Inorganica Chimica Acta, 76 (1983) L157–L158

X-Ray Structure Analysis of the *Cis*- and *Trans*-bis-(*o*-aminophenyldiphenylphosphine)platinum(II)-Cationic Complexes

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Received November 4, 1982

The structures of the neutral *cis*- and *trans*-isomers of $[\mathrm{Pt(NH^{\urcorner})_2}]$, (I) and (II) respectively, containing the deprotonated form of the recently synthesised [1] hybrid ligand *o*-aminophenyldiphenylphosphine ($\mathrm{PNH_2}$) are reported in the preceding paper [2]. We present here a preliminary account of the structures of the *cis*-[III] and *trans*-[IV] isomers of the cationic bis-chelate Pt(II) complexes of the neutral ligand, $[\mathrm{Pt(NH_2)_2}]^{2+}$.

The title cations (III) and (IV) were prepared as the perchlorate and *p*-toluenesulphonate salts, respectively. Crystals of (III) were obtained by treating the yellow *cis*-$[\mathrm{Pt(NH^{\urcorner})_2}]$ in aqueous ethanol with *p*-toluenesulphonic acid until the solution became colourless and they were recrystallised from ethanol. Crystals of (IV) were obtained as a monohydrate when a suspension of *trans*-$[\mathrm{Pt(NH^{\urcorner})_2}]$ (II) in nitromethane was treated with perchloric acid.

Crystals of $[\mathrm{C_{36}H_{32}N_2P_2Pt}][\mathrm{C_6H_7O_3S}]$ (III) were monoclinic, space group $C2/c$, $a = 10.209(2)$, $b = 20.248(4)$, $c = 22.372$ Å, $\beta = 95.53°$, $V = 4603.03$ Å^3, $Z = 4$, $\mu(\text{Mo-K}_\alpha) = 31.06\ \text{cm}^{-1}$. Crystals of $[\mathrm{C_{36}H_{32}N_2P_2Pt}]\cdot 2[\mathrm{ClO_4}]\cdot 2\mathrm{H_2O}$ (IV) were monoclinic, space group $P2_1/c$, $a = 9.467(2)$, $b = 15.267(3)$, $c = 13.031$ Å, $\beta = 101.78°$, $V = 1843.76$ Å^3, $Z = 2$, $\mu(\text{Mo-K}_\alpha) = 39.09\ \text{cm}^{-1}$. The X-ray analyses were carried out using 2380 reflections for (III) and 1812 reflections for (IV) with $I/\sigma(I) \geqslant 3.0$ measured in the θ-range 3–25°. The data collection and method of refinement are as described previously [2]. Anisotropic thermal parameters were assigned to the Pt and P atoms in both structures, to the S atom in (III), and to the N atom and the atoms of the perchlorate counter-ion in (IV). The present R values are 0.0584(III) and 0.0484 (IV).

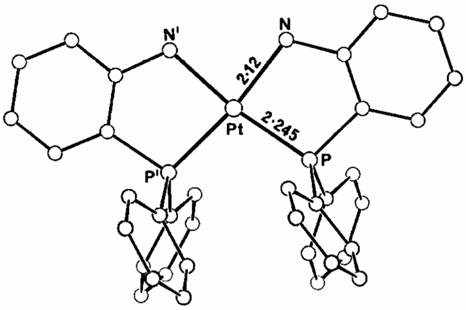

Fig. 1. The structure of the *cis*-isomer of $[\mathrm{Pt(NH_2)_2}]^{2+}$ (III) showing the principal bond lengths (Å). The angles of the coordination sphere are P–Pt–P' 101.3(2), N–Pt–N' 85.9 and P–Pt–N 86.4°.

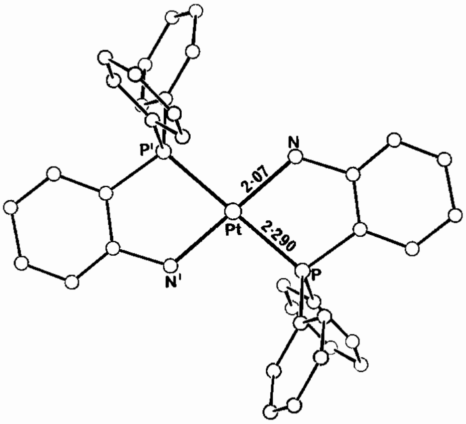

Fig. 2. The structure of the *trans*-isomer of $[\mathrm{Pt(NH_2)}]^{2+}$ (IV) showing the principal bond lengths (Å). The angles of the coordination sphere are P–Pt–N 82.0(4) and P–Pt–N' 98.0(4)°.

In both structures the Pt atoms are on sites of special symmetry; the cations (III) and (IV) have crystallographic C_2 and C_i symmetry respectively. The structures and principal bond lengths are shown in Figs. 1 and 2. The Pt–P bond length in the *trans*-isomer (IV) is 2.290 Å almost identical to that of 2.289 Å in the corresponding neutral *trans*-isomer of $[\mathrm{Pt(NH^{\urcorner})_2}]$ (II) [2]. The Pt–P bond length of 2.245 Å in the *cis*-compound (III) is slightly longer than the mean of 2.240 Å observed in the corresponding neutral *cis*-$[\mathrm{Pt(NH^{\urcorner})_2}]$ compound (I) but this difference is of very low significance (*ca.* 1σ). The Pt–N(amino) bond lengths of 2.12 (III) and 2.07 Å (IV) are significantly longer than the corresponding P–N (amido) bond lengths in the corresponding *cis*- and *trans*-$[\mathrm{Pt(NH^{\urcorner})_2}]$ isomers of 2.02 (I) and 2.04 Å (II).

The conformation of the phenyl rings of the *cis*-phosphine ligands in [III] is similar to that observed

0020-1693/83/0000-0000/$03.00

in the neutral *cis*-[Pt(PN$^-$)$_2$] (I) [2] with the rings of the two halves of the cation in nearly parallel pairs {mean dihedral angle 11.1°}. The P–Pt–P′ angle of 101.3° in (III) is slightly smaller than that in (I) of 104.2°. Even so the only contact of less than 3.4 Å between the *cis*-ligands in (III) is C(22)··· C(32) 3.39 Å.

References

1 M. K. Cooper and J. M. Downes, *Inorg. Chem., 17,* 880 (1978).

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