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Unexpected Behaviour in Derivatives of Barluenga's Reagent, *Hal*(Coll)$_2$*X* (Coll = 2,4,6-trimethyl pyridine, collidine; *Hal* = I, Br; *X* = PF$_6$, ClO$_4$ & BF$_4$)[†]

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For the collidine analogues of Barluenga's Reagent (IPy_2BF_4) reported, a flat cation is necessary for the generation of a modulated phase, in keeping with the "Ratchet Model" theory [Kim *et al., Crystal Growth & Design*, 2014, 14, 6294]. Attempts to study "diffuse modulation" in $Br(Coll)_2ClO_4$ have shown that these non-Bragg features disappear very rapidly on exposure to synchrotron radiation, an effect thought to be caused by the radiation damage disrupting the lattice vibrations that cause the modulation.

Single crystal X-ray diffraction is an incredibly powerful technique: as the technique has developed data collections have been getting faster and faster, and structure determination is becoming increasingly routine. However, with the advent of higher intensity sources and more sensitive detectors, more and more molecular structures are showing features beyond the realms of conventional crystallography.[1–3] These include, super-lattice reflections, incommensurate satellite peaks[4,5] and diffuse features.[6,7] These can affect everything from the smallest molecules to large macrocycles or frameworks.

Although non-Bragg diffraction is well known in solid-state materials, it is still often neglected in molecular systems. For example, out of the 147 entries in the Bilbao Incommensurate Structure Database,[8] only 19 contain carbon and hydrogen. Given the 934,249 structures in the Cambridge Structural Database[9,10] (V5.39, inc. Nov. 2017 & Feb. 2018 updates), this is an abundance that is less than might be expected. There are a number of probable reasons for this, including the fact that most chemical crystallography is primarily concerned with the determination of connectivity and the information required can usually be obtained without addressing the cause of any spurious peaks or disorder. Even in the cases where modulation has been clearly identified for example, dealing with it correctly can be extremely time consuming. As a result, such features are often ignored or sometimes the structure is simply modelled as disordered and the poor end result justified by crystal quality. Often even this is unsatisfactory and many cases are not reported at all.

We estimate that the Oxford Chemical Crystallography Service sees one to two such structures every month, and, while we have made the effort to deal with some of these properly,[11–13] more often than not, the time cost vastly outweighs the benefit. It was with the aim of better understanding this type of structure as well as improving our treatment of them, that we originally embarked in a systematic study[14] of derivatives of Barluenga's Reagent (IPy_2BF_4).[15] IPy_2BF_4, was known to have a structural phase transition on cooling[16] and on closer inspection, we found this transition proceeded *via* a transient modulated phase. Systematically replacing iodine with bromine and exchanging BF_4^- for other small anions, led to the discovery of another modulated phase, the isostructural IPy_2ClO_4, and resulted in the postulation of the "Ratchet Model" as an explanation (Figure 1).[14]

More recently we have extended this study to include the 2,4,6-trimethyl pyridine (collidine, Coll) analogues. $Br(Coll)_2PF_6$ was found to be isostructural with the previously reported[17] triclinic structure of $I(Coll)_2PF_6$ and both exhibited no evidence of modulation on inspection of the raw data and reconstructed reciprocal lattice layers.[‡] The refined structures were also highly ordered

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[†] Electronic Supplementary Information (ESI) available: [Structural files (CIFs), lattice reconstructions and experimental details]. See DOI: 10.1039/b000000x/

[‡] Single crystal X-ray diffraction data were collected at 100 K with copper radiation ($\lambda = 1.54184$ Å) on a (Rigaku) Oxford Diffraction SuperNova A diffractometer fitted with an Oxford CryoSystems Cryostream 700+.[18] Raw frame data were reduced and reciprocal lattice sections reconstructed using CrysAlisPro. The structures were

