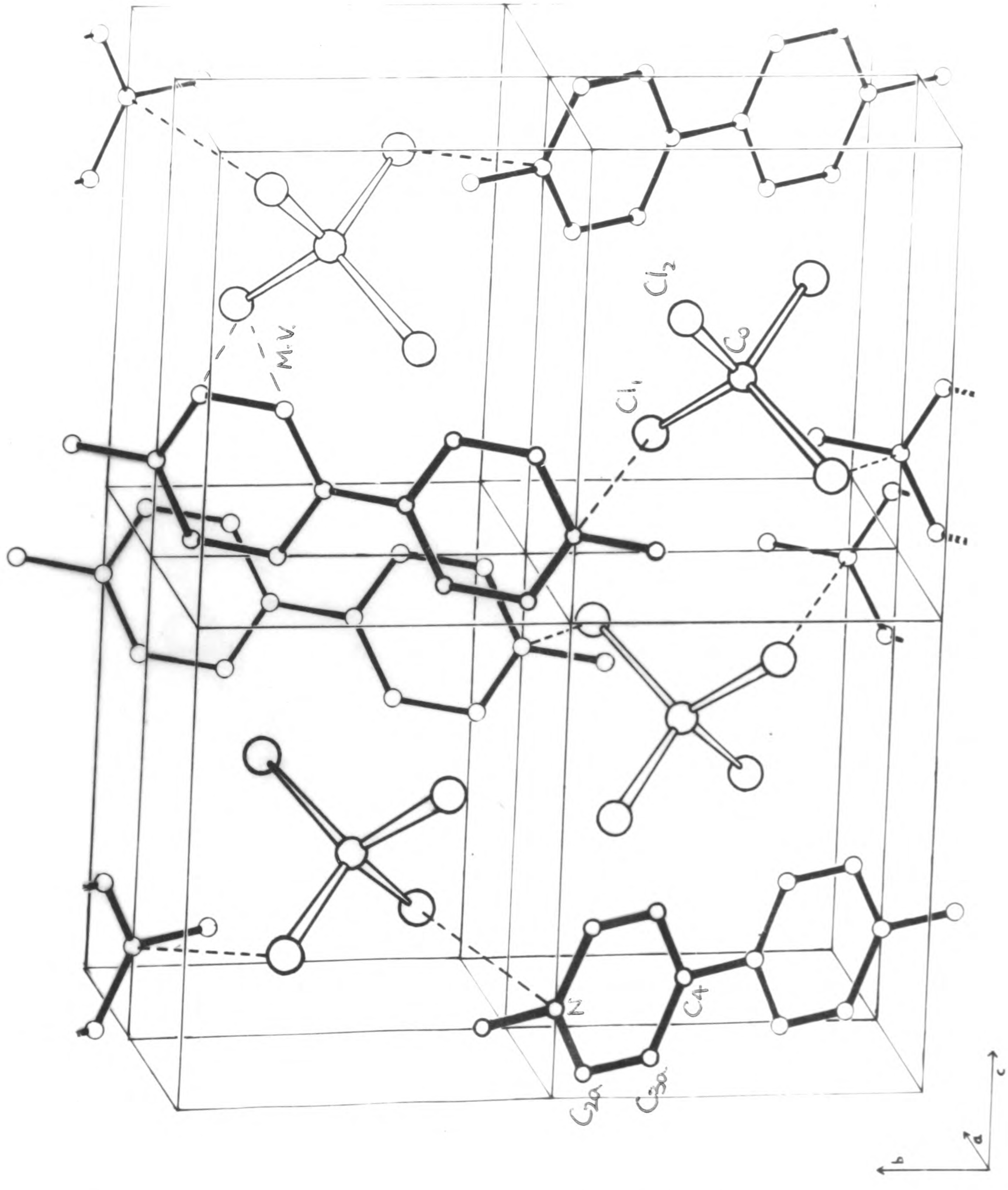


Fig. VI.1. Clinographic view of Paraquat CoCl$_4$ (showing whole cell)

M.V. = the "molecular vice" referred to in the text

The angle shown represents the angle in projection

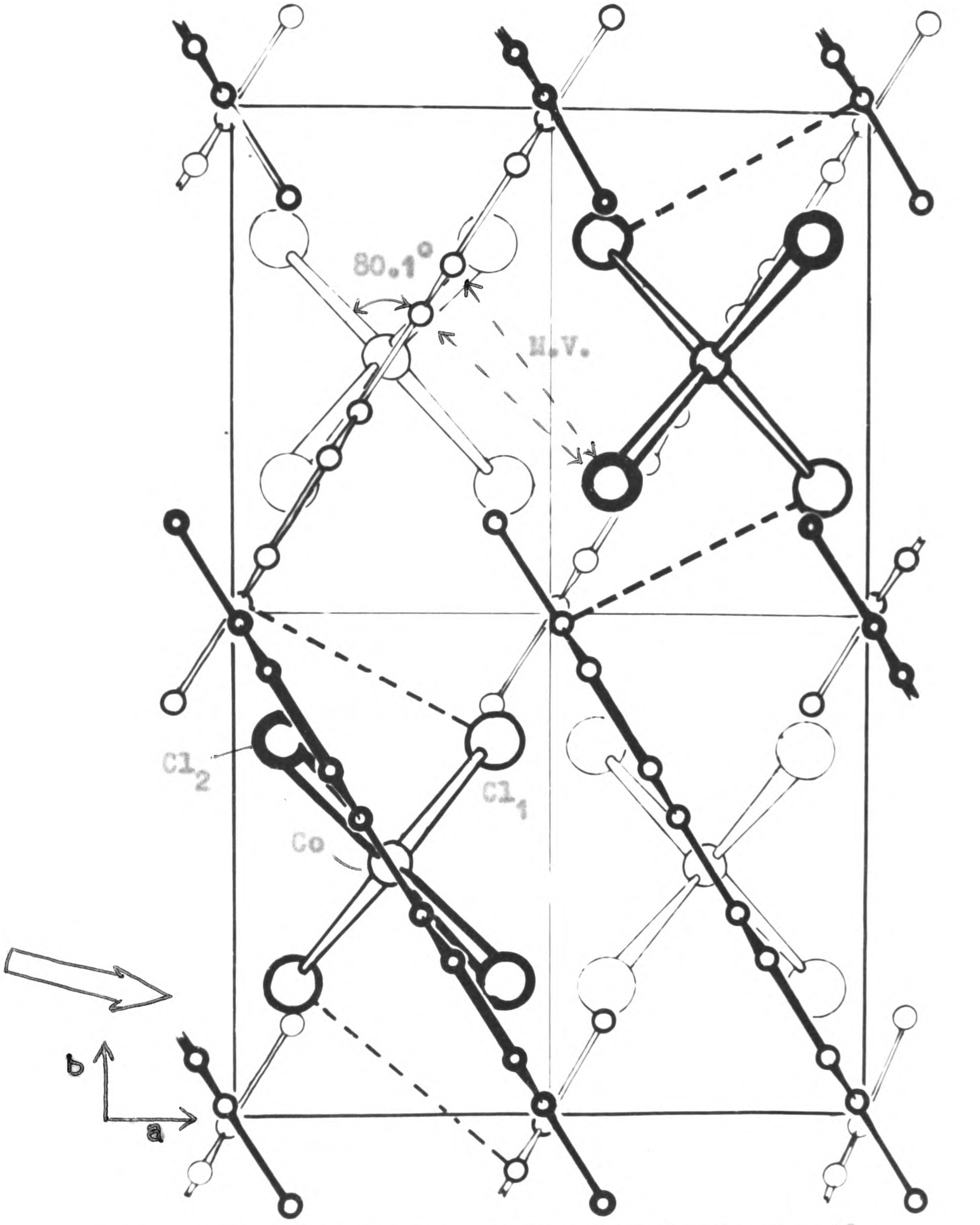


Fig. VI.2. Projection down c for Paraquat $CoCl_4$

(A whole cell is shown. The arrow represents the approximate angle of the clinographic view.)

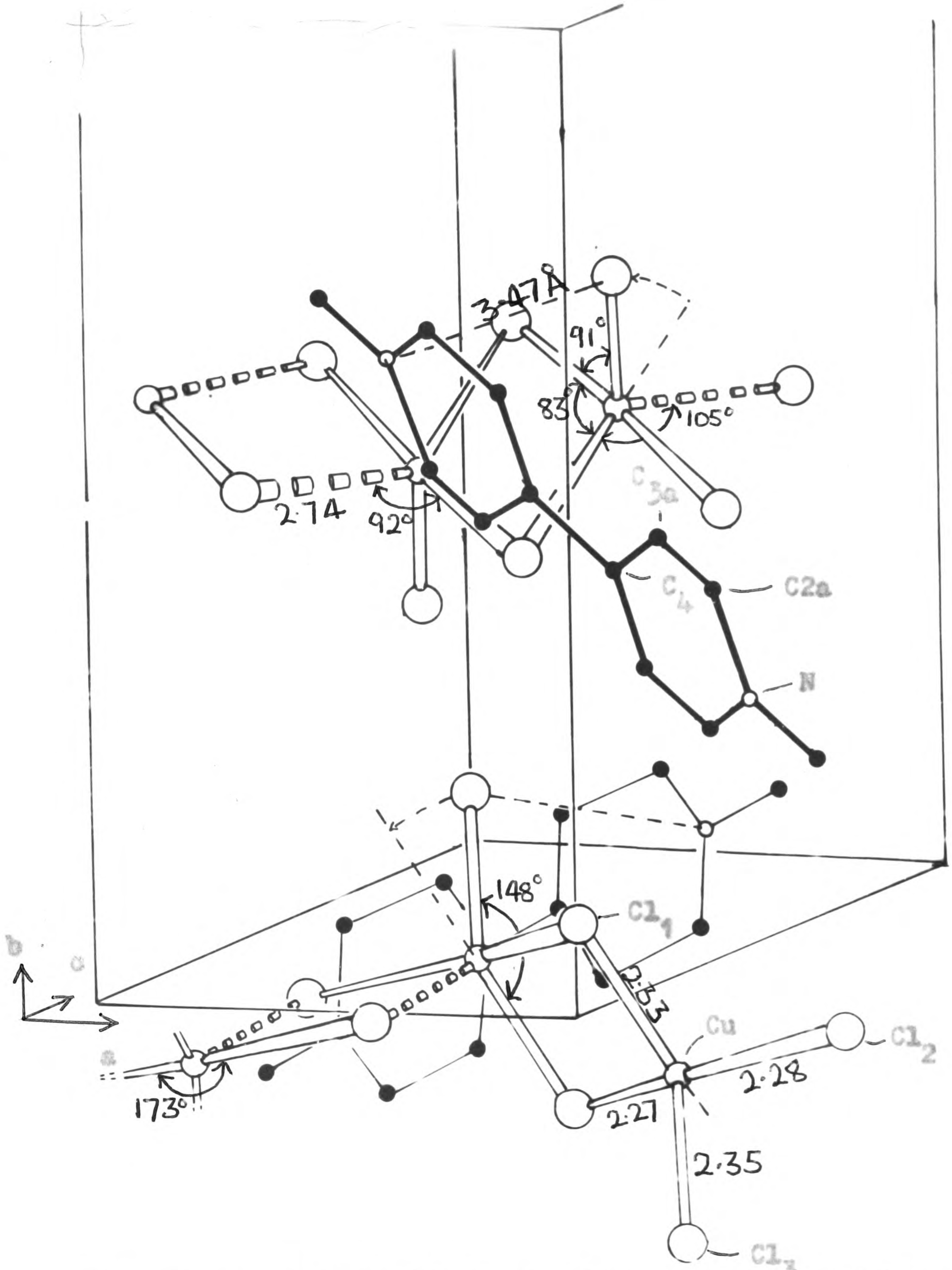


Fig..VI.2. Clinographic Projection of Paraquat Cu_2Cl_6
(A whole cell, but not all its molecules, is shown)

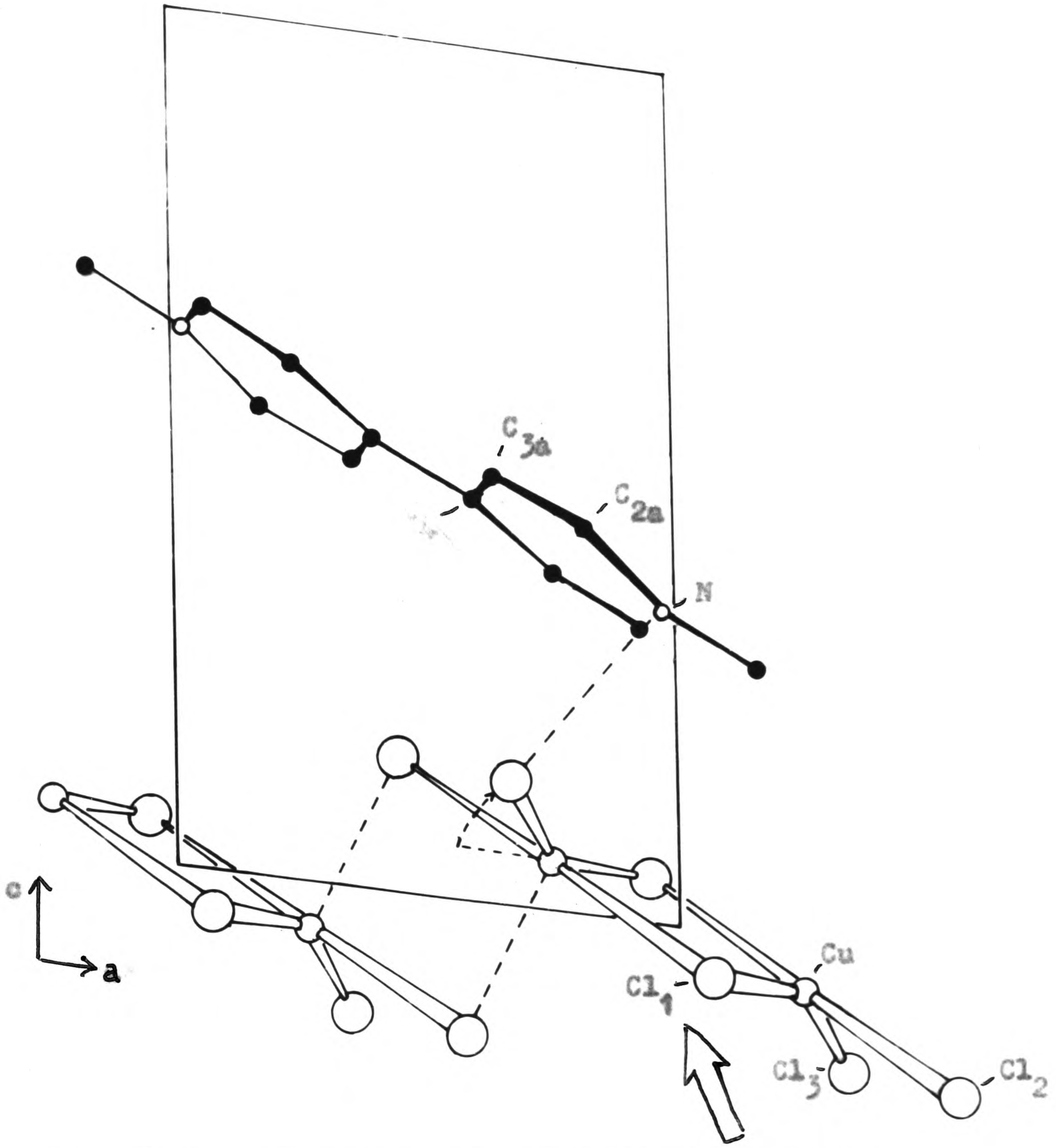


Fig. VI.4. Projection along b for Paraquat Cu_2Cl_6

(A whole cell, but not all its molecules, is shown.)

