The Binding of Neutral Platinum Complexes by Crown Ethers. *X*-Ray Crystal Structures of [*trans*-$PtCl_2(PMe_3)NH_3$.dibenzo-18-crown-6] and [{*trans*-$PtCl_2(PMe_3)NH_3$}$_2$.18-crown-6]

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Summary Complexes of the type *trans*-$PtCl_2(L)NH_3$ where L = PMe_3 (**1**), PEt_3 (**2**), and NH_3 (**3**) co-ordinate to 18-crown-6 (18C6) and dibenzo-18-crown-6 (DB18C6) by hydrogen bonding of their NH_3 ligands, forming the crystalline adducts [(**1**)–DB18C6], [(**2**)–DB18C6], [(**1**)$_2$–18C6], [(**2**)$_2$–18C6], and [(**3**)–18C6]$_n$ which also display considerable stability in solution.

ALTHOUGH we have found[1] recently that $W(CO)_5NH_3$ forms a crystalline 1 : 1 adduct with dibenzo-18-crown-6 (DB18C6), the crystals were not amenable to *X*-ray structural analysis. Here, we report (i) the isolation of crystalline adducts† of *trans*-[$PtCl_2(L)NH_3$][2] [(**1**) L = Me_3P, (**2**) L = Et_3P, (**3**) L = NH_3] with DB18C6 and 18-crown-6 (18C6) and (ii) the *X*-ray crystal structures of (**1**)-DB18C6 and (**1**)$_2$–18C6, and discuss the spectroscopic evidence for the existence of these adducts in solution.

trans-[$PtCl_2(L)NH_3$]

(**1**) L = Me_3P
(**2**) L = Et_3P
(**3**) L = NH_3

Addition of hexane to a CH_2Cl_2 solution (5 cm^3), containing 0·67 mmol of both (**2**) and DB18C6, resulted in the formation of long fibrous needles of a CH_2Cl_2 solvate of [(**2**)–DB18C6]‡ (77%), m.p. 129 °C. Crystalline adducts were also isolated from CH_2Cl_2–hexane containing *equimolar* amounts of the appropriate complex and crown ether: [(**1**)–DB18C6],‡ m.p. 177 °C, [(**1**)$_2$–18C6],‡ m.p. 176 °C, and [(**2**)$_2$–18C6],‡ m.p. 169 °C. It is significant that 18C6 forms 2 : 1 (Pt-ammine : 18C6) rather than 1 : 1 adducts on crystallisation. Recrystallisation of [(**1**)–DB18C6] from CH_2Cl_2–hexane afforded crystals suitable for *X*-ray analysis.§

† Satisfactory elemental analyses were obtained for all the new crystalline adducts.

‡ I.r. (Nujol) and ^1H n.m.r. (CD_2Cl_2) spectroscopic data for selected adducts are as follows: (**1**)–DB18C6, ν 3340, 3280, 3190, and 1600 (NH), and 1140 (CO) cm^{-1}; δ 1·44 [9H, d with ^{195}Pt satellites, *J*(PH) 12 Hz, PMe_3], 3·00 [3H, br s, NH_3], 3·96 and 4·17 [16H, AA′BB′ system, 4 × OCH_2CH_2O], and 6·87 [8H, br s, 2 × C_6H_4]. (**2**)$_2$–18C6, ν 3330, 3265, 3200, and 1635 (NH), and 1115 (CO) cm^{-1}; δ 1·09—1·30 [18H, m, 3 × $(PCH_2CH_3)_3$], 1·72—2·00 [12H, m, 2 × $(PCH_2CH_3)_3$], 3·02 [6H, br s, 2 × NH_3], and 3·65 [24H, s, 6 × OCH_2CH_2O]. [(**3**)–18C6]$_n$ ν 3320, 3215, and 1630 (NH), and 1115 (CO) cm^{-1}.

§ *Crystal data:* (**1**)–DB18C6, $C_{20}H_{24}O_6.C_3H_{12}NPCl_2Pt$, orthorhombic, space group *Pnma*, $a = 18{\cdot}388(2)$, $b = 14{\cdot}745(2)$, $c = 10{\cdot}246(2)$ Å, $U = 2778$ Å^3, $Z = 4$, $\mu(\text{Cu-}K_\alpha) = 121$ cm^{-1}. Of the 2162 independent reflections ($\theta \leqslant 60°$) measured on a diffractometer using Cu-K_α radiation, 175 were classified as unobserved. The structure was solved by the heavy atom method and the absorption-corrected data were refined to give a current $R = 0{\cdot}043$. (**1**)$_2$–18C6, $C_{12}H_{24}O_6.C_6H_{24}N_2P_2Cl_4Pt_2$, monoclinic, space group $P2_1/c$, $a = 11{\cdot}980(1)$, $b = 8{\cdot}632(1)$, $c = 16{\cdot}615(1)$ Å, $\beta = 98{\cdot}20(1)°$, $U = 1701$ Å^3, $Z = 4$, $\mu(\text{Cu-}K_\alpha) = 192$ cm^{-1}. Of the 2140 independent reflections ($\theta \leqslant 55°$) measured on a diffractometer using Cu-K_α radiation, 147 were classified as unobserved. The structure was solved by the heavy atom method and the absorption corrected data were refined to give a current $R = 0{\cdot}043$. The atomic coordinates 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.

