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On the Nucleophilicity of the Sulphur Bridges in Di-μ-sulphido-tetrakis(triphenylphosphine)-diplatinum(II)

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Triply or quadruply bridging sulphido ligand is a common entity among the various transition metal complexes, especially those of biological and catalytic interest [1–11]. Relatively rare is the doubly bridging sulphido counterpart [12–16]. Such rarity is attributed largely to the nucleophilic nature of a μ_2-bridging sulphur. $Pt_2(\mu\text{-}S)_2(PR_3)_4$ (where $PR_3 = PPh_3$ [17] and PMe_2Ph [13, 18]) is included among the well-cited d^8 metal complexes.

Ugo *et al.* [17] reported the formation of the title complex $Pt_2(\mu\text{-}S)_2(PPh_3)_4$ and its dimethylated derivative from a reaction of the former with excess methyl iodide. Subsequent investigations [19, 20], however, did not substantiate its claim for dialkylation, and the product was formulated as $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_3)(PPh_3)_4]^+$. Similar reactions with CH_2Cl_2 and $CHCl_3$ also yielded the monoalkylated derivatives. This raises the question as to why substitution occurs at only one sulphur atom; this phenomenon cannot be attributed to conformational strain or thermal instability as shown from the existence of many stable complexes with two thiol bridges [21–23].

Chatt and Hart [21], in trying to explain the preferential formation of *cis*-$Pt_2(\mu\text{-}SR)_2Cl_2(PR_3)_2$ over the complex with one thiol and one chlorine bridge, suggested the formation of an 'inorganic aromatic ring' involving d_π–p_π interaction in the Pt_2S_2 core. It is possible to draw a parallel to the title complex: if alkylation of one of the sulphur bridges triggers such interaction, as opposed to the electron density being localised on the bridging atoms, the 'aromaticity' of the Pt_2S_2 core would discourage alkylation at the second sulphur atom.

It was also observed that the complex $Pt_2(\mu\text{-}SR)_2Cl_2(PR_3)_2$ is more stable in the *cis*- than in the *trans*-form [22]. The lower stability of the *trans*-derivative was attributed to the high *trans*-influence of the phosphine ligands, thus causing unbalanced bond strengths in the thiol bridges. A form of d_π–p_π–d_π conjugation along the P–Pt–S–Pt–P chain as shown in Fig. 1a was also proposed to account for the stability of the *cis*-complex.

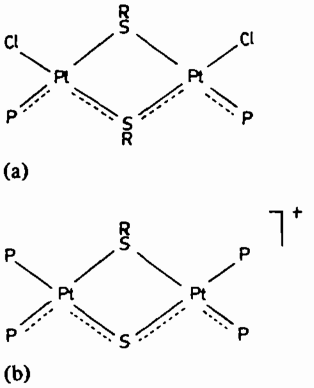

Fig. 1. Possible π-interaction in (a) $Pt_2(\mu\text{-}SR)_2(PR_3)_2(Cl)_2$, and (b) $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PR_3)_4]^+$.

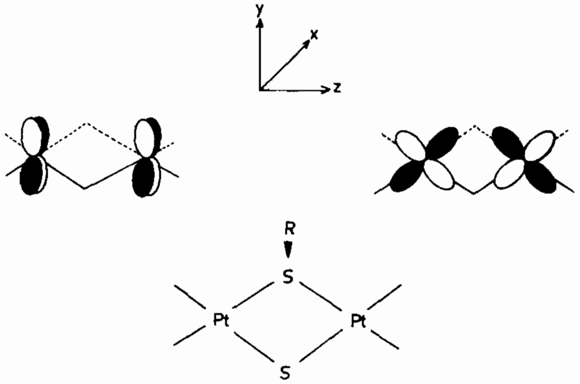

Fig. 2. Out-of-plane metal orbitals in a flat square planar dimer which are symmetrically allowed for π-overlap with bridging ligands.

On alkylation of the title complex, the unsubstituted sulphur atom has relatively higher *trans*-influence than the thiol centre. Applying the above argument, the amount of π-conjugation is expected to be greater on the side with the unsubstituted sulphur (Fig. 1b).