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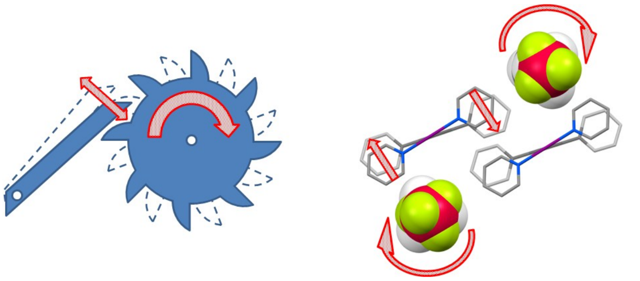

Fig. 1 Schematic of the "Ratchet Model" as originally reported by Kim et al. (left),[14] with part of the structure of Barluenga's Reagent (right). At room temperature the approximately spherical anion spins freely. As the sample is cooled, the lattice contracts and the anion motion is hindered and behaves like a ratchet as the movement of one anion forces the cation to move which subsequently dictates the behaviour of the neighbouring anion. At low temperature, the lattice contracts further, inhibiting this motion, forming an ordered, superstructure phase.

with small, well-defined displacement ellipsoids.

Things were more complex for *Hal*$(Coll)_2ClO_4$ and *Hal*$(Coll)_2BF_4$ (*Hal* = I, Br), however. The structures of both $I(Coll)_2ClO_4$[22] and $Br(Coll)_2ClO_4$[23] had been reported previously and had been found to be isomorphous,[24] crystallising in C2/*c* with one and a half formula units in the asymmetric unit. Redetermining these structures,[§] however, led to the identification of a second polymorph for both $I(Coll)_2ClO_4$ and $Br(Coll)_2ClO_4$.[¶] These were also an isomorphous pair, but with two half molecules in the asymmetric unit and a different structure to those reported by Brayer & James, and Nevrov *et al.* (Table 1). Initially we were concerned that these structures were related by a phase transition, as the original reports were ambient temperature studies. There was no obvious structural relationship, however, and variable temperature studies on both polymorphs (which grew concomitantly) indicated they were not interconvertable under the conditions studied.

Table 1 Unit cell parameters for the two polymorphs of $I(Coll)_2ClO_4$ and $Br(Coll)_2ClO_4$.

	Polymorph I		Polymorph II	
	$I(Coll)_2ClO_4$	$Br(Coll)_2ClO_4{}^a$	$I(Coll)_2ClO_4$	$Br(Coll)_2ClO_4$
REFCODE	BAZNAR[22]	AKOXON[23]		
a/Å	27.844(5)	27.280(30)	29.1027(8)	28.8059(14)
b/Å	11.036(2)	11.028(11)	8.5667(2)	8.5296(3)
c/Å	23.412(7)	23.551(20)	15.9883(5)	15.8383(7)
β/°	126.47(2)	127.19(1)	100.804(3)	99.565(4)
Vol./Å^3	5785.7	5644(9)	3915.47(19)	3837.4(3)
Space Gp.	C2/*c*	C2/*c*	C2/*c*	C2/*c*
Temp./K	Ambient	298(2)	300(2)	300(2)

[a] Cell parameters transformed for comparison with $I(Coll)_2ClO_4$-I; see ESI† for details.

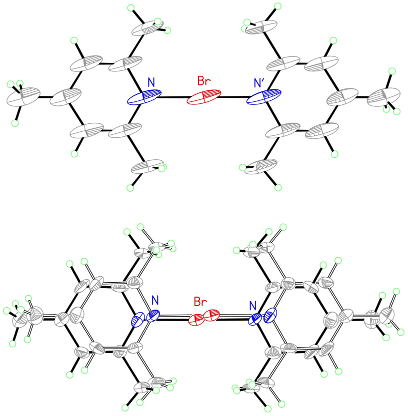

Fig. 2 Displacement ellipsoid plots for the $Br(Coll)_2$ cation in $Br(Coll)_2ClO_4$. The ellipsoids are very prolate when the central bromine atom is modelled occupying a position on the inversion centre such that the two halves of the molecule are related by inversion symmetry (top); when the model breaks the symmetry such that the cation occupies a position 0.3 Å away from the inversion centre the displacement ellipsoids refine freely and are well shaped (bottom). Displacement ellipsoids are drawn at 50% probability; the second half cation and the ClO_4 anion are omitted for clarity in both cases.