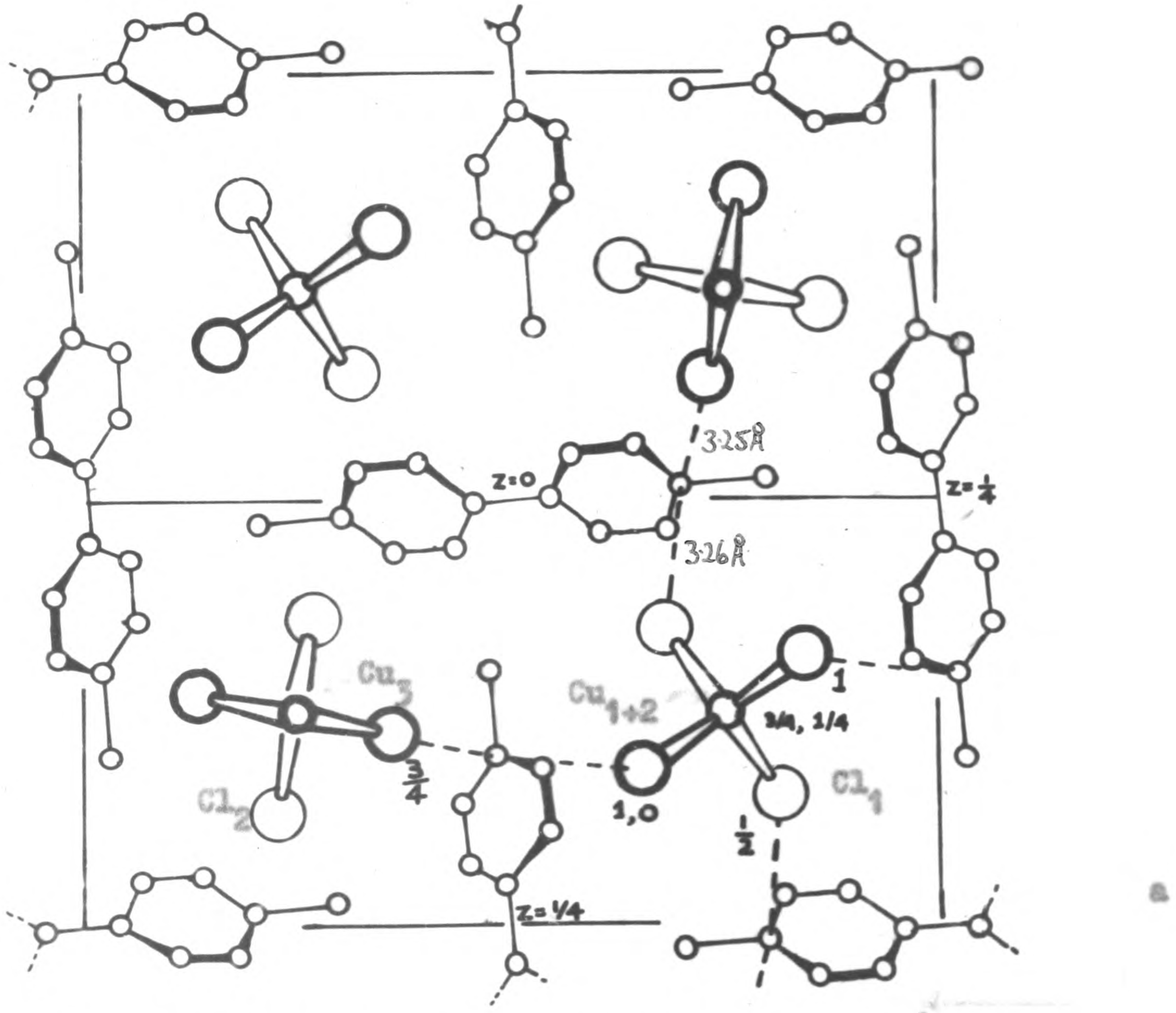


Fig. VI.5. Projection down $\underline{c}$ for Paraquat Cu_2Cl_4

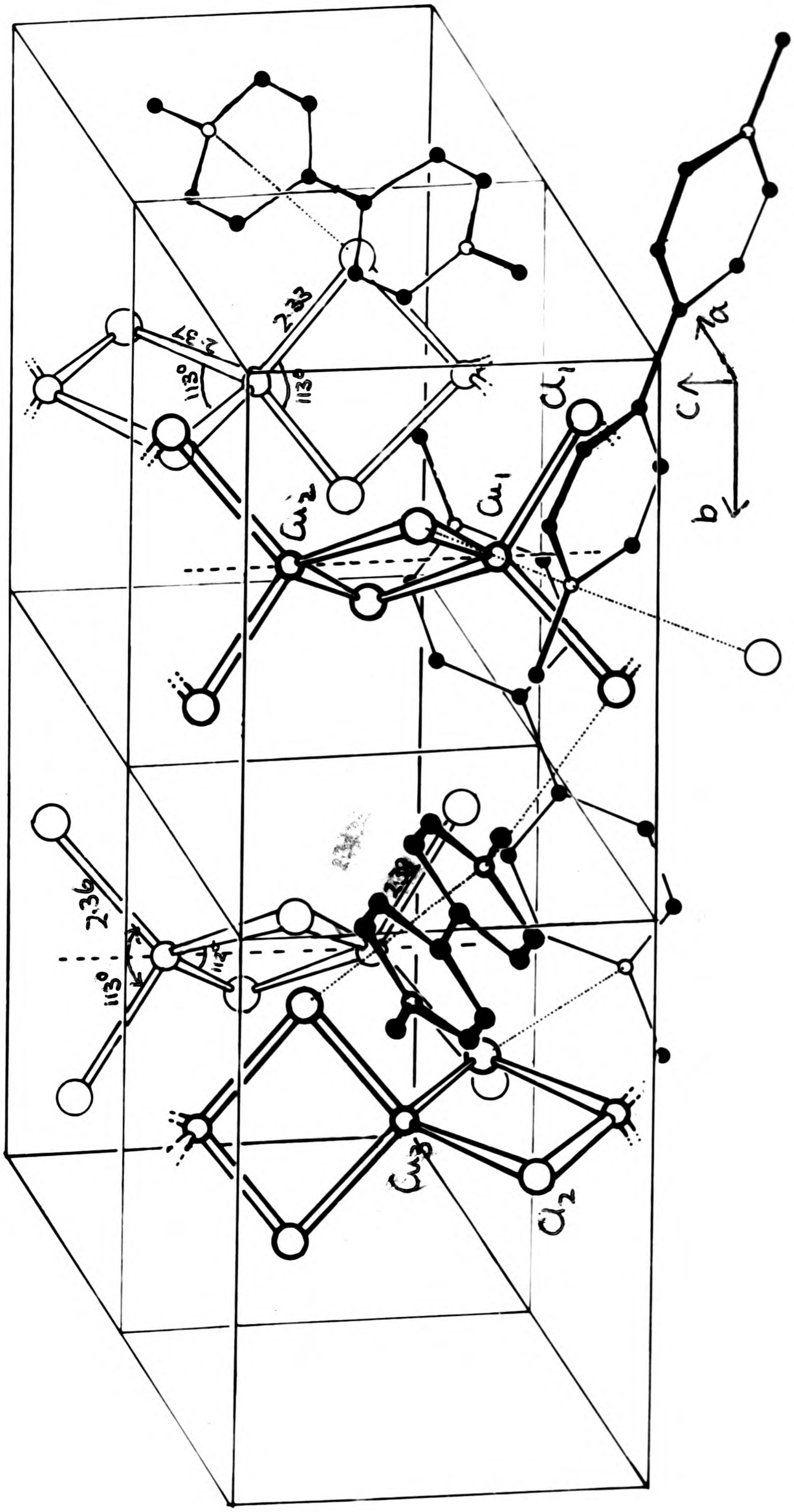


Fig. VI.6. Clinographic view of Paraquat Cu$_2$Cl$_4$

(A whole cell, but not all its moleculer, is shown)

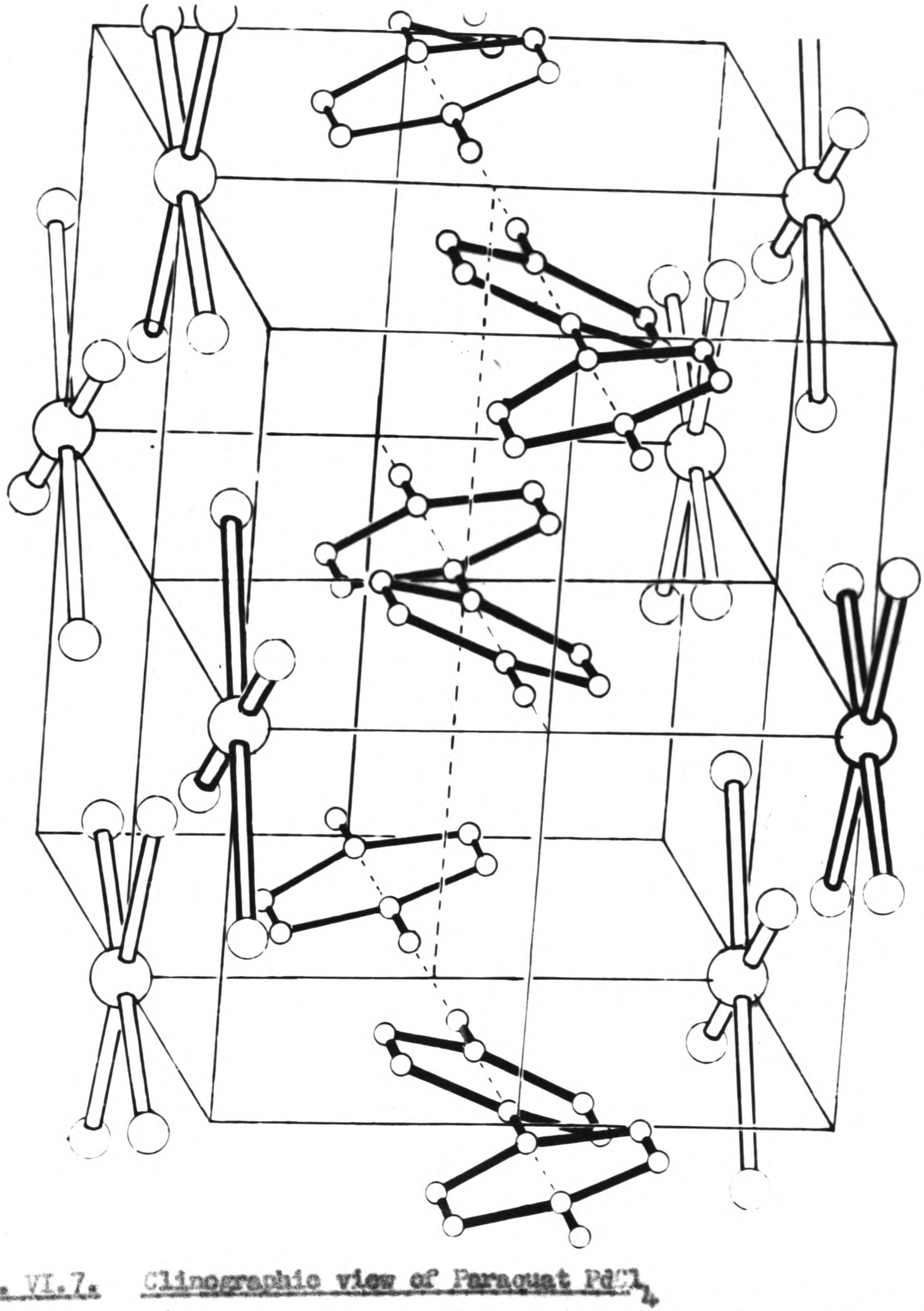
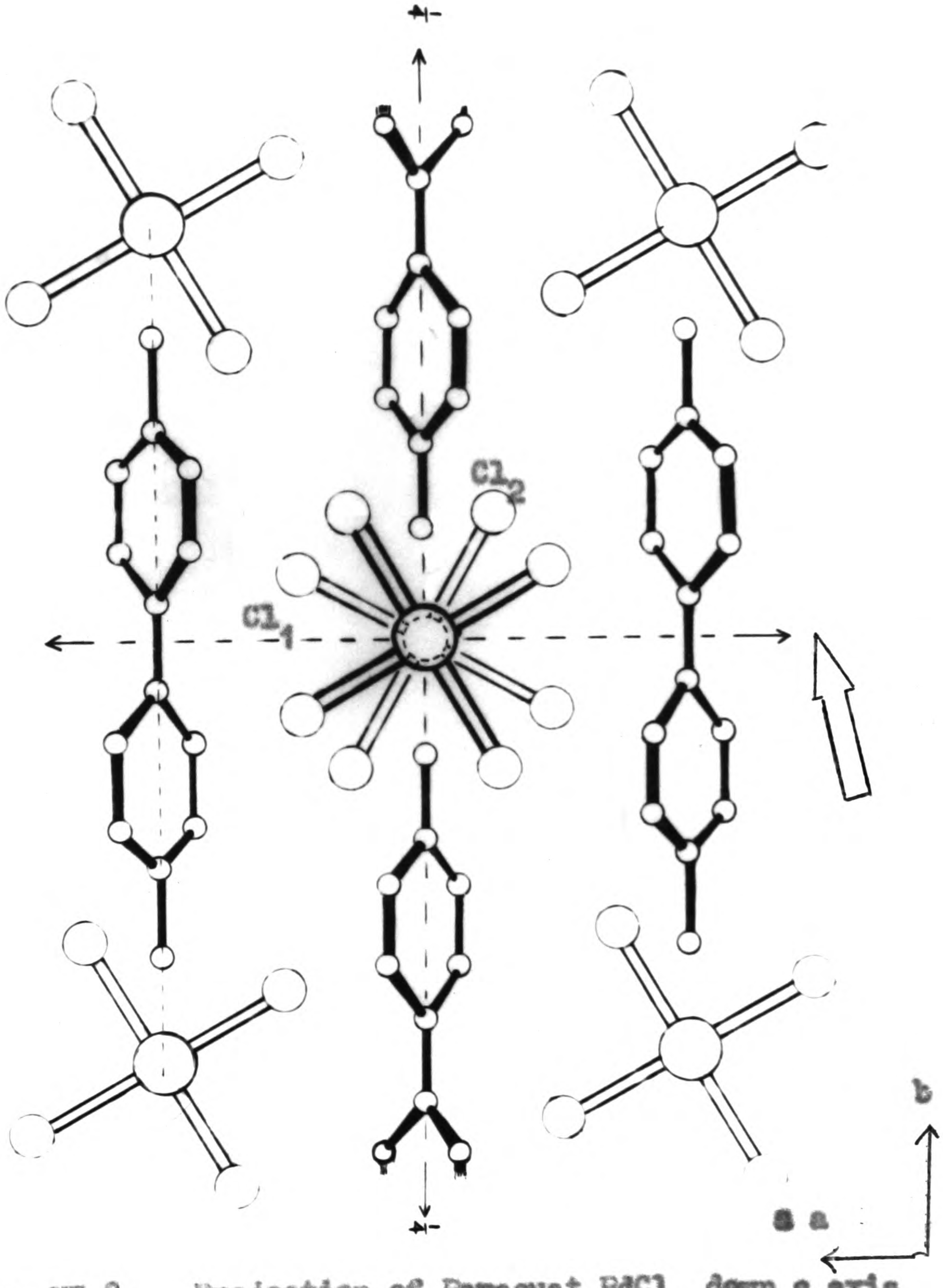


Fig. VI.7. Clinographic view of Paraquat $PdCl_4$

(note position of origin is not at corner of diagram.)



