

Preliminary communication

Complexes of trimethylplatinum(IV) with dithiocarbamates, xanthates
 and cis-maleonitriledithiolate

B. W. Brown, K. Kite, A. J. Nettle and A. F. Psaila

Department of Chemistry, University of Exeter, Exeter EX4 4QD

(Received July 23rd, 1977)

SUMMARY

The dithiocarbamate complexes $[\text{Me}_3\text{Pt}(\text{S}_2\text{CNR}_2)]_2$, $\text{R}_2 = \text{Me}_2, \text{Et}_2, (\text{CH}_2)_4$, are stereochemically rigid in solution, in contrast to the xanthates $[\text{Me}_3\text{Pt}(\text{S}_2\text{COR})]_2$, $\text{R} = \text{Me}, \text{Et}, ^1\text{Pr}, \text{Bz}$, which are non-rigid above -40°C . Sulphur-bridged dimers are postulated. Both types of complex give monomeric 1:1 pyridine adducts containing the bidentate dithioacid ligand. The xanthate ligands are monodentate in $[\text{Me}_2\text{Pt}(\text{S}_2\text{C-OR})\text{bipy}]$, $\text{R} = \text{Me}, \text{CH}_2\text{CF}_3, \text{C}_6\text{H}_{11}$. The complex $(\text{Ph}_4\text{As})_2\{[\text{Me}_3\text{PtS}_2\text{C}_2(\text{CN})_2]_2\}$ contains a dimeric anion.

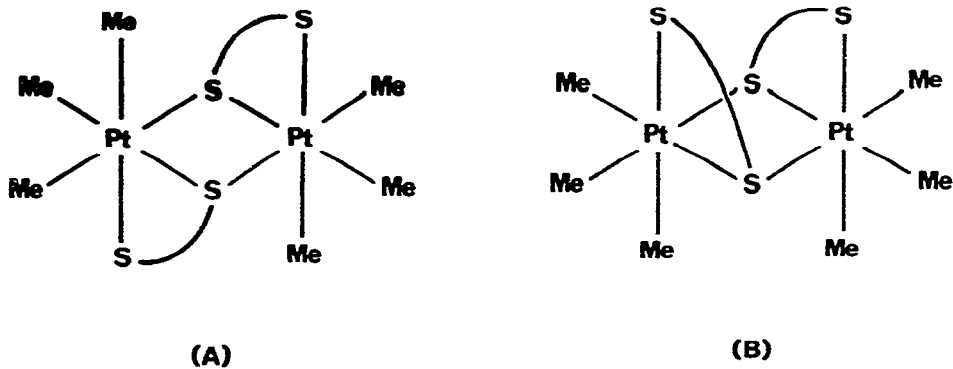
The dimeric β -diketone and β -ketoester complexes of trimethylplatinum(IV) showed a marked difference in stereochemical rigidity in solution [1]. We now report a similar difference between complexes of dithioacid ligands. The dithiocarbamate complexes I; $\text{R}_2 = \text{Me}_2, \text{Et}_2, (\text{CH}_2)_4$, are dimeric in the vapour phase (mass spectrum) and in benzene solution (osmometer, 37°C). The NMR spectra of I in both CDCl_3 and C_6D_6 solutions at 30°C show three methyl-platinum resonances, with $^2\text{J}(\text{}^{195}\text{Pt}-^1\text{H})$ near 76, 70 and 73 Hz from low to high field respectively. A single symmetrically bridged dimer is indicated (Figure 1, A or B) [2], with bridging via the sulphur atoms as in other dimeric dithiocarbamates [3]. The isomers have three non-equivalent methyl groups attached to

each metal atom. For complexes with R = Me and Et, two ligand methyl resonances of equal intensity are seen. As the two NR₂ groups in either dimer are related by a centre of symmetry (A) or a two-fold axis (B), the non-equivalence of the R groups reflects a rigid conformation about the S₂C-N bond.

The xanthate complexes II are low melting, yellow or orange solids. Like I they are dimers in solution (osmometrically in toluene, 37 °C). The NMR spectra of II in CDCl₃ at 30 °C, however, have only broad resonances in the methyl-platinum region, indicating an exchange process among the trans ligands [2]. On cooling the solution, the spectrum sharpens and at -40 °C three resonances of equal intensity are seen. The signal at lowest field has ²J ~ 76 Hz, while the higher field absorptions have almost identical coupling constants in the range 73.0-74.4 Hz. As with I, only one dimer species is present.

Both I and II form monomeric pyridine adducts [Me₃Pt(S₂CNR₂)py] and [Me₃Pt(S₂COR)py]. They have the expected 2:1 pattern of methyl-platinum resonances in solution at 30 °C, with ²J 70.9-72.2 Hz (trans to pyridine), 69.4-71.8 Hz (trans to bidentate dithiocarbamate) and 70.9-72.2 Hz (trans to bidentate xanthate). The ¹H NMR spectra of the 2,2'-bipyridyl complexes [Me₃Pt(S₂COR)bipy], R = Me, CH₂CF₃, C₆H₁₁, at 30 °C in CDCl₃ also show two methyl-platinum resonances, ratio 2:1. They are assignable to methyls trans to bidentate bipyridyl [4] (δ 1.20-1.24; ²J 69.6-70.2 Hz) and to monodentate xanthate (δ 0.28-0.36; ²J 66.4-66.6 Hz) respectively. Attempts to make a bipyridyl adduct of I, R = Me were unsuccessful.

Addition of an aqueous solution of Ph₄AsCl to the deep-red solution formed by mixing (Me₃Pt)₂SO₄ · 4H₂O and Na₂S₂C₂(CN)₂ [5] in aqueous ethanol precipitates an orange-red solid which analyses for (Ph₄As)₂[(Me₃PtS₂C₂(CN)₂]₂. Conductivity measurements in acetone confirm this formulation, and the ¹H NMR spectrum of the complex in this solvent at 30 °C has three methyl-platinum resonances, ratio 1:1:1, with ²J 66.6, 74.0 and 68.2 Hz, consistent with a dimeric anion formed by strong metal-sulphur bridge



bonds. The complex was recovered unchanged after refluxing in pyridine. Two possible structures for the dimeric dithioacid complexes of trimethylplatinum(IV) $[\text{Me}_3\text{Pt}(\text{S}_2\text{CNR}_2)]_2$ (I· (a) $\text{R} = \text{Me}$, (b) $\text{R} = \text{Et}$, (c) $\text{R}_2 = (\text{CH}_2)_4$) and $[\text{Me}_3\text{Pt}(\text{S}_2\text{COR})]_2$ (II, $\text{R} = \text{Me}, \text{Et}, \text{}^i\text{Pr}, \text{Bz}$)

It is notable that these ligands, like the thio- β -diketonates [2] and thiourea [6,7] do not reduce the trimethylplatinum(IV) group.

REFERENCES

1. K. Kite and A. F. Psaila, *J. Organometal. Chem.*, **97** (1975) C33.
2. J. R. Hall and G. A. Swile, *J. Organometal. Chem.*, **47** (1973) 195.
3. D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, (1970) 233
4. D. E. Clegg, J. R. Hall and G. A. Swile, *J. Organometal. Chem.*, **38** (1972) 403.
5. A. Davison and R. H. Holm, *Inorg. Synth.*, **10** (1967) 8
6. V. A. Golovnya and O. M. Ivanova, *Zhur. Neorg. Khim.*, **5** (1958) 1347.
7. K. Kite and A. J. Nettle, Unpublished observations.