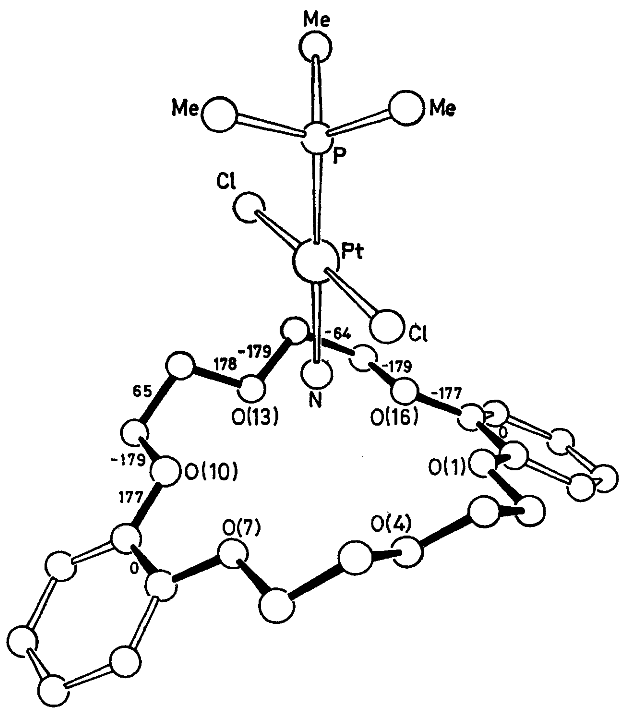


FIGURE 1. Crystal structure of (**1**)–DB18C6. Bond distances: O(4)–C(5) 1·41(2), C(5)–C(6), 1·48(2), C(6)–O(7), 1·44(2), O(7)–C(8) 1·38(2) Å. Bond angles: C(9)–O(10)–C(11) 116(1), C(12)–O(13)–C(14) 113(1)°. Average torsion angle e.s.d. = 1·2°.

This 1:1 adduct (Figure 1) has crystallographic mirror symmetry about the plane bisecting the two aromatic rings and containing the N, Pt, and P atoms, and one of the Me groups. In addition, the DB–18C6 portion has local non-crystallographic C_{2v} symmetry. The NH_3 ligand in (**1**) is involved in three bifurcated hydrogen bonds[3] with the six oxygen atoms in DB18C6 (Figure 2). This binding pattern corresponds (*cf.* Figure 1) to eclipsing of the N–H bonds with the P–C bonds of the PMe_3 ligand. The angles (θ in the caption to Figure 2) of approach of the hydrogen bonds to O(1), O(7), O(10), and O(16) result in approximately trigonal geometry around these aryl oxygen atoms, whereas O(4) and O(13) are oriented away from the NH_3 ligand such that these oxygen atoms enter into an essentially orthogonal hydrogen bonding interaction. By contrast, *X*-ray crystal analysis of $(\mathbf{1})_2$–18C6 revealed (see Figure 3) that the crown adopts its familiar complexing conformation (all-*gauche* with approximately D_{3d} symmetry) with a crystallographic centre of symmetry at its centre and binds two molecules of the platinum ammine, one to each face of the crown. Thus, all six of its oxygen atoms are hydrogen bonded in an approximately trigonal fashion to the two NH_3 ligands. This six-point binding model is to be contrasted with the three-point binding model proposed[4] for the complexation of RNH_3^+ ions by 18C6 in solution and observed[5] for $(PhCH_2NH_3.18C6)^+SCN^-$ in the solid state. Clearly, in [$(\mathbf{1})_2$–18C6] the binding of one *neutral* platinum ammine ligand does not prevent the approach of a second such ligand to the opposite face of the crown. The bifunctional role of the 18C6 in this 2:1 adduct suggested to us that the *trans*-diammine (**3**) should form a linear face-to-face hydrogen bonded polymer with the repeating unit, [(**3**)–18C6]$_n$. Indeed, on mixing *NN*-dimethylformamide solutions of (**3**) and 18C6, a precipitate was formed immediately which dissolved on heating and finally provided pale yellow needles (95%, m.p. 225 °C) with 1:1 stoicheiometry‡ on slow cooling. Unfortunately, the crystals were severely twinned and hence unsuitable for *X*-ray crystallographic analysis. They are also extremely insoluble in a wide range of organic solvents. Fortunately, this is not the case with the other adducts. In fact, convincing i.r. and ^1H n.m.r. spectroscopic evidence was obtained for the existence of stable adducts involving the ammines (**1**) and (**2**) in solution. For example, when the ^1H n.m.r. spectral data¶ for [(**1**)–DB18C6] in CD_2Cl_2 are compared with those for (**1**) and DB18C6, significant