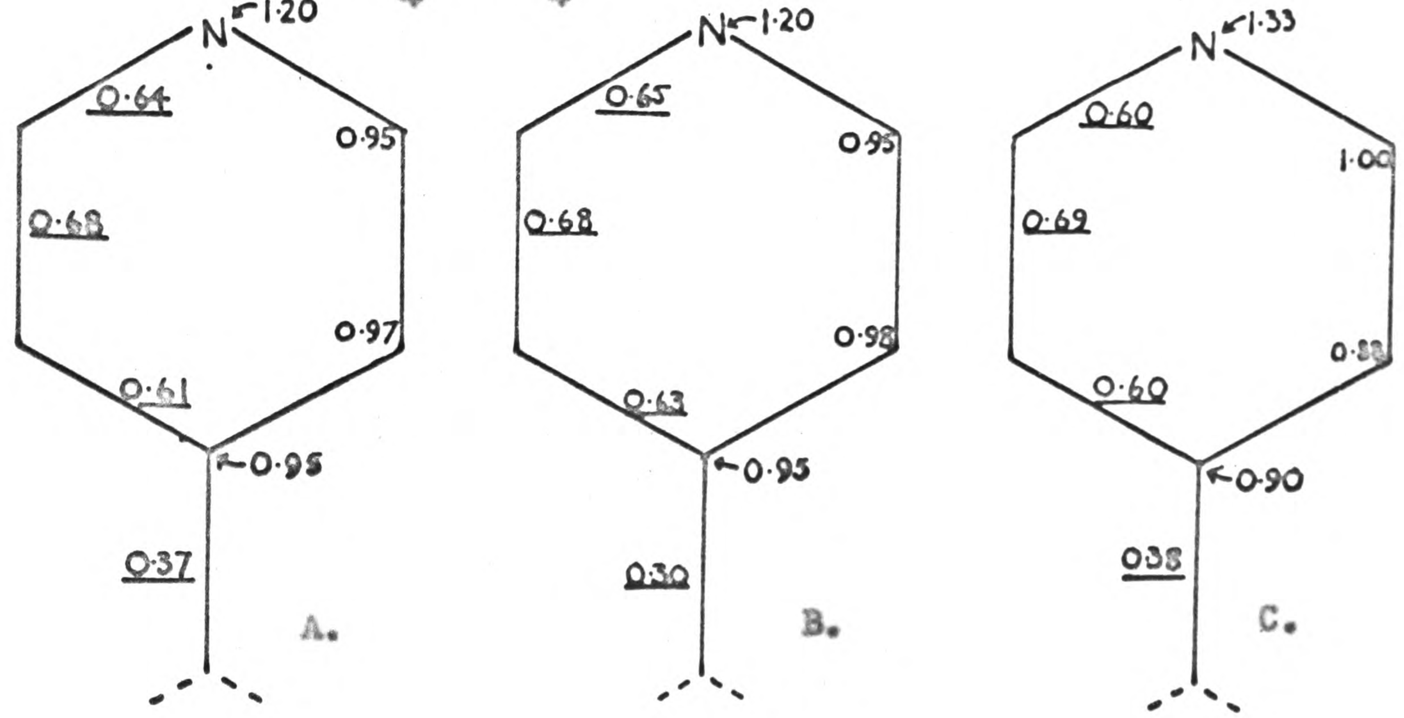
<u>Fig. VI.8.</u> <u>Projection of Paraquat $PdCl_4$ down c axis</u>

(Note that the origin is at the centre of the diagram.)

Crystallographically observed bond orders (I.1.):-

C_2	to	C_3	0.72
C_3	to	C_4	0.62
C_4	to	$C_{4'}$	0.43

DICATION



MONOCATION

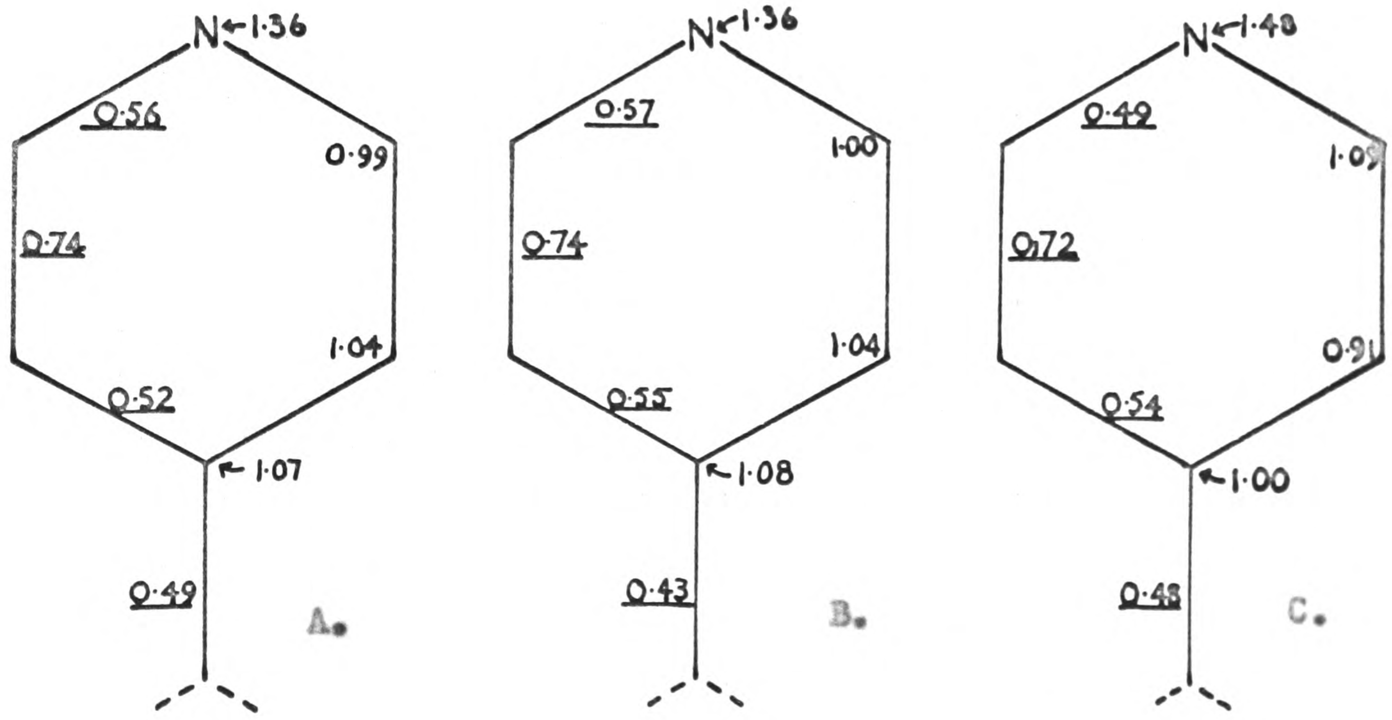


Fig. VI.9. Bond orders and charges calculated by M.O. theory (3 methods)
(for paraquat and its radical monocation)
Crystallographically observed bond orders are also given.

CHAPTER VII.

OBSERVED AND CALCULATED STRUCTURE FACTORS

TABULATION OF STRUCTURE FACTORS

The tables, except VII.3., are arranged in lines of constant h and k. These lines are vertical for the first five tables and horizontal for the last two. They are preceeded by *h k for that line and consist of the triplet, l F_{obs} F_{calc}. Values for F_{obs} have already been multiplied by the layer scales. The numbers given are in electrons multiplied by a factor to make the values more manageable and this factor is given for each table.

All the structures are centrosymmetric, but the cobalthexammine chlorocuprates are referred to a non-centric origin for structure factor calculation. For these the phases, or information to calculate them, are given.

For table VIII.3., $pqCu_2Cl_4$, the constant indices are *l h.

TABLES IN CHAPTER VII.

		Value Tabulated
VII.1	Copper Oxinate.2TCNB	5F
VII.2	Paraquat $CoCl_4$	5F
VII.3	Paraquat Cu_2Cl_4	5F
VII.4	Paraquat $PdCl_4$	2.5F
VII.5	Mixed-Valence (25%Cu(I)) compound	2.5F
VII.6	Paraquat Cu_2Cl_6	0.5F
VII.7	$Co(NH_3)_6{}_4Cu_5Cl_{17}$	0.1F

Table. VII.1. •h k, l $5F_{obs}$ $5F_{calc}$ for CuOx$_2$.2TCNB (M)

• 0 0		
4	31	-18
7	73	-62
8	68	66
9	112	103
10	57	58
11	127	118
12	45	39
13	45	44
14	39	39
15	22	32
16	40	46
17	34	41
• 0 1		
-17	43	41
-15	37	25
-14	39	38
-13	64	60
-10	59	59
-9	53	52
-8	41	-29
-7	140	148
-5	75	82
-4	149	163
4	64	-61
5	17	16
6	39	37
7	76	74
8	116	114
9	73	70
10	179	184
11	114	128
12	28	29
14	42	33
16	39	31
• 0 2		
-17	29	27
-15	47	50
-14	76	83
-10	48	43
-8	97	101
-7	212	222
-6	108	105
-5	38	35
-4	35	38
-3	24	-8
-2	45	-35
0	24	23
3	21	21
5	74	83
6	77	86
7	41	40
9	172	193
10	162	168
11	69	-58
15	22	26
• 0 3		
-17	21	24
-16	28	32
-13	32	-24
-12	28	28
-10	57	53
-9	35	35
-8	53	54
-7	112	111
-6	87	88
-5	94	94
-4	167	169
-3	50	51
-2	155	-164
-1	22	24
0	17	22
1	73	70
2	85	87
3	192	225
4	154	165
5	83	-72
6	33	26
7	65	66
9	95	85
10	28	-24
12	46	55
15	34	27
• 0 4		
-16	30	28
-14	42	38
-13	37	35
-12	51	-46
-11	72	61
-10	141	152
-9	56	53
-8	60	53
-7	79	77
-6	69	66
-5	136	137
-4	82	90
-3	136	-141
-1	69	68
0	119	120
2	143	154
3	87	96
4	75	77
5	45	39
6	29	29
7	38	39
9	43	41
10	32	40
11	30	27
13	41	42
14	30	30
• 0 5		
-16	35	34
-14	28	26
-13	67	58
-12	46	49
-11	145	162
-10	32	34
-9	95	-96
-8	41	31
-7	91	89
-6	76	69
-5	90	83
-2	113	120
-1	56	50
0	132	135
1	87	92
2	91	84
3	100	100
4	77	76
5	73	76
6	52	55
10	47	48
12	37	42
13	37	45
• 0 6		
-16	22	21
-15	32	27
-14	34	31
-13	38	35
-12	43	38
-11	27	23
-7	51	47
-6	54	55
-5	109	106
-4	110	100
-3	52	55
-2	40	34
-1	157	162
0	100	102
3	67	68
• 0 6		
4	57	52
5	51	53
8	50	51
9	36	42
10	26	32
12	28	28
• 0 7		
-14	38	28
-12	50	41
-7	99	98
-6	53	55
-5	28	21
-4	51	50
-3	40	42
-2	90	80
-1	94	94
0	97	-96
1	47	-49
2	47	54
3	62	62
4	59	53
5	35	34
7	38	36
10	22	26
• 0 8		
-12	27	20
-11	35	24
-8	30	30
-7	25	25
-4	42	45
1	22	22
2	28	36
4	37	35
5	36	33
• 0 9		
-9	24	16
-8	29	20
-4	36	29
-3	36	25
-1	23	17
1	21	-15
2	45	37
• 1 -9		
-4	22	23
-1	38	32
1	47	46
2	29	22
3	37	29
4	32	28
6	36	20
7	34	24
• 1 -8		
-7	22	26
-4	37	40
-3	26	27
-2	38	42
-1	39	38
0	46	42
1	49	46
2	52	44
3	43	38
4	49	45
9	42	35
10	45	37
11	43	28
12	23	16
• 1 -7		
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-1	32	22
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2	37	31
3	39	38
4	44	33
5	76	62
6	53	48
7	30	20
8	45	41
9	31	31
10	48	36
11	56	45
12	60	36
13	54	30
• 1 -6		
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-7	38	45
-6	42	45
-5	30	22
-4	68	[illegible]
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-2	45	-43
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2	105	107
3	99	97
4	29	23
5	89	85
6	36	23
7	58	45
8	100	103
14	30	23
• 1 -5		
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-10	38	49
-7	29	33
-5	44	35
-4	70	79
-3	60	60
-2	47	33
-1	87	96
0	27	-23
1	63	56
2	23	22
4	88	66
5	87	73
6	76	64
• 1 -4		
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-10	53	58
-7	48	55
-6	55	53
-5	66	64
-4	85	94
-3	27	28
-2	29	28
-1	78	76
0	75	76
1	91	91
3	39	39
4	51	53
5	24	21
6	136	130
7	72	55
8	40	35
9	75	84
10	49	-33
11	60	51
12	78	73
13	35	30
14	21	24
17	43	38
• 1 -3		
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-15	33	34
-14	30	42
• 1 -3		
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-11	100	114
-10	57	71
-9	36	34
-6	25	20
-5	51	49
-4	131	152
-3	130	148
-2	189	214
-1	111	119
0	140	166
1	55	-46
2	165	174
3	94	100
4	119	127
5	124	124
6	135	141
7	132	126
8	60	63
9	38	25
11	85	79
12	36	35
14	35	30
15	50	45
16	20	23
17	32	21
• 1 -2		
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-13	39	30
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-9	42	34
-8	127	141
-7	74	82
-6	114	123
-5	140	144
-4	96	97
-3	174	184
-1	187	203
0	292	307
1	78	84
2	71	65
3	83	90
4	81	79
5	163	149
6	111	112
7	126	130
8	94	92
9	56	53
10	98	102
11	33	24
12	60	49
13	34	35
14	47	42
15	44	47
16	42	35
17	31	28
• 1 -1		
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-11	113	123
-10	120	132
-9	57	62
-8	122	106
-7	25	19
-6	43	38
-5	177	200
-4	18	19
-3	156	179
-2	114	105
-1	130	121
2	80	-67
3	172	177
4	33	-21
5	128	122
6	197	228
7	146	146
8	122	122
9	36	33
10	58	49
11	40	44
12	62	67
14	45	35
15	34	34
16	26	25
17	25	19
• 1 0		
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-14	38	34
-12	70	64
-11	39	33
-10	56	49
-8	144	149
-7	133	137
-6	102	-91
-4	89	-83
-3	31	34
2	20	22
3	130	148
4	121	123
5	75	-63
6	49	41
7	74	78
8	75	74
9	80	87
10	32	38
11	55	52
14	22	29
17	31	29
• 1 1		
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-16	23	24
-15	28	26
-12	48	50
-11	49	46
-10	38	41
-9	50	51
-8	32	34
-7	99	96
-6	69	74
-5	57	61
-4	142	143
-3	53	-41
2	37	37
3	152	-161
4	50	46
5	22	-8
6	86	94
7	121	126
8	27	-23
9	56	51
10	62	70
11	75	79
13	23	21
17	13	19
• 1 2		
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-16	34	37
-15	39	34
-13	58	53
-11	61	50
-10	35	35
-9	110	111
-8	135	137
-7	145	152
-6	98	96
-5	35	-27
• 1 2		
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-3	49	-42
-1	49	53
0	68	62
1	97	105
3	30	29
4	101	104
5	40	34
6	26	-17
7	138	141
8	109	117
9	54	65
10	89	91
16	27	23
• 1 3		
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-16	39	39
-15	51	41
-14	27	27
-13	39	29
-12	44	41
-11	79	81
-10	43	36
-9	53	51
-8	119	113
-7	112	105
-6	124	124
-5	76	71
-3	121	129
-2	59	58
-1	180	207
0	106	120
1	161	177
2	135	144
3	135	147
4	124	131
5	108	113
6	44	47
7	64	66
8	22	12
9	28	-32
10	96	105
11	30	37
12	24	17
15	22	25
• 1 4		
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-15	28	24
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-10	40	34
-9	55	54
-8	84	79
-7	141	141
-6	108	104
-5	104	108
-4	75	72
-3	72	76
-1	121	126
0	129	138
1	162	172
2	88	98
3	93	102
4	30	29
5	25	21
6	36	39
7	25	27
8	32	33
9	47	60
10	58	65
11	40	42
13	35	40
14	24	32
• 1 5		
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-12	55	47
-10	59	58
-9	27	20
-8	34	25
-7	82	82
-5	35	38
-4	83	78
-3	17	35
-2	105	103
-1	35	30
0	51	50
1	34	36
2	44	49
3	84	92
4	69	71
5	30	34
6	34	40
7	20	14
9	46	51
10	32	35
11	50	57
• 1 6		
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-14	29	26
-13	36	33
-10	63	-54
-8	46	47
-7	52	43
-6	89	75
-5	38	32
-4	60	51
-3	63	57
-2	63	52
0	71	74
2	23	26
3	56	56
4	33	27
6	30	33
9	32	36
10	26	27
• 1 7		
-11	25	16
-9	65	67
-8	29	23
-6	63	63
-5	42	32
-2	38	-37
1	30	-29
2	37	42
3	46	47
5	40	41
6	41	40
• 1 8		
-11	27	21
-10	29	25
-9	34	26
-8	38	28
-7	34	30
-6	20	16
-1	33	35
2	35	40
3	35	39
4	33	34
5	32	35
7	12	16
• 1 9		
-5	35	32
-4	31	27
-3	28	22
-2	35	36
-1	23	22

Table. VII.1.(contd.)

