

Temperature dependence of the spin state and geometry in tricobalt paddlewheel complexes with halide axial ligands

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Trinuclear cobalt paddlewheel complexes, $[\text{Co}_3(\text{dpa})_4\text{X}_2]$ (dpa = the anion of 2,2'-dipyridylamine, $\text{X} = \text{Cl}^-$, Br^- , $-\text{NCS}^-$, $-\text{CN}^-$, $(\text{NC})_2\text{N}^-$), are known to demonstrate a thermally-induced spin-crossover (SCO). Despite a wealth of structural and magnetic information about such complexes, the role of the axial ligand on the characteristic SCO temperature ($T_{1/2}$) remains ambiguous. The situation is complicated by the observation that the solid state geometry of the complexes, symmetric or unsymmetric, with respect to the central cobalt ion, also appears to influence the SCO behavior. In order to seek trends in the relationship between the nature of the axial ligand, geometry and magnetic properties, we have prepared the first examples of tricobalt paddlewheel complexes with axial fluoro and iodo ligands, as well as two new chlorido and bromido solvates. Their SCO properties are discussed in the context of an examination of previously reported chlorido and bromido adducts. The main conclusions are: 1) $T_{1/2}$ values follow the trend $\text{I}^- < \text{Br}^- \approx \text{Cl}^- < \text{F}^-$; 2) while the molecular geometry is predominantly guided by crystal packing for the Cl^- , Br^- and I^- derivatives, the presence of an axial fluoride may favor a more symmetric core; and 3) the magnetic characterization of a second example of an unsymmetric complex supports the observation that they display dramatically lower $T_{1/2}$ values than their symmetric analogues; and 4) SCO in crystallographically symmetric compounds apparently occurs without loss of molecular or crystallographic symmetry, while a gradual geometric transformation linking the temperature dependence of quasi-symmetric to unsymmetric in crystallographically unconstrained compounds was found.

Introduction

Complexes consisting of three or more linearly-disposed metal ions, "extended metal atom chains" (EMACs) or "metal strings", have been intensively studied with respect to their electronic, magnetic, and single-molecule conductive properties.¹⁻³ The simplest examples are trinuclear complexes supported by four 2,2'-dipyridylamine anions (dpa), where the axial positions are most often occupied by halide or pseudohalide ligands. Chromium and cobalt derivatives have the particularity of presenting either symmetric metal cores, where $\Delta_{\text{M-M}}$, the difference between the intermetallic distances, is less than 0.05 Å,¹ or dramatically unsymmetric cores, where $\Delta_{\text{M-M}}$ has been found to reach up to 0.65 Å.⁴ In trinuclear chromium complexes, the preferred geometry appears to depend on the nature of the axial ligands; stronger

σ -donors tend to stabilize the symmetric arrangement and weaker donors the unsymmetric form.^{5,6}

The effect of the axial ligand on the conformation of the tricobalt core is less well understood. Remarkably, $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$ can present a symmetric (*s*- $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$) or unsymmetric core (*u*- $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$), depending the crystalline environment (Chart 1).^{7,8} All evidence to date points to this variability being a solid state phenomenon; in solution, only *s*- $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$ has been detected,⁹ while a Hirshfeld surface analysis demonstrated the importance of intermolecular interactions on the geometry of $[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$.¹⁰ Geometric plasticity is not restricted to the chlorido adducts; in the case of $[\text{Co}_3(\text{dpa})_4\text{Br}_2]$, for which three solvates have been crystallographically characterized, two of the structures are rigorously symmetric at room temperature, while the third is markedly unsymmetric.¹¹ Conversely, all of the reported complexes with stronger-field axial ligands ($-\text{CN}^-$, $-\text{NCS}^-$, $(\text{NC})_2\text{CN}^-$) are highly symmetric¹² suggesting that, like for the

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Electronic Supplementary Information (ESI) available: Thermal ellipsoid plot of $1[\text{BF}_4] \cdot 4\text{CH}_2\text{Cl}_2$, diagrams showing intramolecular interactions for $1 \cdot 2\text{CH}_2\text{Cl}_2$, $3 \cdot \text{Et}_2\text{O}$ and $4 \cdot \text{Et}_2\text{O}$, crystal data and refinement and selected bond distance and angles tables for newly reported compounds, $\chi^2 T$ vs. T plots and fits for previously reported compounds. See DOI: 10.1039/x0xx00000x

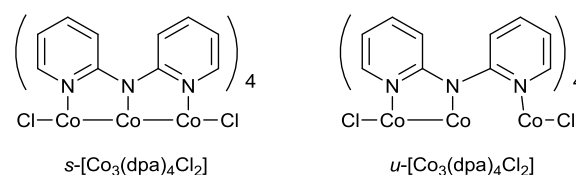


Chart 1.

trichromium analogues, the ligand field may play a role in the core geometry.

This question is not purely academic, as it directly influences the spin-crossover (SCO) behaviour found in many tricobalt complexes.^{7,8} For example, while the dichloromethane solvates of both *s*- and *u*-[Co₃(dpa)₄Cl₂] show a thermally-induced SCO, there are significant differences in their solid state magnetic signatures. Symmetric [Co₃(dpa)₄Cl₂]·CH₂Cl₂ was reported to display an *S* = 1/2 ground state with *g* ≈ 2.3, and the temperature where 50% of the complexes are in the high spin state, *T*_{1/2}, equal to 329 K.⁷ On the other hand, the unsymmetric form, [Co₃(dpa)₄Cl₂]·2CH₂Cl₂, presented a low-temperature plateau with $\chi T \approx 1 \text{ cm}^3 \text{ K mol}^{-1}$, indicating an *S* = 1/2 ground state with *g* ≈ 3.2. This material displays a SCO at relatively low temperature, with an asymptotic curve reaching ~2.5 cm³ K mol⁻¹, indicating significant population of the *S* = 3/2 excited state at high temperatures.⁷

