Mixed Metal Complexes containing a Novel Chelating Sulphur Ligand

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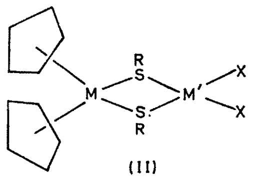
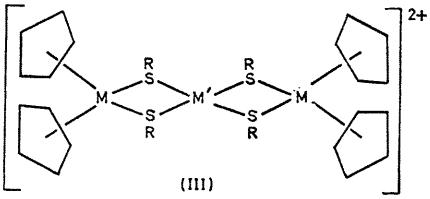
Summary Complexes $(\pi\text{-}C_5H_5)_2M(SR)_2$ are versatile ligands, forming a wide range of mixed metal complexes, some of which contain metal–metal bonds.

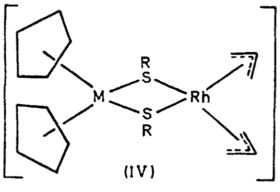
WE have found that the bis-thiolato-complexes $(\pi\text{-}C_5H_5)_2M(SR)_2$[1](I) (where M=Mo or W, and R=Me, Et, Bu^n, Allyl, or Ph) can act as chelating ligands forming crystalline, mixed-metal derivatives.



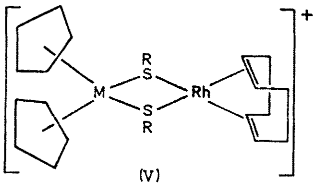
(II)



(III)



(IV)



(V)

Whilst simple dithiol ligands do not form simple neutral derivatives with cobalt and iron dihalides, the complexes (I) react readily with $M'X_2$ in anhydrous ethanol or tetrahydrofuran to give well characterised compounds of the stoicheiometry (II).

Examples of complexes (II) are, where M'=Fe, M=Mo, R=Me or Bu^n and X=Cl; where M' = Co, M=Mo or W, R=Me or Bu^n and X=Cl, Br, or SCN. The electronic spectra of the cobalt complexes (in dichloromethane solutions) indicates an essentially tetrahedral environment for the cobalt atom. The magnetic moment of the complex $(\pi\text{-}C_5H_5)_2Mo(SBu^n)_2CoBr_2$over the range −185—100° shows that the Curie Law is obeyed and gives μ_{293} = 4·35 B.M. which is consistent with tetrahedral symmetry for the metal.

With the nickel sub-group metals two series of complexes are formed. These are binuclear species of the type (II) and the trinuclear species (III) which have been characterised as the Cl^-, Br^-, or the PF_6^- salts. Examples are, where M=Mo or W, R=Me, and M'=Pd or Pt for the dinuclear derivatives, and M'=Ni, Pd, or Pt for the trinuclear derivatives (III).

The reaction of the bis-thiolato-complexes (I) with the dimeric compounds $[RhCl(allyl)_2]_2$ and [RhCl cyclo-octa-1,5-diene]$_2$ gives the compounds (IV) and (V) respectively, which were characterised as the hexafluorophosphate salts and where M=Mo or W and R=Me.

Treatment of the complexes (I; R = Ph) with the Group VI hexacarbonyls gives crystalline compounds of stoicheiometry $(\pi\text{-}C_5H_5)_2M(SR)_2M'(CO)_3$ (VI) where M=Mo or W and M'=Cr, Mo, or W. In the case of the complexes (VI) it appears that the complex (I) acts as a 6-electron ligand to the $M'(CO)_3$, presumably making use of the metal lone pair which is known to be available in the hydrides $(\pi\text{-}C_5H_5)_2MH_2$ (M=Mo or W)[2]

We thank N.A.T.O. for a research grant (to A.R.D.).

(*Received, July 3rd,* 1969; *Com.* 966.)

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[1] M. L. H. Green and W. E. Lindsell, *J. Chem. Soc.* (*A*), **1967**, 1455; and M. L. H. Green, M. Harriss and W. E. Lindsell, *ibid.*, **1969**, 1453.

[2] M. L. H. Green, J. H. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, **1961**, 4854.