h k, l	$5F_{obs}$	$5F_{calc}$
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0	37	35
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3	22	24
• 2 -9		
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-1	29	21
0	33	30
1	23	22
4	33	27
5	29	23
7	18	17
8	22	21
9	21	14
• 2 -8		
-5	26	26
-4	44	39
-3	45	40
0	41	30
1	46	40
2	42	26
3	46	40
5	22	13
7	30	24
8	29	23
10	43	38
11	49	38
• 2 -7		
-10	23	26
-8	28	34
-6	31	30
-3	72	73
-2	66	53
-1	47	-50
0	25	-12
1	35	32
2	25	24
6	51	54
7	46	47
8	27	21
9	30	24
11	44	30
13	26	20
14	35	28
• 2 -6		
-12	17	23
-9	40	49
-8	35	38
-6	42	40
-5	69	59
-4	75	77
-3	28	30
-2	77	-80
-1	121	-105
0	142	141
1	113	92
2	30	30
3	66	50
4	81	62
5	84	81
6	123	111
11	57	45
• 2 -5		
-13	36	35
-11	42	50
-10	43	50
-9	48	48
-6	63	60
-5	58	53
-4	85	92
-3	22	11
-2	43	29
-1	134	132
0	124	128
1	81	74
2	113	105
3	104	99
4	125	110
5	56	49
6	66	59
7	79	85
8	25	-22
9	53	-59
10	49	41
11	44	45
12	66	59
13	48	43
14	44	30
15	28	27
16	38	33
• 2 -4		
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-13	39	46
-12	22	24
-11	47	48
-10	28	24
-8	37	29
-7	41	53
-6	79	74
-5	93	87
-4	104	104
-3	163	149
-2	95	94
-1	162	154
0	84	78
2	24	-23
4	149	129
5	120	107
6	86	82
7	36	26
8	91	-94
9	69	79
10	197	216
11	36	34
12	64	47
13	40	34
14	26	24
15	57	49
16	32	24
• 2 -3		
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-14	23	26
-12	49	52
-10	53	53
-8	39	42
-7	63	56
-5	71	79
-4	135	120
-2	81	70
-1	172	156
0	139	136
1	63	-53
2	176	-148
3	119	118
4	154	143
5	92	96
6	132	131
7	101	87
8	68	66
10	53	41
12	36	37
13	50	43
15	33	24
• 2 -2		
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-13	51	52
-12	65	-59
-11	40	-36
-10	117	128
-9	43	40
-8	42	41
-7	34	28
-6	102	-79
-2	99	88
-1	55	-38
0	80	74
1	96	-79
2	69	66
3	139	116
4	75	74
5	50	52
6	130	118
7	93	87
8	48	49
9	71	73
11	29	26
12	51	-56
13	29	26
14	39	44
15	25	33
16	27	30
• 2 -1		
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-12	45	-24
-11	156	164
-10	129	141
-9	35	27
-8	59	55
-7	99	111
-6	84	80
-5	70	66
3	51	49
4	49	48
5	121	120
6	232	241
7	74	81
9	39	40
13	48	64
14	42	41
16	34	28
• 2 0		
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-16	25	14
-15	31	29
-12	109	111
-11	120	127
-10	70	70
-9	144	132
-7	22	-13
-6	78	73
-5	36	-29
3	31	37
4	25	32
5	221	239
6	84	91
7	31	-22
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10	52	52
12	42	42
13	20	25
14	24	24
16	36	39
• 2 1		
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-16	23	28
-15	22	25
-14	46	49
-12	83	76
-11	47	53
-10	108	101
-9	34	40
-8	33	-14
-7	158	150
-6	128	116
-5	37	-13
-4	62	60
-3	58	66
0	52	54
1	149	-133
2	168	172
3	59	50
4	114	117
5	95	95
6	54	-51
7	71	71
8	70	70
9	51	55
10	118	117
11	44	45
13	47	44
15	39	44
16	31	34
• 2 2		
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-11	45	51
-10	26	32
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-5	133	150
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-2	190	205
-1	105	114
0	158	179
1	77	85
2	47	43
4	34	30
5	86	88
6	93	98
7	29	32
8	43	56
9	174	201
10	82	103
13	23	20
15	36	26
• 2 3		
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-11	39	40
-10	33	39
-9	63	70
-8	108	121
-7	74	75
-6	31	33
-5	63	64
-4	97	95
-2	128	143
-1	30	25
0	109	120
1	107	-92
2	68	77
4	45	49
6	42	48
8	136	160
9	100	108
10	55	-60
14	31	30
• 2 4		
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-11	40	38
-10	34	30
-9	45	50
• 2 4		
-8	86	86
-7	65	66
-6	87	77
-5	143	133
-4	23	20
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0	23	27
1	77	81
2	122	113
3	82	87
6	43	45
8	47	44
• 2 5		
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-13	45	-40
-12	73	70
-11	111	129
-8	46	43
-7	45	48
-6	106	96
-5	47	48
-4	90	-80
-3	13	18
-2	23	18
-1	66	68
1	75	80
2	64	63
3	45	49
4	36	38
6	26	33
• 2 6		
-15	22	21
-14	42	43
-13	41	40
-12	75	77
-10	53	-43
-9	14	21
-8	62	57
-6	40	38
-5	37	37
-4	40	37
-3	38	39
-2	32	34
-1	82	88
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1	33	35
2	49	63
3	44	51
4	46	53
5	32	38
• 2 7		
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-6	57	60
-1	50	52
2	31	38
3	41	44
7	30	32
8	24	24
• 2 8		
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-5	36	38
-4	28	34
-3	40	42
-2	28	39
-1	43	-45
1	43	46
2	30	36
3	26	30
• 2 9		
-3	18	20
-2	19	19
-1	24	22
• 3 -9		
0	44	38
2	38	26
3	29	22
6	26	21
8	32	23
• 3 -8		
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0	43	47
1	36	31
2	37	30
3	46	48
4	38	30
5	19	13
6	25	21
9	31	20
10	44	34
11	29	20
• 3 -7		
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-7	27	24
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-4	40	46
-3	35	38
-2	31	25
-1	83	74
0	46	44
1	65	53
2	42	36
3	34	33
6	37	30
7	35	23
8	36	32
9	38	32
10	39	29
11	33	22
12	53	45
13	16	13
• 3 -6		
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-8	23	30
-7	66	72
-6	45	44
-5	57	55
-4	99	91
-3	25	23
-2	18	15
-1	66	70
0	68	-55
1	45	40
2	92	82
3	66	48
4	112	91
5	53	51
7	70	63
8	44	42
9	59	43
10	66	53
11	44	34
12	37	28
13	30	22
• 3 -5		
-11	23	31
-10	30	28
-8	38	42
-7	40	43
-6	40	33
-5	70	69
-4	50	50
-3	31	-28
-2	68	60
-1	57	47
0	57	41
• 3 -5		
1	70	70
2	102	95
3	37	32
4	101	94
5	86	63
6	71	62
7	93	89
8	29	-17
10	39	25
11	49	33
12	27	25
13	39	30
15	25	23
• 3 -4		
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-11	43	50
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-7	28	25
-6	52	45
-5	98	102
-4	94	85
-3	43	34
-2	81	77
-1	37	-31
0	68	65
1	19	19
2	108	94
3	94	81
4	32	30
5	66	67
6	26	25
8	48	35
11	54	50
12	38	34
13	43	42
14	34	34
16	17	10
• 3 -3		
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-12	30	36
-11	55	57
-10	34	34
-9	25	27
-8	38	44
-7	41	42
-6	29	24
-5	58	60
-4	23	26
-3	55	51
-2	92	83
-1	99	104
1	16	-11
3	81	75
4	54	47
5	122	113
6	87	73
7	42	45
8	67	77
9	41	-36
10	56	45
11	67	62
12	26	19
14	28	22
16	38	36
• 3 -2		
-16	23	24
-12	102	124
-11	44	55
-9	21	18
-7	35	37
-6	87	84
-5	131	116
-4	111	104
-3	169	152
-2	74	62
-1	168	171
1	154	147
2	82	74
3	76	75
4	119	116
5	122	108
6	134	116
7	58	55
9	24	24
10	38	42
11	32	25
12	23	20
13	36	26
14	40	40
15	21	21
16	20	11
• 3 -1		
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-15	21	25
-12	70	69
-11	40	34
-10	59	60
-9	137	138
-8	65	72
-7	52	49
-6	132	115
-5	74	65
-4	152	153
0	95	100
1	8	10
2	136	138
3	61	55
4	82	81
5	103	99
6	118	105
7	114	114
8	54	57
9	73	73
11	60	50
12	29	34
13	44	40
14	38	43
15	40	37
16	31	26
• 3 0		
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-13	38	50
-12	98	102
-11	108	115
-9	63	58
-8	99	97
-7	52	52
-6	144	138
-4	39	42
-3	123	106
1	26	-21
2	109	109
3	98	97
4	110	111
5	146	159
6	93	91
7	77	72
8	50	48
9	53	50
10	62	65
11	52	54
13	35	26
14	34	26
15	25	22
16	31	22
• 3 1		
-17	18	26
-16	22	29
-15	25	31

Table VII.1.(cont.)

*h k, l	$5F_{obs}$	$5F_{calc}$
• 3 1		
-13	40	37
-12	25	26
-11	37	44
-10	29	32
-9	84	87
-8	83	80
-7	47	-36
-5	47	47
-4	42	33
-3	176	171
-2	165	175
-1	144	126
1	94	98
2	52	50
3	70	71
4	71	-66
5	23	26
6	104	117
7	60	63
8	64	72
9	22	23
10	58	46
15	19	22
• 3 2		
-16	21	23
-13	25	29
-12	28	32
-10	27	32
-9	36	43
-8	95	99
-7	102	106
-5	88	85
-4	25	18
-3	121	116
-2	101	92
0	48	-36
1	63	63
2	58	-46
3	63	62
4	52	47
6	61	58
8	44	55
9	79	86
10	47	60
• 3 3		
-16	22	25
-14	26	30
-12	38	43
-11	32	33
-10	54	58
-9	83	83
-8	77	79
-7	63	69
-6	31	25
-5	31	38
-4	16	-11
-3	30	-20
-2	49	52
-1	55	55
0	71	72
1	106	122
2	23	27
3	43	39
4	50	53
6	98	104
7	82	99
9	47	46
• 3 4		
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-16	31	33
-13	43	47
-12	41	46
-11	18	20
-10	22	28
-9	52	55
-8	69	69
-7	67	68
-6	56	56
-5	22	18
-4	95	88
-3	22	23
-2	66	73
-1	45	51
0	93	106
1	88	96
2	100	116
3	70	73
4	43	46
6	26	21
9	50	64
10	26	30
• 3 5		
-14	28	33
-13	63	73
-11	21	27
-10	36	42
-9	36	39
-8	83	95
-7	63	65
-6	35	41
-5	37	40
-3	33	31
-2	79	81
-1	81	83
0	76	84
1	36	42
2	45	54
3	32	32
5	29	36
8	33	38
9	24	28
10	41	44
11	19	25
• 3 6		
-15	17	23
-14	33	36
-13	34	38
-12	21	23
-11	20	20
-8	32	38
-7	32	34
-6	29	30
-5	47	54
-4	26	30
-3	64	66
-1	39	39
0	35	35
1	35	39
2	47	57
3	45	49
8	33	33
9	27	28
• 3 7		
-11	38	-39
-9	41	44
-8	20	17
-7	40	44
-6	12	16
-5	21	25
-4	66	71
-3	40	39
-1	37	39
2	39	40
5	24	25
• 3 8		
-10	24	30
-7	34	37
-6	29	26
-5	30	28
• 3 8		
-4	43	45
-3	27	-27
1	21	22
2	26	27
4	24	30
• 4 -9		
-1	34	34
0	50	43
1	49	40
4	21	18
6	19	13
• 4 -8		
-6	11	-10
-4	62	56
-3	18	16
-2	19	18
-1	28	28
0	25	27
1	34	26
2	36	30
3	30	26
4	30	25
7	38	29
8	22	11
9	47	32
10	44	35
• 4 -7		
-9	13	17
-6	41	41
-5	28	27
-4	28	33
-3	23	23
-2	38	32
-1	38	28
0	48	42
1	24	14
2	65	49
3	26	24
6	25	26
7	30	27
9	46	38
10	69	46
• 4 -6		
-9	33	41
-8	22	22
-7	22	24
-6	44	44
-5	42	42
-4	88	90
-3	67	53
-2	109	-106
-1	33	-21
0	59	55
1	35	31
2	60	56
5	86	84
6	64	61
7	17	12
8	29	25
10	40	36
12	26	22
13	34	23
• 4 -5		
-10	51	59
-9	27	29
-7	34	37
-6	44	41
-5	69	69
-3	81	-75
-2	67	-61
-1	129	124
0	78	62
1	29	29
2	59	51
3	110	92
4	84	76
5	82	70
6	31	24
10	32	26
• 4 -4		
-13	18	26
-12	38	52
-11	33	40
-10	21	25
-7	46	52
-6	48	47
-5	66	70
-4	45	35
-3	45	33
-2	122	117
-1	83	73
0	114	101
1	125	104
2	55	45
3	86	75
4	72	60
5	72	66
6	99	99
7	61	-61
8	105	-103
9	84	72
10	58	54
11	66	61
12	49	42
13	22	18
14	32	27
• 4 -3		
-15	33	49
-13	23	26
-12	34	41
-11	30	39
-9	33	31
-8	41	41
-7	54	50
-6	79	77
-5	73	75
-4	137	144
-3	71	67
-2	120	109
-1	105	103
0	175	149
1	50	-41
3	118	111
4	89	84
5	62	61
6	39	32
7	47	-37
8	82	91
9	168	169
10	23	15
11	33	28
12	50	43
13	32	26
14	59	44
15	23	21
• 4 -2		
-16	13	19
-14	36	53
-13	46	54
-11	44	45
-9	39	41
-8	79	70
-7	36	-22
-6	28	40
-5	164	140
-4	174	157
-3	141	119
-2	135	114
-1	114	109
• 4 -2		
0	51	-36
1	86	-60
2	106	106
3	113	119
4	89	91
5	117	118
6	77	74
7	48	47
8	83	81
9	44	35
10	52	50
12	29	23
13	22	13
14	24	21
15	20	19
• 4 -1		
-14	29	27
-13	61	-62
-11	102	119
-10	37	43
-9	16	10
-8	41	38
-6	192	168
-5	220	217
-4	65	-39
-3	79	79
-2	23	18
0	23	26
1	25	30
2	40	35
3	46	46
4	22	25
5	103	112
6	108	107
7	40	44
8	55	61
9	28	35
10	17	12
11	43	-44
12	31	30
13	48	50
14	14	23
15	26	24
• 4 0		
-14	27	-23
-12	101	113
-11	64	74
-10	51	59
-9	57	57
-8	57	56
-7	53	47
-6	19	-22
-5	38	41
-4	91	74
1	23	23
2	54	57
4	86	95
5	140	160
6	40	49
8	25	28
9	22	28
10	23	-21
12	27	36
13	30	26
15	26	22
• 4 1		
-13	60	68
-12	54	65
-11	45	52
-10	91	87
-9	20	-14
-7	77	76
-5	63	56
-4	56	-35
0	47	62
1	55	59
3	30	29
4	139	158
5	30	33
6	26	-14
7	34	40
9	39	44
• 4 2		
-13	39	39
-12	37	42
-11	60	69
-8	87	84
-7	61	53
-5	58	53
-4	58	78
-3	149	154
-1	30	46
0	19	-3
1	107	111
2	45	47
3	25	23
4	30	32
6	46	48
8	40	45
9	76	84
10	33	44
12	31	31
• 4 3		
-16	41	49
-15	31	42
-12	24	26
-9	84	99
-8	94	105
-7	50	57
-6	54	63
-5	52	51
-4	26	22
-3	103	115
-2	69	65
-1	125	149
0	29	31
1	39	-18
2	52	54
3	57	53
4	49	59
5	57	61
7	30	47
9	46	55
• 4 4.		
-16	23	32
-12	21	25
-11	19	22
-10	28	33
-9	55	59
-8	41	48
-6	66	61
-5	90	85
-3	47	54
-2	41	39
-1	48	57
0	19	-3
1	57	67
2	105	127
3	24	29
5	38	44
7	67	83
8	44	47
9	23	-27
11	17	22
• 4 5		
-14	18	-14
-13	28	-26
-12	42	39
-11	28	31
• 4 5		
-10	27	34
-9	48	46
-8	25	30
-7	52	53
-6	99	89
-4	37	-25
-2	46	52
0	39	46
1	51	57
2	36	42
5	20	22
7	23	24
8	14	24
9	22	26
• 4 6		
-13	51	52
-12	64	71
-9	29	31
-8	27	31
-7	46	44
-5	30	-29
-2	28	32
-1	20	19
0	28	32
1	28	34
2	24	30
3	21	27
4	27	34
8	18	18
• 4 7		
-9	22	21
-7	17	20
-6	35	37
-5	23	25
-4	18	-10
-3	25	28
-2	58	58
-1	34	36
2	22	26
3	28	32
4	18	19
5	17	-17
• 4 8		
-8	30	36
-7	18	23
-6	20	26
-4	18	17
-3	74	79
-1	37	-28
1	19	22
• 5 -8		
-4	18	-16
-1	43	37
0	22	17
1	22	18
2	22	19
5	39	28
6	25	16
7	25	16
• 5 -7		
-3	23	21
0	49	39
1	44	34
2	54	50
3	38	28
8	39	26
9	40	31
• 5 -6		
-8	28	31
-7	36	40
-6	33	36
-5	47	50
-4	30	31
-2	90	88
-1	29	25
0	29	29
1	31	29
3	34	24
4	42	39
5	25	19
6	28	20
8	26	22
9	49	33
10	45	26
11	50	39
12	22	15
• 5 -5		
-11	21	27
-9	25	27
-8	43	55
-7	37	37
-6	58	55
-5	79	80
-2	47	51
-1	28	-20
0	52	43
1	114	94
2	62	41
3	77	73
4	50	45
6	79	72
7	50	42
8	36	29
9	52	38
10	44	29
11	36	22
12	51	31
• 5 -4		
-12	29	32
-11	30	29
-9	25	28
-8	28	31
-7	26	26
-6	54	54
-5	47	51
-3	91	83
-2	59	44
-1	63	55
0	35	26
1	73	71
2	69	58
3	85	76
5	63	54
6	36	35
9	36	24
10	44	37
11	22	19
12	39	28
• 5 -3		
-14	21	26
-12	32	36
-8	36	39
-7	48	46
-6	88	84
-5	73	68
-4	24	21
-3	56	48
-2	22	19
-1	63	57
0	23	19
1	51	46
2	59	56
4	56	57
5	42	33
7	65	65
10	46	50
11	41	36
12	35	31
13	32	29

