Electronic Ground States of the Trigonal-prismatic Rhenium Complexes, Tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium, and Tris(toluene-3,4-dithiolato)rhenium

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The electron paramagnetic resonance spectra of the trigonal prismatic complexes, $[Re(S_2C_2Ph_2)_3]$ and $[Re(tdt)_3]$ (tdt = toluene-3,4-dithiolate), are characteristic of sulphur-containing organic radicals and they show that the unpaired electron in these compounds is in a non-bonding molecular orbital derived from the ligand π orbitals. E.p.r. properties, visible-u.v. absorption spectra, voltammetric properties, the magnetic properties of ions derived from $[Re(S_2C_2R_2)_3]$, and the unusually high electrical conductivities exhibited by the solids are all consistent with an electronic ground state configuration $(3a_1')^2(4e')^4(2a_2')^1$ for these complexes.

CRYSTALLOGRAPHIC analysis[1,2] shows that in tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium, $[Re(S_2C_2Ph_2)_3]$, the central rhenium atom is surrounded (Figure 1) by an almost perfect trigonal prism of six sulphur atoms. The co-ordination geometry of the complex is D_{3h} and the overall molecular symmetry belongs very nearly to the point group C_{3h}. The phenyl rings are twisted out of the planes of the chelate rings and do not appear to conjugate with the rest of the structure.

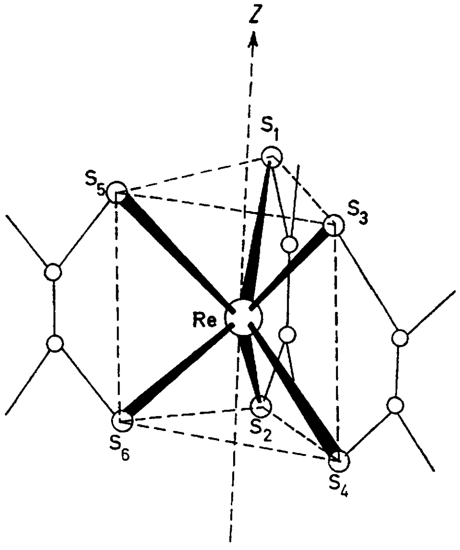

FIGURE 1 $[Re(S_2C_2Ph_2)_3]$

Molecular orbitals for this complex can be constructed from a basis obtained from the 5*d*, 6*s*, and 6*p* rhenium orbitals and 24 ligand orbitals. These ligand orbitals fall into the following three categories. (i) Six σ-orbitals are derived from the sulphur sp^2 hybrids which point in towards the central rhenium atom. (ii) Six π_h-orbitals are derived from the sulphur sp^2 hybrids oriented at 120° to the σ-orbitals. (iii) Twelve π_v-orbitals are derived from the three sets of four ligand π-orbitals which lie at right angles to the planes of each of the three chelate rings. These are delocalised over the S–C–C–S frameworks and are designated in order of increasing energy as $1\pi_v$, $2\pi_v$, $3\pi_v$, and $4\pi_v$, respectively. The ligand $3\pi_v$ and the 5*d* orbitals of rhenium have comparable energies. The other π_v energies are quite different and interactions between them and the 5*d* orbitals are ignored.

In the D_{3h} group these 33 basis orbitals fall into the symmetry classes listed in references 3 and 6. Standard Hückel calculations lead to the energy levels and molecular orbitals available to the complex, and the electronic configuration for its ground state can be obtained by feeding 43 electrons into these levels. Two groups of workers have, separately, carried out such calculations and have reached rather different conclusions regarding the location of the unpaired electron in the rhenium ' trisdithiolates.'

Schrauzer and Mayweg have derived[3,4] the partial energy-level diagram shown in Figure 2a and they conclude that the electronic configuration for the ground states of the neutral complexes $[M(S_2C_2R_2)_3]$ (M = Cr, Mo, or W) is $(3a_1')^2(4e')^4$. In these, the $4e'$ molecular orbital is formed from a linear combination of the lowest antibonding (E') ligand π-orbital (41%), the sulphur sp^2 (17%), and the metal *d* and *p* orbitals of E' symmetry (25 and 17% respectively). The next lowest unoccupied molecular orbitals are the $5e'$ and $2a_2'$ orbitals. The $5e'$ orbitals are ' composed similarly as $4e'$, but over a relatively broad range of metal input Coulomb terms always have somewhat greater metal character than $4e'$.' $2a_2'$ Is a pure ligand π-molecular orbital, and the relative energies of the $5e'$ and $2a_2'$ orbitals depend critically on the input parameters employed in the Hückel calculation. Paramagnetic resonance measurements on the monoanions $[M(S_2C_2R_2)_3]^-$ (M = Cr, Mo, or W) indicate significant metal character and are consistent with the ground-state configuration $(3a_1')^2(4e')^4(5e')^1$, and, furthermore, they definitely rule out the configuration $(3a_1')^2(4e')^4(2a_2')^1$ in these ions.