If we ever hope to exploit the SCO properties of dpa-based tricobalt complexes, it is necessary to better understand the role of the ligand environment on the core geometry and magnetic behaviour. To this end, we have completed the series of halide adducts with the first examples of the fluorido and iodido complexes of [Co₃(dpa)₄X₂], namely [Co₃(dpa)₄F₂]·2CH₂Cl₂, (**1**·2CH₂Cl₂), [Co₃(dpa)₄I₂]·C₂H₄Cl₂ (**4**·C₂H₄Cl₂) and [Co₃(dpa)₄I₂]·Et₂O (**4**·Et₂O). During this work, we also obtained new solvates of the chlorido and bromido adducts, [Co₃(dpa)₄Cl₂]·Et₂O (**2**·Et₂O) and [Co₃(dpa)₄Br₂]·Et₂O (**3**·Et₂O). To contextualize their structural and magnetic temperature dependence, we have examined the magnetic data for a number of previously reported chlorido⁸ and bromido¹¹ adducts, and report the previously-undetermined thermodynamic parameters characterizing their SCO behaviour.

Experimental section

Materials

All reactions were carried out under an inert atmosphere of argon or nitrogen using standard Schlenk and glove box techniques. Anhydrous CoCl₂ from Fisher Chemicals was stored at 120°C, NaI and AgBF₄ from Alfa Aesar were dried under vacuum (10⁻³ mbar) for 12 h and stored in a glovebox, anhydrous tetrabutylammonium fluoride (TBAF) solution (1 M in THF) and CoBr₂ from Sigma Aldrich were stored in a nitrogen atmosphere. Dichloromethane (CH₂Cl₂), diethyl ether (Et₂O) and acetonitrile (MeCN) were purified using an Inert Technologies solvent purification system. Anhydrous dimethylformamide (DMF), *n*-hexane and 1,2-dichloroethane (C₂H₄Cl₂) were purchased from Acros and degassed prior to use. [Co₃(dpa)₄Cl₂]·*n*CH₂Cl₂ (*n* = 1, 2) was prepared according to the literature procedure.¹³

Physical measurements

CHN elemental analyses were performed by the Service d'Analyse Élémentaire, UMR 7565, Université de Lorraine, France and by PLACAMAT, UMS 3626, Université de Bordeaux.

IR spectra were measured on a Nicolet 6700 FT-IR using a Smart iTR accessory between 550 and 4000 cm⁻¹.

Crystallography

Single crystals suitable for X-ray diffraction were selected under immersion oil in ambient conditions and attached to a MiTeGen microloop. For structures at 350 K, the crystals were fixed to a pin using Apiezon AP101 grease. The crystals were mounted and centred in the X-ray beam using a video camera. Data collection was performed on a Bruker APEXII Quasar diffractometer with Mo K α (λ = 0.71073 Å) radiation. The data were collected using a routine to survey reciprocal space, and were indexed by the APEX2 program.¹⁴ Data were reduced and integrated using SAINT¹⁴ and an absorption correction was applied using SADABS.¹⁵ The structures were solved using direct methods and refined by least-squares refinement on *F*² followed by difference Fourier synthesis.¹⁶ All hydrogen atoms were introduced at idealized positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients. Crystal and refinement data are given in Tables S1-S5.

Magnetic measurements

Magnetic measurements were carried out with an MPMS-XL Quantum Design SQUID magnetometer, working between 1.8 and 400 K with applied dc fields ranging from -7 to 7 T. Measurements were performed on freshly filtered polycrystalline samples of **1**·2CH₂Cl₂ (22.97 mg), **2**·Et₂O (20.82 mg), **3**·Et₂O (22.10 mg), **4**·C₂H₄Cl₂ (17.94 mg) and **4**·Et₂O (17.43 mg) sealed a polypropylene bag (3×0.5×0.02 cm). Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to confirm the absence of any bulk ferromagnetic impurities. The magnetic data were corrected for the sample holder and the intrinsic diamagnetic contributions.

Synthesis

[Co₃(dpa)₄F₂]·2CH₂Cl₂, **1·2CH₂Cl₂.** Addition of AgBF₄ (0.070 g, 0.36 mmol) to a CH₂Cl₂ solution (15 mL) of [Co₃(dpa)₄Cl₂] (0.15 g, 0.16 mmol) afforded a dark green-brown solution that was stirred at room temperature for 16 h. The resulting solution was filtered over Celite and a 1 M THF solution of TBAF (0.48 mL, 0.48 mmol) was added dropwise to the filtrate. After standing overnight, dark brown crystals were filtered off and washed with hexane. Yield: 0.10 g (59%). Elemental analysis Calcd for C₄₂H₃₆N₁₂Co₃Cl₄F₂ (%): C 47.35, H 3.41, N 15.78 Found C 47.69, H 3.70, N 15.99. FT-IR ($\bar{\nu}$, cm⁻¹): 1602s, 1590s, 1546m, 1466w, 1450w, 1419m, 1360s, 1308s, 1281m, 1150s, 1053w, 1023s, 882m, 756m, 737m, 649w.

[Co₃(dpa)₄Cl₂]·Et₂O, **2·Et₂O.** [Co₃(dpa)₄Cl₂] (0.05 g) was dissolved in DMF (5 mL) and filtered over Celite. Crystals were obtained from the DMF solution layered with diethyl ether within 4 days. Yield: 45 mg, (90%) Elemental analysis Calcd for C₄₄H₄₂N₁₂Co₃Cl₂O (%): C 52.71, H 4.22, N 16.76 Found: C 52.85, H 4.50, N 16.47. FT-IR ($\bar{\nu}$, cm⁻¹): 1603s, 1591s, 1546m, 1468s, 1457s, 1416s, 1363s, 1313s, 1279m, 1251w, 1152s, 1104m, 1041w, 1018s, 932w, 884s, 779w, 762s, 740s, 639w, 565w.

