Crown Ethers as Second-sphere Ligands. The Interactions of Transition-metal Ammines with 18-Crown-6 and Dibenzo-18-Crown-6 †

Howard M. Colquhoun and David F. Lewis
New Science Group, Imperial Chemical Industries PLC, The Heath, Runcorn WA7 4QE
J. Fraser Stoddart
Department of Chemistry, The University, Sheffield S3 7HF
David J. Williams
Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

Neutral and cationic transition-metal ammines interact with crown ethers in aqueous and non-aqueous solution *via* (N–H · · · O) hydrogen-bond formation to give discrete or polymeric adducts which are readily isolated by crystallisation. Dibenzo-18-crown-6 generally yields discrete 1 : 1 (metal complex : crown) adducts in which only one face of the macrocycle interacts with an ammine ligand, whereas 18-crown-6 often binds two such ligands, one to each face of the crown ether. The resulting adducts are then either polymeric or of 2 : 1 (metal complex : crown) stoicheiometry. Ammines which yield isolable adducts include $[W(CO)_5(NH_3)]$, *trans*-$[PtCl_2(PMe_3)(NH_3)]$, *trans*-$[PtCl_2(NH_3)_2]$, $[Co(NH_3)_6][PF_6]_3$, $[Cu(NH_3)_4(H_2O)][PF_6]_2$, and $[Pt(H_2NCH_2CH_2NH_2)_2][PF_6]_2$. Such adduct formation provides the basis for a novel method of separating different transition metals; for example, 18-crown-6 selectively precipitates the copper(II) complex (as a polymeric 1 : 1 adduct) in the presence of an equimolar amount of the cobalt(III) ammine.

Macrocyclic polyethers,[1] which are class ' a ' or ' hard ' ligands, do not readily form complexes with transition metals in low oxidation states, since such metals normally provide only class ' b ' or ' soft ' co-ordination sites. However, because of the demonstrated[2] ability of crown ethers to bind primary alkylammonium ions (RNH_3^+) *via* multiple hydrogen-bond formation [Figure 1(*a*)], it occurred to us that a similar type of interaction might occur with ligating ammonia ($M \leftarrow NH_3^{\delta+}$) and thus provide a means of binding transition-metal *complexes* to crown ethers [Figure 1(*b*)].

Although a small number of transition-metal aqua-complexes, in which crown ethers form polymeric structures by hydrogen bonding to aqua-ligands, had been characterised crystallographically[3] before our work began, there was no evidence for stabilising host–guest interactions in solution. In addition, the generality of this type of adduct formation between protic ligands in the first co-ordination sphere of a transition-metal complex and crown ethers does not seem to have been appreciated.

Hydrogen bonding between ammine ligands and anions or solvent molecules is a well established phenomenon.[4] A particularly useful i.r. spectroscopic method for detecting such interactions was developed by Chatt and co-workers,[4,5] who found, for example, that the carbonyl-stretching frequency of the ruthenium(II) complex $[Ru(NH_3)_5(CO)]^{2+}$ decreases as the hydrogen-bonding ability of the anion or solvent increases. This observation may be readily understood on the grounds that hydrogen bonding involves a net donation of electron density from the anion or solvent lone pairs to the ammine hydrogen atoms, so producing an overall increase in electron density on the metal complex. The extent of electron transfer from the metal *d* orbitals to CO π-antibonding orbitals is thereby increased and results in a lower CO stretching frequency.

Since a cationic transition-metal complex containing a *single* ammine ligand approximates most closely to a primary alkylammonium ion, we examined initially the interaction between dibenzo-18-crown-6 and $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)]^+$, a cationic complex which contains both i.r. [ν(CO)] and ^1H n.m.r. (C_5H_5) spectroscopic probes. Part of this work has been published in preliminary form.[6,7]

Experimental

Materials and Methods.—Literature procedures were used to prepare $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)][BPh_4]$,[8] $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_5N)][PF_6]$,[9] $[W(CO)_5(NH_3)]$,[10] $[PtCl_2(PR_3)(NH_3)]$ (R = Me or Et),[11] *cis*- and *trans*-$[PtCl_2(NH_3)_2]$,[12] $[Pt(H_2NCH_2CH_2NH_2)_2]Cl_2$,[13] $[Cu(NH_3)_4(H_2O)][SO_4]$,[14] and $[Co(NH_3)_6]Cl_3$.[15] Hexafluorophosphate salts were obtained by metathetical reactions with $[NH_4][PF_6]$. Dibenzo-18-crown-6 ($C_{20}H_{24}O_6$) was obtained *via* the ICI Fine Chemicals Service, and 18-crown-6 ($C_{12}H_{24}O_6$) was purchased from Aldrich. Infrared (i.r.) spectra were determined using Perkin-Elmer PE 197 and PE 580 instruments, and nuclear magnetic resonance (n.m.r.) spectra were obtained on JEOL FX 100, Perkin-Elmer R 34, and Bruker WH 400 spectrometers. Microanalyses were carried out by the Characterisation and Measurement Group of ICI Mond Division. Melting points were determined in air using a hot-stage microscope and are uncorrected.