Stiefel, Eisenberg, Rosenberg, and Gray,[5,6] independently and almost simultaneously, carried out similar calculations on $[Re(S_2C_2Ph_2)_3]$. Their ordering of the molecular orbitals differs from that of Schrauzer and Mayweg and they conclude that the ground state electronic configuration is $(4e')^4(2a_2')^2(3a')^1$; part of their energy-level diagram is shown in Figure 2b.

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[1] R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, 1965, **87**, 3776.

[2] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 1966, **5**, 411.

[3] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, 1966, **88**, 3235.

[4] E. J. Rosa and G. N. Schrauzer, *J. Phys. Chem.*, 1969, **73**, 3132.

[5] H. B. Gray, *Trans. N.Y. Acad. Sci.*, 1966 [2], **28**, 898.

[6] E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **88**, 2956.

Their ($3a_1'$) orbital is largely metal $5d_{z^2}$ in character. Their ($4e'$) orbital contains considerable $5d$ and $3\pi_v$ character, and it is thoroughly delocalised over the d_{xy}, $d_{x^2-y^2}$ and $3\pi_v$ basis orbitals. ($2a_2'$) Is a non-bonding linear combination of the ligand $3\pi_v$ orbitals.

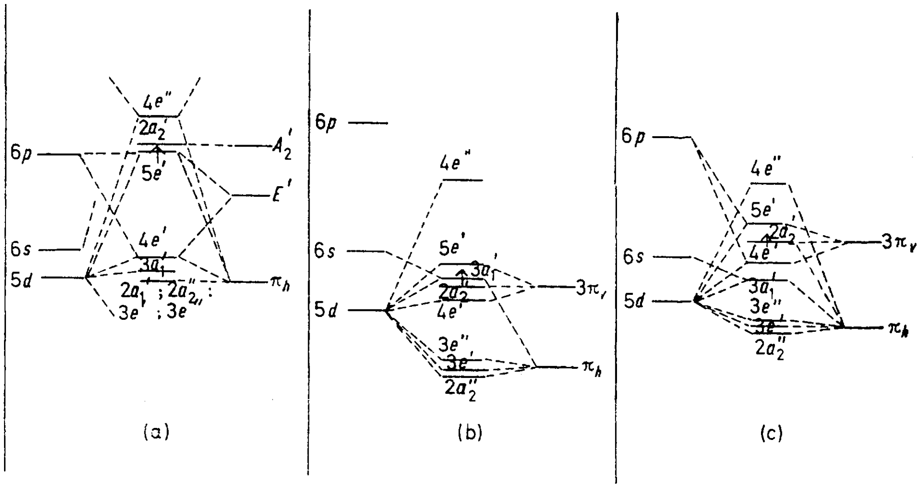

FIGURE 2 Energy level diagrams

Spin Hamiltonian parameters for [ReOCl$_4$], [Re(S$_2$C$_2$Ph$_2$)$_3$], and [Re(tdt)$_3$] at 77 K; tdt = toluene-3,4-dithiolate. All hyperfine tensor components are in units of cm^{-1}

Compound	Solvent	g_{11}	g_{22}	g_{33}	T_{11}	T_{22}	T_{33}	Q'
[ReOCl$_4$]	CCl$_4$	1·974	1·708	1·708	−0·0636	−0·0323	−0·0323	±0·0020
[Re(S$_2$C$_2$Ph$_2$)$_3$]	CHCl$_3$	2·0376	2·0182	1·9963	−0·0001	+0·0003	−0·0002	
[Re(tdt)$_3$]	CHCl$_3$	2·048	2·0132	1·9892	−0·0001	+0·0003	−0·0002	

We believe that the electron paramagnetic resonance spectra of [Re(S$_2$C$_2$Ph$_2$)$_3$] and [Re(tdt)$_3$] (tdt = toluene-3,4-dithiolate) are not consistent with either of the ground-state configurations $(3a_1')^2(4e)^4(5e')^1$ or $(4e')^4(2a_2')^2(3a_1')^1$ proposed by these two groups of workers, but are consistent with the configuration $(3a_1')^2(4e')^4(2a_2')^1$ rejected by the first group.

