

Formation and X-Ray Crystal Structure of $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2 \cdot 18\text{-crown-6}]_n^{2+} [\text{PF}_6^-]_{2n}$. A Hydrogen Bonded Stepped-chain Copolymer

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Summary X-Ray crystallography reveals that the [bis-(ethylenediamine)platinum(II)] dication forms a chain copolymer with 18-crown-6 in which the metal complex is sandwiched between two crown molecules that are displaced laterally such that each ethylenediamine ligand is involved in only two hydrogen bonds to oxygen atoms and each 18-crown-6 ring in only four hydrogen bonds.

To date, water¹ and ammonia² co-ordinated to transition metals have provided sources of hydrogen atoms which are capable of hydrogen bonding with crown ether oxygen atoms to form crystalline adducts. In the case of the transition metal amines, these adducts are also stable in solution. Clearly, however, there is a wide range of potential ligands which are able to form hydrogen bonds and thereby co-ordinate crown ethers in the second sphere. Since ethylenediamine is a common chelating ligand which contains acidic hydrogen atoms, we have investigated the ability of $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+} [\text{PF}_6^-]_2$ to interact with 18-crown-6 (18C6) in aqueous solution. Here, we report the isolation and crystal structure of the 1:1 adduct $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2 \cdot 18\text{C6}]_n^{2+} [\text{PF}_6^-]_{2n}$.

An aqueous solution (5 cm³) of $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+} [\text{PF}_6^-]_2$ (0.40 mmol) was added to 18C6 (0.76 mmol) dissolved in water (2 cm³) and the solution was cooled to 5 °C. After 1 h, crystals of a 1:1 adduct[†] (49%, m.p. 201 °C) were isolated. The structure (Figure) was determined by X-ray analysis.[§] Bond distances, angles, and other geometrical parameters are summarised in the caption to the Figure. The structure is probably best described as a hydrogen bonded stepped-chain copolymer formed between the $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2]^{2+}$ dication and 18C6 in which (i) only one hydrogen atom associated with each

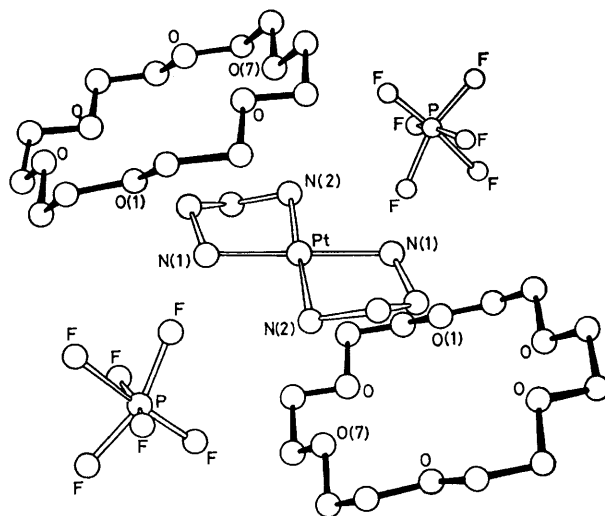


FIGURE. Crystal structure of $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2 \cdot 18\text{C6}]_n^{2+} [\text{PF}_6^-]_{2n}$. Bond distances: C-C, 1.46–1.54(2), C-O, 1.40–1.43(2) Å. Bond angles at O(1) 113(1), O(4) 109(1), O(7) 109(1)°. Torsional angles: |O-C-C-O| 64.1–67.1(1.5), |C-C-O-C| 173.5–176.4(1.1)°. Hydrogen bond distances, $R(\text{N} \cdots \text{O})$ (Å); angles (θ°) between COC planes and (a) NO vectors and (b) HO vectors: N(1)-H \cdots O(1) 3.07; (a) 31, (b) 41. N(2)-H \cdots O(7) 3.02; (a) 30, (b) 35.

amino-group, and (ii) only four of the six crown ether oxygen atoms are involved in hydrogen bonding. The Pt atom and the centre of the 18C6 ring, which adopts the all-*gauche* conformation with approximately D_{3d} symmetry, are located on crystallographic centres of symmetry. The PF_6^- ion is in a general position and is disordered.

The structure of $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2 \cdot 18\text{C6}]_n^{2+} [\text{PF}_6^-]_{2n}$ was not unambiguously predictable from the examination

[†] Prepared by addition of $[\text{NH}_4^+ \text{PF}_6^-]_{\text{aq}}$ to the dichloride (F. Basolo, J. C. Bailar, and B. R. Tarr, *J. Am. Chem. Soc.*, 1950, **72** 2433).

[‡] A satisfactory elemental analysis was obtained for the 1:1 adduct, $\nu(\text{Nujol})$ 3305, 3220, 3140, and 1600 (NH), 1115 (CO), and 820 (PF) cm^{-1} .

[§] *Crystal data*: $[\text{Pt}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_2 \cdot 18\text{C6}]_n^{2+} [\text{PF}_6^-]_{2n}$, monoclinic, space group $P2_1/c$, $a = 8.705(1)$, $b = 10.248(1)$, $c = 16.535(1)$ Å, $\beta = 100.09(1)^\circ$, $U = 1452$ Å³, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 111$ cm^{-1} . Of the 2165 independent reflections ($\theta \leq 60^\circ$) measured on a diffractometer using Cu-K α radiation, 236 were classified as unobserved. The structure was solved by the heavy atom method and the absorption-corrected data were refined to give a current $R = 0.066$. 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.

of space-filling molecular models and is surprising, perhaps, in its under-utilisation of hydrogen bonding with respect to both the $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ ligands and the 18C6 rings. It may be significant, however, that the 'unused' N-H bonds are adjacent to $[\text{PF}_6]^-$ ions in the crystal and could thus form weak hydrogen bonds to fluorine atoms.

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² H. M. Colquhoun and J. F. Stoddart, *J. Chem. Soc., Chem. Commun.*, 1981, 612; H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, preceding two communications.