Amminepentacarbonyltungsten(0)–*Dibenzo*-18-*crown*-6 (1/1). —A solution containing $[W(CO)_5(NH_3)]$ (0.34 g, 1 mmol) and dibenzo-18-crown-6 (0.36 g, 1 mmol) in benzene (20 cm^3) was

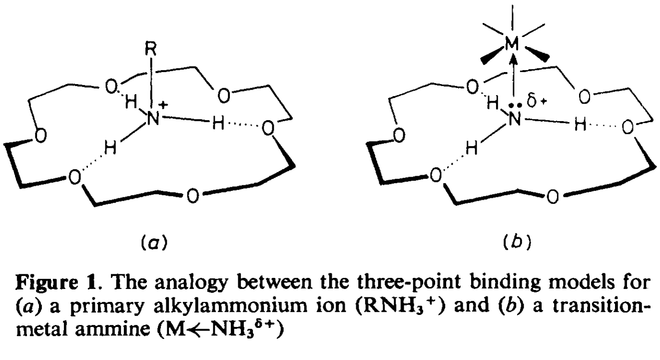

Figure 1. The analogy between the three-point binding models for (*a*) a primary alkylammonium ion (RNH_3^+) and (*b*) a transition-metal ammine ($M \leftarrow NH_3^{\delta+}$)

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† 1,4,7,10,13,16-Hexaoxacyclo-octadecane and 6,7,9,10,17,18,-20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclo-octadecin.

filtered and treated, dropwise with stirring, with hexane until crystallisation began. On standing at room temperature for 5 h, well formed yellow *crystals* appeared and these were filtered off, washed with hexane, and dried in air. The yield was 0.41 g (58%) (Found: C, 45.9; H, 4.0; N, 1.7. Calc. for $C_{25}H_{27}NO_{11}W \cdot 0.5C_6H_6$: C, 45.8; H, 4.1; N, 1.9%). On standing for several days, the crystals lost the benzene of crystallisation and became opaque.

Amminedichloro(triethylphosphine)platinum(II)*–Dibenzo-*18-*crown-*6*–Dichloromethane* (1/1/1).—A solution of *trans*-$[PtCl_2(PEt_3)(NH_3)]$ (0.27 g, 0.67 mmol) and dibenzo-18-crown-6 (0.25 g, 0.69 mmol) in dichloromethane (5 cm^3) was filtered and treated, dropwise with stirring, with hexane until a faint permanent precipitate was evident. After standing for 0.5 h, the *adduct* had crystallised in the form of long, fibrous needles which were filtered off, washed with hexane, and dried. The yield was 0.40 g (77%), m.p. 129 °C (Found: C, 38.5; H, 5.2; N, 1.9, Calc. for $C_{26}H_{42}Cl_2NO_6PPt \cdot CH_2Cl_2$: C, 38.3; H, 5.2; N, 1.7%).

The following adducts were prepared similarly: $[PtCl_2(PMe_3)(NH_3)] \cdot C_{20}H_{24}O_6$, m.p. 177 °C (Found: C, 38.7; H, 5.0; N, 1.8. Calc.: C, 38.7; H, 5.0; N, 2.0%); $2[PtCl_2(PEt_3)(NH_3)] \cdot C_{12}H_{24}O_6$, m.p. 169 °C (Found: C, 27.5; H, 6.2; N, 2.6. Calc.: C, 27.0; H, 5.6; N, 2.6%); and $2[PtCl_2(PMe_3)(NH_3)] \cdot C_{12}H_{24}O_6$, m.p. 176° C (Found: C, 22.7; H, 5.4; N, 2.9. Calc.: C, 22.0; H, 4.9; N, 2.8%).

Polymeric trans-*Bis(ammine)dichloroplatinum*(II)–18-*Crown-*6 (1/1).—A solution of *trans*-$[PtCl_2(NH_3)_2]$ (0.30 g, 1 mmol) in dimethylformamide (dmf) (30 cm^3) was treated with a solution of 18-crown-6 (0.26 g, 1 mmol) in dmf (10 cm^3) at room temperature. A precipitate formed immediately, but redissolved on boiling. Slow cooling of this solution yielded pale yellow needles of the *adduct*, which were filtered off, washed with cold dmf and diethyl ether, and dried under vacuum. The yield was 0.53 g (95%), m.p. 225 °C [Found: C, 25.7; H, 5.2; N, 4.9. Calc. for $(C_{12}H_{30}Cl_2N_2O_6Pt)_n$: C, 25.5; H, 5.3; N, 5.0%].

Polymeric Tetra-ammineaquacopper(II) *Bis(hexafluorophosphate)*–18-*Crown-*6 (1/1).—A solution of $[Cu(NH_3)_4(H_2O)][PF_6]_2$ (0.95 g, 2.16 mmol) in the minimum volume of 3 mol dm^{-3} aqueous ammonia was treated with a solution of 18-crown-6 (0.57 g, 2.16 mmol) in water (2 cm^3). The mixture was allowed to stand at room temperature for 3 h, and the resulting deep blue *crystals* were filtered off, washed with a little ice-water and diethyl ether, and dried on the filter. The yield was 0.52 g (34%), m.p. 183 °C [Found: C, 20.9; H, 5.4; N, 8.1. Calc. for $(C_{12}H_{38}CuF_{12}N_4O_7P_2)_n$: C, 20.5; H, 5.4; N, 8.1%].

