Inorganica Chimica Acta, 26 (1978) L13–L14

Platinum(II) Complex Containing a Seven Membered Chelate Ring: X-Ray Molecular Structure of Chloro-(dimethylsulphoxide)(1,4-diaminobutane)platinum(II) Chloride

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Received November 12, 1977

Complexes of the type [Pt(N–N)(dmso)Cl]Cl containing chelate rings of increasing size (dmso = dimethylsulphoxide; N–N = chelated 1,2-diaminoethane (en), 1,3-diaminopropane (tn) and 1,4-diaminobutane (bn)) have been synthesized [1] to investigate the chelate effect from a kinetic point of view by measuring the rates of ring opening and closure [2] under the strong *trans* labilising effect of the S-bonded dimethylsulphoxide. Since ring size and flexibility affect markedly the chelation phenomenon we undertook a single-crystal structure analysis of the 1,4-diaminobutane complex [Pt(dmso)(bn)Cl]Cl which contains the rare seven-membered chelate ring.

Crystal Data

The crystals are triclinic with unit-cell dimensions a = 6,747(7), b = 13.46(1), c = 7.511(7) Å, α = 107.7(1), β = 89.7(2), γ = 104.0(1)°, space group $P\bar{1}$ and Z = 2, D_c = 2.28. A total of 2008 independent reflexions were measured ($\theta \leqslant 28$) on a Siemens automatic diffractometer. The structure was solved by Patterson and Fourier methods and full matrix least-squares refinement has reached R = 0.080, with anisotropic temperature factors for Pt, Cl and S atoms only (Table I).

The crystals are built up by $[Pt(dmso)(nb)Cl]^+$ cations and Cl^- anions. Each Cl^- anion is surrounded by four N–H groups of three adjacent cations, with Cl···N distances ranging from 3.25(3) to 3.39(2) Å. The figure shows the structure of the cation in which the unusual 7-membered chelate ring is formed, with Pt coordinated by the two nitrogen atoms of the diamine. The coordination around Pt is completed by Cl and by the S atom of the dmso ligand. The stereochemistry of Pt is the usual square planar with a slightly tetrahedral distortion. One H atom, bonded to C(2), occupies nearly an axial position, 2.85 Å far away from Pt. The opposite axial position is occupied by the other H atom (Pt···H, 2.84 Å) bonded to C(2) of the cation in the unit cell immediately above along the X-axis. Thus the cation is quasi 6-co-ordinate in the solid state.

Coordination bond lengths and angles are given in the Figure. The Pt–Cl distance of 2.307(9) Å is close to the values found in the $[PtCl_3(dmso)]^-$ anion [3] (2.297(5)–2.318(5) Å) and the Pt–S bond length

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TABLE. Atomic Coordinates.

Atom	Atomic co-ordinates			E.s.d.'s		
	X/a	Y/b	Z/c	S(X)	S(Y)	S(Z)
Pt	0.2800	0.2347	0.1704	0.0001	0.0001	0.0002
Cl1	0.3819	0.1088	−0.0711	0.0012	0.0007	0.0013
Cl2	0.5700	0.4204	0.7065	0.0013	0.0007	0.0013
S	0.2621	0.1367	0.3614	0.0011	0.0006	0.0012
O	0.1458	0.1685	0.5274	0.0040	0.0019	0.0038
N1	0.2054	0.3568	0.3803	0.0040	0.0022	0.0043
N2	0.2765	0.3219	0.0127	0.0035	0.0016	0.0025
C1	−0.0162	0.3465	0.3958	0.0044	0.0027	0.0049
C2	−0.1397	0.3123	0.2288	0.0067	0.0048	0.0108
C3	−0.0733	0.3681	0.1058	0.0066	0.0043	0.0074
C4	0.0728	0.3296	−0.0821	0.0056	0.0027	0.0057
C5	0.1607	−0.0066	0.2465	0.0057	0.0026	0.0056
C6	0.5079	0.1346	0.4619	0.0062	0.0028	0.0054
H1C1	−0.0708	0.2894	0.4706			
H2C1	−0.0355	0.4245	0.4764			
H1C2	−0.1459	0.2284	0.1601			
H2C2	−0.2916	0.3208	0.2633			
H1C3	−0.2107	0.3765	0.0451			
H2C3	−0.0152	0.4462	0.1916			
H1C4	−0.0055	0.2525	−0.1792			
H2C4	0.1066	0.3892	−0.1545			

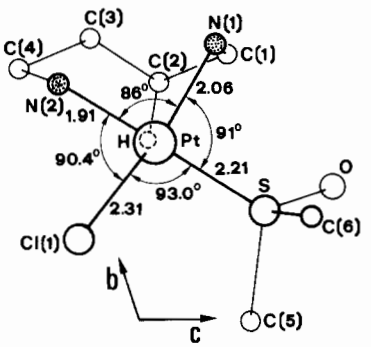

Figure. A view of the $[Pt(dmso)(bn)Cl]^-$ cation together with co-ordination bond lengths and angles. E.s.d.'s are 0.01 Å for Pt–S and Pt–Cl and 0.03–0.04 Å for the other bond lengths; 0.3° for angles involving Pt, S and Cl and 2–3° for the others.

of 2.21(1) Å is similar to the values reported in $[PtCl_3(dmso)]^-$ (2.193 Å) and in *cis*-$[PtCl_2(dmso)_2]$ (2,244 and 2.229 Å) [4]. The other bond lengths and angles are of too low accuracy to be discussed.

The chelate 7-membered ring assumes a twist-chair conformation very similar to that found in bis-(L-ornithinato)palladium(II) [5], with noticeable internal strain. The torsional angles around the bonds in the chain N(1)–$(CH_2)_4$–N(2) are 41, 50, 97, 60 and 56° respectively, the central angle being close to that of 102° found in the Pd compound.

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