Hydrogen Bonding by Cisplatin Derivatives: Evidence for the Formation of N–H · · · · Cl and N–H · · · · Pt Bonds in $[NPr^n_4]_2\{[PtCl_4]\cdot cis\text{-}[PtCl_2(NH_2Me)_2]\}$

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Neutron diffraction shows that the title compound contains both N–H · · · · Cl and N–H · · · · Pt bonds in the solid; such hydrogen bonding is considered to be responsible for the high solubility in dichloromethane of this and related adducts involving *cis*-$[PtX_2L_2]$ (X = Cl or Br, L = NH_2Me or $NHMe_2$) complexes which are otherwise practically insoluble.

In this communication we draw attention to two apparently disparate aspects of platinum chemistry. First we show that *cis*-bis-amine–platinum(II) complexes can hydrogen bond to a variety of anionic substrates, including metal complexes. Colquhoun, Stoddart, and Williams[1] have recently highlighted the importance of such interactions in the general context of second-sphere co-ordination, an example being the adduct formed between two *cis*-$[PtCl_2(NH_3)_2]$ units (cisplatin, the important antitumour drug[2]) and one 18C6 crown ether molecule.[3] Secondly, we show crystallographic evidence (neutron data) for intermolecular N–H · · · · Pt bonding perpendicular to the primary co-ordination square-plane of a platinum(II) complex. There are many examples (*e.g.* ref. 4) where weak interactions exist in solids between a hydrogen atom (usually bound to carbon) and a Pt^{II} centre, and these may be considered as models for the early stages of activation of C–H bonds in cyclometallation reactions. It is in this light that we consider the nature of the N–H · · · · Pt bond in the title compound.

The product (**1**) studied here resulted from the reaction of methylamine with $[NPr^n_4]_2[Pt_2Cl_6]$ in *N*,*N*-dimethylformamide. Although analytically it accorded with the intended complex $[NPr^n_4][PtCl_3(NH_2Me)]$, a CD_2Cl_2 solution of it gave two ^{195}Pt n.m.r. signals at 2 286 and 2 980 p.p.m. (to high frequency of Ξ $^{195}Pt = 21.4$ MHz).[5] The higher shift is similar to that of $[NPr^n_4]_2[PtCl_4]$ (3 045 p.p.m.); the lower signal is broad, as is typical for ^{195}Pt bonded to ^{14}N, and its shift may be compared to that of *cis*-$[PtCl_2(NH_3)_2]$ (2 416 p.p.m. in dimethyl sulphoxide).[6] The value of $^3J(PtH)$ for the methylamine ligand is 48.8 Hz, much higher than 34.3 Hz observed for *trans*-$[PtCl_2(NH_2Me)_2]$ suggesting the *cis*-configuration even though *cis*-$[PtCl_2(NH_2Me)_2]$ alone is virtually insoluble in CH_2Cl_2. These results suggested the formulation of (**1**) as $[NPr^n_4]_2\{[PtCl_4]$*cis*-$[PtCl_2(NH_2Me)_2]\}$ an unusual type of double salt which retains its integrity in solution.

The complex can more conveniently be prepared by dissolving the *cis*-bis-amine complex in a CH_2Cl_2 solution of $[NPr^n_4]_2[PtCl_4]$, and by comparable means we have obtained similar complexes (**2**)—(**4**).

$[NPr^n_4]_2\{[PtCl_4]$*cis*-$[PtCl_2(NH_2Me)_2]\}$
(**1**)

$[NPr^n_4]_2\{[PtCl_4]$*cis*-$[PtCl_2(NHMe_2)_2]\}$
(**2**)

$[NPr^n_4]_2\{[PtBr_4]$*cis*-$[PtBr_2(NH_2Me)_2]\}$
(**3**)

$[NPr^n_4]_2\{[PtBr_4]$*cis*-$[PtBr_2(NHMe_2)_2]\}$
(**4**)

We have investigated the linkage involved in these complex anions by crystal structure analysis of (**1**) at low temperature (20 K), using neutron data in order to locate hydrogen atoms accurately; the geometry is shown in Figure 1.† Each platinum atom has the usual planar primary co-ordination structure with in-plane bond angles close to 90°. The most remarkable features of the structure are two short hydrogen contacts H(11) · · · · Pt(1), 2.262(11); H(22) · · · · Cl(13), 2.318(12) Å, which link the two constituent platinum species together. The latter contact has similar dimensions to other Pt–N–H · · · · Cl–Pt hydrogen bonds inferred from *X*-ray diffraction [N · · · · Cl 3.270 Å in (**1**); 3.30 Å in cisplatin;[7] 3.31 Å in the cisplatin–crown ether adduct[3]].

The N(1)–H(11) vector makes an angle of 79.5° to the $PtCl_4$ plane, and Pt(1) · · · · H(11)–N(1) at 167.1(9)° is much closer to linearity than the more conventional Cl · · · · H–N hydrogen bond Cl(13) · · · · H(22)–N(2) of 151.0(12)°. An intramolecular N–H · · · · Pt contact was recently characterised by *X*-ray diffraction in *cis*-$[Pt\{o\text{-}Ph_2PC_6H_4NC(O)\text{-}C_6H_4\}\text{-}\{o\text{-}Ph_2PC_6H_4NHC(O)Ph\}$[8] [Pt · · · · H, 2.318(22); Pt · · · · N, 3.24 Å; *cf.* Pt · · · · N 3.277 Å in (**1**)] which the authors termed 'agostic'.[9]