Polymeric Hexa-amminecobalt(III) *Tris(hexafluorophosphate)*–18-*Crown-*6 (2/3).—To a solution of $[Co(NH_3)_6][PF_6]_3$ (0.60 g, 1.0 mmol) in water (20 cm^3) was added a solution of 18-crown-6 (0.52 g, 2.0 mmol) in water (5 cm^3). An orange crystalline precipitate formed at room temperature. After 1 h, the *crystals* were filtered off, washed with water and diethyl ether, and dried. The yield was 0.54 g (54%), m.p. >250 °C [Found: C, 21.4; H, 4.6; N, 7.7. Calc. for $(C_{36}H_{108}Co_2F_{36}N_{12}O_{18}P_6)_n$: C, 21.8; H, 5.4; N, 8.5%].

Separation of $[Cu(NH_3)_4(H_2O)][PF_6]_2$ *from* $[Co(NH_3)_6][PF_6]_3$ *by Reaction with* 18-*Crown-*6.—A solution containing $[Cu(NH_3)_4(H_2O)][PF_6]_2$ (0.84 g, 2.0 mmol) and $[Co(NH_3)_6][PF_6]_3$ (1.20 g, 2.0 mmol) in 3 mol dm^{-3} aqueous ammonia (40 cm^3) was treated with 18-crown-6 (0.57 g, 2.16 mmol) in water (5 cm^3). After this mixture had been held at 5 °C for 0.5 h, the blue crystals of the copper adduct were filtered off, washed with diethyl ether, and dried. The yield was 1.27 g (93%). This material was shaken with 1 mol dm^{-3} aqueous HCl and the resulting suspension was extracted with dichloromethane (2 × 150 cm^3). The organic layer was separated, dried over molecular sieves (3A), and evaporated to dryness, giving 0.52 g (86%) of solid $[NH_4][PF_6] \cdot C_{12}H_{24}O_6$. On adding 0.95 g (2.23 mmol) of this ammonium adduct to the mixed ammine solution described above, and shaking vigorously for 1 h, a 93% yield of the crystalline copper adduct was obtained.

Polymeric Bis(ethylenediamine)platinum(II) *Bis(hexafluorophosphate)*–18-*Crown-*6 (1/1).—To a solution of $[Pt(H_2NCH_2CH_2NH_2)_2][PF_6]_2$ (0.24 g, 0.40 mmol) in water (5 cm^3) was added 18-crown-6 (0.20 g, 0.76 mmol) in water (3 cm^3). The solution was cooled to 5 °C and after 1 h the colourless crystalline *precipitate* was filtered off, washed with a little ice-water and diethyl ether, and dried under vacuum. The yield was 0.17 g (49%), m.p. 201 °C [Found: C, 21.9; H, 4.6; N, 6.4. Calc. for $(C_{16}H_{40}F_{12}N_4O_6P_2Pt)_n$: C, 22.1; H, 4.6; N, 6.4%].

Results and Discussion

The i.r. spectrum of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)][BPh_4]$ in dichloromethane solution exhibits two strong CO stretching frequencies, a symmetric vibration at 2 065 cm^{-1} and an antisymmetric mode at 2 018 cm^{-1}. Addition of 1 mol equivalent of dibenzo-18-crown-6 resulted in a shift of these bands to 2 057 and 2 010 cm^{-1}, respectively. Addition of excess of crown ether produced no further change in the carbonyl region of the spectrum. In contrast, the analogous pyridine complex, $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_5H_5N)][PF_6]$, showed *no* shift in frequencies for the CO stretching absorptions on addition of the crown ether, confirming our conclusion that the observed shifts in the spectrum of the ammine complex are a result of specific hydrogen-bonding interactions between the crown ether and the ammine ligand.

The ^1H n.m.r. spectrum of $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)][BPh_4]$ in CD_2Cl_2 similarly showed significant changes on addition of 1 mol equivalent of dibenzo-18-crown-6, the NH_3 resonance shifting from δ 1.52 to 2.15 (consistent with hydrogen-bond formation) and the C_5H_5 resonance moving upfield from δ 4.72 to 4.52, perhaps as a result of shielding by the aromatic rings of the crown. Support for this conclusion comes from the observed shift to *lower* field (δ 4.96) of the C_5H_5 resonance in $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)][BPh_4] \cdot C_{20}H_{24}O_6$. Small shifts are also found in the ^1H n.m.r. resonances of dibenzo-18-crown-6 on addition of the cationic iron ammine. On cooling down a solution of equimolar amounts of crown and complex in CD_2Cl_2, the signal at δ 3.95 (assigned to the CH_2OCH_2 protons of the crown) separated into two resonances ($T_c = -50$ °C, $\Delta\nu = 50$ Hz) at 190 °C. The derived $\Delta G_c^{\ddagger}$ value of 10.8 kcal mol^{-1} (45.2 kJ mol^{-1}) provides an approximate measure of the binding energy of the adduct, since the averaging process involves dissociation of the iron complex from one face of the crown ether and subsequent re-association with the opposite homotopic face.