[Co₃(dpa)₄Br₂]·Et₂O, 3·Et₂O. This reaction is a modification of that previously published for [Co₃(dpa)₄Br₂],¹¹ except that the resulting solid from the reaction was extracted with DMF. Crystals were obtained from the DMF solution layered with diethyl ether. Yield: 0.68 g (62%) Elemental analysis Calcd for C₄₄H₄₂N₁₂Co₃Br₂O (%) : C 48.42, H 3.88, N 15.40 Found: C 48.74, H 4.08, N 15.61. FT-IR ($\bar{\nu}$, cm⁻¹): 1603s, 1591s, 1546m, 1467s, 1456s, 1416s, 1362s, 1313s, 1279m, 1250w, 1164w, 1152s, 1104s, 1042w, 1018s, 964w, 933w, 885s, 843w, 761s, 739s, 647w, 563w.

[Co₃(dpa)₄I₂]·C₂H₄Cl₂, 4·C₂H₄Cl₂. [Co₃(dpa)₄Cl₂] (0.20 g, 0.22 mmol) and NaI (1.65 g, 11.0 mmol) were dissolved in MeCN (15 mL) and stirred at room temperature for 16 h. A deep red-brown solution and a white precipitate (NaCl) were obtained. The solvent was removed under vacuum and the solid was extracted with 1,2-dichloroethane. After standing overnight at -15°C, red-brown crystals were collected and washed several times with hexane. Yield: 0.15 g (56%) Elemental analysis Calcd for C₄₂H₃₆N₁₂Co₃I₂Cl₂ (%) : C 41.68, H 3.00, N 13.89 Found C 41.62 H 3.05 N 13.92. FT-IR ($\bar{\nu}$, cm⁻¹): 1603s, 1593s, 1547s, 1454s, 1418s, 1370s, 1313s, 1236w, 1162w, 1146m, 947w, 925m, 886s, 769m, 751m, 729m, 670m, 573w, 557w.

[Co₃(dpa)₄I₂]·Et₂O, 4·Et₂O. The reaction was carried out under similar conditions as for 4·C₂H₄Cl₂, but the solid was extracted with CH₂Cl₂ and filtered over Celite. The CH₂Cl₂ was then removed under vacuum and the remaining solid was extracted with acetonitrile and layered with diethyl ether to yield brown crystals. Yield: 0.19 g (73%) Elemental analysis Calcd for C₄₄H₄₂N₁₂Co₃I₂O (%) : C 44.58, H 3.57, N 14.18 Found C 44.92 H 3.38 N 14.37. FT-IR ($\bar{\nu}$, cm⁻¹): 1604s, 1591s, 1548m, 1455s, 1420s, 1368s, 1312s, 1167m, 1148s, 1107m, 1045w, 1017m, 1004w, 925w, 885m, 756s, 734s, 636s, 580w.

Results

Synthesis

The fluoro adduct [Co₃(dpa)₄F₂]·2CH₂Cl₂, 1·2CH₂Cl₂, was synthesized from [Co₃(dpa)₄(BF₄)₂], prepared *in situ* by combining AgBF₄ and [Co₃(dpa)₄Cl₂]¹³ in CH₂Cl₂ and stirring for several hours. The dark green solution was then filtered to remove AgCl and treated with tetrabutylammonium fluoride in THF, giving a deep orange solution, from which an orange solid crystallized rapidly as 1·2CH₂Cl₂ in 59% yield. Attempts to synthesize 1 directly from [Co₃(dpa)₄Cl₂] using 2 eq. of AgF gave a mixture of [Co₃(dpa)₄F₂] and [Co₃(dpa)₄Cl₂] complexes, while 3 eq. yielded a mixture of products, including the oxidized 1[BF₄]₄·4CH₂Cl₂, which was crystallographically characterized (Fig. S1, Tables S6 and S12). Attempts to cleanly synthesize this latter compound by oxidation of 1·2CH₂Cl₂ with NOBF₄ were unsuccessful.

Compounds 2·Et₂O and 3·Et₂O were obtained from recrystallization of [Co₃(dpa)₄Cl₂] and [Co₃(dpa)₄Br₂],¹¹ respectively, from DMF/Et₂O.

The iodo adduct [Co₃(dpa)₄I₂], 4, was obtained from treating [Co₃(dpa)₄Cl₂] with a large excess of NaI in MeCN. After stirring overnight, the solvent was removed under reduced pressure and the reddish-brown solid was extracted with C₂H₄Cl₂. When

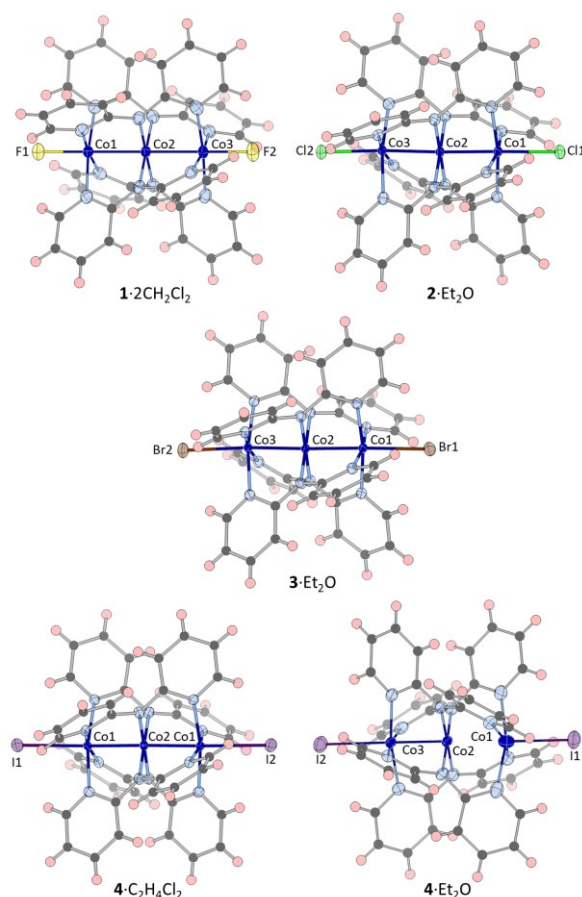


Figure 1. Ball and stick representations of the new structures of 1-3 from X-ray diffraction data at 85 K. Solvents of crystallization have been omitted.

the solution was cooled to -15 °C, brown needles of 4·C₂H₄Cl₂ were obtained in 56% yield. For 4·Et₂O, the solid was first extracted with CH₂Cl₂ and filtered to remove excess NaI and NaCl. The CH₂Cl₂ was in turn evaporated under reduced pressure, the solid extracted with MeCN and layered with Et₂O, yielding a crop of 4·Et₂O as brown plates in 73% yield.