Table VII.1.(cont.) •h k, l $5F_{obs}$ $5F_{calc}$

• 5	-2	
-13	30	35
-12	50	56
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-10	26	29
-6	43	44
-5	33	34
-4	69	61
-3	60	46
-2	76	77
-1	37	-39
1	23	23
2	60	56
3	53	52
4	67	68
5	73	68
6	48	53
7	41	48
• 5	-1	
-13	61	80
-10	26	25
-7	75	69
-6	64	47
-5	53	44
-4	86	87
-3	45	43
-2	108	114
-1	38	34
1	43	47
2	50	47
3	70	74
4	69	67
5	66	57
6	37	37
• 5	0	
-13	37	43
-12	58	65
-11	42	54
-10	66	64
-9	41	44
-7	96	81
-6	55	55
-5	64	65
-4	81	83
-3	93	102
-2	71	75
-1	74	93
0	12	12
1	52	67
2	36	30

3	40	37
4	74	78
5	63	73
• 5	1	
-16	17	19
-14	32	42
-13	55	57
-12	60	65
-10	36	36
-9	80	90
-8	34	32
-7	43	48
-4	73	76
-3	125	136
-2	56	52
-1	115	119
0	26	30
1	60	62
2	85	107
3	55	57
4	45	48
5	34	50
• 5	2	
-16	12	18
-14	21	20
-13	26	27
-10	29	35
-9	28	36
-7	23	25
-6	50	49
-5	24	23
-4	93	96
-3	118	111
-2	98	101
-1	67	83
• 5	3	
-10	31	38
-9	63	62
-8	67	67
-6	51	50
-5	37	33
-4	41	43
-3	37	38
• 5	4	
-13	26	27
-11	24	25
-10	33	39
-9	38	41
-8	31	36
-3	25	35

• 5	5	
-14	25	39
-13	21	23
-9	36	39
-8	41	44
-7	28	33
• 6	-8	
-2	25	34
-1	29	33
0	28	29
3	21	20
• 6	-7	
-2	27	26
-1	32	35
0	34	27
1	41	36
5	21	14
6	30	25
8	34	24
• 6	-6	
-7	33	37
-4	60	63
-3	33	28
-1	29	32
1	43	49
2	34	32
5	33	32
8	41	26
• 6	-5	
-10	28	37
-7	27	37
-6	42	50
-5	61	72
-4	30	28
-3	86	-103
-1	56	58
1	26	26
2	23	15
4	80	80
5	62	52
9	46	33
10	28	19
11	27	15
• 6	-4	
-11	35	47
-6	40	46
-4	52	-8
-2	68	71
-1	37	33
0	47	42

• 6	-4	
1	50	43
2	75	70
3	55	48
4	29	30
5	55	49
6	35	30
7	35	-24
11	25	17
• 6	-3	
-12	17	26
-8	23	29
-7	32	35
-6	29	34
-5	42	43
-4	36	29
-3	63	65
-2	35	32
-1	86	87
0	74	63
2	46	45
3	56	56
4	48	47
5	67	60
6	67	-64
7	91	-83
8	91	81
9	59	49
10	44	36
11	38	29
• 6	-2	
-14	17	34
-13	16	28
-9	35	37
-8	32	29
-6	33	39
-5	64	83
-4	44	47
-3	59	67
-2	83	88
-1	93	87
0	47	-39
2	68	65
3	49	49
4	51	49
5	40	35
7	64	62
8	92	82
11	45	35
12	29	20

• 6	-1	
-14	26	31
-13	25	-27
-12	24	34
-9	38	43
-8	37	-28
-6	116	131
-5	80	93
-4	61	81
-3	48	54
3	41	47
4	64	62
5	59	52
6	38	30
7	55	49
12	27	17
• 6	0	
-14	39	-39
-12	55	70
-9	29	37
-8	36	41
-7	76	78
-6	69	89
-4	55	66
-2	42	60
1	22	13
2	26	29
4	83	81
5	74	78
6	32	30
7	37	35
8	42	34
10	27	-19
11	28	24
12	44	36
• 6	1	
-13	57	61
-12	27	35
-11	36	56
-10	32	36
-8	26	29
-6	44	47
-5	73	85
-4	73	-67
-3	63	-30
-1	39	40
0	45	44
1	37	31
2	19	-2
3	69	67

4	94	93
• 6	2	
-14	24	30
-12	26	36
-11	39	43
-5	38	-17
-4	90	-75
-2	150	145
-1	19	3
1	24	22
2	30	23
3	72	75
9	20	13
• 6	3	
-14	13	19
-13	19	23
-12	24	32
-9	41	46
-8	27	30
-6	37	32
-5	23	28
-4	70	65
-3	81	82
-2	25	42
-1	28	31
0	39	35
4	30	28
6	33	-16
7	39	38
8	65	54
9	92	31
• 6	4	
-10	46	48
-9	46	48
-6	32	31
-4	46	52
-3	37	33
-2	63	72
0	29	-14
1	45	49
2	49	41
4	25	29
6	29	35
7	92	91
8	22	18
• 6	5	
-10	26	31
-3	28	30
0	41	39
1	60	54
4	21	23
[illegible]	[illegible]	10

Table. VII.2.

*h k, l $5F_{obs}$ $5F_{calc}$ for Paraquat $CoCl_4$

• 0 0		
6	168	-227
12	101	116
14	163	-183
16	62	61
• 0 1		
5	85	-79
7	130	195
11	112	110
13	108	125
• 0 2		
4	90	79
6	103	-165
12	71	-36
16	84	-94
• 0 3		
1	236	-245
3	354	-315
5	119	-172
9	65	-63
11	225	-226
13	178	-169
• 0 4		
0	288	-363
2	209	203
6	490	449
8	189	159
10	70	78
14	17	122
16	82	112
• 0 5		
1	389	-361
5	716	748
7	175	120
9	134	-113
11	113	-113
13	242	285
15	127	119
• 0 6		
0	316	317
2	43	-13
4	632	-628
6	273	-237
10	305	329
12	69	-58
14	138	-120
• 0 7		
1	116	51
3	329	-307
5	699	-723
7	252	-243
9	156	100
11	156	-180
11	180	-180
13	182	-177
15	133	-153
• 0 8		
2	51	36
6	98	-72
8	161	-145
10	71	60
12	112	122
• 0 9		
1	348	303
3	220	189
5	223	212
7	192	177
9	113	139
11	209	194
13	100	96
• 0 10		
0	398	395
2	72	42
4	77	34
6	83	87
8	201	205
• 0 11		
1	603	-581
3	64	-54
5	210	153
9	317	-342
11	150	-136
• 0 12		
0	228	-136
2	313	-273
4	109	92
8	233	-279
10	179	-193
• 0 13		
1	218	197
5	133	-119
7	172	174
9	193	185
• 0 14		
0	309	269
2	213	198
4	71	46
6	70	29
8	144	135
10	149	153
12	57	85
• 0 15		
7	149	-151
• 0 16		
0	156	-128
2	69	-68
4	258	-265
6	185	-157
2 18		
4	248	224
6	191	180
8	44	-41
• 0 19		
3	95	75
5	111	98
• 0 20		
4	76	-100
• 1 1		
2	136	139
3	247	-249
4	71	71
5	61	-11
6	247	214
7	369	-354
8	183	-160
9	397	-432
10	119	-127
11	175	-175
14	86	103
15	62	-64
• 1 2		
1	129	-131
2	374	-400
4	168	-162
5	125	-135
6	121	83
7	405	-399
9	79	-70
10	138	-123
11	182	194
12	87	-100
13	68	60
• 1 3		
2	397	480
3	214	232
4	246	212
5	296	267
6	124	-112
7	249	241
8	292	-267
• 1 3		
9	139	141
10	130	129
11	88	68
12	87	96
15	60	64
16	46	-70
• 1 4		
0	80	50
1	398	-509
2	153	154
3	293	-273
4	345	357
5	49	45
6	310	283
7	314	295
8	62	45
9	82	-80
10	122	121
11	113	-117
12	193	234
14	116	124
15	80	86
• 1 5		
1	47	-12
2	344	-378
3	230	-234
4	150	-140
5	275	-291
6	134	110
7	151	-150
8	169	160
9	48	-49
10	71	68
11	72	-55
12	121	-126
13	102	-86
14	56	-53
15	69	-74
• 1 6		
0	72	25
2	195	-205
3	113	-100
4	485	-543
5	92	-85
6	366	-398
8	65	-59
9	170	167
10	50	-47
12	161	-176
13	63	-82
14	141	-155
15	75	-72
• 1 7		
1	33	-13
2	101	-84
3	50	53
4	227	-195
5	56	51
6	159	167
8	126	104
10	152	-171
11	122	127
13	50	67
15	65	63
• 1 8		
0	79	-83
1	50	21
2	363	339
3	85	-56
4	454	521
5	157	132
6	259	297
7	81	-58
8	98	113
9	87	76
10	72	-35
11	110	-109
12	91	66
14	138	135
• 1 9		
1	95	75
2	558	569
3	91	-48
4	127	121
5	44	-29
6	308	-299
7	128	115
8	206	-213
9	152	179
12	204	226
• 1 10		
0	347	-341
1	156	145
2	224	-208
3	97	78
4	78	-75
5	47	63
6	118	-128
7	86	-84
8	196	-199
10	190	-198
12	100	-101
13	59	62
• 1 11		
1	248	-238
2	197	-170
3	80	-62
6	141	118
7	124	-123
9	149	-162
10	106	-72
11	75	-58
12	75	-53
• 1 12		
0	270	255
1	90	-85
2	158	136
6	72	56
8	186	187
9	83	89
10	141	136
• 1 13		
1	375	376
3	71	64
4	124	-95
6	88	90
7	86	56
9	157	148
11	123	126
• 1 14		
0	257	-268
1	312	-336
2	113	-104
3	183	-183
4	88	62
7	143	151
8	78	-77
9	72	51
10	73	-76
11	94	-98
• 1 15		
1	50	-47
2	167	141
3	166	-172
5	175	-148
7	13	-117
8	101	-84
9	83	-83
11	57	-72
• 1 16		
1	110	97
3	186	190
5	64	-42
7	166	-138
• 1 17		
1	46	1
3	154	154
5	205	192
7	85	78
• 1 18		
2	58	58
4	92	88
6	55	47
• 1 19		
2	98	88
3	140	-128
5	142	-155
6	42	-57
• 1 20		
0	86	-81
2	44	-34
3	97	-109
• 2 0		
1	327	-404
3	279	-268
4	381	-456
6	422	-394
7	157	142
8	144	-156
11	157	-208
12	90	-88
14	175	-173
15	113	134
16	61	-59
• 2 1		
1	109	172
3	121	83
4	127	133
5	401	-360
6	162	-142
7	50	-40
8	222	-205
9	84	-52
12	108	103
15	90	-53
16	63	-69
• 2 2		
0	303	304
1	103	157
2	136	151
3	200	186
4	462	470
5	213	-174
7	168	-162
8	199	185
9	59	71
10	126	127
11	91	103
12	155	156
14	138	110
15	83	-65
16	51	68
• 2 3		
1	95	84
2	661	-708
3	176	196
4	229	-258
5	269	295
6	338	345
7	186	200
8	231	251
9	85	87
10	142	-111
11	91	21
12	178	-181
• 2 4		
0	490	-559
1	396	-377
2	224	-275
3	379	-362
4	107	-109
5	133	124
7	229	231
8	222	-242
9	126	116
10	191	-211
11	111	-110
12	153	-162
13	100	-116
• 2 5		
1	485	-517
2	351	345
3	198	-181
4	61	43
5	198	-189
6	277	-261
7	197	-200
8	166	-174
9	124	-111
10	143	154
11	157	-165
12	123	151
14	82	-83
15	71	-78
• 2 6		
0	261	250
1	313	-308
2	253	234
3	129	-102
5	184	184
6	150	160
7	57	49
9	109	71
10	129	124
11	64	-84
• 2 7		
1	440	433
2	133	97
3	253	241
4	85	86
5	73	-15
7	166	170
8	151	-166
9	325	350
10	111	-127
11	153	173
12	101	79
13	104	118
14	84	31
• 2 8		
0	104	97
1	324	272
2	83	69
3	422	395
5	95	-75
7	321	-308
11	162	173
13	49	56
• 2 9		
1	248	-204
2	73	53
3	226	-245
5	191	-201
7	177	-177
9	182	-168
11	122	-94
13	30	-105
• 2 10		
2	143	-118
• 2 10		
1	231	-211
2	228	-220
3	330	-326
5	85	31
6	88	-59
7	239	282
10	106	-83
11	149	-172
• 2 11		
1	116	93
2	83	82
3	239	256
4	86	-67
5	226	217
7	182	164
• 2 12		
0	105	103
2	87	-23
3	88	-40
4	228	251
5	91	-109
6	203	201
8	88	69
9	103	102
11	48	19
• 2 13		
2	110	-94
3	92	-65
5	170	-164
6	142	158
10	86	-106
12	51	-36
• 2 14		
0	64	-66
1	64	71
2	129	-127
3	129	116
4	102	-130
6	174	-176
7	118	-84
8	96	-85
• 2 15		
2	102	183
4	107	39
6	184	-183
8	123	-114
10	87	87
• 2 16		
0	150	145
2	119	109
5	97	75
6	92	68
8	75	82
• 2 17		
2	125	-126
3	77	11
• 2 18		
0	168	-161
2	86	-74
• 2 19		
1	84	-87
2	71	-57
• 3 1		
1	113	-113
2	146	171
3	347	426
4	144	-126
6	67	-84
7	188	209
8	80	-65
9	121	-108
10	89	79
11	110	114
13	219	229
14	48	-26
15	141	138
• 3 2		
0	50	-38
1	142	-130
2	149	122
3	290	281
4	167	172
5	61	28
6	263	298
7	91	63
8	128	135
9	106	-65
10	110	-124
13	50	56
• 3 3		
1	264	-292
2	106	-86
3	463	-464
4	166	-172
5	155	-142
6	110	63
7	93	-75
8	58	-37
9	138	-128
10	64	-81
11	127	-135
13	110	-117
14	81	64
15	58	-45
• 3 4		
0	302	-302
1	57	43
2	248	-230
3	189	209
4	60	-39
5	132	-113
6	88	-98
7	55	29
8	312	-349
10	180	-178
11	63	86
13	54	-32
15	69	-64
• 3 5		
1	430	408
2	78	-55
3	59	48
5	138	-124
7	98	74
9	218	230
11	125	165
13	92	33
• 3 6		
0	700	741
1	101	-93
2	396	403
3	140	-142
4	180	-160
6	95	-65
8	340	383
10	322	347
12	57	61
• 3 7		
1	64	-53
2	60	25
5	76	64
7	148	-154
8	65	73
9	111	-104
14	95	-69
• 3 8		
1	155	114
2	170	-161
3	52	61

Table. VII.2. (cont.)