The neutral, zerovalent tungsten complex $[W(CO)_5(NH_3)]$ provided further evidence for the association of metal ammines with crown ethers in solution. A benzene solution of this complex shows i.r. bands [ν(CO)] at 2 067 ($A_1^{(2)}$), 1 923 (E), and 1 900 cm^{-1} ($A_1^{(1)}$), but addition of 1 mol equivalent of dibenzo-18-crown-16 resulted in significant shifts of all three frequencies to lower wavenumber to 2 057, 1 912, and 1 880 cm^{-1}, respectively.* A 1 : 1 adduct of $[W(CO)_5(NH_3)]$

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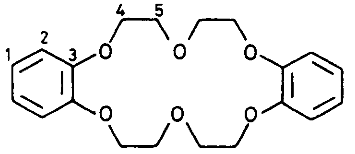
* The assignments of the i.r. bands of the complex and the adduct were inadvertently reversed in our original communication.[6]

Table 1. ^{13}C N.m.r. spectroscopic data * for $[W(CO)_5(NH_3)]\cdot C_{20}H_{24}O_6\cdot 0.5C_6H_6$

	δ values (p.p.m. relative to $SiMe_4$)						
Species	CO(*cis*)	CO(*trans*)	C-1	C-2	C-3	C-4	C-5
$[W(CO)_5(NH_3)]$	198.7	200.6	—	—	—	—	—
$C_{20}H_{24}O_6$ 	—	—	114.2	121.5	149.8	70.2	69.3
$[W(CO)_5(NH_3)]\cdot C_{20}H_{24}O_6$	198.7	200.9	112.2	121.5	147.8	69.8	67.2

* Recorded in CD_2Cl_2 at ambient temperature on a Bruker WH400 spectrometer using $SiMe_4$ as internal standard and lock.

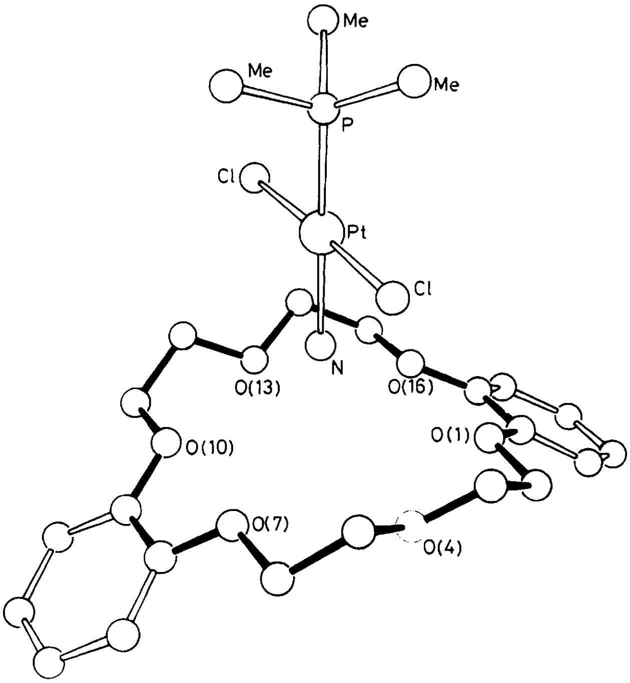


Figure 2. The crystal structure of $[PtCl_2(PMe_3)(NH_3)]\cdot C_{20}H_{24}O_6$. The NH_3 ligand is involved in three bifurcated hydrogen bonds to the six oxygen atoms of the crown

with this crown crystallised from benzene solution on slow addition of hexane, and was found to contain 0.5 mol equivalent of benzene of crystallisation. The ^{13}C n.m.r. spectrum of this adduct in C_6D_6 solution showed only small changes in the chemical shifts of tungsten carbonyl resonances relative to those of the free complex. However, upfield shifts of up to 2 p.p.m. were observed in the crown resonances on adduct formation (Table 1). Crystals of this adduct were unfortunately not suitable for *X*-ray analysis.

Neutral platinum(II) ammines of the form *trans*-$[PtCl_2(L)(NH_3)]$ (L = PMe_3 or PEt_3) similarly yielded crystalline adducts with both crowns on addition of hexane to dichloromethane solutions containing equimolar amounts of crown and metal complex. Although adducts with dibenzo-18-crown-6 had the expected 1 : 1 stoicheiometry, those involving 18-crown-6 were found (Table 2) to contain 2 mol of platinum complex per mol of crown ether suggesting that this crown is capable of binding *two* ammine ligands, one on each face of the macrocycle. The structures, shown in Figure 2 and 3 respectively, of $[PtCl_2(PMe_3)(NH_3)]\cdot C_{20}H_{24}O_6$ and $2[PtCl_2(PMe_3)(NH_3)]\cdot C_{12}H_{24}O_6$, which have been determined by *X*-ray crystallography, confirm this suggestion. The principal structural features have been reported previously [7] but here it is important to note that, in both adducts, the platinum complex is bound to the macrocycle *via* the NH_3 ligand which forms bifurcated (Figure 2) and direct (Figure 3) hydrogen bonds to ethereal oxygen atoms (N ··· O distances = 3.04—3.41 Å).