Crystal structures

Diffraction data for crystals of 1·2CH₂Cl₂, 2·Et₂O, 3·Et₂O, 4·Et₂O and 4·C₂H₄Cl₂ were collected at a minimum of three temperatures from 85 K. Diagrams of the structures at 85 K are represented in Figure 1 and selected bond distances are given in Tables 1-3.

The fluoro adduct 1·2CH₂Cl₂ crystallizes in the space group C2/c with the tricobalt complex on a general position. The Co-Co distances are similar at 85 K, with a difference ($\Delta_{\text{Co-Co}}$) of only 0.0109(8) Å, and the Co-Co and Co-F distances remain essentially constant with increasing temperature (Table 1). In

Table 1. Selected bond distances (Å) for 1·2CH ₂ Cl ₂ .			
T (K)	85	120	250
Co(1)-Co(2)	2.3265(6)	2.3257(6)	2.3304(9)
Co(2)-Co(3)	2.3156(6)	2.3157(6)	2.3153(9)
Co(1)-F(1)	2.011(1)	2.0084(19)	2.016(3)
Co(3)-F(2)	2.005(1)	2.005(2)	2.007(3)

Table 2. Selected bond distances (Å) for **2**·Et₂O and **3**·Et₂O.

2 ·Et ₂ O				
T (K)	85	120	298	350
Co(1)–Co(2)	2.3323(2)	2.3312(3)	2.3752(5)	2.3964(6)
Co(2)–Co(3)	2.3209(2)	2.3198(3)	2.3299(5)	2.3397(6)
Co(1)–Cl(1)	2.4816(4)	2.4823(4)	2.4574(7)	2.4350(9)
Co(3)–Cl(2)	2.4430(3)	2.4443(4)	2.4471(7)	2.4412(9)
3 ·Et ₂ O				
T (K)	85	120	298	350
Co(1)–Co(2)	2.3303(2)	2.3295(2)	2.3691(6)	2.3862(7)
Co(2)–Co(3)	2.3162(2)	2.3162(2)	2.3218(5)	2.3308(7)
Co(1)–Br(1)	2.6852(2)	2.6890(2)	2.6363(6)	2.6096(7)
Co(3)–Br(2)	2.6167(2)	2.6205(2)	2.6081(6)	2.6002(7)

the crystal packing, the dichloromethane molecules interact with the axial fluoro ions through C–H...F hydrogen bonds, forming a one-dimensional motif (Fig. S2). Notably, the ligand-solvent interactions are not identical on both sides of the complex, and the closer contact between the dichloromethane molecule and fluoro ion is associated with the slightly longer Co–Co distance. This compound has the unusual feature of having quite similar Co–N_{pyr} and Co–N_{amide} distances (Table S7); all other known examples of tricobalt EMACs have much shorter Co–amide distances with respect to the Co–pyridine distances.

[Co₃(dpa)₄Cl₂]·Et₂O (**2**·Et₂O) and [Co₃(dpa)₄Br₂]·Et₂O (**3**·Et₂O) are isostructural, crystallizing in the space group *P*2₁/*c*, with almost equal Co–Co distances at 85 K ($\Delta_{\text{Co-Co}} = 0.0114(3)$ and $0.0141(3)$ Å, respectively, Table 2). The slight asymmetry of the trimetallic core is associated with pairwise X...H–C interactions between neighbouring molecules in the crystal packing (Fig. S3). The two complexes display the same temperature dependence; specifically, both the longer Co–Co distance and the longer Co–N distances increase with increasing temperature, while the other Co–Co and Co–N distances remain essentially the same (Table 2, S8 and S9). However, this divergence does not hold with respect to the Co–Cl and Co–Br distances, which are more alike at 350 K ($\Delta_{\text{Co-X}} = 0.006(1)$ and $0.009(1)$ Å) than at 85 K ($\Delta_{\text{Co-X}} = 0.0386(5)$ and $0.0685(3)$ Å).

Two [Co₃(dpa)₄I₂] solvates were crystallographically characterized. Compound **4**·Et₂O (*C*2/*c*) has highly dissimilar Co–Co distances at 85 K with $\Delta_{\text{Co-Co}} = 0.1353(4)$ Å (Table 3). This asymmetry is associated with a short contact of *ca.* 3 Å between the iodido ligand coordinated to the cobalt ion participating in the long Co–Co distance and the ether solvent (Fig. S4), reminiscent of the asymmetric solvent interactions

Table 3. Selected bond distances (Å) for **4**·Et₂O and **4**·C₂H₄Cl₂

4 ·Et ₂ O				
T (K)	85	170	240	298
Co(1)–Co(2)	2.4295(3)	2.4504(8)	2.4645(4)	2.4680(15)
Co(2)–Co(3)	2.2942(3)	2.2928(8)	2.2937(4)	2.3047(14)
Co(1)–I(1)	2.7728(3)	2.7535(7)	2.7449(3)	2.7542(13)
Co(3)–I(2)	2.8620(3)	2.8620(7)	2.8719(3)	2.8702(13)
4 ·C ₂ H ₄ Cl ₂				
T (K)	85	120	298	
Co(1)–Co(2)	2.3146(3)	2.3111(4)	2.3558(5)	
Co(1)–I(1)	2.8904(4)	2.8925(4)	2.8447(6)	