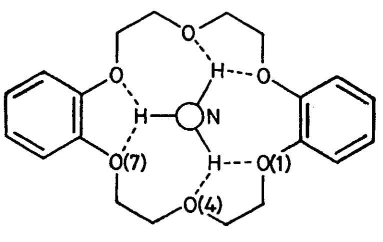


FIGURE 2. Diagrammatic representation of the bifurcated hydrogen bonding pattern in (**1**)–DB18C6 portraying the observed positions of the hydrogen atoms in a weighted difference electron density map although these positions have not been refined. Hydrogen bond distances, $R(N \cdots\cdots O)$ (Å); angles (θ°) between COC planes and (a) NO vectors and (b) HO vectors: O(1) 3·41; (a) 6, (b) 7. O(4) 3·36; (a) 89, (b) 81. O(7) 3·32; (a) 4, (b) 12. These hydrogen bond parameters are based on calculated hydrogen positions placed tetrahedrally 1·0 Å from the nitrogen atom.

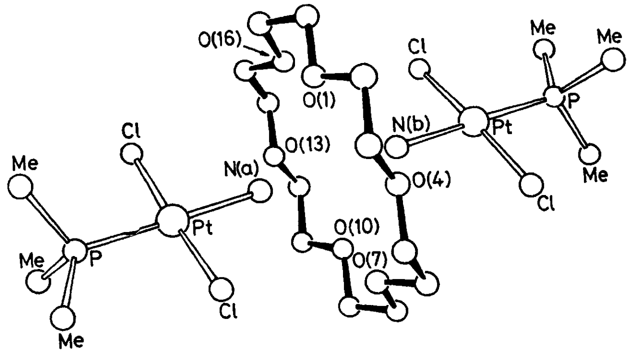
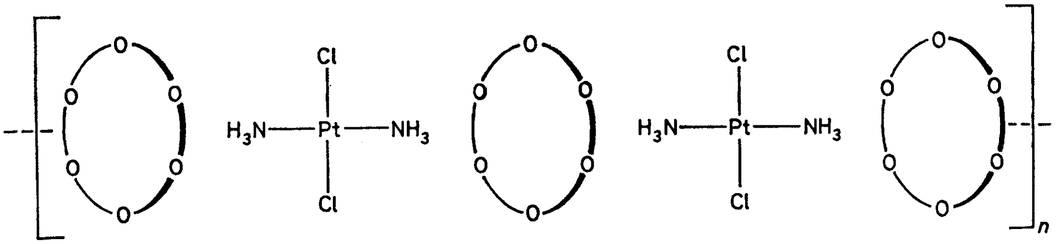


FIGURE 3. Crystal structure of $(\mathbf{1})_2$–18C6. Bond distances: C–C 1·43—1·51(2) C–O 1·40—1·45(2) Å. Bond angles at O(1) 114(1), O(7) 112(1), O(13) 112(1)°. Torsional angles: |O–C–C–O| 68·7—69·2(1·2), |C–C–O–C| 176·4—179·7(1·2)°. Hydrogen bond distances, $R(N \cdots\cdots O)$ (Å); angles (θ°) between COC planes and NO vectors: O(1) 3·04; 10. O(7) 3·21; 11. O(13) 3·31; 16. Although the hydrogen positions are poorly resolved in the difference electron density map, it does indicate that a staggered relationship exists between the NH_3 and PMe_3 ligands. Thus, the N(a)–H bonds are directed towards O(1), O(7), and O(13) and the N(b)–H bonds towards O(4), O(10), and O(16). Distance $R(a)N \cdots\cdots N(b)]$, 3·48 Å.

¶ ^1H N.m.r. spectroscopic data: $Me_3PPtCl_2NH_3$ (**1**), $\delta(CD_2Cl_2)$ 1·54 [9H, d with ^{195}Pt satellites, *J*(PH) 12 Hz, PMe_3] and 2·70 [3H, br s, NH_3]. DB18C6, $\delta(CD_2Cl_2)$ 3·95 and 4·13 [16H, AA′BB′ system, 4 × OCH_2CH_2O] and 6·86 [8H, br s, 2 × C_6H_4].



[(3)-18C6]$_n$

chemical shift changes are evident upon formation of the 1 : 1 adduct. Moreover on cooling the solution, the signal at δ 3·96 arising from the $-CH_2OCH_2-$protons separates ($T_c = -106$ °C) into two resonances ($\Delta\nu$ = *ca.* 66 Hz) at -108 °C. The derived $\Delta G_c^\ddagger$ value of 7·9 kcal mol^{-1} for the process involving exchange of (**1**) between the homotopic faces of DB18C6 indicates, as expected, that the adduct formed in solution is weaker for this neutral platinum ammine than it is in the case of the cationic iron ammine $[Fe(\eta\text{-}C_5H_5)(CO)_2NH_3]^+[BPh_4]^-$ studied previously.[1]

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