Initial refinement of the structure of the second polymorph for $Br(Coll)_2ClO_4$ yielded very prolate ellipsoids for all the non-hydrogen atoms in one half cation (Figure 2). Modelling this as disordered suggests a translation within the unit cell corresponding to approximately 0.6 Å such that the cation occupies a position 0.3 Å away from the inversion centre. A similar effect was seen for $Br(Coll)_2BF_4$ and examination of the reconstructed reciprocal lattice layers showed the presence of diffuse scattering for both samples (Figure 3). No diffuse features were visible for $I(Coll)_2ClO_4$, though on close inspection of $I(Coll)_2ClO_4$ there was just a suggestion of prolate ellipsoids present in the same half cation that might have been put down to crystal quality or absorption effects without knowledge of the behaviour in the bromine analogues. In $Br(Coll)_2ClO_4$ and $Br(Coll)_2BF_4$, the diffuse features intensified at low temperature and it was thought that similar effects might be visible on cooling $I(Coll)_2ClO_4$ below 100 K. Many attempts were made to prepare samples of $I(Coll)_2BF_4$, but these were found to be unstable.

In order to see if the diffuse features would sharpen into satellite reflections on cooling below 100 K, data were collected for $Br(Coll)_2ClO_4$ using I19-1 at Diamond Light Source.[25][||] Unexpectedly, there were no satellite reflections or diffuse features evident at 30 K. Remarkably, it was not possible to reproduce the diffuse features at 100 K at I19-1 either, even when the same sample and even the same crystal was used and data collected in Oxford clearly showed the non-Bragg scattering. It seemed unlikely that 20 miles and 24 hrs could explain the difference, and on closer inspection of the individual raw images collected using I19-1, while most were devoid of extra features, the first images of some data

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solved using SuperFlip[19] and refined using the CRYSTALS software suite.[20,21] See the ESI† for further details.

[§] Single crystal X-ray diffraction data for $I(Coll)_2ClO_4$ and $Br(Coll)_2ClO_4$ were collected as for $I(Coll)_2PF_6$ and $Br(Coll)_2PF_6$. See the ESI† for further details.

[¶] Polymorphs I & II were obtained concomitantly from DCM at room temperature, however, reducing the temperature seemed to encourage growth of polymorph I.

[||] Single crystal diffraction data for $I(Coll)_2ClO_4$ and $Br(Coll)_2ClO_4$ were collected using synchrotron radiation ($\lambda = 0.6889$ Å) at 30 K using an Oxford CryoSystems HeliX[26]. See the ESI† for further details.

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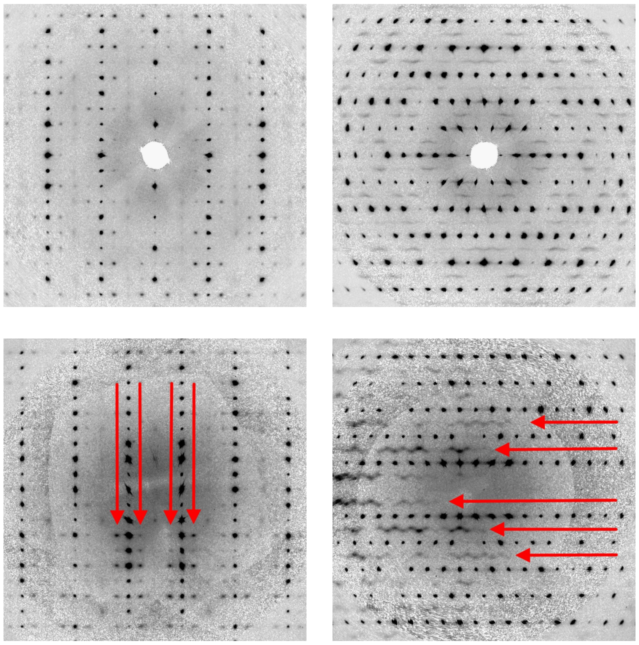

Fig. 3 Selected reciprocal lattice reconstructions from laboratory X-ray diffraction data: the $0kl$ and $hk0$ layers for Br(Coll)$_2$BF$_4$ (top left and right respectively) the $3kl$ and $hk3$ layers for Br(Coll)$_2$ClO$_4$ (bottom left and right respectively, diffuse features are marked in red).

collections suggested the diffuse scattering may be disappearing during data collection.

