

Weak Forces in Inorganic Lattices: Anion Roles in Lattice Assembly

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Application of the concepts of supramolecular chemistry¹ demands an understanding of the nature of the labile and frequently weak forces which control the assembly of molecular aggregates, including crystalline solids.²⁻⁶ Particularly useful to the chemist in analysing these forces is their association with particular constituents of the molecules involved, hydrogen-bonding⁷ and aromatic stacking interactions⁸ being two rather well-known examples of forces identified in this way. The relative facility with which crystallographic information may be obtained today has led to the provision of a vast amount of data suitable for such analysis, though it must be noted that all intermolecular forces have a common origin in the interactions between positive and negative particles (nuclei and electrons, for the chemist),^{2,6} so that their full quantitative treatment may ultimately require a more general approach, even if subsequently the results can be recast in terms associated with particular structural features.^{2,9}

Here, we report the crystal structures of two copper(II) complexes of different but closely related macrocyclic polyamines, one complex containing pyridine-2,6-dicarboxylate (dipicolinate = dipic²⁻) anion in its monoprotonated form (Hdipic⁻) and the other chloride and hexafluorophosphate anions, the focus in our analysis of the structures being the different forms of interaction involving the anions. One of the macrocyclic ligands is a known¹⁰ species (**A**, Fig. 1) and

the other (**B**) a derivative of a polyamino alcohol characterised as its Co(III) complex in earlier work.¹¹ We consider that the detailed analysis of closely related systems where a single factor may be predominant in determining any differences, to be useful as a preliminary step to the ultimately quantitative dissection of all supramolecular forces.

Experimental

Syntheses

[Cu(A)(Hdipic)₂·H₂O (1). A sample of [Cu(A)](ClO₄)₂ available from earlier work^{10a} was dissolved in the minimum volume of water and excess sodium hydrogen dipicolinate dissolved in to cause slow deposition of pink crystals of **1** suitable for a structure determination. Anal. Calc. for C₂₆H₃₆CuN₈O₁₃: C, 42.65; H, 4.96; N, 15.30. Found: C, 42.5; H, 5.0; N, 15.6%.

[Cu(B)Cl(OH₂)]PF₆ (2). The open-chain precursor N₄ ligand, **L** (=2,2-bis(2-aminoethylaminomethyl)propan-1-ol), was isolated from its Co(III) complex prepared in earlier work.¹¹ [Co(L)Cl](ClO₄)₂ (5.0 g) was dissolved in water (200 mL), Zn powder (10 g) added, and then 3 mol L⁻¹ HCl (100 mL) was added dropwise under vigorous stirring. The initially red solution rapidly became almost colourless. After filtering off unreacted Zn powder, the solution was diluted to 2 L and applied to a column of H⁺ form Dowex 50W-x2 resin. The column was washed with water (200 mL) and eluted with 1.0 mol L⁻¹ HCl (500 mL) to remove Zn(II) before the protonated ligand was eluted with 4 mol L⁻¹ HCl. The eluate was evaporated to dryness under reduced pressure to give a white powder. Yield, 3.3 g. It was used as follows without further purification. Crude **L**·4HCl (2.1 g) was suspended in methanol (200 mL) and neutralised with NaOH (0.96 g) before CuCl₂·2H₂O (1.1 g) in methanol (100 mL) was added to give a deep blue solution. Formaldehyde (5.1 g), nitroethane (0.9 g) and triethylamine (1.6 g) were then added before heating at reflux for 3 days. After cooling to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue dissolved in water (500 mL), filtered and absorbed onto SP-Sephadex 25 (Na⁺ form). Elution with 0.3 mol L⁻¹ NaCl revealed one major blue-violet band. Its eluate was taken to dryness under reduced pressure and the residue freed of NaCl by extraction into methanol. Evaporation of this extract provided a violet

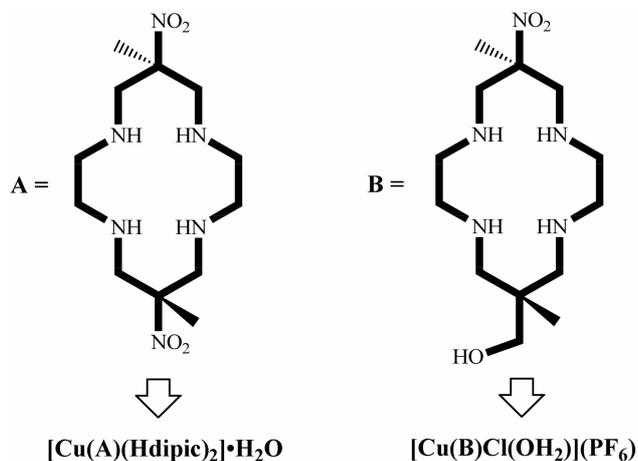


Figure 1. Ligands giving rise to the complexes studied in the present work.