observed in [Co₃(dpa)₄Cl₂]·2CH₂Cl₂.¹⁰ The temperature dependence of **4**·Et₂O is characterized by an increase of the asymmetry due to a divergence of the Co–Co, Co–Cl and average terminal Co–N bond distances with increasing temperature. This asymmetrization implicates only one half of the molecule: the longer Co–Co and terminal Co–N (Table S10) distances increase and the shorter Co–I distance decreases from 85 to 298 K, while the other distances do not change substantially. In this way, the bond distances in **4**·Et₂O are highly dissimilar at 298 K, although they are still far from convergence at 85 K. It should be noted that this is the same trend previously observed in the unsymmetric chlorido adduct **2**·2CH₂Cl₂,⁷ although it is less pronounced in the iodido adduct. The central cobalt ion in **4**·C₂H₄Cl₂ is bisected by a 2-fold rotation axis, yielding crystallographically equivalent Co–Co, Co–X and terminal average Co–N distances. The complex in **4**·C₂H₄Cl₂ exhibits a non-negligible increase of 0.0412(6) Å in the Co–Co distance from 85 to 300 K. This modification is concomitant with an increase in the average terminal Co–N distance (Table S11) and a decrease in the Co–X distance with increasing temperature. This structural temperature dependence has been previously observed in the likewise rigorously symmetric compounds **2**·THF and **2**·cyclohexane, both of which show a thermally-induced SCO.⁸ We will revisit the relationship between the structural temperature dependence and the SCO in the discussion section.

Temperature dependence of the magnetic susceptibility

Variable temperature *dc* magnetic susceptibility measurements were carried out on freshly-filtered polycrystalline samples of **1**·2CH₂Cl₂, **2**·Et₂O, **3**·Et₂O, **4**·Et₂O and **4**·C₂H₄Cl₂ from 1.85 K to a maximum temperature dictated by the respective thermal stability of the compounds, as determined by verifying the reversibility of the curves above 300 K (Fig. 2). As shown in the χT vs. *T* plots, all compounds exhibit a low temperature plateau around 0.55 cm³ mol^{−1} K, corresponding to a doublet ground state with *g* values of *ca.* 2.4. The magnetic susceptibility data were fit to the ideal solution model (Eq. 1),¹⁷ with *S*_{LS} = 1/2 and *S*_{HS} = 3/2. The

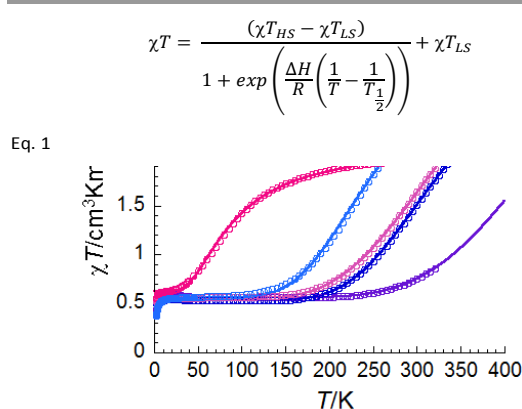


Figure 2. χT versus *T* plots at 1000 Oe for the newly reported compounds, where χ is the magnetic susceptibility equal to *M*/*H* per mole of complex. Lines are the fits to the ideal solution model (Eq. 1).

Table 4. Thermodynamic parameters from fitting of the magnetic susceptibility data to the ideal solution model (Eq. 1).

	ΔH (kJmol ⁻¹)	ΔS (Jmol ⁻¹ K ⁻¹)	g_{LS}	g_{HS}	$T_{1/2}$ (K)
1·2CH ₂ Cl ₂	18.6(5)	40.4	2.45(5)	2.66 ^a	460(10)
2·Et ₂ O	14.6(5)	43.6	2.39(5)	2.66 ^a	335(5)
3·Et ₂ O	13.3(5)	40.9	2.44(5)	2.66 ^a	325(5)
4·Et ₂ O	1.5(2)	12.3	2.59(5)	2.32(5)	122(5)
4·C ₂ H ₄ Cl ₂	9.5(5)	36.5	2.45(5)	2.66(5)	260(5)
2·CH ₂ Cl ₂	18.0 ^b	54.7 ^b	2.35(2) ^b	2.35(2) ^b	329 ^b
	16.0(5)	44.8	2.39(5)	2.66 ^a	357(5)
2·2CH ₂ Cl ₂	n.r. ^b	n.r. ^b	3.21(2) ^b	2.51(2) ^b	n.r. ^b
	1.6(2)	8.3	3.37(5)	2.76(5)	193(5)
2·1.75C ₇ H ₈ · 0.5C ₆ H ₁₄ ^c	6.6(5)	28.7	2.41(5)	2.66 ^a	230(5)
2·C ₄ H ₈ O ^c	11.6(5)	39.7	2.37(5)	2.66 ^a	292(5)
2·C ₆ H ₆ ^c	12.6(5)	43.6	2.36(5)	2.66 ^a	289(5)
2·C ₆ H ₁₂ ^c	9.1(5)	33.3	2.46(5)	2.66 ^a	273(5)
3·CH ₂ Cl ₂ ^d	14.9(5)	34.5	2.38(5)	2.66 ^a	431(5)
3·1.75C ₇ H ₈ · 0.5C ₆ H ₁₄ ^d	8.0(5)	33.2	2.41(5)	2.66 ^a	241(5)
3·C ₆ H ₁₂ ^d	8.2(5)	40.4	2.49(5)	2.66 ^a	203(5)

^a g_{HS} was fixed in the fitting process. ^b Values from ref. 7. ^c Data from ref. 8. ^d Data from ref 11. n.r. = not reported.

resulting thermodynamic parameters are given in Table 4. To complement these results, the thermodynamic parameters from a (re)fitting of the magnetic data for several previously-reported compounds have been included (χT vs. T plots are presented in Fig. S5 and S6). As the value of χT_{HS} could not always be determined from the experimental data and taking 4·C₂H₄Cl₂ as a reference, the g_{HS} value was fixed at 2.66 for all compounds except 4·Et₂O, 4·C₂H₄Cl₂ and 2·2CH₂Cl₂. The ΔH , $T_{1/2}$ and g_{LS} parameters were allowed to refine freely.