It is also possible to invoke a qualitative molecular orbital model to predict an enhanced π-interaction. Figure 2 shows the two molecular orbitals in which π-overlap is involved for the limiting flat square planar model [24]. This is also applicable to the title complex which has a hinged square planar geometry [18]. In forming the alkylated derivative, the sulphur atom concerned utilises the p-orbitals in the x and y directions, hence decreasing its contribution to the π-MO. The overlap at the other sulphur bridge would therefore increase, resulting in greater delocalisation of electron density and a consequent reduction in nucleophilicity.

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Alkylation at the second sulphur bridge may also be inhibited by steric forces. Crystallographic studies on some thiol bridged complexes show that the alkyl substituents adopt an anti-conformation [20, 22] probably for steric reasons. Similar studies on $Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4$ [18] and $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_3)(PPh_3)_4]PF_6$ [20] demonstrated the hinged square planar geometry for both compounds with the dihedral angle equal to 121° and 138° respectively. For the latter, the alkyl substituent points away from the hinging distortion. It can therefore be inferred that alkylation of the title complex incurs steric hindrance due to the alkyl substituent on one side, and to the closing up of the two coordination planes on the other, thus blocking the attack of a second electrophile.

Finally, it is possible that statistical and entropic considerations contribute towards the observed resistance to dialkylation.

The two sulphur bridges are capable of functioning as donor ligands to a single metal centre, as demonstrated in the isolation of $[LMPt_2(\mu_3\text{-}S)_2(PPh_3)_4]^{2+}$ (where ML = Ni(dppp), Pd(dppe) and Hg(dppe)* [12, 25] and $[L_nMPt_2(\mu_3\text{-}S)_2(PPh_3)_4]^+$ (where ML_n = $Au(PPh_3)$ and $Pd(PPh_3)Cl)$ [26, 27]. This may be possible since the sulphur atoms, being spaced apart at an optimal distance, coordinate simultaneously to the metal ion, in which case the projected π-interaction would not be triggered. The tendency for 4-coordinate Pd^{2+}, Ni^{2+} and Hg^{2+} and 3-coordinate Au^+ provides added stability for these systems.

The mode of coordination of the sulphur atoms in the platinum–silver complex $[Ag_2Pt_4(\mu_3\text{-}S)_4(PPh_3)_8]^{2+}$ (Fig. 3) [26] can be rationalised in terms of the greater electrophilicity and smaller size of the silver ion compared to alkyl halides. Furthermore, each silver bridge adopts a linear 2-coordinate geometry; coordination to one site each of two complexes draws the other two sites together, thus facilitating the coordination of the second silver ion.

Sulphur dioxide reversibly attacks the sulphur sites in the title complex to yield $Pt_2(\mu\text{-}S_2O_2)_2(PPh_3)_4$ [17, 19]. The loose coordination of SO_2 in this adduct probably has no significant electronic effect on the bonding properties of the system; this probably explains why attachment at both sulphur atoms is possible.

It is probable that all the above factors contribute towards the stability of the monoalkylated derivative of the title complex. Before a more vigorous treatment can be presented, the isolation of other d^8 sulphido and thiolato complexes, such as $Ni_2(\mu\text{-}S)_2(PR_3)_4$, $NiPt(\mu\text{-}S)_2(PR_3)_4$ and $Ni_2(\mu\text{-}S)(\mu\text{-}SR)(PR'_3)_4$, remains a synthetic challenge.

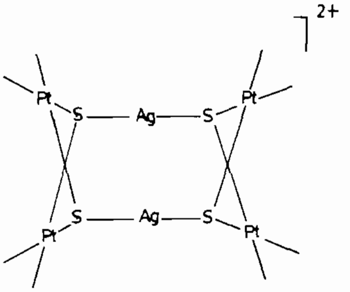

Fig. 3. Molecular skeleton of $[Ag_2Pt_4(\mu_3\text{-}S)_4(PPh_3)_8]^{2+}$.

Acknowledgements

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