solid. Yield, 1.5 g. Pink crystals of **2** suitable for a structure determination were obtained by adding NH_4PF_6 to an aqueous solution of this chloride. Anal. Calc. for $\text{C}_{13}\text{H}_{31}\text{ClCuF}_6\text{N}_5\text{O}_4\text{P}$: C, 27.62; H, 5.53; N, 12.39. Found: C, 27.5; H, 5.7; N, 12.3%. Electronic spectrum: λ_{max} , $\log \epsilon_{\text{max}}$ in water, 610 nm (sh), $1.74 \text{ M}^{-1} \text{ cm}^{-1}$ and 511 nm, $2.03 \text{ M}^{-1} \text{ cm}^{-1}$. IR spectrum (KBr disc): 1553 cm^{-1} (NO_2) and 3393 cm^{-1} (OH).

Crystallography. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer¹² with graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystals were introduced into glass capillaries with a protective "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. The data (φ - and ω -scans) were processed with HKL2000.¹³ The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least squares on F^2 with SHELXL-97.¹⁴ Absorption effects were corrected empirically with SCALEPACK.¹³ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to nitrogen and oxygen atoms were found on Fourier-difference maps and all the others were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom. The absolute configuration in **2** was determined [Flack parameter $-0.011(10)$]. The molecular plots were drawn with SHELXTL¹⁵ and Balls & Sticks.¹⁶

Crystal data for **1**. $\text{C}_{26}\text{H}_{36}\text{CuN}_8\text{O}_{13}$, $M = 732.17$, monoclinic, space group $C2/c$, $a = 22.2238(14)$, $b = 8.2641(5)$, $c = 18.2014(9) \text{ \AA}$, $\beta = 118.505(4)^\circ$, $V = 2937.6(3) \text{ \AA}^3$, $Z = 4$. Refinement of 220 parameters on 2744 independent reflections out of 10460 measured reflections ($R_{\text{int}} = 0.028$) led to $R_1 = 0.039$, $wR_2 = 0.107$, $S = 1.025$, $\Delta\rho_{\text{min}} = -0.48$, $\Delta\rho_{\text{max}} = 0.46 \text{ e \AA}^{-3}$.

Crystal data for **2**. $\text{C}_{13}\text{H}_{31}\text{ClCuF}_6\text{N}_5\text{O}_4\text{P}$, $M = 565.39$, hexagonal, space group $P6_5$, $a = b = 9.8829(6)$, $c = 38.7657(18) \text{ \AA}$, $V = 3279.0(3) \text{ \AA}^3$, $Z = 6$. Refinement of 283 parameters on 4115 independent reflections out of 75387 measured reflections ($R_{\text{int}} = 0.027$) led to $R_1 = 0.030$, $wR_2 = 0.079$, $S = 0.884$, $\Delta\rho_{\text{min}} = -0.24$, $\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-644416 and 644417. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The complex **1**, $[\text{Cu}(\text{A})(\text{Hdipic})_2]\cdot\text{H}_2\text{O}$ (Fig. 2), contains the anticipated predominant isomer of the ligand **A**, with the macrocycle in the usual "trans-III" conformation¹⁷ for such cyclam derivatives and the nitro substituents, again as usual, being axially oriented.^{10,18} Dipicolinate, in its various protonated forms, is well known to adopt a range of coordinated

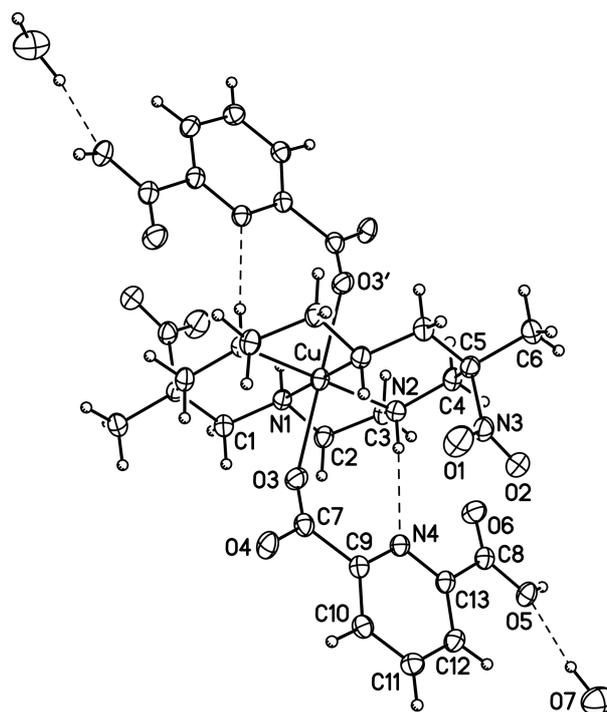


Figure 2. View of complex **1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Symmetry code: $1/2 - x, 1/2 - y, -z$.