Discussion

In this study, we wished to explore the relationship between the axial ligand, the molecular geometry and the spin-crossover properties of dpa-based tricobalt EMACs. We will approach these questions in succession, and first examine the role of the axial ligand on the molecular geometry. Based on the data presented here and found in the literature, there does not appear to be a correlation between the nature of the axial ligand and the molecular geometry for the chlorido, bromido and iodido adducts, which, at room temperature, range from rigorously symmetric to quite unsymmetric, depending on the solvent of crystallization. Concerning the fluorido adduct, so far only one example is known. In 1·2CH₂Cl₂, the difference in Co-Co distances, Δ_{Co-Co} , is less than 0.05 Å, and this complex is therefore considered “symmetric”, or more precisely “quasi-symmetric”, as Δ_{Co-Co} , while small, is nonzero.

These results, taken together, are consistent with the observation that the geometry of complexes with weaker axial ligands is sensitive to crystal packing, while the presence of relatively strong field axial ligands favours symmetric or quasi-symmetric structures. Specifically, the symmetry in

[Co₃(dpa)₄(CN)₂].CH₂Cl₂ is crystallographically enforced, while all the known –NCS[–] and –(NC)₂C[–] adducts have similar Co–Co distances, with the largest variation being 0.04 Å.⁹ An alternative hypothesis concerning the fluorido adduct is that the low polarizability of this anion does not lend itself to significant interactions with other moieties that can distort the {Co₃} core. Undoubtedly, further examples of tricobalt complexes with axial fluorido ligands should be sought in an effort to clarify this observation.

The deconvolution of packing and electronic effects on the core geometry is unfortunately complicated by the lack of an isostructural series for the four halide analogues to date. While the chlorido and bromido adducts are often isostructural,^{8,11} the fluorido and the iodido adducts do not follow the same pattern. For example, 1·2CH₂Cl₂ (C2/c) is not isostructural with 2·2CH₂Cl₂ ($I\bar{4}$), and while 2·Et₂O and 3·Et₂O (P2₁/c) are isostructural, the iodido adduct 4·Et₂O (C2/c) is not. We can conclude that obtaining an isostructural series is not a trivial task, and may indeed be impossible, due to the varying sizes of the axial ligands under consideration. Nonetheless, for the isostructural pairs 2/3·Et₂O and 2/3·1.75toluene·0.5hexane, the core symmetries and temperature dependences within each pair are comparable. Likewise, their spin crossover properties are similar, with almost identical $T_{1/2}$ values, ~330 K for the diethyl ether solvates and ~235 K for the toluene/hexane solvates (Table 4). This observation suggests that the SCO behaviour in the chlorido and bromido adducts is principally a result of molecular geometry and crystal packing, and that the similar ligand field of the Cl[–] and Br[–] anions does not allow us to differentiate any electronic effect for these axial ligands. Indeed, the important influence of the molecular geometry on the spin-crossover properties has been previously observed in the disparate behaviour of the respective symmetric and unsymmetric complexes 2·CH₂Cl₂ and 2·2CH₂Cl₂.⁷ We now have a second comparative example in the form of two iodido complexes, where the dichloroethane solvate is rigorously symmetric and the diethyl ether solvate is unsymmetric. From

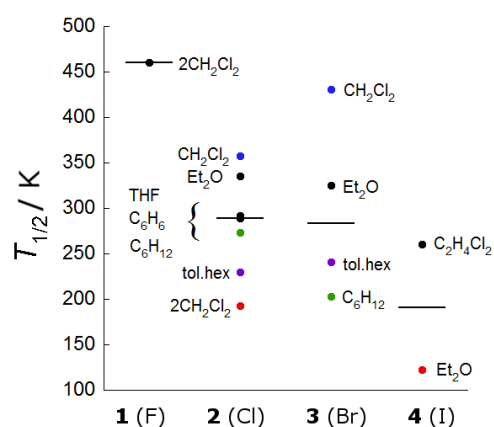


Figure 3. Distribution of $T_{1/2}$ values for all reported compounds. Black lines represent the median and coloured dots are discussed in the text.

Table 5. Change in distances (in Å) with increasing T for compounds with crystallographically enforced symmetry at reported temperatures.

	2·THF	2·C ₆ H ₁₂	3·C ₆ H ₁₂	3·CH ₂ Cl ₂	4·C ₂ H ₄ Cl ₂
δT (K)	120-295	213-295	110-298	111-240	85-298
Co(1)–Co(2)	0.037(1)	0.031(1)	0.064(1)	0.007(1)	0.041(1)
Co(1)–X(1)	–0.017(1)	–0.014(1)	–0.054(1)	0.043(1)	–0.046(1)
Co(1)–N _{avg}	0.038(3)	0.031(4)	0.060(3)	0.015(9)	0.042(3)
Co(2)–N _{avg}	0.009(3)	0.009(4)	0.011(3)	0.005(9)	0.006(3)
$T_{1/2}$ (K)	292(5)	273(5)	203(5)	431(5)	260(5)
Ref.	8		11		This work

Figure 3, which collects the $T_{1/2}$ values for all measured compounds, it can be seen that the $T_{1/2}$ values for the unsymmetric 2·2CH₂Cl₂ and 4·Et₂O (in red) are significantly lower than those of their more symmetric analogues.

While there is considerable overlap between the series, the $T_{1/2}$ values generally follow the trend $F^- > Cl^- \approx Br^- > I^-$. The impact of the fluoro ligands in stabilizing the $S = 1/2$ spin state has been previously seen in a series of one-dimensional polymers of alternating $[(Co_3(dpa)_4)]^{2+}$ and MF_6^{2-} units, which also demonstrated very high spin-crossover temperatures ($T_{1/2} > 400$ K).^{18,19} It should also be mentioned that the structure of 1·2CH₂Cl₂ does not display any significant geometric changes up to 250 K, a temperature where the compound remains fully in the low spin state, suggesting that our assumption that the changes in geometry are indeed representative of the spin-crossover phenomenon is reasonable.