Variable-temperature ^{1}H n.m.r. studies of $[PtCl_2(PMe_3)(NH_3)]\cdot C_{20}H_{24}O_6$ indicate a free energy of activation of 7.9 kcal mol^{-1} (33.8 kJ mol^{-1}) for dissociative exchange of the metal complex between the homotopic faces of the crown. This value, some 2 kcal mol^{-1} lower than that for the same process involving $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(NH_3)]^+$, indicates that, as expected, the adduct formed in solution between a crown ether and a neutral ammine is less strongly bound than that formed between a crown ether and a cationic ammine in which N–H bond polarisation will be enhanced by the overall positive charge.

Direct evidence for the chemical significance of transition-metal ammine–crown ether interactions was provided by the action of 18-crown-6 on *trans*-$[PtCl_2(NH_3)_2]$. On mixing solutions of the two components in dimethylformamide (dmf) at room temperature an adduct precipitated immediately in essentially quantitative yield. The adduct could be recrystallised from hot dmf, and it analysed as $\{[PtCl_2(NH_3)_2]\cdot C_{12}H_{24}O_6\}_n$. The crystals proved unsuitable for *X*-ray analysis, but, in view of the known structure of 2 *trans*-$[PtCl_2(PMe_3)(NH_3)]\cdot C_{12}H_{24}O_6$ (Figure 3) and the insoluble nature of the adduct in all solvents except hot dmf, a linear polymeric structure (Figure 4) seems highly probable. In keeping with this structural proposal, the *cis* isomer of $[PtCl_2(NH_3)_2]$, which is geometrically incapable of forming a linear polymer, failed to give a precipitate on addition of 18-crown-6 to a solution of the complex in dmf. We thus have, in principle, a technique for separating geometrical isomers of transition-metal ammines by adduct formation with crown ethers.

Adduct formation has been observed even in aqueous solutions, where the competition for hydrogen-bond formation to ammonia ligands and to crown ethers from solvent water might have been expected to inhibit ammine–crown ether hydrogen-bond formation. First, we examined the interaction of 18-crown-6 with the ' cuprammonium ' ion $[Cu(NH_3)_4(H_2O)]^{2+}$, as its hexafluorophosphate salt. A deep blue crystalline material, which slowly precipitated at room temperature from a solution of the two components (equimolar amounts) in 3 mol dm^{-3} aqueous ammonia, analysed

Table 2. ^1H N.m.r. spectroscopic data * for platinum(II) adducts with dibenzo-18-crown-6 ($C_{20}H_{24}O_6$) and 18-crown-6 ($C_{12}H_{24}O_6$)

Species	^1H N.m.r. data (δ values, J in Hz)
trans-$[PtCl_2(PMe_3)(NH_3)]$	1.54 (9 H, d with ^{195}Pt satellites, $^2J_{PH}$ 12, PMe_3) and 2.70 (3 H, br s, NH_3)
trans-$[PtCl_2(PEt_3)(NH_3)]$	1.15 (9 H, d × t, $^3J_{PH}$ 20, $^3J_{HH}$ 7, 3 × CH_2CH_3), 1.72—2.00 (6 H, m, 3 × CH_2Me), and 2.69 (3 H, br s, NH_3)
$C_{12}H_{24}O_6$	3.58 (s, 12 × OCH_2)
$C_{20}H_{24}O_6$	3.95 and 4.13 (16 H, AA′BB′ system, 4 × OCH_2CH_2O) and 6.86 (8 H, br s, 2 × C_6H_4)
2 *trans*-$[PtCl_2(PMe_3)(NH_3)]\cdot C_{12}H_{24}O_6$	1.49 (18 H, d with ^{195}Pt satellites, $^2J_{PH}$ 12, 2 × PMe_3), 3.33 (6 H, br s, 2 × NH_3), and 3.63 (24 H, s, 12 × OCH_2)
trans-$[PtCl_2(PMe_3)(NH_3)]\cdot C_{20}H_{24}O_6$	1.44 (9 H, d with ^{195}Pt satellites, $^2J_{PH}$ 12, PMe_3), 3.00 (3 H, br s, NH_3), 3.96 and 4.17 (16 H, AA′BB′ system, 4 × OCH_2CH_2O), and 6.87 (8 H, br s, 2 × C_6H_4)
2 *trans*-$[PtCl_2(PEt_3)(NH_3)]\cdot C_{12}H_{24}O_6$	1.15 (18 H, d × t, $^3J_{PH}$ 20, $^3J_{HH}$ 7, 6 × CH_2CH_3), 1.72—2.00 (12 H, m, 6 × CH_2CH_3), 3.02 (6 H, br s, 2 × NH_3), and 3.65 (24 H, s, 12 × OCH_2)
trans-$[PtCl_2(PEt_3)(NH_3)]\cdot C_{20}H_{24}O_6$	1.07 (9 H, d × t, $^3J_{PH}$ 20, $^3J_{HH}$ 7, 3 × CH_2CH_3), 1.60—1.90 (6 H, m, 3 × CH_2Me), 3.00 (3 H, br s, NH_3), 3.96 and 4.16 (16 H, AA′BB′ system, 4 × OCH_2CH_2O), and 6.85 (8 H, br s, 2 × C_6H_4)

