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Isolation and Structure Determination of an Unusual Dinuclear Platinum(II) Complex Containing a Bridging N,N-Dimethyl Dithiocarbamate

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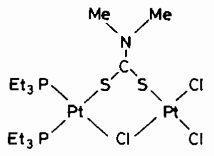
Although a variety of transition metal complexes with dithiocarbamate ligands have been isolated in recent years [1], only a few similar complexes of platinum and palladium are known [2–4]. In almost all these platinum–dithiocarbamate complexes, the dithiocarbamate ligands are coordinated to platinum atom in bidentate fashion through the sulfur atoms. Due to our continuing interest in the studies of mixed ligands complexes of transition metals [5–8], it was thought worthwhile to synthesize some new complexes containing mixed phosphine and dithiocarbamate ligands. In the course of this study, we have been able to isolate an unusual dinuclear platinum complex with a bridging N,N-dimethyldithiocarbamate group. The preparation and the X-ray structure of this novel complex is being presented here.

From the reaction of $[Pt_2Cl_4(PEt_3)_2]$ with sodium N,N-dimethyldithiocarbamate, NaS_2CNMe_2, (eqn. 1) in CH_2Cl_2 at room temperature, bright yellow crystals of the mixed ligand complex, $[Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)]$ (*1*) are isolated in almost quantitative yield by the addition of hexane to the supernatent solution (*Anal.* Found: C, 20.8; H, 4.20; Cl, 12.9; P, 7.35%; Mol. wt., 841, Calcd. for (*1*): C, 21.1; H, 4.22; Cl, 12.5; P, 7.27%; Mol. wt., 853; M.p. 195–8 °C).

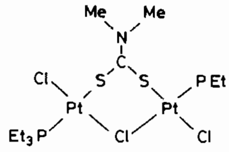
$$Pt_2Cl_4(PEt_3)_2 + NaS_2CNMe_2 \rightarrow Pt_2Cl_3(PEt_3)_2(S_2CNMe_2) + NaCl \qquad (1)$$

Infrared spectrum of the complex shows a strong band at ~1580 cm^{-1} suggesting the presence of considerable double-bond character in the C–N bond of the coordinated dithiocarbamate. ^1H NMR spectrum (300 MHZ spectrum in $CDCl_3$) shows signals due to methyl protons of PEt_3 as two sets of multiplets centered at δ 1.16 ppm (9 H) and δ 1.21 ppm (9 H) in 1:1 ratio. The methylene group protons of PEt_3 are also observed as two sets of multiplets in 1:1 ratio at δ 2.02 ppm (6 H) and δ 1.86 ppm (6 H). This indicates the presence of two non-equivalent PEt_3 groups in the complex. The non-equivalency is probably caused due to the presence of dissimilar (or magnetically non-equivalent) *trans*-groups, *e.g.*, in structure A where both phosphines are coordinated to the same platinum nuclei in an unsymmetrical dinuclear complex or in structure B or C where PEt_3 groups are coordinated to two different platinum nuclei having the dissimilar geometries. Interestingly the methyl protons of N,N-dimethyldithiocarbamate group also appear as two equally intense singlets at δ 3.32 (3 H) and δ 3.57 ppm (3 H). This indicates that both methyl groups are non-equivalent; thus suggesting the existence of non-equivalent sulfur atoms and also the presence of some double-bond characters in the C–N bond. This is in support of the structure in which the two sulfur atoms are coordinated to the non-equivalent platinum nuclei in the dinuclear complex.

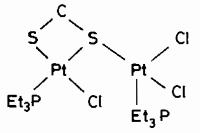
Although ^1H NMR spectrum rules out the possibility of the unsymmetrical and symmetrical structures such as D and E respectively, it certainly does not rule out the other possible structures (A thru C). Furthermore, the possibility of several other structural configurations (geometries) possible for the dimeric complex with a dithiocarbamate bridged between two platinums cannot be neglected.



