

Isolation and X-Ray Crystal Structure of $[\text{Cu}(\text{NH}_3)_4\text{H}_2\text{O} \cdot 18\text{-crown-6}]_n^{2+} [\text{PF}_6]_{2n}^-$ A Linear Face-to-face Hydrogen Bonded Chain Copolymer

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Summary X-Ray crystallography reveals that the [aquo-(tetra-ammine)copper] $^{2+}$ ion forms a chain copolymer with 18-crown-6 in which each individual crown molecule is involved in no fewer than ten hydrogen bonds with four ammine ligands co-ordinated to the copper(II) centres in adjacent ions.

We have proposed¹ that the crystalline 1:1 adduct formed between *trans*-PtCl₂(NH₃)₂ and 18-crown-6 (18C6) has the structure of a regular alternating copolymer represented by the repeating unit, [*trans*-PtCl₂(NH₃)₂ · 18C6]_n. It is envisaged that alternating 18C6 molecules in this structure serve as bifunctional six-point binding sites for two ammine ligands associated with adjacent *trans*-PtCl₂(NH₃)₂ complexes. We have now examined the consequences for adduct formation with 18C6 of increasing the number of ammine ligands co-ordinated to the transition metal. In complexes such as [Cu(NH₃)₄(H₂O)]²⁺, the aquo-ligand and all four ammine ligands attached to copper contain acidic hydrogen atoms potentially able to form hydrogen bonds

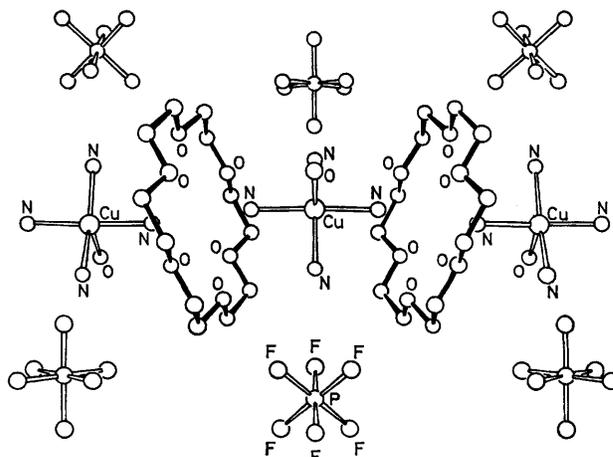


FIGURE 1. The crystal structure of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O}) \cdot 18\text{C6}]_n^{2+} [\text{PF}_6]_{2n}^-$.

with the oxygen atoms of 18C6. This communication describes the isolation and crystal structure of the 1:1 adduct, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})\cdot 18\text{C6}]_n^{2+}[\text{PF}_6]_{2n}^-$.

Addition of an aqueous solution (2 cm³) of 18C6 (2.16 mmol) to $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}[\text{PF}_6]_2^-$ (2.16 mmol) dissolved in the minimum volume of 3M aqueous ammonia afforded, on standing at room temperature for 3 h, deep blue crystals of a 1:1 adduct† (34%, m.p. 183 °C). X-Ray analysis‡ revealed (Figure 1) that the adduct does indeed have a copolymeric structure in which 18C6 molecules alternate with $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ ions. The details of the hydrogen bonding interactions are summarised in Figures 2 and 3.

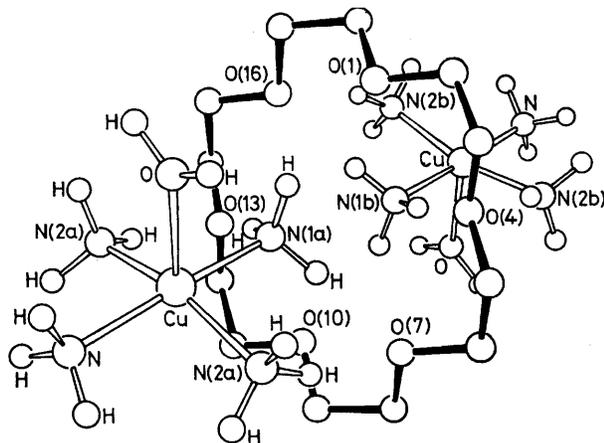


FIGURE 2. The structural detail and selected geometrical parameters associated with the ten-point binding site in the solid state. Bond distances: C-C 1.46(1) and 1.47(1), C-O, 1.40–1.44(1), Cu-N(1) 2.04(1), Cu-N(2) 2.03(1), Cu-O 2.29(1) Å. Bond angle at O(1) and O(7) 111(1)°. Torsional angles: $|\text{O}-\text{C}-\text{O}|$ 63.0–66.8(7), $|\text{C}-\text{C}-\text{O}-\text{C}|$ 176.9–179.5(7)°. Distance $R[\text{N}(1\text{a}) \cdots \text{N}(1\text{b})]$, 3.37 Å.