A few compounds show anomalous behaviour and deserve further comment. The crystallographically symmetrical ($\Delta_{Co-Co} = 0$) 3·CH₂Cl₂ has an exceptionally high $T_{1/2}$ value compared to its congener 2·CH₂Cl₂ (431 K vs. 357 K, blue dots in Fig. 3). Although the two complexes are isostructural near room temperature, 2·CH₂Cl₂ undergoes a phase change which breaks the equivalence of the Co–Co distances at lower temperatures. But this does not explain the unusual temperature dependence observed in 3·CH₂Cl₂. Unlike the other rigorously symmetric compounds 2·THF, 2·C₆H₁₂, 3·C₆H₁₂ and 4·C₂H₄Cl₂ where the Co–X distance *decreases* with increasing temperature (Table 5), in 3·CH₂Cl₂, the Co–X distance in 3·CH₂Cl₂ significantly *increases* with temperature. The reason for this uncharacteristic temperature dependence is not clear from the packing diagrams, but is likely related to the unusual $T_{1/2}$ value, and theoretical calculations may help elucidate this behaviour.

Remaining within the crystallographically symmetric series, we note that 3·C₆H₁₂ displays a particularly low $T_{1/2}$ value compared to the chlorido analogue 2·C₆H₁₂ (203 K vs. 273 K, green dots in Fig. 3). These complexes are not isostructural and 2·C₆H₁₂ undergoes a phase transition between 120 and 213 K, which is clearly observable in the χT vs. T plot (Fig. S7). Nonetheless, they follow the same temperature dependence and both compounds begin their spin-crossover around 100 K, but the conversion in 2·C₆H₁₂ is broader than in 3·C₆H₁₂ (Fig. S7). Comparing the structures at 120 (2·C₆H₁₂) and 110 K

Table 6. Change in distances (in Å) with increasing T for quasi-symmetric or unsymmetric compounds.

	1·2CH ₂ Cl ₂	2·Et ₂ O ^a	3·Et ₂ O ^a
δT (K)	85-250	85-298	85-298
Co(1)–Co(2)	0.004(1)	0.043(1)	0.039(1)
Co(2)–Co(3)	0.000(1)	0.009(1)	0.006(1)
Co(1)–X(1)	0.005(3)	–0.024(1)	–0.049(1)
Co(3)–X(2)	0.002(3)	0.004(1)	–0.009(1)
Co(1)–N _{avg}	–0.001(3)	0.041(2)	0.041(3)
Co(2)–N _{avg}	–0.002(3)	0.006(2)	0.010(3)
Co(3)–N _{avg}	–0.001(3)	0.014(2)	0.012(3)
$T_{1/2}$ (K)	460(10)	335(5)	325(5)
Ref.	This work	This work	This work

	2·1.75tol-0.5hex		3·1.75tol-0.5hex	
δT (K)	90-298 ^b		110-295 ^c	
Co(1)–Co(2)	0.105(2)	0.122(2)	0.080(2)	0.031(2)
Co(2)–Co(3)	0.000(2)	–0.002(2)	0.003(2)	0.004(2)
Co(1)–X(1)	–0.080(4)	–0.075(4)	–0.080(2)	–0.028(1)
Co(3)–X(2)	0.000(4)	–0.014(4)	0.006(1)	0.007(1)
Co(1)–N _{avg}	0.095(10)	0.111(10)	0.075(7)	0.027(6)
Co(2)–N _{avg}	0.008(10)	0.007(10)	0.009(6)	0.008(6)
Co(3)–N _{avg}	0.017(10)	0.006(11)	0.002(6)	0.004(6)
$T_{1/2}$ (K)	230(5)		241(5)	
Ref.	8		11	

Compound	2·C ₆ H ₆ ^b	2·2CH ₂ Cl ₂	4·Et ₂ O
$\delta d(\text{pm})/\delta T(\text{K})$	170-316	133-298	85-298
Co(1)–Co(2)	0.039(1)	0.038(2)	0.031(1)
Co(2)–Co(3)	0.028(1)	0.023(2)	0.004(1)
Co(1)–X(1)	–0.029(2)	–0.040(2)	–0.028(3)
Co(3)–X(2)	0.003(2)	–0.018(2)	0.007(2)
Co(1)–N _{avg}	0.028(6)	0.032(7)	0.027(6)
Co(2)–N _{avg}	0.001(6)	0.004(7)	0.008(6)
Co(3)–N _{avg}	0.023(6)	0.027(8)	0.004(6)
$T_{1/2}$ (K)	289(5)	193(5)	122(5)
Ref.	8	7	This work

^a Values only given to 298 K for better comparison with other complexes. ^b Two molecules in the asymmetric unit. ^c Two molecules in the asymmetric unit between 170–260 K and one molecule at 316 K, due to a phase transition. The values were obtained by taking the difference between the distances for the unique molecule at 316 K and the two independent molecules at 170 K.

(3·C₆H₁₂), we note that two short contacts of 2.28 and 2.30 Å are found between the complexes in 3·C₆H₁₂, while only one comparable contact (2.26 Å) is found in 2·C₆H₁₂. An increased cooperativity between trinuclear complexes in 3·C₆H₁₂ may thus explain its more “abrupt” thermal conversion to the high spin state.²⁰