h	k	l	$5F_{obs}$	$5F_{calc}$
• 3	8			
		4	77	9
		6	146	-134
		7	231	-249
		8	155	-140
		10	249	-262
• 3	9			
		2	120	-110
		3	96	-92
		6	138	126
		8	64	94
		10	121	-81
		11	97	-119
		13	104	-129
• 3	10			
		0	112	-62
		1	98	68
		2	140	125
		4	329	330
		6	260	243
		7	64	-87
		8	110	91
• 3	11			
		3	193	195
		5	228	236
		7	90	44
• 3	12			
		0	175	164
		1	108	-65
		4	330	-338
		6	220	-224
		7	63	69
• 3	13			
		1	110	73
		2	110	-105
		3	319	-310
		4	156	-154
		5	253	-254
		6	62	74
		7	134	-139
		8	57	45
• 3	14			
		0	110	-77
		1	64	36
		2	127	99
		3	219	209
		4	139	130
		7	112	-69
		10	66	-47
• 3	15			
		1	152	147
		2	87	-48
		4	103	-81
		5	141	131
		7	88	110
		9	101	94
• 3	17			
		1	206	-239
• 4	0			
		1	31	38
		2	89	84
		3	394	419
		5	136	124
		6	298	355
		7	160	-162
		8	61	15
		9	45	-64
		10	80	-89
		11	64	-36
		12	170	150
		13	84	91
		14	189	186
• 4	1			
		1	115	106
		2	219	236
		3	91	72
		4	180	-134
		5	175	-127
		6	64	-55
		7	81	84
		8	114	-107
		9	101	118
		11	64	57
		12	104	103
• 4	2			
		1	33	39
		2	243	-255
		3	156	124
		4	330	-373
		6	294	-315
		7	71	-49
		8	62	-14
		10	92	-71
		12	169	-173
		14	123	-129
• 4	3			
		1	250	-284
		2	311	-338
		3	85	-67
		4	176	-138
		5	49	21
		6	195	185
		7	155	-182
		8	181	180
		9	177	-211
		12	132	-120
• 4	4			
		0	155	141
		1	226	-211
		2	221	236
		3	270	-271
		4	110	104
		7	127	102
		8	100	62
		9	92	92
		10	122	116
		12	91	111
		14	47	64
• 4	5			
		1	531	569
		3	57	-8
		4	50	-49
		5	107	-68
		6	91	76
		7	178	165
		8	78	74
		9	299	332
		10	91	49
		14	136	-102
• 4	6			
		0	414	-377
		1	97	-74
		2	125	-118
		3	117	101
		4	37	14
		6	146	156
		7	230	-221
		8	194	-194
		10	101	-122
		13	55	58
• 4	7			
		1	331	-331
		2	174	144
		3	146	-142
		4	69	58
		5	72	-37
		6	62	57
		7	239	-217
		8	65	-76
• 4	7			
		9	215	-249
		10	63	-56
		11	82	-122
		12	51	60
		13	42	13
• 4	8			
		0	114	115
		1	157	147
		3	241	234
		4	138	-157
		7	203	-221
		8	80	107
		9	78	-52
		11	88	88
		12	59	-77
		13	82	64
• 4	9			
		1	168	171
		3	203	179
		5	184	168
		7	166	161
		9	99	122
		11	74	88
		13	54	45
• 4	10			
		0	74	-46
		1	114	-92
		2	62	52
		3	159	-135
		4	270	272
		5	46	40
		6	80	35
		7	195	200
		11	97	-75
		12	71	102
• 4	11			
		1	63	-23
		2	135	-121
		3	199	-166
		4	195	-193
		5	284	-309
		8	97	91
		9	57	25
• 4	12			
		2	138	-131
		4	153	-143
		6	149	-152
		9	74	61
		10	65	-47
• 4	13			
		3	152	163
		4	91	-73
		5	117	143
		11	42	56
• 4	14			
		0	128	96
		1	78	60
		2	142	108
		3	108	88
		4	106	121
		6	89	113
		7	83	-69
		8	67	77
		10	54	54
• 4	15			
		2	170	147
		3	83	-84
		4	151	130
		6	108	-90
		8	96	-86
• 4	16			
		0	206	-199
		2	95	-88
		3	53	-35
		4	62	-60
• 4	17			
		1	35	-37
		2	68	-51
		4	61	6
		6	59	50
• 4	18			
		0	139	155
		2	93	88
		3	56	-35
		4	47	-47
• 5	1			
		2	168	169
		3	276	-267
		5	65	-37
		6	59	-81
		7	100	-115
		9	158	-183
		10	94	126
		11	189	-168
		13	134	-117
• 5	2			
		1	269	-250
		2	64	-59
		3	236	-255
		5	102	-87
		7	242	261
		8	67	-75
		10	133	-143
		11	140	-116
• 5	3			
		1	102	80
		2	120	-117
		3	195	205
		4	88	-85
		5	291	305
		6	242	214
		7	144	140
		8	125	141
		9	83	34
		10	66	-52
		11	44	47
		12	123	-114
		13	84	88
• 5	4			
		0	251	265
		1	154	145
		2	167	167
		3	212	238
		4	54	54
		5	213	-204
		6	132	119
		7	160	-177
		8	143	135
		10	103	134
		11	155	141
		13	52	33
• 5	5			
		1	34	7
		2	136	131
		3	140	-125
		4	57	79
		5	241	-248
		7	140	-130
• 5	6			
		0	136	-106
		1	52	-41
		2	137	-130
		3	56	-50
		4	222	-232
		5	88	117
		6	256	-256
		7	67	62
		8	143	-117
		11	57	-74
• 5	7			
		1	69	57
		2	142	118
		3	42	-45
		4	98	71
		5	102	82
		6	199	-197
		8	116	-107
		10	61	69
		12	100	85
• 5	8			
		0	147	149
		1	113	62
		2	230	226
		4	165	141
		5	105	80
		6	106	70
		8	175	195
		10	71	74
		12	74	82
• 5	9			
		1	142	-123
		2	352	-376
		3	103	81
		4	105	-106
		5	247	261
		6	135	144
		8	121	126
		9	96	-97
		10	109	-92
		12	67	-79
• 5	10			
		0	186	-213
		2	170	-170
		3	82	-58
		4	107	-72
		5	67	37
		6	82	-61
		8	62	-91
		10	101	-119
• 5	11			
		1	83	-53
		2	117	146
		3	117	-98
		5	115	-115
		6	113	-124
		7	62	-58
		8	41	-54
		10	77	65
		11	42	-43
• 5	12			
		0	135	130
		1	48	-43
		2	143	134
		3	67	-45
		7	72	58
		8	76	65
		10	91	81
• 5	13			
		1	155	133
		2	92	74
		3	79	50
		4	63	45
		5	129	121
		9	66	66
• 5	14			
		1	108	96
		2	76	51
		3	155	143
		4	144	-144
		5	137	-122
		6	137	-125
		7	126	-104
		8	54	43
• 5	15			
		1	153	-133
		3	103	-99
		5	60	-5
		6	76	65
		7	67	-76
• 5	16			
		0	96	-90
		1	102	-93
		3	106	-116
		6	30	36
• 5	17			
		1	58	53
		3	57	74
• 6	0			
		2	264	-233
		3	269	274
		4	115	87
		5	115	-85
		6	186	-142
		7	291	-339
		8	163	-172
		10	232	-243
• 6	1			
		1	185	-178
		5	115	100
		6	176	135
		9	92	-81
• 6	2			
		0	276	322
		2	203	200
		3	117	-119
		4	93	58
		8	199	220
		10	138	138
• 6	3			
		1	138	157
		2	102	103
		3	101	102
		5	85	60
		6	110	-114
		10	86	70
• 6	4			
		2	71	-39
		4	278	-273
		8	93	-70
• 6	5			
		2	203	-201
		3	275	-268
		4	181	-180
		5	190	-177
		6	114	150
		10	116	-107
• 6	6			
		0	79	-62
		1	98	72
		2	130	96
		3	209	183
		6	114	98
		7	115	-118
• 6	7			
		2	138	155
		3	199	199
		5	361	416
• 6	8			
		1	110	-68
		3	92	-67
		5	115	65
• 6	9			
		1	160	-146
		3	148	-118
		5	114	-124
• 6	11			
		1	186	185
		6	118	118
• 6	12			
		0	231	241
		2	127	117
		6	94	-57
• 6	13			
		1	135	-133
		2	133	109

••••••••••••••

Table VII.3.

*1 h, k 5F$_{obs}$ 5F$_{calc}$ for Paraquat Cu$_2$Cl$_4$

• 0 0		
6	324	-358
8	550	610
10	664	-738
12	388	389
14	193	-230
16	211	225
18	110	-107
20	174	132
• 0 1		
3	420	-471
5	439	398
7	566	-616
9	367	356
11	134	103
13	269	-231
15	52	43
17	188	168
19	103	-91
• 0 2		
2	546	1128
4	525	-663
6	430	463
8	724	-864
10	778	879
12	694	-729
14	365	390
16	204	-226
18	99	114
20	54	-46
• 0 3		
1	458	511
3	204	-174
5	29	38
7	307	233
9	369	-343
11	282	-246
17	224	-231
19	160	172
• 0 4		
2	554	-748
4	492	615
6	468	-499
8	664	712
10	368	-409
12	277	286
14	238	-240
16	261	237
18	95	-87
20	56	61
• 0 5		
1	246	228
3	549	556
5	450	-414
7	129	105
11	67	70
13	333	-305
15	73	42
17	113	108
19	92	-76
• 0 6		
2	391	452
4	421	-490
6	640	767
8	603	-571
10	255	250
12	160	-160
14	52	55
16	175	-133
18	111	92
• 0 7		
1	231	-188
3	287	-278
5	613	628
7	109	-76
9	92	-67
11	50	38
13	74	-58
17	43	58
• 0 8		
2	810	-923
4	664	769
8	473	489
10	140	-141
12	164	-128
14	102	-104
16	217	215
18	182	-167
• 0 9		
1	295	250
3	269	207
5	141	103
7	121	-98
9	251	212
11	146	-160
13	73	-42
17	75	-81
19	32	57
• 0 10		
2	490	473
4	326	-344
6	597	668
8	442	-511
10	258	261
12	116	-149
14	152	163
16	259	-278
18	165	165
• 0 11		
5	143	-134
7	206	178
9	137	-126
11	90	108
15	118	150
• 0 12		
2	197	-196
4	139	154
6	232	-261
8	293	325
10	314	-341
12	69	75
14	213	-227
16	84	87
• 0 13		
1	86	-71
5	154	141
7	104	-90
9	126	-149
11	175	184
13	60	-27
15	66	-62
• 0 14		
4	90	76
6	127	129
8	222	-238
10	173	173
12	60	-66
14	95	79
• 0 15		
1	127	141
9	124	124
11	156	-181
13	119	58
• 0 16		
2	88	-105
4	71	58
6	217	-217
8	111	99
10	127	-148
12	55	48
• 0 17		
1	109	68
3	68	55
5	65	60
9	65	-40
11	66	83
• 0 18		
2	262	238
4	301	-253
6	236	204
8	146	-120
• 0 19		
1	117	122
3	84	-92
7	102	105
9	88	-117
• 0 20		
2	93	-63
4	205	178
6	112	-125
• 0 21		
1	48	-45
• 1 0		
1	173	-163
2	202	-194
3	141	-160
4	222	-223
5	517	561
6	125	-116
7	98	-64
8	62	63
9	39	38
10	150	-141
11	45	-38
12	95	77
13	204	195
15	51	-54
16	132	-147
17	47	-52
18	43	55
19	92	89
20	30	28
• 1 1		
1	304	318
2	339	-325
3	260	231
4	651	-822
5	394	360
6	52	43
7	33	19
8	175	-172
10	42	43
11	63	53
12	125	-135
14	169	186
15	153	-164
16	50	-51
17	82	72
18	74	-52
• 1 2		
1	73	86
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10	42	-45
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12	135	-100
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12	152	139
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20	55	69
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7	88	87
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14	229	-208
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17	46	-10
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5	33	-4
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9	266	223
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17	44	-58
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19	33	-22
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9	275	243
10	185	-177
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12	112	-101
14	125	120
16	47	-54
17	114	117
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6	39	21
8	230	-213
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12	72	-63
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17	78	-76
19	31	36
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8	116	88
9	138	-138
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11	102	-101
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12	51	24
13	78	-81
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16	49	-22
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8	114	117
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11	86	-97
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13	45	54
14	129	142
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8	88	93
10	69	60
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7	113	-133
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15	58	-58
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6	86	101
8	116	-128
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14	41	60
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7	46	68
8	98	-93
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7	109	-123
10	45	59
• 1 18		
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3	59	72
6	75	-78
• 1 19		
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4	49	48
5	33	-28
7	38	44
• 1 20		
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2	50	20
3	61	-57
• 2 0		
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5	261	-275
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7	37	-20
8	341	-364
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10	84	94
11	63	55
12	140	111
13	107	-101
14	198	-227
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16	59	-43
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20	28	21
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• 2 1		
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10	27	32
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13	76	69
14	31	-33
15	177	-168
17	116	111
19	96	-89
20	24	24
• 2 2		
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2	233	224
3	243	-256
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5	44	46
6	177	-149
7	251	-262
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13	69	68
14	31	9
16	125	115
18	171	-173
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9	231	-248
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12	86	-90
13	124	-110
14	83	67
15	83	67
19	130	112
• 2 4		
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3	374	389
4	215	177
5	289	-294
6	81	-57
7	46	74
8	175	-148
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12	175	165
13	117	-106
14	146	-114
15	30	29
16	91	-93
18	154	160
• 2 5		
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6	362	-348
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9	404	408
10	111	-102
11	443	-407
12	195	161
13	304	304
14	62	-50
15	182	-189
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17	99	103
18	62	49
19	97	-100
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2	39	87
3	331	-353
4	451	-458
5	217	211
6	307	276
7	240	-208
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10	88	-76
11	204	-171
12	82	-75
13	108	96
14	69	54
15	93	-91
18	46	-21
• 2 7		
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4	204	-197
5	259	-290
6	72	67
7	155	173
8	32	-92
9	400	-380
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11	447	482
12	159	-148
13	365	-363
14	109	99
15	149	148
16	37	-44
17	23	-42
18	50	54
19	56	68
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3	177	153
4	253	241
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6	116	-103
8	122	-91
9	42	-42
10	119	100
11	88	89
12	76	-84
13	92	-85
15	39	56
16	61	76
18	58	-72
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2	139	-143
3	228	-261
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5	166	192
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9	318	304
10	62	-46
11	429	-394
12	98	74
13	328	320
14	40	-36
17	47	-47
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3	169	-178
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6	254	-239
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9	44	-28
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11	128	-95
12	43	-20
13	29	30
14	38	-52
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6	53	47
7	169	151
8	44	27
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10	31	24
11	125	108
12	51	-42
13	82	-81
17	26	44
• 2 12		
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3	96	98
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12	39	29
14	56	60
16	60	-71
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5	348	386
6	44	-61
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9	42	46
10	96	-85
11	184	-164
12	36	41
13	106	97
15	44	-51
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3	132	-130
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5	107	119
6	111	-116
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11	94	-90
12	154	-145
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14	28	-19
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5	196	-237
7	111	130
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10	65	61
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12	70	-67
13	90	-92
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12	58	79
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7	23	-41
9	80	81
10	61	-60
11	83	-93
• 2 18		
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• 2 20		
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Table VII.3.(cont.)