forms¹⁹ and unidentate binding through carboxylate- O is not unusual. The Cu- O bond length of $2.391(2) \text{ \AA}$ is relatively short for an axial ligand of a tetragonally elongated Cu(II) complex²⁰ and thus is suggestive of a moderately strong coordination interaction. The dipicolinate ligands are also involved in at least three proton coordination (H-bonding) interactions. The pyridine- N centre serves as an acceptor of an H-bond from a secondary, coordinated NH group of the macrocycle [$\text{N}2\cdots\text{N}4$ $3.200(3) \text{ \AA}$, $\text{H}2\cdots\text{N}4$ 2.32 \AA , $\text{N}2\cdots\text{H}2\cdots\text{N}4$ 175°], this NH perhaps also being involved in donor H-bonding to the unprotonated oxygen of the pendent carboxylate group [$\text{N}2\cdots\text{O}6$ $3.092(3) \text{ \AA}$, shorter than $\text{N}2\cdots\text{N}4$ but $\text{H}2\cdots\text{O}6$ 2.59 \AA and $\text{N}2\cdots\text{H}2\cdots\text{O}6$ 117°]. The adjacent NH unit on the same side of the macrocycle mean plane may be involved in H-bonding to a nitro- O atom [$\text{N}1\cdots\text{O}1'$ $2.864(3) \text{ \AA}$, $\text{H}1\cdots\text{O}1'$ 2.27 \AA , but the angle $\text{N}1\cdots\text{H}1\cdots\text{O}1'$, 123° , is rather small; symmetry code $1/2 - x, 1/2 - y, -z$]. The protonated oxygen atom of the pendent carboxylate unit appears to be involved in both donor and acceptor interactions, the former involving the unbound oxygen of the coordinated carboxylate group of an adjacent complex [$\text{O}5\cdots\text{O}4'$ $2.459(2) \text{ \AA}$, $\text{H}5\cdots\text{O}4'$ 1.63 \AA , $\text{O}5\cdots\text{H}5\cdots\text{O}4'$ 173° , symmetry code: $1/2 x, 1 - y, z - 1/2$] and the latter the water molecule of the asymmetric unit [$\text{O}7\cdots\text{O}5$ $2.894(3) \text{ \AA}$, $\text{H}7\cdots\text{O}5$ 1.92 \AA , $\text{O}7\cdots\text{H}7\cdots\text{O}5$ 169°].

In addition to its H-bonding interactions, the dipicolinate ligand may be involved in both intra- and inter-molecular stacking interactions. The mean plane of the macrocycle nitro substituent lies close to that of the dipicolinate on the same side of the macrocycle, though with a slight tilt which

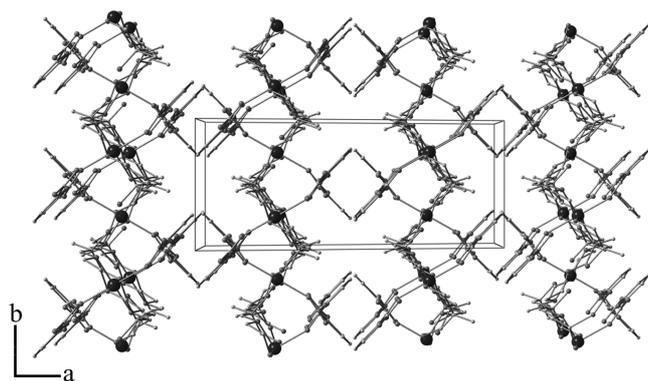


Figure 3. View of the packing in complex **1**. Hydrogen atoms and water molecules are omitted.

brings the oxygen atom O2 within 3.087(3) Å of O6 in the (pendent) carboxylate group, 3.115(3) Å of carboxylate-C and 3.205(3) Å of N4. The nitro group and the dipicolinate ring atoms do not overlap in projection perpendicular to the ring, however, and, as seen in the other structure considered presently (see ahead), the nitro group orientation with respect to the rest of the macrocycle is essentially identical in the absence of dipicolinate. As well, nitro groups of adjacent complex molecules are involved in O...O contacts of 2.745 Å, indicating this to be a much more important interaction. A more conventional form of parallel-displaced π -stacking (in which there is overlap in projection) involves parallel dipicolinate units of separate complex ions, a view of the lattice down *c* (Fig. 3) showing channels of square cross section which result from these interactions [centroid...centroid distance 3.59 Å, offset 1.25 Å]. The array here is very similar to that seen in the Pb(II) complex of the isomeric pyridine-2,3-dicarboxylate,²¹ with parallel pairs of dipicolinate anions alternating orthogonally down *c*. These pairs overlap considerably in projection, though the closest atom contacts are about 3.4 Å and thus are not particularly short. Each pair is linked to the next by the water molecule, which symmetrically bridges unbound oxygen atoms of coordinated carboxylate units on separate metal centres and indeed is also symmetrically disposed between two methyl groups at a distance suggestive of a weak CH...O interactions (H...O 2.503 Å).^{7c}

