Tris-maleonitrile-dithiolate Metal Complexes

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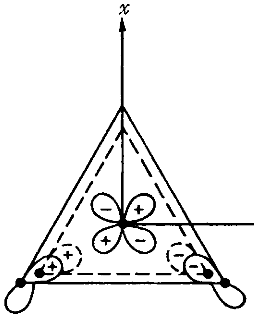
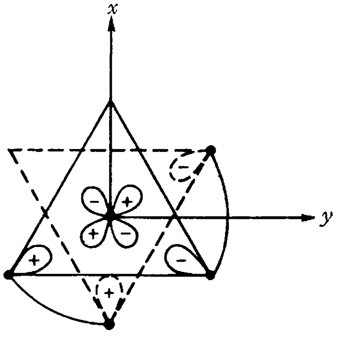
IONS of the first-row transition-metal series may give either bis- or tris-substituted maleonitrile-dithiolate (MNT) complexes[1,2] even in the presence of an excess of ligand. The bis-substituted compounds appear to predominate with the elements Fe, Co,[3] Ni, and Cu whereas tris-complexes are known for V and Cr. In this communication we report the preparation and possible structures of new tris-complexes of manganese, iron, molybdenum, and tungsten.

A green crystalline complex, $[Ph_3PMe]_2[Mn(MNT)_3]$, is obtained by the reaction of manganous salts with Na_2MNT in ethanol, followed by precipitation on addition of $[Ph_3PMe]I$. The compound is a 2 : 1 electrolyte in nitromethane and is paramagnetic, $\mu_{eff} = 4{\cdot}97 \pm 0{\cdot}05$ B.M. A re-investigation of the Fe–MNT system in aqueous acetone (Fe^{3+}: MNT^{2-} mole ratios 1 : 2) afforded first, with $[Ph_3PMe]Br$, the known complex,[4] $[Ph_3PMe][Fe(MNT)_2]$, which is deep red, but if an acetone solution containing the reactants and the cation is warmed in air for a short while and water then added to cause crystallisation, a dark green crystalline complex, $[Ph_3PMe]_2[Fe(MNT)_3]$, is obtained. This new compound, also isolated as the Ph_4P^+ salt, is a 2 : 1 electrolyte in nitromethane and is paramagnetic, $\mu_{eff} = 2{\cdot}70 \pm 0{\cdot}1$ B.M. (measured using the Ph_4P^+ complex). Once isolated, the two compounds do not appear to be interconvertible.



D_{3h}



D_3

FIGURE

One component of the doubly degenerate interaction between ligand σ_+ combinations and metal d_{xy}, $d_{x^2-y^2}$ orbitals for D_{3h} and D_3 symmetry.

$MoCl_5$ and WCl_6 react with an excess of Na_2MNT in tetrahydrofuran to give complex ions $[Mo(MNT)_3]^{2-}$ (green) and $[W(MNT)_3]^{2-}$ (magenta) respectively. Isolated as the Ph_4P^+ salts they are both diamagnetic and 2 : 1 electrolytes in nitromethane and acetone. No evidence was found for bis-complexes in Group VI or VII and it seems likely that coexistence of bis- and tris-substituted species occurs in the cobalt and iron groups. Comparison of the *X*-ray powder patterns of the first-row complexes, $[M(MNT)_3]^{2-}$, where M = V, Mn, and Fe, with Ph_4P^+ as cation, indicates that these compounds are isomorphous and probably isostructural.

The complexes can be described as in the formal oxidation state +4 but both the magnetic moment of the manganese compound, which is field-independent, and the methods by which the complexes were synthesised (Mn and Fe by "oxidation" and Mo and W by "reduction") make it inadvisable to place any literal interpretation on this formalism. This difficulty is, of course, also apparent in other related dithiolato-systems, *e.g.*, $V(S_2C_2Ph_2)_3$ in which the vanadium is in the formal +6 oxidation state.

The complex $Re(S_2C_2Ph_2)_3$ has the eclipsed (D_{3h}) rather than the staggered (D_3) configuration.[5] The eclipsed configuration is not imposed by crystal forces but is retained in solution and, indeed may be adopted by many tris-dithiolate complexes.[6] In order to examine the nature of the bonding in these complexes we have evaluated the corresponding overlap integrals in the two geometries using the expressions for group overlap integrals given by one of us elsewhere.[7] The combination of sulphur orbitals on any one ligand which is involved in only σ-type interaction with the metal orbitals, and which is symmetric with respect to a twofold rotation, is denoted σ_+; σ_-, π_+, and π_- are defined in an analogous way. These orbitals are used as a basis set for either point group. In the Table we give overlap integrals for interactions which are common to both geometries together with those additional overlaps which occur for the D_3 configuration alone.