*l h, k $5F_{obs}$ $5F_{calc}$

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8	172	165
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10	153	-154
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12	29	12
13	98	-101
14	120	123
15	40	44
16	90	-116
19	46	-45
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5	200	-210
6	143	-143
7	161	164
9	51	-49
10	38	-36
11	98	114
12	88	93
13	106	-86
14	87	-98
15	56	-66
17	112	82
18	44	39
19	19	-10
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3	144	-137
4	88	-85
5	181	195
6	207	-188
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9	63	72
10	109	-133
14	120	-147
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16	37	41
18	19	-7
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5	180	175
6	117	-137
7	237	256
9	112	-105
10	55	-67
11	50	58
12	128	-133
13	118	124
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15	67	-74
16	25	-17
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7	86	-93
8	57	-69
9	120	131
10	97	113
11	71	77
12	66	-57
13	78	-61
14	40	-38
15	47	34
16	99	88
17	31	22
19	16	35
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3	224	214
4	21	-20
5	115	-94
6	47	45
7	314	-300
8	134	-125
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10	70	81
11	137	-140
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13	185	-166
14	85	-58
15	88	77
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18	28	24
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5	81	-75
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9	126	-122
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12	51	-51
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18	35	30
• 3 7		
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8	145	142
9	152	-136
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13	80	58
16	62	69
18	20	-35
• 3 8		
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5	26	-28
6	61	-62
8	160	135
9	72	62
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13	48	-30
14	52	-43
15	41	-45
16	88	72
17	52	61
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5	188	-184
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8	77	-68
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12	84	70
13	38	-29
14	24	-24
15	31	-25
16	18	-18
17	28	31
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8	122	-102
9	29	26
11	102	-94
12	123	127
13	66	61
14	68	-77
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10	56	45
11	101	-105
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13	33	-48
14	46	46
15	47	34
16	11	23
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• 3 12		
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15	23	28
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• 3 18		
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7	22	-15
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8	149	135
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12	163	166
14	73	-92
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9	37	36
10	238	-233
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12	83	97
13	161	-163
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15	47	57
16	81	74
17	79	61
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4	84	-138
5	99	127
6	62	58
7	212	-257
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10	262	305
11	149	-154
12	246	-292
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14	172	177
15	107	-102
16	68	-58
17	123	102
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8	184	-187
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10	217	238
11	164	-174
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14	106	113
15	40	-28
16	85	-65
17	99	-98
• 4 4		
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3	44	-17
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5	137	-120
6	145	-174
7	117	111
8	173	180
9	229	-248
10	213	-166
12	144	127
13	69	-71
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17	111	-98
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13	152	-133
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17	34	33
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12	26	-18
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16	76	-56
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7	171	-157
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11	27	18
16	35	-16
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5	291	-303
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8	196	184
9	165	-140
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16	83	88
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14	68	61
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7	38	29
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14	54	56
• 4 12		
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15	80	-90
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13	84	-78
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8	248	-251
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12	22	18
13	53	71
14	115	-136
15	25	28
• 5 5		
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3	140	130
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9	34	37
15	76	115
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6	79	-57
7	72	-66
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10	149	-127
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12	29	-21
14	68	66
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3	33	11
4	66	-60
6	24	-15
7	68	-72
8	24	-38
9	47	45
• 5 8		
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8	74	-63
• 5 9		
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3	215	-224
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7	96	105
11	55	-44
12	47	-46
13	46	58
• 5 10		
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5	47	-50
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8	91	-98
10	109	108
12	34	-45
• 5 11		
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8	49	-16
9	41	56
10	39	-44
11	58	61
• 5 13		
5	69	-62
7	68	88
9	20	-33
• 5 14		
2	58	60
6	76	-85
7	16	-15
• 5 15		
1	98	98

•••••••••••••••

Table VII.4.

*h k, l 2.5F_{obs} 2.5F_{calc} for Paraquat $PdCl_4$

• 0 0		
8	1186	1253
10	815	685
12	1172	1101
14	303	406
16	506	556
• 0 2		
4	1056	862
6	759	642
8	739	628
10	639	544
12	303	326
14	368	371
16	220	258
• 0 4		
0	51	51
2	136	102
4	211	230
8	307	212
10	154	122
12	162	105
14	145	100
16	170	111
• 0 6		
0	162	244
2	775	888
4	525	470
6	545	523
8	458	403
10	509	489
12	294	206
14	373	363
• 0 8		
0	691	692
2	377	418
4	582	553
6	419	432
8	435	426
10	322	297
12	328	347
14	235	216
• 0 10		
0	432	423
2	397	369
4	154	139
6	507	552
10	238	263
12	214	225
14	140	158
• 0 12		
0	511	503
2	733	703
4	536	614
6	461	471
8	465	520
10	412	457
12	251	293
• 0 14		
0	483	488
2	467	513
4	424	469
6	421	446
8	389	393
• 0 16		
0	81	92
4	145	163
• 1 1		
6	649	660
8	789	776
10	646	627
12	409	372
14	440	445
16	294	310
• 1 2		
3	304	259
• 1 3		
4	115	135
6	779	751
8	162	150
10	366	338
12	307	267
14	174	198
16	87	120
• 1 4		
1	493	655
3	554	534
5	567	491
7	405	390
9	278	294
11	234	259
• 1 5		
0	554	711
2	580	679
4	603	619
6	626	564
8	528	474
10	402	393
12	358	344
14	260	272
16	204	227
• 1 6		
1	156	145
3	162	151
5	106	116
7	123	103
• 1 7		
0	995	1085
2	658	624
4	717	754
6	705	715
8	538	562
10	432	424
12	445	508
14	249	278
• 1 8		
1	495	-438
3	552	-554
5	363	-365
7	319	-334
9	333	-365
11	184	-223
13	156	-197
• 1 9		
0	405	337
2	358	363
4	584	609
8	512	506
10	189	216
12	199	194
14	204	195
• 1 10		
1	253	-209
3	184	-128
5	189	-186
7	137	-156
• 1 11		
0	350	318
2	423	378
4	304	288
6	333	337
8	230	240
10	284	256
12	179	193
• 1 12		
1	194	157
3	194	187
5	137	140
7	130	130
9	115	139
• 1 12		
11	87	94
• 1 13		
0	604	552
2	485	417
4	475	442
6	465	444
8	398	364
10	294	303
• 1 15		
0	281	276
2	278	297
4	238	228
6	278	300
8	208	193
• 2 0		
2	629	-607
4	532	517
6	261	200
8	406	338
12	503	435
16	237	200
• 2 1		
1	149	-212
3	694	-696
5	168	-146
7	179	-169
9	326	-332
15	155	-169
• 2 2		
4	483	514
6	430	435
8	446	418
10	418	388
12	241	234
14	280	279
16	195	198
• 2 3		
1	63	-60
3	110	-102
• 2 4		
6	703	695
8	751	703
10	560	530
12	437	449
14	294	362
• 2 5		
1	383	444
3	364	380
5	386	357
7	335	298
9	265	239
11	195	213
13	127	171
15	100	133
• 2 6		
0	598	668
2	866	1148
4	701	745
6	742	789
8	554	584
10	556	632
12	297	346
14	323	436
• 2 7		
1	229	-183
5	168	-160
7	127	-124
• 2 8		
0	754	764
2	513	538
4	583	645
6	470	503
8	459	498
10	307	360
12	323	380
14	233	254
• 2 9		
1	323	-283
3	220	-180
5	265	-253
7	241	-216
11	127	-169
13	100	-127
• 2 10		
0	344	367
2	418	394
4	134	173
6	538	505
8	134	136
10	307	289
12	224	219
• 2 11		
1	273	224
5	241	211
7	195	171
11	179	149
• 2 12		
2	241	252
4	195	195
6	134	129
8	174	183
10	200	177
• 2 14		
0	257	226
2	283	249
4	241	220
6	245	221
8	237	191
• 2 15		
1	162	-122
3	155	-130
5	134	-111
7	110	-104
• 2 16		
0	425	351
2	347	282
4	432	382
• 3 1		
4	356	420
6	314	315
8	330	336
10	314	300
12	211	180
14	263	222
16	172	153
• 3 2		
1	693	-782
3	247	-249
5	579	-618
7	448	-463
9	162	-171
11	325	-341
13	167	-234
• 3 3		
2	962	1128
4	767	739
6	1055	991
8	604	564
10	579	636
12	455	463
14	414	421
16	229	287
• 3 4		
1	152	-147
3	275	-232
5	91	-109
7	107	-103
9	115	-126
• 3 5		
0	593	702
2	620	688
4	645	635
6	569	563
8	515	491
10	442	413
12	312	352
14	269	287
• 3 6		
1	122	116
3	162	143
5	99	95
7	115	91
• 3 7		
0	435	500
2	240	254
4	361	374
6	278	296
8	272	287
10	172	181
12	243	253
14	115	125
• 3 8		
1	207	177
3	107	-124
5	162	165
• 3 9		
0	622	633
2	493	481
4	654	698
6	322	312
8	507	573
10	304	320
12	295	353
14	215	248
• 3 10		
1	167	108
3	295	258
9	162	178
13	57	57
• 3 11		
0	441	422
2	521	475
4	427	391
6	437	421
8	319	329
10	319	329
12	253	259
• 3 12		
3	122	130
9	91	98
• 3 13		
0	207	201
2	115	128
4	162	162
6	146	146
8	152	138
10	122	104
• 3 14		
1	218	-160
3	233	-170
5	167	-142
7	141	-129
9	141	-122
• 3 15		
0	266	250
2	260	290
4	253	225
6	298	274
• 3 16		
1	128	-100
3	146	-129
• 4 0		
2	278	276
4	840	867
6	310	281
8	582	618
10	176	211
12	406	423
14	146	147
16	193	270
• 4 1		
1	158	185
3	293	-286
5	187	168
7	86	93
9	141	-148
11	108	104
15	71	-69
• 4 2		
2	746	957
4	740	782
6	757	757
8	569	602
10	459	551
12	402	423
14	297	376
16	187	288
• 4 3		
1	50	-60
3	112	-97
• 4 4		
0	692	749
2	630	639
4	744	672
6	579	545
8	609	526
10	439	412
12	351	388
• 4 5		
1	100	-108
3	132	-133
5	122	-90
7	93	-84
• 4 6		
0	112	-82
2	112	168
4	122	-58
6	132	142
10	146	115
14	132	97
• 4 7		
3	176	175
9	106	117
• 4 8		
0	367	353
2	247	234
4	324	328
6	229	209
8	273	265
10	193	175
12	209	198
• 4 9		
1	100	72
3	200	176
9	137	123
• 4 10		
0	706	610
2	760	783
4	585	564
6	688	687
8	432	466
10	471	531
12	335	353
• 4 11		
1	106	53
3	180	-162
7	93	28
• 4 11		
9	141	-117
• 4 12		
0	442	395
2	439	431
4	416	377
6	399	373
8	327	315
10	308	298
• 4 13		
1	93	-47
5	86	-45
• 4 14		
0	226	197
2	237	208
4	206	183
6	200	192
• 5 1		
2	551	557
4	490	492
6	530	537
8	388	379
10	345	361
12	243	312
14	209	248
• 5 2		
3	663	666
5	335	324
7	298	315
9	385	437
11	128	197
13	132	193
• 5 3		
0	423	507
2	703	789
4	515	540
6	547	595
8	397	443
10	412	486
12	222	290
14	296	349
• 5 4		
1	105	82
5	74	72
• 5 5		
0	334	406
2	327	413
4	344	392
6	331	342
8	317	321
10	238	277
12	222	234
14	212	205
• 5 6		
1	184	-157
3	136	-121
5	148	-142
7	128	-121
9	93	-91
11	81	-95
13	66	-72
• 5 7		
0	322	295
2	247	235
4	347	317
6	181	167
8	243	266
10	148	163
12	193	178
• 5 8		
1	87	102
3	155	-133
5	93	108
7	93	72
11	124	88
13	57	44
• 5 9		
0	638	614
2	364	305
4	544	495
6	377	346
8	367	401
10	277	229
12	375	353
• 5 10		
1	206	-167
5	155	-157
7	119	-125
11	105	-106
• 5 11		
0	456	403
0	0	446
4	405	379
6	398	395
8	347	321
10	326	312
• 5 12		
1	193	-143
3	119	-74
5	178	-134
7	155	-116
9	66	-57
• 5 13		
0	296	250
2	258	241
4	290	260
6	217	193
• 5 14		
1	243	163
3	178	144
5	184	148
• 5 15		
0	241	194
• 6 0		
6	83	23
8	545	499
10	188	171
12	234	240
• 6 1		
3	148	100
5	298	298
7	253	241
9	98	80
11	157	201
13	122	137
• 6 2		
2	291	347
4	382	279
6	364	359
8	231	228
10	248	241
12	199	217
• 6 3		
3	199	158
5	202	158
7	128	141
9	98	110
11	90	102
13	64	83
• 6 4		
2	387	435
4	531	464
6	452	416
8	356	372
10	288	293
12	261	303
• 6 5		
3	185	-181
5	181	-151
7	165	-140
• 6 5		
9	133	-135
11	83	-105
13	74	-91
• 6 6		
2	694	703
4	585	515
6	690	675
8	401	415
10	411	475
12	324	353
• 6 8		
2	480	424
4	513	472
6	401	345
8	415	392
10	313	298
12	236	272
• 6 9		
3	133	109
11	52	30
• 6 10		
2	326	295
4	128	135
6	173	162
8	104	133
10	222	207
• 6 11		
1	128	-99
3	234	-222
5	83	-82
7	74	-90
9	133	-165
• 6 12		
0	165	221
2	143	177
4	133	150
6	199	224
• 6 14		
0	269	239
2	271	241
• 7 1		
2	369	412
4	351	373
6	453	485
8	309	298
10	261	306
12	321	309
• 7 2		
1	116	-107
3	52	-14
5	108	-98
7	95	-76
• 7 3		
0	67	48
2	329	326
4	226	172
6	201	162
8	182	160
10	220	208
12	67	49
• 7 4		
1	191	-166
3	218	-187
5	198	-145
7	155	-134
9	147	-132
11	95	-92
• 7 5		
0	452	448
2	441	455
4	459	436
6	391	382
8	344	362
10	321	314
12	228	262
• 7 7		
0	519	547
2	502	562
4	555	601
6	391	421
8	480	511
10	363	383
• 7 8		
1	218	195
3	120	107
5	179	180
7	164	152
9	90	77
• 7 9		
0	349	402
2	67	68
4	187	227
6	184	215
8	161	177
• 7 10		
1	95	69
3	112	113
5	85	58
7	52	57

Table VII.5.

*h k, l 2.5F_{obs} 2.5F_{calc} for the 25% (Cu(I)) m.v.compound

• 0 0			
12	3796	3638	180
16	3132	3194	0
• 0 2			
2	449	388	0
6	318	514	-180
10	455	577	-180
14	792	840	0
• 0 4			
4	3281	3141	0
8	2196	1996	-180
12	2715	2609	0
16	1803	1888	-180
20	1029	1013	0
24	956	844	-180
• 0 6			
10	635	779	0
14	513	530	180
18	318	288	-180
• 0 8			
8	3766	3724	0
12	2234	2196	-180
16	988	886	0
20	1179	1056	-180
24	1106	1023	0
• 0 10			
14	857	830	-180
• 0 12			
12	2483	2430	0
16	1342	1490	-180
20	718	933	0
• 0 14			
18	280	356	0
• 0 16			
16	1350	1318	0
• 1 3			
5	1150	1188	135
7	1498	1494	45
11	449	478	-135
13	309	44	-45
15	410	318	-135
17	443	500	-45
• 1 5			
7	443	422	135
9	550	607	-135
11	259	136	135
• 1 7			
9	710	661	-45
11	608	475	45
13	270	314	-135
15	417	446	45
17	389	260	135
21	309	283	135
• 1 9			
11	183	164	-45
13	167	123	-135
15	237	79	-45
19	225	181	-45
• 2 2			
4	497	483	0
6	694	930	-90
8	730	1056	-180
10	237	269	-90
12	259	479	-0
14	734	680	90
22	410	325	-90
18	270	122	90
• 2 4			
4	585	650	-90
6	183	63	-0
8	938	905	90
10	519	380	-180
14	248	273	180
• 2 6			
6	575	487	-90
8	270	384	-0
10	237	210	-90
14	917	982	90
18	359	583	-90
• 2 8			
8	167	113	90
10	1093	1086	0
14	248	301	180
16	212	80	-90
• 2 10			
12	248	382	180
14	237	217	-90
18	617	593	90
• 2 14			
14	524	528	-90
• 3 5			
7	631	544	45
9	130	142	135
11	485	485	45
13	604	617	-45
15	309	337	-135
21	318	197	135
• 3 7			
9	367	301	-135
11	686	634	135
• 3 7			
13	367	356	-135
17	225	270	45
19	300	190	-45
• 3 9			
11	474	467	-135
• 3 7			
21	290	127	45
• 4 4			
4	3744	3756	-180
6	2832	2832	-90
8	3365	3403	0
10	1391	1720	90
12	2037	2243	180
14	590	688	90
16	1514	1770	0
18	545	559	-90
20	1318	1330	-180
• 4 6			
6	270	193	-180
10	237	44	-0
12	956	924	90
• 4 8			
8	3575	3504	180
12	1753	1830	0
16	1465	1457	-180
20	1395	1340	0
24	745	764	180
• 4 10			
10	318	297	0
12	640	604	-90
14	367	216	-0
18	335	132	-180
• 4 12			
12	1595	1565	-180
14	343	377	-90
16	1224	1166	-0
18	374	333	90
20	892	901	180
24	813	688	0
• 4 16			
16	944	1006	180
• 5 7			
9	270	161	135
11	212	158	-135
13	270	219	-45
15	183	1	45
• 5 9			
11	580	684	-45
13	502	485	45
15	326	355	135
• 5 11			
13	455	381	-45
15	462	452	-135
• 6 6			
6	973	1131	90
10	410	242	90
12	309	213	0
14	474	161	-90
18	540	583	-90
• 6 8			
8	343	321	-90
10	690	644	180
14	410	279	0
16	382	186	90
• 6 10			
10	580	479	-90
14	212	120	90
18	212	76	90
• 6 12			
12	335	383	-90
• 6 14			
14	270	612	-90
16	248	151	-180
18	343	619	90
• 7 9			
11	259	295	-135
15	167	294	45
• 7 11			
15	270	235	-45
• 8 8			
8	2084	2194	0
12	1253	1384	-180
16	1732	1754	0
20	1333	1240	180
• 8 10			
10	813	960	-180
• 8 12			
12	1230	1275	0
16	1264	1077	180
20	902	762	0
24	635	556	-180
• 8 14			
14	318	363	-180
• 8 16			
16	682	729	0
20	799	785	-180
• 10 10			
12	335	468	-0
• 10 12			
18	212	187	180
• 10 14			
18	443	512	-90
• 12 12			
12	1842	1861	180
18	335	178	-90
20	535	577	-180
• 12 16			
16	622	829	-180

••••••••••••••

Table VII. 6.