* Recorded in CD_2Cl_2 at ambient temperature on a Perkin-Elmer R34 spectrometer using $SiMe_4$ as internal standard and lock.

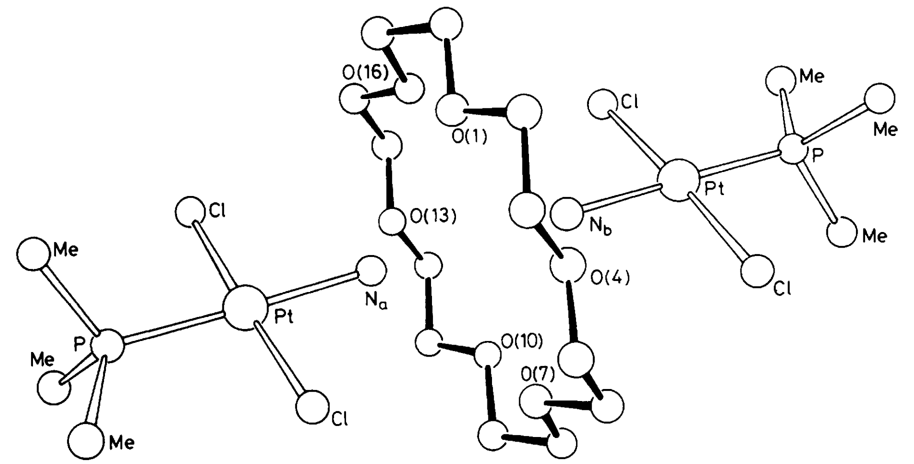


Figure 3. The crystal structure of $2[PtCl_2(PMe_3)(NH_3)]\cdot C_{12}H_{24}O_6$. All six oxygen atoms are hydrogen bonded directly to the two NH_3 ligands [N_a–H to O(1), O(7), and O(13); N_b–H to O(4), O(10), and O(16)]

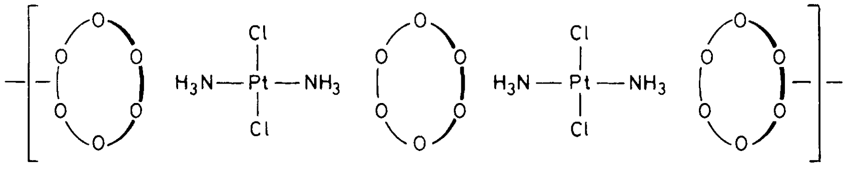


Figure 4. The proposed structure of $\{[PtCl_2(NH_3)_2]\cdot C_{12}H_{24}O_6\}_n$

for the 1 : 1 adduct $\{[Cu(NH_3)_4(H_2O)][PF_6]_2\cdot C_{12}H_{24}O_6\}_n$. The adduct was obtained more readily and in higher yield by cooling the solution to *ca.* 5 °C. The solid-state i.r. spectrum of this adduct showed significant frequency shifts in bands assigned to N–H stretching (*ca.* 3 300 cm^{-1}) and bending (*ca.* 1 620 cm^{-1}) vibrations relative to those in the free complex. However, the O–H stretching absorptions were virtually unaffected in keeping with the known *X*-ray crystal structure of the adduct.[7] In this case, a linear, polymeric structure was found (Figure 5) in which the crown ether forms hydrogen bonds solely to ammine ligands (N ··· O distances = 3.06—3.28 Å), leaving the aqua-ligand to interact only very weakly, if at all, with a fluorine atom of $[PF_6]^-$.