In addition to the six hydrogen bonds between the 18C6 oxygen atoms and N(1a) and N(1b), a further four hydrogen bonds are formed between the N(2a) and N(2b) ammine ligands to O(7) and O(13), and O(4) and O(16), respectively. Thus, individual 18C6 molecules are involved in no fewer than *ten* hydrogen bonds, O(1) and O(10) each accepting

one hydrogen bond with trigonal geometry, and O(4), O(7), O(13), and O(16) all accepting two hydrogen bonds, one each from the N(1) ammine ligands with approximately trigonal geometry and one each from N(2) ammine ligands with approximately tetrahedral geometry (Figure 3).

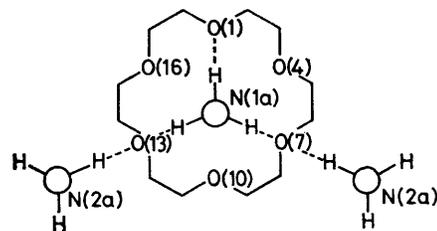


FIGURE 3. Diagrammatic representation of one-half of the hydrogen bonding pattern associated with the ten-point binding site. Hydrogen bond distances, $R(\text{N} \cdots \text{O})$ (Å); angles (θ), between COC planes and (a) NO vectors and (b) HO vectors: N(1a)-H \cdots O(1) 3.27; (a) 12, (b) 1. N(1a)-H \cdots O(7) 3.06; (a) 11, (b) 11. N(2a)-H \cdots O(7) 3.28; (a) 43, (b) 48.

Presumably, these hydrogen bonding interactions involving the N(2a) and N(2b) ammine ligands are responsible for the relative tilt of alternate 18C6 rings (Figure 1). The structure has high crystallographic symmetry with the Cu^{2+} ion located on a special position. The $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ ion has C_{2v} symmetry (*mm*), the 18C6 has C_{2h} symmetry (*2/m*), and the PF_6^- ion has C_s symmetry (*m*) and is disordered within the mirror plane. Alternate $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})]^{2+}$ ions are related by a centre of symmetry located at the centre of the crown which adopts the characteristic all-*gauche* conformation with approximately D_{3d} symmetry. The aquo-ligand is co-ordinated trigonally to the Cu^{2+} ions but does not participate in hydrogen bonding interactions§ with 18C6. Thus, the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})\cdot 18\text{C6}]_n^{2+}[\text{PF}_6]_{2n}^-$ chain copolymer displays a structure related to that of the $[\text{MnNO}_3(\text{H}_2\text{O})_5\cdot 18\text{C6}]_n^+[\text{NO}_3]_n^-[\text{H}_2\text{O}]_n$ adduct² in which four of the five aquo-ligands participate in hydrogen bonding to 18C6 molecules.

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† A satisfactory elemental analysis was obtained for the 1:1 adduct, $\nu(\text{Nujol})$ 3640 and 3555 (OH), 3355, 3270, and 3205 (NH), 1635 (NH and OH), 1100 (CO), and 830 (PF) cm^{-1} .

‡ Crystals of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})\cdot 18\text{C6}]_n^{2+}[\text{PF}_6]_{2n}^-$ are orthorhombic, space group *Cmcm*, $a = 19.275(2)$, $b = 10.018(1)$, $c = 14.672(1)$ Å, $U = 2833$ Å³, $Z = 4$, $\mu(\text{Cu}-K\alpha) = 31$ cm^{-1} . Of the 972 independent reflections ($\theta \leq 55^\circ$) measured on a diffractometer using Cu- $K\alpha$ radiation, 51 were classified as unobserved. The structure was solved by the heavy atom method and the absorption corrected data were refined to give a current $R = 0.064$. All hydrogen positions were unambiguously located in a weighted difference electron density map. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ However, there are close approaches (3.05 and 3.08 Å) of two of the fluorine atoms in a PF_6^- ion to the oxygen atom of the aquo-ligand.

¹H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, preceding communication.

²A. Knöchel, J. Kopf, J. Oehler, and G. Rudolph, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 61.