We now turn our attention to compounds where the symmetry of the metal core is not crystallographically enforced (Table 6). For these compounds, excluding 1·2CH₂Cl₂ and 4·Et₂O, for which the $T_{1/2}$ values are likely influenced by the electronic effect of the axial ligands, the $T_{1/2}$ values range

from 193 to 357 K. As might be expected based on the low $T_{1/2}$ values displayed by the unsymmetric compounds **2**·2CH₂Cl₂ and **4**·Et₂O, there is a correlation between SCO temperature and the asymmetry of the complex in the chlorido and bromide series. For example, if we compare $\Delta_{\text{Co-Co}}$ values from crystallographic data collected around room temperature, we find that large differences in Co–Co distances are associated with lower $T_{1/2}$ values (Fig. 4). The linear fit is slightly better when the average of the two $\Delta_{\text{Co-Co}}$ values for the two molecules in the asymmetric unit of **2**·1.75toluene·0.5hexane (0.161 and 0.130 Å) and **3**·1.75toluene·0.5hexane (0.157 and 0.109 Å) are used (Fig. S8). Compound **2**·C₆H₆ has a lower than expected $T_{1/2}$ for being a quite symmetrical compound (0.025 Å at 316 K). But here again, the temperature dependence for **2**·C₆H₆ is atypical, in that both the Co–Co and terminal Co–N distances expand with increasing temperature, mirroring the behaviour for the crystallographically symmetric compounds. Interestingly, the χT vs. T curve is almost superimposable on that of the crystallographically symmetric **2**·C₄H₈O.⁸ Notably, the isostructural compounds **2**·1.75toluene·0.5hexane and **3**·1.75toluene·0.5hexane demonstrate $T_{1/2}$ values (violet dots in Fig. 3) intermediate between the quasi-symmetric and unsymmetric complexes. These complexes exhibit a marked temperature dependence, transforming from almost symmetric to unsymmetric within the measured temperature range. This observation, as well as the relationship between $\Delta_{\text{Co-Co}}$ and $T_{1/2}$ described above, suggests that the distinction between “(quasi)-symmetric” and “unsymmetric” compounds may not be very meaningful. Rather, it seems reasonable, based on observed trends, that the compounds in Table 6 would theoretically all be quite symmetric in the low temperature limit and unsymmetric in the high temperature limit, as exemplified by **2**/**3**·1.75toluene·0.5hexane, where the transformation happens to occur within a measurable temperature range. To explore this idea, we plotted previously published structural data for unsymmetric **2**·2CH₂Cl₂ and the new data from (quasi)-symmetric **2**·Et₂O in Figure 5. The two data sets have been aligned (requiring an offset of 0.02 Å) to emphasize the point that the trends for **2**·Et₂O are simply an extrapolation of

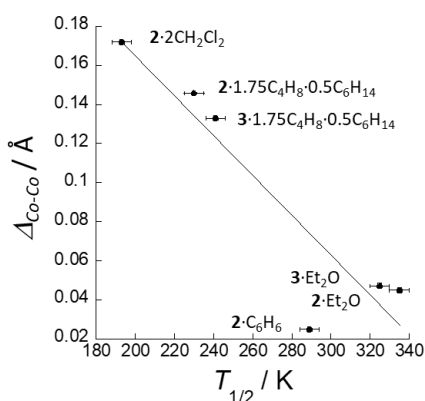


Figure 4. Correlation between $T_{1/2}$ and the differences in Co–Co bond distances for structures obtained close to room temperature (295 – 316

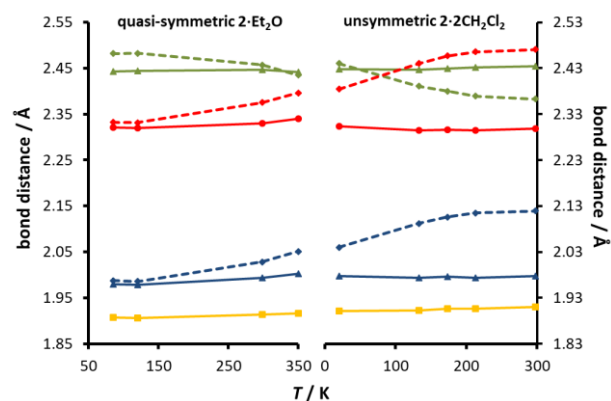


Figure 5. Comparison of the structural data from X-ray crystallography on two distinct crystals, the quasi-symmetric and unsymmetric forms of Co₃dpa₄Cl₂.

those for **2**·2CH₂Cl₂. This not only suggests that the same states are implicated in the spin-crossover for both the (quasi)-symmetric and unsymmetric compounds, but provides experimental evidence for the shallow ²B potential energy state proposed by Pantazis et al.,²¹ which links the symmetric ²A low spin state with the unsymmetric ⁴B high spin state and accounts for the gradual geometric changes previously observed for **2**·2CH₂Cl₂. In this view, the location of the complex on the ²B surface at a given temperature determines both the $T_{1/2}$ value and the asymmetry of the core, a relationship which is consistent with experimental evidence for crystallographically unconstrained compounds. However, the temperature dependence of the crystallographically symmetrical complexes implies the existence of a low-lying symmetrical quartet state, which is not present in the current theoretical picture. Experimental and theoretical work on rigorously symmetrical complexes is underway.

Conclusions

The synthesis of fluoro and iodo adducts of tricobalt paddlewheel complexes has been accomplished for the first time, allowing a more comprehensive investigation of the influence of the axial ligands on their core geometry and spin-crossover properties. Although the relationship between axial ligands, geometry and the spin-crossover properties is far from simple, several conclusions can be derived. While there is quite a bit of overlap in the $T_{1/2}$ values among the four halide series, the presence of iodo ligands tends to stabilize the high spin state compared to their congeners, while fluoro ligands favour a much higher $T_{1/2}$ value. The structural geometry of complexes with I[−], Br[−] and Cl[−] ligands appears to be mainly a function of the crystal packing, while the only example of a fluoro compound is quite symmetric. Higher asymmetry in the tricobalt core is associated with destabilization of the low spin state, as exemplified by lower $T_{1/2}$ values, suggesting a continuum of core geometries consistent with the previous theoretical calculations.

These conclusions are offered with the caveat that the picture could easily evolve with the discovery of new halide adducts, and work is currently focused on efforts to obtain genuinely unsymmetric examples in the fluoro and bromido series.

Conflicts of interest

There are no conflicts of interest to declare.

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Notes and references

‡ The compound **2**·Et₂O was reported as a communication to the Cambridge Structural Database by M. Shatruk, RefCode GOJRIL.

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