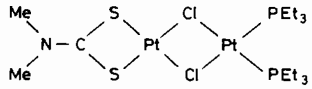
A



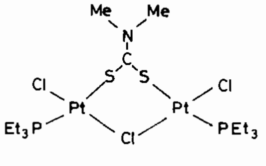
B



C



D



E

In order to assign a correct structure of the complex *1*, an X-ray crystal structure determination has been carried out.

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The complex crystallizes in the orthohombic space group *Pbca* with eight molecules per unit cell; the lattice constants are $a = 27.316(7)$, 'b = 14,279(2), $c = 13.925(3)$ Å. Intensity data were collected on a $P2_1$ four-circle automated diffractometer with $MoK\bar{\alpha}$ radiation. A total of 4827 independant reflections were measured. Intensities were corrected for Lorentz, polarization, and absorption effects. The structure was determined using heavy-atom techniques and refined by full-matrix least-squares procedures. The final R value was 0.078 for 2732 observations with $F \geqslant 30 (F)$ and 226 variables.

A perspective view of the molecule *1* is presented in Fig. 1 where the most relevant atoms are labeled. In the compound both platinum atoms (Pt_1 and Pt_2 in Fig. 1) are four coordinated. Pt_2 is surrounded in an approximately planar fashion by PEt_3 and chlorine (Cl_3) at mutually *trans* positions, a chlorine (Cl_2) and a sulfur (S_1) of the dithiocarbamate group. This sulfur is also coordinated to the second platinum (Pt_1) with PEt_3 at the *trans* position. The other sulfur atom (S_2) of dithiocarbamate is attached to Pt_1 with a chlorine (Cl_1) at the *trans* position. This platinum (Pt_1) has a distorted square planner geometry. The shorter bond length of N_1–C_{13} (1.34 Å) is in agreement of a partial double bond character.

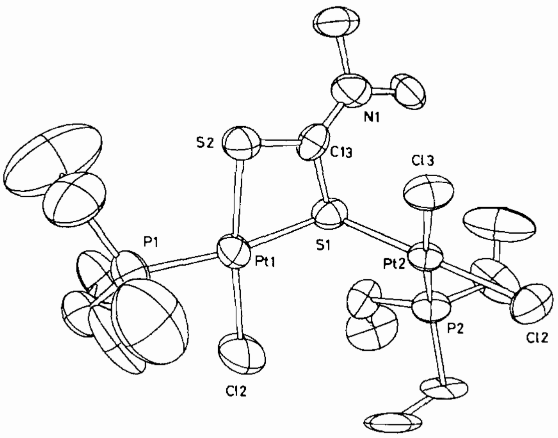

Fig. 1. OERTEP drawing of the complex $[Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)]$. Principal bond lengths (Å) are: Pt_1–P_1 = 2.226(8), Pt_1–Cl_1 = 2.314(8), Pt_1–S_1 = 2.370(7), Pt_1–S_2 = 2.277(6), S_2–C_{13} = 1.658(26), S_1–C_{13} = 1.742(25), Pt_2–S_1 = 2.292(7), Pt_2–P_2 = 2.234(6), Pt_2–Cl_2 = 2.315(7), Pt_2–Cl_3 = 2.369(6), N_1–C_{13} = 1.342(30) and angles (°): P_1–Pt_1–Cl_1 = 89.1(3), P_1–Pt_1–S_1 = 170.7(3), S_1–Pt_1–Cl_1 = 97.8(3), P_1–Pt_1–S_2 = 98.6(3), S_1–Pt_1–S_2 = 78.8(3), S_2–Pt_1–Cl_1 = 172.3(3), Pt_1–S_1–Pt_2 = 115.6(3), Cl_3–Pt_2–Cl_2 = 89.3(2), Cl_2–Pt_2–P_2 = 87.1(3), Cl_3–Pt_2–P_2 = 175.8(3), S_1–Pt_2–P_2 = 92.5(3), S_1–Pt_2–Cl_3 = 91.1(2), N_1–C_{13}–S_1 = 121.8(2.0), N_1–C_{13}–S_2 = 126.0(2.0), S_2–C_{13}–S_1 = 112.2(1.6).

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