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Preliminary communication

NMR EVIDENCE FOR SINGLE-SITE AND SYNCHRONOUS DOUBLE-SITE INVERSION AT PYRAMIDAL SULPHUR ATOMS IN MONO- AND BINUCLEAR COMPLEXES OF TRIMETHYLPLATINUM(IV) HALIDES WITH BIDENTATE THIOETHERS

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Summary

Adducts of the type Me_3PtXL (X = Cl, Br, I; L = $MeSCH_2CH_2SMe$) exhibit pyramidal inversion at individual sulphur atoms, whereas the adducts $(Me_3PtX)_2L'$ (L′ = $MeSCH_2SMe$, X = Cl, Br, I) exhibit both ring inversion, and synchronous inversion about both sulphur atoms.

Reactions of the tetrameric complexes $(Me_3PtX)_4$ with monodentate Lewis bases give successive cleavage of the Pt—X bonds to form three types of adduct [1, 2], the halogen bridged $(Me_3PtXL)_2$, the mononuclear $[Me_3PtXL_2]$, and $[Me_3PtL_3]^+X^-$. In our investigation of the action of bidentate sulphur ligands we find that 2,5-dithiahexane behaves in a manner analogous to ethylenediamine and give the monomer $[Me_3Pt(MeSCH_2CH_2SMe)X]$ (Fig. 1a). In contrast 2,4-dithiapentane gives only the binuclear complexes $[(Me_3PtX)_2MeSCH_2SMe]$, which we believe to have the novel structure illustrated in Fig. 1b.

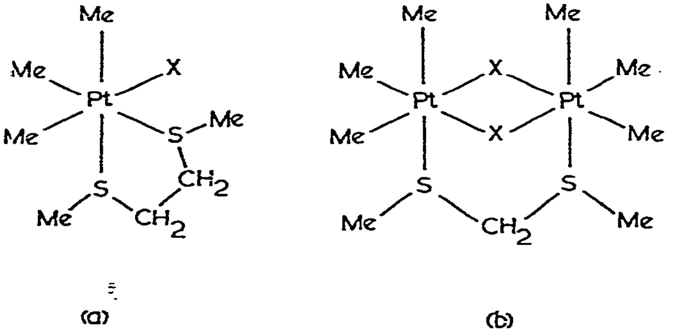

Fig. 1. Me_3PtX complexes of (a) 2,5-dithiahexane and (b) 2,4-dithiapentane (X = Cl, Br, I).

Variable temperature NMR spectra of these mono- and bi-nuclear species can be fully explained in terms of ring and/or sulphur inversion, and it would appear that in the bi-nuclear species there is synchronous inversion at both sulphur atoms. In the mono-nuclear complexes a 5-membered ring pseudorotational vibration [3] cannot account for the observed spectral changes, and is likely to be very fast on the NMR time scale even at low temperatures. Temperature dependent changes in the S—Me proton signals can, however, be fully explained on the basis of independent inversion at either sulphur atom, as illustrated in Fig. 2.

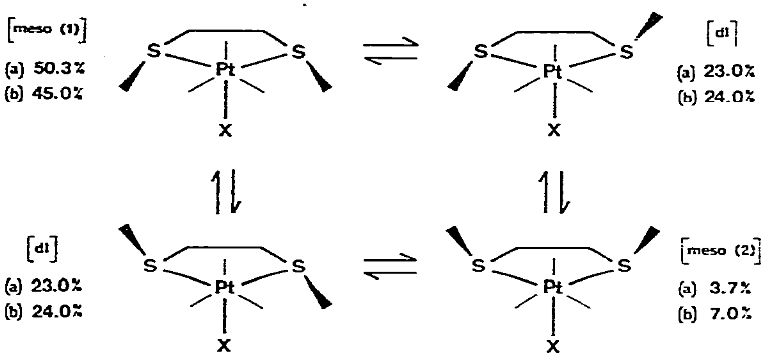

Fig. 2. Isomers of [$Me_3PtXMeSCH_2CH_2SMe$] formed by the independent inversion of either sulphur atom. Populations of isomers, (a) X = Cl, (b) X = Br, essentially temperature independent.

In the binuclear complexes the sulphur atom inversion and the inversion of the —S—CH_2—S— portion of the six-membered S—CH_2—S—Pt—X—Pt ring will cause predictably different types of environment averaging of both the S—Me and Pt—Me protons. The proton NMR spectra of these binuclear complexes at ca. −90°C show both the sulphur atom and the ring inversion processes to be slow on the NMR time scale. Further, only the *dl*-isomer illustrated in Fig. 3 is present.

On warming, both dynamic processes increase in rate, until at ca. −50°C both are fast on the NMR time scale. Although ring inversion is the faster of the two, we observe that both processes contribute to the observed line shapes of the

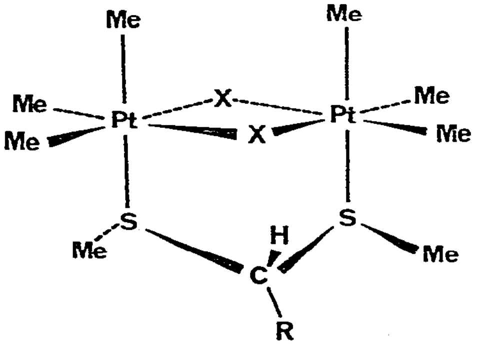

Fig. 3. *dl*-Isomer of complexes [$(Me_3PtX)_2MeSCH(R)SMe$].

S—Me and Pt—Me resonances for an appreciable portion of the temperature range, (−95 to −50°C). Nevertheless, by a detailed analysis [4] of the S—Me and the equatorial Pt—Me absorptions, the activation parameters for the two processes can be separately deduced for the chloro and bromo binuclear complexes (but not for the iodo complex). Initial results show that the activation energies for sulphur inversion in the binuclear complexes $[(Me_3PtX)_2MeSCH_2SMe]$, ($X =$ Cl, Br), are 40.6 ± 3.0 and 48.9 ± 2.4 kJ mol^{-1} respectively, these values being 4 and 11 kJ mol^{-1} greater than the corresponding ring inversion energies.

The two possible *meso* isomers are not detected at any temperature, and thus the sulphur inversion energies are considered to refer to simultaneous inversion at both sulphur atoms such that the *dl*-isomer illustrated in Fig. 3 is converted into its mirror image form. Single-site sulphur inversion would necessarily lead to the formation of the *meso*-isomers, for which we can find no evidence, and further, the band shape changes of the equatorial Pt—Me resonances can only be fully interpreted in terms of a synchronous inversion at both sulphur atoms. Although such a phenomenon has been postulated [5—7], this appears to be the first clear demonstration of its existence, which here doubtless stems from the conformational restrictions placed upon the single site process.

The binuclear compounds $[(Me_3PtX)_2MeSCH(Me)SMe]$ ($X =$ Cl, Br) have been isolated, and here the low temperature NMR spectra are compatible with only a single configurational isomer (Fig. 3, R = Me). The non-formation of the other Me-substituted isomer, presumably due to steric factors, prevents the detection of any ring inversion process. In this case all line shape changes with temperature are explicable solely in terms of synchronous inversion at both sulphur atoms.

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