The nature of the Pt · · · · H–N interaction raises a question. Its nearly linear geometry is typical of three-centre four-electron (3c–4e) hydrogen bonds in contrast to all M–H–M, M–H–B, and M–H–C 3c–2e bonds accurately characterised which are bent, usually having angles of *ca.* 110 ± 20° at H. However Z–H · · · · Pt interactions (Z = N or C) imply a 3c–2e description if they are termed agostic.[8,9] Use of the filled Pt $5d_{z^2}$ orbital in the interaction would make hydrogen bonding (with an electrostatic component) the more appropriate description. Use of the Pt $6p_z$ orbital, which is also of allowable symmetry but is empty, would support the description of the bonding as agostic. The geometry of the linkage, and the ability of *cis*-$[PtCl_2(NH_2Me)_2]$ to hydrogen bond to other substrates, leads us to favour a 3c–4e description of the Pt · · · · H–N bond. We note that *both* $6p_z$ and $5d_{z^2}$ may be involved in this interaction.

Without doubt the Cl · · · · H–N hydrogen bonding is an important feature because the *cis*-$[PtCl_2L_2]$ complexes can also be rendered highly soluble in CH_2Cl_2 (>0.2 mol dm^{-3}) by $[NPr^n_4]Cl$, $[NBu^n_4]_2[PtCl_6]$, and other doubly charged chloroanionic salts such as $[NPr^n_4]_2[CoCl_4]$. *trans*-$[PtCl_2(NH_3)_2]$

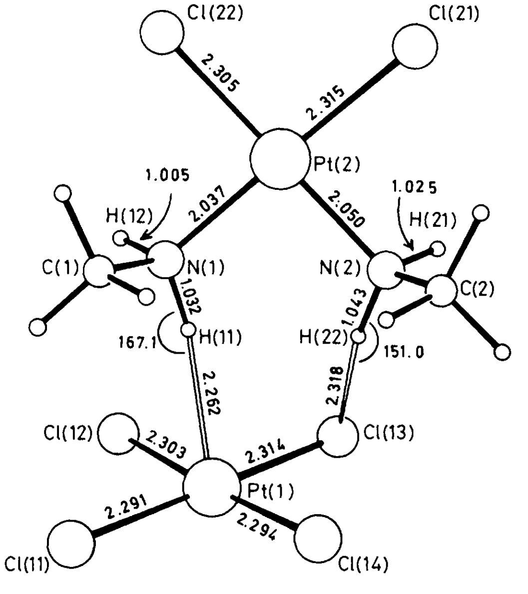

Figure 1. Molecular structure of the anion of (**1**). $\{[PtCl_4]$*cis*-$[PtCl_2(NH_2Me)_2]\}$. Important geometric parameters include: bond lenghs (Å) Pt(1)–Cl(11) 2.291(5), Pt(1)–Cl(12) 2.303(5), Pt(1)–Cl(13) 2.314(5), Pt(1)–Cl(14) 2.294(5), Pt(1) · · · H(11) 2.262(11), Pt(2)–N(1) 2.037(5), Pt(2)–N(2) 2.050(5), Pt(2)–Cl(21) 2.315(5), Pt(2)–Cl(22) 2.305(5), Cl(13) · · · H(22) 2.318(12), N(1)–H(11) 1.032(11), N(1)–H(12) 1.005(12), N(2)–H(21) 1.025(13), N(2)–H(22) 1.043 (12); bond angles (°) Cl(11)–Pt(1)–Cl(12) 90.4(2), Cl(11)–Pt(1)–Cl(14) 89.9(2), Cl(12)–Pt(1)–Cl(13) 89.4(2), Cl(13)–Pt(1)–Cl(14) 90.2(2), Cl(21)–Pt(2)–Cl(22) 93.9(2), N(1)–Pt(2)–N(2) 92.6(2), Pt(1)–Cl(13) · · · H(22) 78.4(4), N(1)–H(11) · · · Pt(1) 167.1(9), N(2)–H(22) · · · Cl(13) 151.0(12).

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† *Crystal Data:* $[NPr^n_4]_2\{[PtCl_4]$*cis*-$[PtCl_2(NH_2Me)_2]\}$, $C_{26}H_{66}Cl_6N_4Pt_2$, $M = 1037.7$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.680(4)$, $b = 11.926(2)$, $c = 15.350(15)$ Å, $\alpha = 93.88(4)$, $\beta = 100.57(5)$, $\gamma = 96.58(4)°$, $U = 1901(2)$ Å^3, $Z = 2$, $D_c = 1.813$ g cm^{-3}, $\lambda = 1.15933(8)$ Å neutrons, Ge(220) monochromator, $T = 20$ K, $\mu_N(\lambda = 1.15933) = 3.22$ cm^{-1}. The structure was initially solved and refined on the basis of *X*-ray data collected at 293 K. We report here the results of a neutron diffraction experiment at the Brookhaven National Laboratory High Flux Beam Reactor. Data were collected at 20 K for a unique hemisphere of reciprocal space in the range $5 < 2\theta < 82°$ and refined by full matrix least squares to $R = 0.12$ for 5244 unique data ($I > 0$) [$R = 0.079$ for data with $I > 3\sigma(I)$]. The propyl chains of one $[NPr^n_4]$ cation show two-fold disorder, but all atoms of the complex dianion were satisfactorily located and refined. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

does not possess significant antitumour activity, and we note the corresponding complexes with NH_2Me and $NHMe_2$ do not show any solubility enhancement in CH_2Cl_2 with any of the salts which promote it with their *cis* counterparts.

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