Observed and Calculated Structure Factors for $pqCu_2Cl_6$ (see p. 28)

*0,0;l= ,2,4,6,8;(58,72)(24,38)(23,19)(30,-27)

*0,1;l=1to8;(42,53)(30,-22)(32,26)(46,36)(10,-8)(25,-20)(45,-40)(4,4)

*0,2;l=0to8;(51,66)(4,1)(41,39)(37,28)(21,-15)(24,-21)(17,-12)(31,-26)(4,4)

*0,3;l=1to8;(6,7)(13,-14)(16,-14)(8,-11)(40,-32)(49,-49)(12,10)(32,32)

*0,4;l=0to6;(38,-33)(10,8)(4,1)(35,-29)(25,-20)(59,-59)(13,-14)

*0,5;l=1to6;(12,-8)(7,8)(5,9)(59,-61)(7,-6)(51,-55)

*0,6;l=0to5;(22,20)(18,18)(12,-13)(20,-23)(11,11)(40,-34)

*0,7;l=1;(24,-28)

*1,-7;l=0to3;(16,-18)(14,-16)(2,4)(16,14)

*1,-6;l=1to5;(13,15)(15,-16)(31,33)(2,2)(14,12)

*1,-5;l=0to5;(36,47)(3,-7)(45,49)(37,-36)(5,0)(8,-7)

*1,-4;l=1to7;(42,51)(23,-21)(45,47)(20,-40)(3,-5)(22,20)(29,-24)

*1,-3;l=1to7;(32,24)(52,58)(26,-27)(24,20)(22,-22)(12,10)(18,18)

*1,-2;l=1to8;(33,36)(52,-56)(36,-27)(8,5)(3,-2)(7,-9)(37,-34)(6,-7)

*1,-1;l=0to8;(31,35)(13,-12)(15,11)(7,2)(25,-16)(43,-40)(20,-17)(37,-31)(12,11)

*1,0;l=1to8;(4,-2)(47,-48)(37,-31)(28,-24)(45,-40)(64,-66)(19,15)(12,11)

*1,1;l=0to8;(36,-48)(19,-13)(4,-3)(40,-35)(45,-38)(65,-68)(25,-23)(66,-69)(36,-31)

*1,2;l=1to7;(10,-8)(8,6)(13,8)(49,-47)(35,-26)(52,-50)(23,21)

*1,3;l=0to7;(4,2)(44,44)(7,-10)(10,-7)(17,-13)(26,-20)(3,4)(12,-8)

*1,4;l=1to4;(36,-38)(29,25)(44,-43)(4,8)

*1,5;l=0to4;(35,-36)(18,16)(48,-50)(54,53)(18,-13)

*1,6;l=1;(55,-59)

*2,-3;l=1to7;(12,-13)(44,-46)(48,-52)(35,-34)(30,-30)(54,-56)(15,14)

*2,-2;l=0to8;(31,-34)(35,-36)(11,-10)(31,-27)(39,-35)(46,-41)(19,-18)(50,-51)(35,33)

*2,-1;l=1to8;(4,-6)(3,4)(5,2)(14,-14)(43,-38)(24,-21)(30,28)(21,-17)

*2,0;l=2to8;(3,-3)(24,16)(37,-34)(13,10)(15,-11)(14,13)(42,42)

*2,1;l=1to7;(31,-35)(46,47)(48,-50)(10,11)(1,0)(44,40)(5,-1)

*2,2;l=0to7;(16,-23)(34,34)(53,-59)(63,68)(29,-21)(44,38)(7,4)(14,12)

Table VII.6 (cont.)

*2,3;l=1to5;(36,-33)(20,-19)(38,-37)(31,31)(3,2)
*2,4;l=0to5;(19,-19)(1,2)(19,-13)(51,51)(12,10)(16,14)
*2,5;l=1to3;(13,11)(17,19)(34,36)
*2,6;l=0,1;(4,-2)(15,18)
*3,-5;l=0to6;(13,-8)(33,-35)(15,-15)(13,-14)(19,-23)(7,-8)(2,-5)
*3,-4;l=1to7;(6,-7)(1,-1)(1,1)(23,20)(31,-34)(10,7)(20,22)
*3,-3;l=0to7;(17,-23)(21,22)(2,0)(28,27)(37,-36)(38,33)(17,-16)(33,32)
*3,-2;l=1to7;(18,-21)(42,42)(34,-31)(20,-16)(35,-30)(56,61)(12,10)
*3,-1;l=2to7;(50,-41)(55,48)(29,-21)(43,37)(3,-2)(29,25)
*3,0;l=1to7;(20,13)(24,21)(28,-24)(24,23)(9,-6)(3,-1)(5,-5)
*3,1;l=0to6;(30,35)(14,10)(3,6)(48,46)(26,18)(17,15)(5,3)
*3,2;l=1to6;(41, 49)(22,20)(38,36)(50,52)(4,5)(21,-19)
*3,3;l=0to6;(19,16)(9,11)(47,56)(33,35)(29,26)(21,20)(2,-2)
*3,4;l=1to4;(10,10)(27,32)(36,41)(11,12)
*3,5;l=0,1;(4,2)(19,26)
*4,-4;l=2to6;(6,-8)(14,14)(14,-16)(25,22)(9,-10)
*4,-2;l=1to7;(11,10)(27,24)(21,21)(20,16)(11,11)(6,-8)(9,5)
*4,-1;l=1to7;(64,67)(19,16)(28,21)(42,39)(13,13)(28,-28)(16,-14)
*4,0;l=0to7;(22,29)(4,-4)(52,47)(35,31)(14,12)10,10)(11,-11)(13,-16)
*4,1;l=1to6;(4,4)(21,19)(32,27)(11,7)(14,-16)(15,-13)
*4,2;l=0to6;(11,-15)(16,23)(8,10)(12,-11)(6,5)(38,-34)(3,-2)
*4,3;l=1to5;(2,4)(9,-9)(4,3)(42,-44)(19,20)
*4,4;l=0to3;(13,-17)(3,6)10,-12)(24,-26)
*4,5;l=1;(12,17)

The F values are 0.5x absolute value in electrons.

Table VII.7.

Structure Factors (x0.1) for Cobalthexammine Chlorocuprate(I).

The calculated values are based on the parameters in Table V.2. but related to a non-centrosymmetric origin at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$. The phase can be calculated from the relationship:

$$\alpha = (x+2)\pi/4 \pm \pi/2 ,$$ where the sign is given below, and x= h+k+l (mod 4). The table is arranged as:

$*h,k;(l,F_{obs}, F_{calc})_1(l,F_{obs},F_{calc})_2$ &c.

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*0,0;(8,18,25)(12,109,-98)(16,117,111)(24,29,24)(28,46,-40)(
*0,2;(6,33,32)(10,33,16)(14,34,25)(18,10,13)
*0,4;(4,118,166)(8,73,-73)(12,124,128)(16,79,-76)(20,59,62)(24,33,-32)(28,35,35)(32,15,-16)
*0,6;(8,13,11)
*0,8;(4,77,-83)(8,142,185)(12,76,-74)(16,68,70)(20,66,-65)(24,54,55)(28,11,-12)
*0,10;(2,28,-13)(6,53,75)(14,14,-7)(18,12,-6)(22,19,17)(26,18,22)
*0,12;(4,137,135)(8,79,-85)(12,77,79)(16,39,-35)(20,43,41)(24,26,-23)
*0,14;(2,37,38)(10,16,-14)(14,22,22)(18,18,22)
*0,16;(4,76,-69)(8,67,67)(12,41,-43)(16,54,59)(20,27,-25)(24,23,20)
*0,18;(2,11,17)(6,11,-7)(10,17,14)(14,17,19)(22,12,-6)
*0,20;(4,36,-34)(8,56,66)(12,25,-23)(16,21,16)
*0,22;(6,15,14)(10,26,28)(18,11,-7)
*0,24;(4,36,-34)(8,56,66)(12,25,-23)(16,21,16)
*0,26;(10,13,2)
*0,28;(4,34,31)(12,43,30)(16,19,-21)
*0,32;(4,14,-14)
*1,1;(9,34,30)(11,15,-12)(13,36,-28)(15,28,25)(17,22,-25)(19,12,12)
*1,3;(3,19,-27)(5,37,30)(7,52,46)(9,18,19)(11,16,-13)(13,27,-21)(15,28,-21)(17,11,10)(19,11,-7)(21,11,10)
*1,5;(3,42,-42)(5,31,-29)(7,29,37)(9,14,-15)(11,26,21)(13,13,-14)(15,10,3)(17,12,11)
*1,7;(3,48,-41)(5,20,5)(13,20,-19)(17,19,10)(21,15,14)
*1,9;(7,45,48)(9,31,-36)(11,14,15)(13,18,-18)(15,18,-21)(17,11,14)
*1,11;(3,13,-5)(5,23,-20)(7,38,-41)(9,17,21)(11,18,-20)(13,27,30)(15,23,24)

Table VII.7.(cont.)

*1,13;(3,28,24)(5,10,0)(7,18,-10)(9,14,10)(11,20,-4)(15,11,12)(17,20,-22)

*1,15;(3,30,26)(5,15,18)(7,11,-10)(9,14,-5)(11,15,-3)(13,13,16)
(15,19,-28)(17,13,-3)

*1,17;(3,11,11)(5,13,-11)(7,21,22)(13,15,3)(15,17,18)

*1,19;(3,13,-16)(9,10,-13)

*1,21;(3,10,6)(7,14,11)(9,12,-12) *1,25;(7,16,15)

*2,2;(4,41,42)(6,26,27)(12,11,11)(14,26,-23)(16,3,29)(22,25,24)

*2,4;(6,35,35)(8,57,-67)(12,29,28)(14,14,15)(16,15,14)(18,22,22)
(22,12,9)(28,11,-15)

*2,6;(6,35,32)(8,31,36)(12,23,27)(14,24,-22)(24,12,12)

*2,8;(4,44,16)(6,22,8)(10,54,63)(12,11,5)(22,12,5)

*2,10;(4,17,19)(8,39,29)(12,22,4)(14,15,17)(20,19,19)

*2,12;(4,22,-11)(6,16,5)(10,32,40)(14,11,7)

*2,14;(6,26,-27)(10,14,13)(12,15,19)(18,15,14)

*2,16;(8,15,16)(10,17,-20)(14,11,12)

*2,18;(4,19,16)(14,11,17)(16,19,19)

*2,20;(6,13,12)(10,12,2) *2,22;(4,14,14)

*2,24;(6,12,11) *2,30;(6,14,-14)

*3,3;(3,53,56)(9,15,-12)(17,16,-11)(19,15,12)(23,20,20)

*3,5;(5,57,55)(7,35,9)(9,10,4)(11,36,-30)(13,16,-15)(15,28,-28)
(19,24,7)(21,16,21)

*3,7;(5,45,-47)(9,29,-31)(11,23,20)(13,12,0)(15,18,22)(19,16,-7)

*3,9;(5,12,13)(11,11,4)(13,12,8)(15,12,-10)(19,16,-11)

*3,11;(5,40,-39)(7,17,8)(9,10,11)(11,14,-11)(15,22,23)

*3,13;(5,14,8)(7,16,-18)(9,14,19)(13,16,15)(19,12,-3)

*3,15;(5,24,-16)(9,9,5)(11,20,14)

*3,17;(11,11,-6)(17,16,15)

*3,19;(5,28,27)(7,20,18)(9,18,-14) *3,21;(1,11,10)(5,13,0)

*4,4;(4,104,-116)(6,70,71)(8,123,151)(10,30,-25)(12,81,-81)(14,48,-49)
(16,81,83)(18,37,37)(20,51,-43)(22,10,9)(24,43,43)(28,19,-19)

*4,6;(6,13,5)(8,26,22)(10,23,12)(12,43,-48)(14,14,16)(16,11,-11)
(20,16,19)

*4,8;(6,29,-30)(8,103,-110)(10,11,15)(12,83,90)(14,18,11)(16,47,-48)
(18,10,12)(20,63,61)(22,15,-13)(24,29,-28)(28,22,27)

*4,10;(6,32,36)(10,28,27)(12,11,11)(14,20,22)

*4,12;(6,30,-30)(8,85,94)(12,63,-61)(14,25,12)(16,65,66)(18,22,-25)
(20,30,-30)(24,35,35)(26,12,11)(28,27,-20)

Table VII.7.(cont.)

*4,14;(6,16,16)(8,20,-16)(10,16,8)(12,37,43)(20,15,-20)(24,10,-7)

*4,16;(6,10,-6)(8,46,-44)(12,65,67)(16,42,-41)(18,12,-11)(20,34,36)
(24,20,-20)
*4,18;(12,19,-14)(20,11,8)

*4,20;(8,61,58)(12,30,-30)(14,13,-7)(16,36,38)(20,26,-24)(24,22,22)

*4,22;(8,14,7)(12,11,-5) *4,28;(8,22,26)(12,22,-22)
*4,24;(8,30,-30)(12,33,35)(16,20,-19)(20,21,22)

*5,5;(5,22,24)(9,10,7)(11,35,-31)(13,27,-27)
*5,7;(11,18,-19)(17,12,7)(19,11,-12)
*5,9;(9,26,-18)(11,26,27)(17,13,-9)
*5,11;(7,12,4)(9,26,25)(13,16,11)(19,11,-12)(21,11,5)
*5,13;(11,22,27)(15,10,12)(*5,15;(13,9,11)
*5,17;(7,18,19)(9,17,-19)(11,9,8)

*6,6;(6,14,-19)(8,28,28)(10,18,-18)(12,19,20)(14,25,20)(16,12,11)
*6,8;(14,16,18)(16,15,-15)(18,23,27)(24,9,9)
*6,10;(8,23,28)(10,11,9)(12,19,21)(16,20,13)(
*6,12;(10,16,-11)(12,21,20)(14,11,10)(16,16,16)(18,13,14)
*6,14;(8,15,14)(14,12,-4)(18,11,-13)
*6,16;(8,13,9)(10,28,32)(12,11,-5)(14,10,10)(18,10,-7)
*6,18;(12,10,6)(14,12,-11) *6,20;(10,17,19)(12,10,-12)

*7,7;(7,41,41)(13,28,-27)
*7,9;(9,30,-31)(11,17,17)(13,15,14)(15,15,-16)(17,27,31)19,13,-10)
*7,11;(15,12,15)(17,17,-19) *7,13;(9,20,24)(11,15,-14)(13,18,18)
*7,15;(9,15,-14)(11,9,2)(15,10,10)
*7,17;(9,19,10)(11,12,-6) *7,19;(9,16,-20)(11,18,20)

*8,8;(8,83,90)(12,50,-52)(16,66,71)(20,27,-25)(24,22,22)(28,22,-24)
*8,10;(14,19,16)(18,27,30)
*8,12;(12,78,80)(16,51,-51)(20,40,46) *8,14;(10,26,32)
*8,16;(12,51,-46)(14,12,10)(16,47,44)(20,27,-28)
*8,18;(10,20,17) *8,20;(12,41,43)(16,28,-28)(20,20,22)
*8,22;(10,12,-12)(14,12,13)(18,10,12)
*8,24;(12,24,-25)(14,11,-7)(16,31,36)(20,15,-12)