To investigate this further a 45° wedge of data was collected repeatedly on the same crystal and clearly indicated that the diffuse features disappeared within 200 s (Figure 4). This effect was entirely repeatable. Given that the only variable in the experiment was the dosage of X-rays from the high intensity synchrotron radiation at Diamond, the ionisation events due to the photo-electric effect[27] or Compton Scattering[28] were suspected to be responsible, even though only 1% of the beam was being used. Radiation damage is a very well known problem in macromolecular crystallography,[29–31] and is also seen in small molecule studies using synchrotron radiation.[32,33] Typical characteristics of beam damage include a loss of high resolution data, an increase in the mosaic spread, an expansion in the unit cell and a reduction of intensity for particular reflections.[34] The Bragg reflections for Br(Coll)$_2$ClO$_4$ do show signs of beam damage, but not on this time-scale; it seems the radiation affects the diffuse satellites first.

We found this observation very interesting, firstly because this has potential implications for structural studies of amorphous materials where analysis of pair distribution functions depend on the diffuse scattering. Secondly, we wondered whether we could rationalise the effect of the radiation damage given our understanding of the cause of the modulation in these materials as described by the “Ratchet Model”. At high temperatures, the anion tumbles freely, but on cooling the space available decreases and the structure behaves like a “Ratchet” where the anion acts as a spinning cog and the cation acts as a pawl. This hindered rotation creates a low energy vibration that travels through the structure leading to long range ordering and the appearance of satellite reflections. On cooling further, the balance between the decreasing amount of thermal energy available and the increasingly constricted space available for rotation eventually prevents the propagation of vibrations through the lattice and the structure settles into a new low symmetry state. Applying the concept of the “Ratchet Model” further, the loss of the diffuse satellites implies the damage to the structure disrupts the low energy modes.

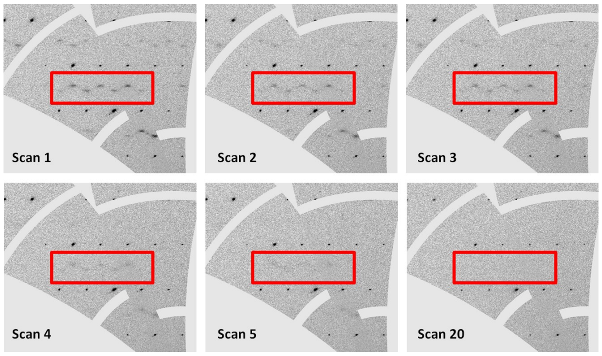

Fig. 4 Reciprocal lattice reconstruction of the $hk1$ layer from a 45° wedge of data collected using synchrotron radiation. Each scan was collected using 1 s/°; the diffuse scattering has almost completely disappeared by the fifth scan, i.e. in less than four minutes.

There are a number of possible mechanisms for this. Data at Diamond were collected close to the bromine absorption edge which suggested that the damage would initially affect the cation. This could lead to a weakening of the Br—N bond making the cation less stiff leading to a softening of the vibrational modes. On the other hand, comparing the structures for the two polymorphs of I(Coll)$_2$ClO$_4$ and Br(Coll)$_2$ClO$_4$, it became apparent that Polymorph II comprised two half molecules in the asymmetric unit and as both halogen atoms occupied a position on an inversion centre, both cations were rigorously flat. In Polymorph I this was not the case, and although one molecule was located on an inversion centre and therefore flat, the other exhibited a significant twist (dihedral angles** of 33.0(1)° and 31.8(2)° for I(Coll)$_2$ClO$_4$ and Br(Coll)$_2$ClO$_4$ respectively at 300 K). There was no evidence for diffuse scattering or modulation in reciprocal lattice reconstructions for Polymorph I of *Hal*(Coll)$_2$ClO$_4$ or indeed either of *Hal*(Coll)$_2$PF$_6$ (see ESI†); this twisting could disrupt the “Ratchet” type behaviour. It is therefore also possible that the radiation damage in Br(Coll)$_2$ClO$_4$ causes a twisting of the cations so that the collidine rings are no longer coplanar, causing a loss of the diffuse scattering/modulation in these structures.