Only the overlap integral between E' combinations of σ_+ orbitals with d_{xy} and $d_{x^2-y^2}$ orbitals on the metal is greater for the D_{3h} rather than the D_3 configuration. There will be little difference between the zeroth-order energies of the interacting orbitals in the two geometries, so we conclude that the occurence of the D_{3h} geometry indicates that the σ_+ (E') interaction is the most important bonding interaction. The relative orientation of the σ_+, d_{xy}, and $d_{x^2-y^2}$ orbitals for the two geometries are shown in the Figure.

TABLE

Overlap integrals of D_{3h} *and* D_3 *symmetries*

(*a*) *Common interactions*

Ligand orbital type	D_{3h} ($\theta = 49°$)		D_3 ($\theta = 60{\cdot}7°$)	
	Symmetry	Overlap	Symmetry	Overlap
σ_+	A'_1 (z^2)	$0{\cdot}357S_\sigma$	A_1 (z^2)	$0{\cdot}345S_\sigma$
	E' (xy, x^2-y^2)	$0{\cdot}854S_\sigma$	E (xy,$x^2 - y^2$)	$0{\cdot}570S_\sigma$
σ_-	E'' (xz,yz)	$0{\cdot}858S_\sigma$	E (xz,yz)	$0{\cdot}946S_\sigma$
π_-	E' (xy,x^2-y^2)	$0{\cdot}495S_\pi$	E (xy,x^2-y^2)	$0{\cdot}977S_\pi$
π_+	E'' (xz, yz)	$0{\cdot}656S_\pi$	E (xz,yz)	$0{\cdot}819S_\pi$

(*b*) *Interactions which occur in* D_3 *only*

Ligand orbital type	Symmetry	Overlap
σ_+	E (xz,yz)	$0{\cdot}640S_\sigma$
σ_-	E (xy,x^2-y^2)	$0{\cdot}988S_\sigma$
π_-	E (xz,yz)	$0{\cdot}870S_\pi$
π_+	A_1(z^2)	$1{\cdot}381S_\pi$
	E (xy,x^2-y^2)	$0{\cdot}564S_\pi$

The data in this table is obtained assuming that the sulphur–sulphur separation in a ligand molecule is the same in the two geometries. Similarly, the metal–sulphur bond distance is taken as constant. θ is the angle between the threefold rotation axis and a metal–sulphur bond axis.

All π-bonding interactions favour the D_3 configuration; the extent to which any interaction contributes to molecular stability depends upon the zeroth-order energy separation of the interacting orbitals as well as on their overlap integral. Whilst the overlap data in this communication is applicable to other tris-dithiolate complexes, it should be noted that the zeroth-order π-orbital energies of a $R_2C_2S_2$ ligand, in particular, will depend on the nature of R. However, it has been shown[6] that toluene-3,4-dithiolato-complexes of Re, Mo, and W bear a marked similarity to $Re(S_2C_2Ph_2)_3$ and it has been suggested[3,6] that the dissimilarity of the electronic spectra of $[Co(MNT)_3]^3$ to those of typical octahedral Co^{3+} systems may be explained by the assumption of a trigonal prismatic structure.

That trigonal prismatic arrangements among 2nd- and 3rd-row transition-metal sulphur compounds are not unique to dithiolato-complexes has been pointed out,[5] MoS_2 and WS_2 being the best known examples. It is significant that NiAs also has a trigonal prismatic structure[8] and that the sulphides MS, (M = Ni, Co, Fe, Cr, V, and Ti) are similar; MnS has a staggered arrangement of sulphur atoms.

Detailed magnetic and single-crystal *X*-ray studies are now in progress.

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[1] $[S_2C_2(CN)_2]^{2-}$; *cis*-1,2-Dicyanoethylene-1,2-dithiolate; (MNT^{2-}).

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[3] $[Co(MNT)_3]^{3-}$ reported by C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray. *J. Amer. Chem. Soc.*, 1964, **86**, 2958, and confirmed by the present authors.

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[6] E. I. Steifel and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, **87**, 4012.

[7] S. F. A. Kettle, *Inorg. Chem.*, in the press.

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