An apparently similar adduct was obtained from the cobalt-

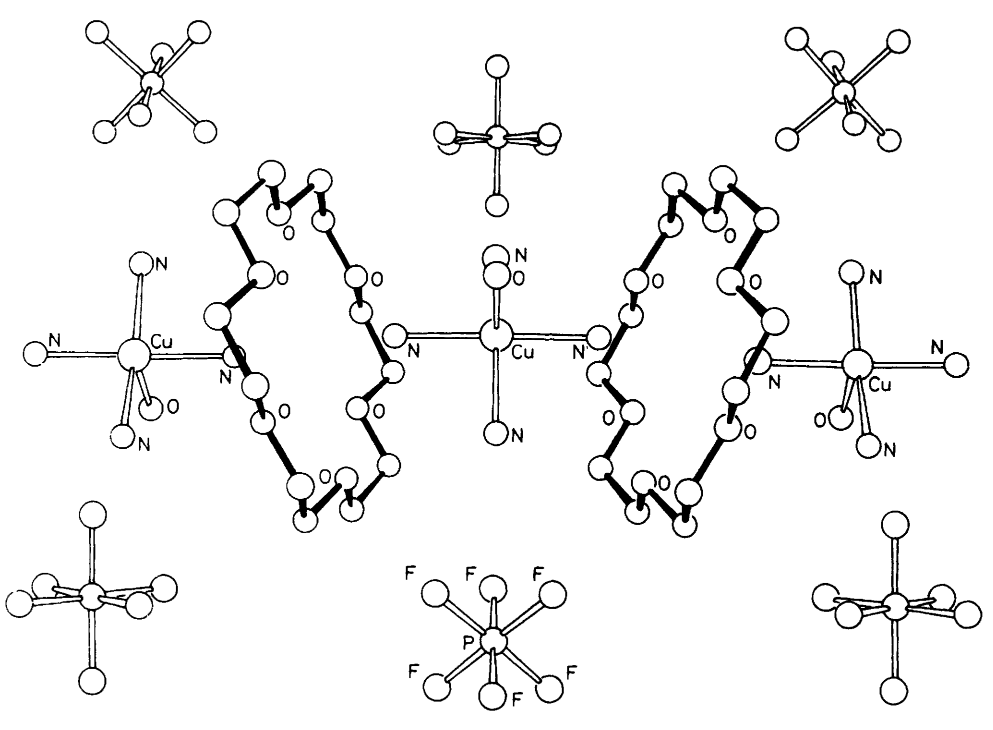
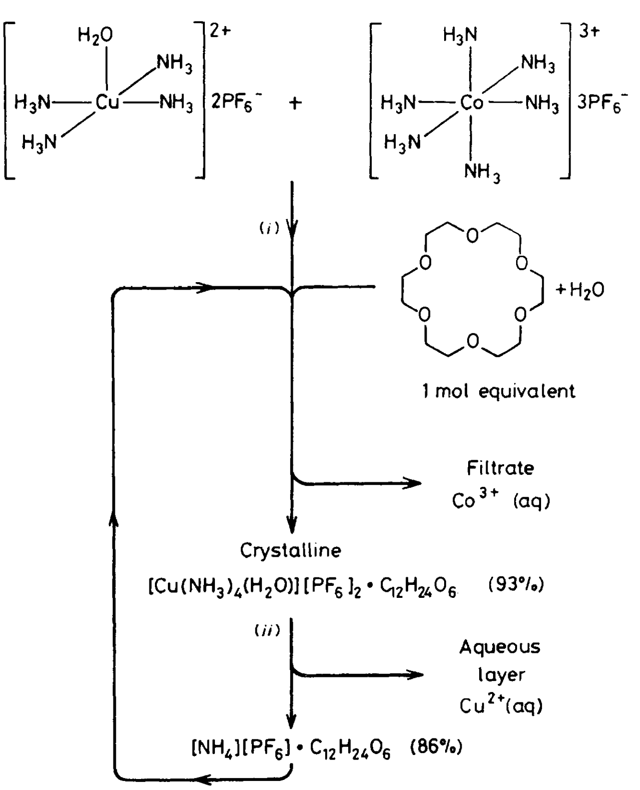


Figure 5. The crystal structure of $\{[Cu(NH_3)_4(H_2O)][PF_6]_2{\cdot}C_{12}H_{24}O_6\}_n$

(III) complex $[Co(NH_3)_6][PF_6]_3$, which yielded a crystalline orange precipitate on addition of a two-fold molar excess of 18-crown-6 to its aqueous solution. The adduct analysed approximately as $\{2[Co(NH_3)_6][PF_6]_3{\cdot}3C_{12}H_{24}O_6\}_n$. Although the exact nature of this material has not been investigated further, a two- or three-dimensional polymeric structure seems possible. A further example of the selectivity of crown ether–transition-metal ammine interactions was found when 1 mol equivalent of 18-crown-6 was added to a solution containing 1 mol equivalent each of $[Co(NH_3)_6][PF_6]_3$ and $[Cu(NH_3)_4(H_2O)][PF_6]_2$ in 3 mol dm^{-3} aqueous ammonia (excess of ammonia is required to stabilise the 'cuprammonium' ion). The 1 : 1 *copper* adduct was precipitated exclusively in >90% yield and could thus be separated from the cobalt-containing solution by filtration. The adduct, on treatment with hydrochloric acid [equation (1)], yielded aqueous copper(II) and

$$[Cu(NH_3)_4(H_2O)][PF_6]_2{\cdot}C_{12}H_{24}O_6 + 4HCl \longrightarrow Cu^{2+} + 3NH_4^+ + H_2O + 4Cl^- + PF_6^- + [NH_4][PF_6]{\cdot}C_{12}H_{24}O_6\downarrow \quad (1)$$

insoluble $[NH_4][PF_6]{\cdot}C_{12}H_{24}O_6$ which was recovered by extraction with dichloromethane. The ammonium hexafluorophosphate adduct with 18-crown-6 could be used instead of free crown to separate $[Cu(NH_3)_4(H_2O)]^{2+}$ from $[Co(NH_3)_6]^{3+}$. On stirring a suspension of the ammonium adduct in 3 mol dm^{-3} aqueous ammonia containing equimolar amounts of the two ammines, exchange of $[Cu(NH_3)_4(H_2O)]^{2+}$ for $[NH_4]^+$ occurred and a blue precipitate of the *copper* adduct slowly replaced the white ammonium adduct. A cyclic system is thus achieved.[16] The overall sequence of events in this novel approach to metal-ion separation is summarised in the Scheme.