The conformation of the macrocycle **B** present in [Cu(**B**)(OH₂)Cl]PF₆ (Fig. 4) is very similar to that of **A** in [Cu(**A**)(Hdipic)₂·H₂O], with both methyl substituents again equatorially disposed. As noted above, the orientation of the nitro substituent in **B** is very similar to that of the two such substituents in **A**, indicating that it is not determined by stacking with dipicolinate in that case. The short nitro-*O*/nitro-*O* contacts seen for the complex of **A**, however, are not seen in the complex of **B** and instead there are multiple nitro-*O*/PF₆ contacts which must influence the orientation of the nitro group. These are not the only contacts of the fluorine atoms of the hexafluorophosphate anions, and they are far from the shortest, which appear to be a consequence of H-bonding to the coordinated water [O4...F4' 2.902(3) Å,

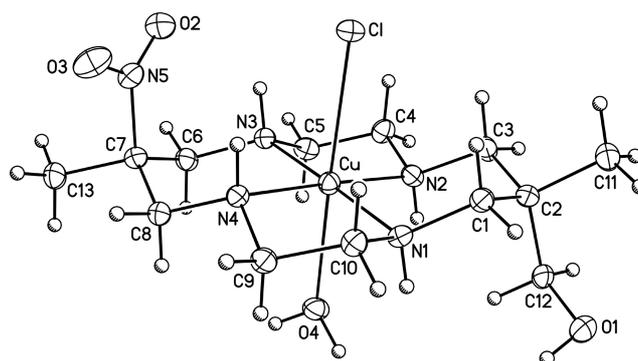


Figure 4. View of complex **2**. Displacement ellipsoids are drawn at the 30% probability level. The counter-ions are omitted.

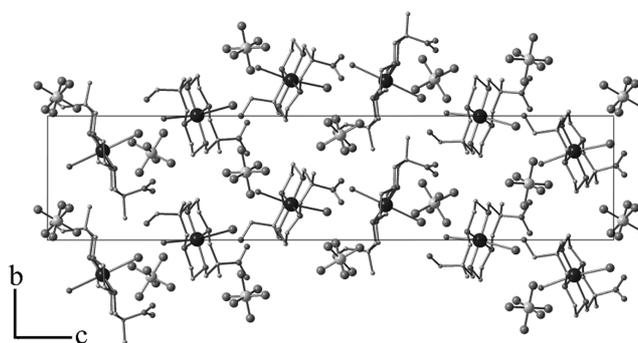


Figure 5. View of the packing in complex **2**. Hydrogen atoms and water molecules are omitted.

H4A...F4' 2.08 Å, O4-H4A...F4' 168°, symmetry code: ' $x + 1, y, z$ '). Another F contact (of 3.21 Å) is to coordinated Cl, the relatively long bond of this atom to Cu [2.7212(8) Å] being associated with its additional contacts to coordinated water [O4...Cl' 3.131(2) Å, H4B...Cl' 2.38 Å, O4-H4B...Cl' 144°, symmetry code: " $x - y + 1, x, z - 1/6$] and to the hydroxymethyl substituent of **B** [O1...Cl' 3.260(3) Å, H1...Cl' 2.49 Å, O1-H1...Cl' 143°], as well as to one of its NH centres [N1...Cl' 3.248(3) Å, H1N...Cl' 2.36 Å, N1-H1N...Cl' 168°].

Conclusions

A general issue concerning lattices incorporating metal ions capable of electronic and/or magnetic interactions is the proximity of the metal ion centres. While the separations in the present instances are too large for any interactions to be apparent, it is clear that they are significantly influenced by differing interactions of the closely similar macrocycle complex cations with their environments. In complex **1**, the shortest Cu...Cu separation, 8.2641(5) Å, involves the pairs of cations between which there are short nitro-*O* contacts. Given that such contacts do not persist in **2**, so that they cannot be considered due to major forces at work, it may be that the complex array in **1** reflects the exigencies of the dipicolinate stacking interactions. In **2**, the shortest Cu...Cu contacts are 7.0428(3) Å within a spiral chain of cations

linked by the H-bonding interactions of the chloride ligand. Obviously, major forces, such as bridging ligand coordination, can be used to bring metal ion centres much closer but these weaker interactions do not have negligible consequences and their control may well be a means to achieve subtle variations in electronic and magnetic properties of metal complexes. Indeed, it is well-established in the case of spin state changes of Fe(II) complexes that quite minor changes in solid state structures can have dramatic consequences.²²

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