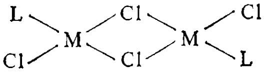
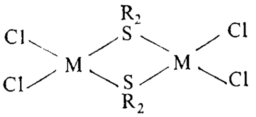
The Dibasic Nature of Dialkyl Sulphides in $(R_2S)_2Pt_2X_4$ (X = Cl or Br): a Distinction between Corresponding Platinum and Palladium Complexes

By P. L. GOGGIN,* R. J. GOODFELLOW, D. L. SALES, J. STOKES, and P. WOODWARD

(*Department of Inorganic Chemistry, The University, Bristol, 8*)

COMPOUNDS $(Me_2S)_2Pt_2Cl_4$ and $(Et_2S)_2Pt_2Cl_4$ have colour and solubility properties[1] markedly different from those expected on comparison with other platinum(II) complexes. We have found that their infrared spectra (500—200 cm.$^{-1}$) differ from those of other platinum and palladium complexes, $L_2M_2Cl_4$,[2] including their palladium analogues, in having no absorptions which can be assigned to the stretching of the bridging Pt–Cl bonds of structure (I). The spectra agree well with the only alternative square-planar structure (II), in which the dialkyl sulphide acts as a dibasic ligand. The band at about 420 cm.$^{-1}$ in these complexes and their bromo-analogues can only be assigned as Pt–S stretching although this is considerably higher than for the related assignment in $(Me_2S)_2$-Pd_2Cl_4 (340 cm.$^{-1}$)[2] or for *cis*-$(Me_2S)_2PtBr_2$ (317 and 305 cm.$^{-1}$).[3] That a ligand should be more strongly bound to a metal when bridging than when terminal is surprising and we felt that further confirmation of the structure was necessary. We have now completed the single-crystal *X*-ray analyses of $(Me_2S)_2Pd_2Br_4$ and $(Et_2S)_2Pt_2Br_4$; (bromides were chosen in preference to chlorides so as to give unequivocal distinction in electron density between halogen and sulphur).


(I)


(II)

Crystal data:

(i) $(Me_2S)_2Pd_2Br_4$: monoclinic, $P2_1/n$, $a = 6·00$, $b = 10·49$, $c = 11·47$ Å, $\beta = 107°35'$, $Z = 2$. $R = 6·7\%$;

(ii) $(Et_2S)_2Pt_2Br_4$: monoclinic, $P2_1/n$, $a = 7·36$, $b = 13·45$, $c = 9·20$ Å, $\beta = 104°6'$, $Z = 2$. $R = 6·2\%$.

In both crystals the molecule is required to possess a centre of symmetry. The structural refinement shows further that both molecules have a planar skeleton based on two bridged square-planar metal atoms, and that whereas $(Me_2S)_2Pd_2Br_4$ is Br-bridged, with dimethyl sulphide ligands in a *trans*-configuration, $(Et_2S)_2Pt_2Br_4$, is indeed symmetrically *S*-bridged with S–C bonds symmetrically related to the plane of the molecule. Important bond distances are:

Pd–Br (terminal) = 2·40 ± 0·004,
Pd–Br (bridging) = 2·44 ± 0·004 (mean),
Pd–S (terminal) = 2·30 ± 0·02,
Pt–Br (terminal) = 2·39 ± 0·006,
Pt–S (bridging) = 2·23 ± 0·01 Å.

It is noteworthy that in $(Me_2S)_2Pd_2Br_4$ the S–C bonds are not symmetrically related to the plane of the molecule; one bond lies close to the plane and the other in a plane nearly perpendicular to it. Since it is generally found that chemically equivalent Pt–X and Pd–X bond lengths are within 0·01 Å of each other, the relative lengths of the Pt–S and Pd–S bonds in these structures implies significantly stronger bonding when the ligand is bridging than when it is terminal, in agreement with the infrared evidence.

A monobasic dialkyl sulphide possesses one lone-pair of electrons which, with platinum and palladium, would be capable of interacting repulsively with non-bonded *d*-electrons of the metal. If this lone-pair were accommodated in a bonding orbital with the metal, as must be the case in these platinum dimers, this repulsion would be eliminated allowing formation of a shorter and stronger bond. In contrast, the number of lone-pair repulsions with non-bonded *d*-electrons would not be reduced by transferring a halide from a terminal to a bridging position since the remaining lone-pairs could interact with interaxial *d*-electrons of *two* metal atoms. The position of the S–C bonds in the palladium compound likewise suggests that repulsion between the lone-pair and the d_{xy}, d_{xz}, and d_{yz} orbitals of the metal is being minimised. It is not obvious why these palladium and platinum complexes adopt different structures, though the explanation may lie in the spatial dissimilarity of the 4*d* and 5*d* orbitals.

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