Scheme. A cyclic process for separation of Cu^{II} from Co^{III}. (*i*) 4 mol dm^{-3} aqueous ammonia followed by 18-crown-6, cooling to 0 °C, filtration; (*ii*) 1 mol dm^{-3} HCl, extraction with CH_2Cl_2, separation, evaporation of CH_2Cl_2

Although the NH_3 ligand clearly provides a very suitable binding site for crown ethers, there exists a wide range of other first-sphere ligands which are potentially able to form hydrogen bonds and thereby co-ordinate with crown ethers in the second sphere. Since ethylenediamine is known to show 'acidic' behaviour in certain platinum complexes,[17] we examined the ability of $[Pt(H_2NCH_2CH_2NH_2)_2][PF_6]_2$ to interact with 18-crown-6 in aqueous solution. On cooling a solution of the two components (1 : 2 molar ratio of metal

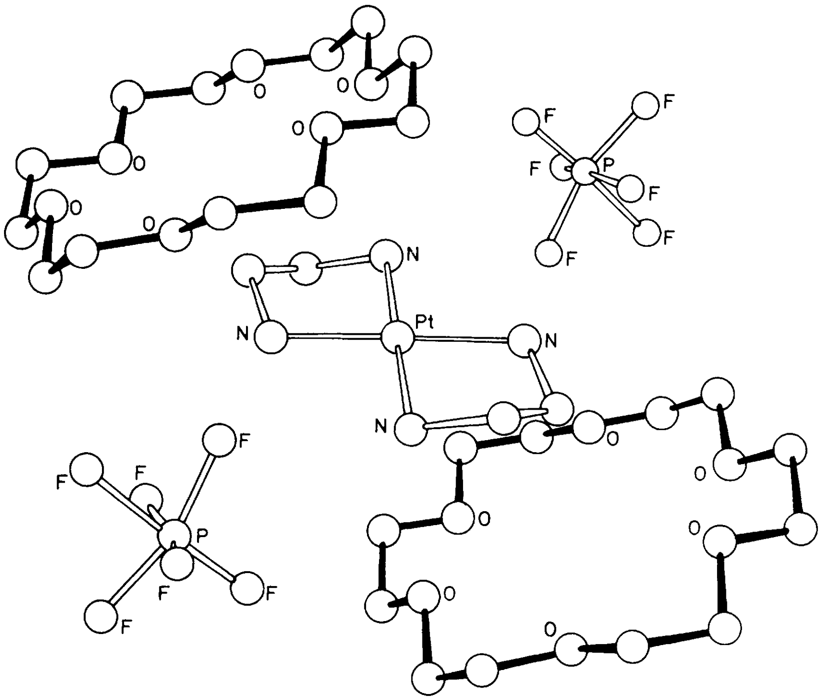


Figure 6. The crystal structure of $\{[Pt(H_2NCH_2CH_2NH_2)_2][PF_6]_2 \cdot C_{12}H_{24}O_6\}_n$

complex : crown) a colourless crystalline adduct was precipitated in *ca.* 50% yield. It analysed for the 1 : 1 adduct, $\{[Pt(H_2NCH_2CH_2NH_2)_2][PF_6]_2 \cdot C_{12}H_{24}O_6\}_n$. A polymeric ' stepped-sandwich ' structure (Figure 6) has been determined crystallographically for this material.[7] Only one hydrogen atom of each amino-group and only four of the six crown ether oxygen atoms are involved in hydrogen bonding (ignoring possible weak interactions between $[PF_6]^-$ counter ions and the co-ordinated amino-groups).

We believe that many other primary ligands, such as acetonitrile,[18] will form second-sphere complexes with crown ethers. Recently, we have also discovered that by using much larger macrocyclic polyethers such as dibenzo-30-crown-10 * more than one primary ligand may be bound within the cavity of the macrocycle. Indeed, the 2,2′-bipyridyl complex $[Pt(bipy)(NH_3)_2][PF_6]_2$ is readily solubilised in dichloromethane by addition of this crown and the *X*-ray crystal structure of the resulting 1 : 1 adduct [19] reveals almost complete encapsulation of the metal complex. Here, both hydrogen-bonding and $\pi \rightarrow \pi$ charge-transfer interactions play significant roles in binding the two components together.

Thus, second-sphere co-ordination by macrocyclic ligands such as crown ethers provides a novel method of modifying the physical and chemical properties of transition-metal complexes. It may also prove to be a valuable approach to the study of non-covalent bonding interactions in general.

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