In order to investigate the effect of radiation further, powder diffraction data were collected for Br(Coll)$_2$ClO$_4$ on I11 at Diamond Light Source.[36]†† This showed an expansion of the unit cell commensurate with radiation effects reported previously[34] and a gradual change in the intensity of some reflections, with a second phase growing in over time (Figure 5). The cell parameters and

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** The angles between the two C$_5$N*Hal* planes were calculated using PLATON.[35]

†† Data were collected at 300 K[18] on a sample mounted onto the outside surface of a glass capillary[37] and spun. A wide-angle position sensitive consisting of Mythen-2 Si strip modules and two 5 s scans were summed together[38] such that scans were recorded at approximately 10.9 s intervals. The wavelength was set to the zirconium absorption edge and refined from a silicon standard to $\lambda = 0.686907$ Å (18.0 KeV).

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intensities of the new phase were consistent with the previously reported structure of collidinium perchlorate,[39] but the structure determined for collidinium bromide† was not consistent with the remaining, unindexed peaks. However, it is quite likely that single crystals from solution would have a different structure to powder prepared by decomposition. The poor signal to noise due to fluorescence and other sample related issues† meant that it was not possible to follow the structural changes in detail.

One concern was the possibility that heating caused by the intense synchrotron radiation, was leading to sample degradation. Previous studies[40,41] have shown that sample heating caused by interaction with a synchrotron beam is of the order of a few Kelvin and our own investigation of a sample of silicon powder showed no significant change in the unit cell parameters when exposed to repeat scans. However, the heat capacity and conductivity of silicon would be expected to be very different to that of $Br(Coll)_2ClO_4$, and additionally, our study of $Br(Coll)_2ClO_4$ was carried out close to the bromine absorption edge. It is very difficult to decouple the effects of temperature and radiation damage in a given sample, but as the appearance of the diffuse satellites seen in the single crystal diffraction data for $Br(Coll)_2ClO_4$ was clearly temperature dependent two tests were carried out. Firstly, a single crystal of $Br(Coll)_2ClO_4$ was exposed for twenty 45° scans to ensure the diffuse scattering had been eliminated. Then the crystal left at 100 K for one hour before one single further scan was carried out: there was no visible diffuse scattering. This was then repeated with only six scans, which eliminated almost all of the diffuse scattering, and after half an hour at 100 K, there was no visible increase in the intensity of the non-Bragg features.

Given these results, we therefore concluded that the synchrotron radiation caused damage that disrupts the transfer of vibrations through the crystal lattice, leading to a loss of the diffuse modulation. The exact mechanism for this is the subject of ongoing research, but the fact that the structure appears to change so rapidly at the start of a data collection has significant implications for those studying structure-property correlations and using X-ray radiation, especially synchrotron radiation, as a probe.

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Conflicts of interest

There are no conflicts to declare.

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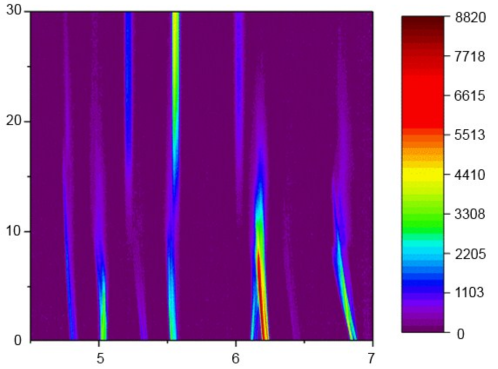

Fig. 5 Contour map showing the 4.5-7.0° region of the first thirty powder X-ray diffraction patterns for $Br(Coll)_2ClO_4$. The initial shift of the peaks to higher d-spacing can be seen as well as the appearance of the new phase.

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