Electron paramagnetic resonance spectra of [ReOCl$_4$], of [Re(S$_2$C$_2$Ph$_2$)$_3$], and of [Re(tdt)$_3$] are shown in Figure 3, and spin-Hamiltonian parameters defined by

$$\mathscr{H} = \beta H.g.S + S.T.I + Q_{zz}'[I_z^2 - \tfrac{1}{3}I(I+1)]$$

are listed in the Table. Spectra calculated from these parameters are shown in Figure 3. In [ReOCl$_4$], the unpaired electron is in a molecular orbital which is a linear combination of the $5d_{xy}$ orbital of rhenium (66%) and a group orbital (33%) derived from chloride ion $3p_x$ and $3p_y$ orbitals.[7] Strong spin–orbit coupling in ReOCl$_4$ causes the principal components of the g-tensor to differ very markedly from 2·002 and hyperfine interactions in this compound are very large. The spectra of the tris(dithiolato)rhenium complexes are quite different. The small g-tensor anisotropy is very characteristic of sulphur-containing organic radicals[8] and the vanishingly small rhenium nuclear hyperfine coupling, almost certainly a direct dipolar coupling, sets an upper limit of the order of 0·1% to the rhenium contribution to the molecular orbital containing the unpaired electron in these 'dithiolates.' The e.p.r. spectra show that the unpaired electron in the rhenium complexes is in the non-bonding $2a_2'$ molecular orbital derived from the ligand $3\pi_v$ orbitals.

The apparently conflicting two sets of molecular orbital calculations and these e.p.r. deductions can be made self-consistent by averaging the Coulomb energies used by the two groups of workers[3,6] for the corresponding basis orbitals. This produces the correlation

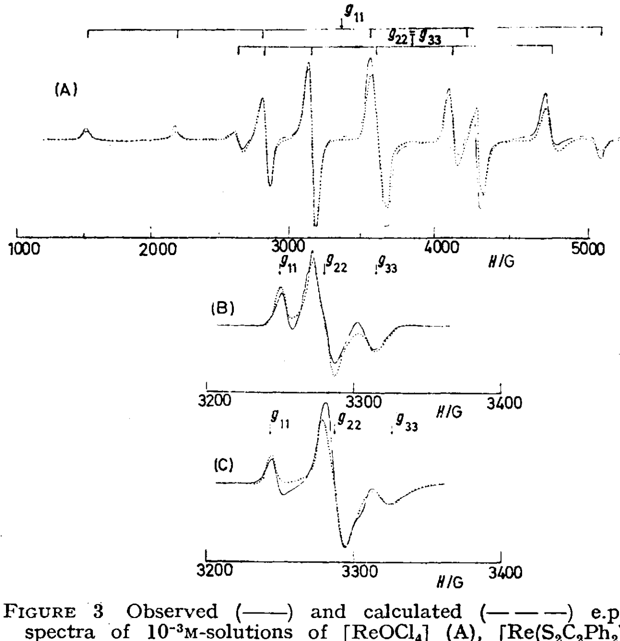

FIGURE 3 Observed (——) and calculated (— — —) e.p.r. spectra of 10^{-3}M-solutions of [ReOCl$_4$] (A), [Re(S$_2$C$_2$Ph$_2$)$_3$] (B), and [Re(tdt)$_3$] (C) at 77 K

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[7] A. H. Al-Mowali and A. L. Porte, *J.C.S. Dalton*, 1975, 50.

[8] P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen and Co. Ltd., London, 1967, p. 349 and references therein.

diagram shown in Figure 2c and leads to a ground state electronic configuration $(3a_1')^2(4e')^4(2a_2')^1$ for $[Re(S_2C_2R_2)_3]$ complexes. This configuration is not inconsistent with the visible–u.v. absorption spectra[6] or with the voltammetric properties[6] of the rhenium trisdithiolates, and it accounts for the magnetic properties[9] of the species $[Re(S_2C_2R_2)_3]^0$, $[Re(S_2C_2R_2)_3]^{-1}$, and $[Re(S_2C_2R_2)_3]^{-2}$. Furthermore, in this configuration the most loosely bound electron is placed on the outside of these complexes, *i.e.* in that region where it can most readily exchange and take part in redox reactions with neighbouring molecules. The interesting discovery[4] that the specific resistances of the solid complexes $[Re(S_2C_2R_2)_3]$ fall in the range $10^3 < \rho < 10^8$ Ω cm whereas the corresponding properties of the molybdenum and tungsten analogues fall in the range $10^{12} < \rho < 10^{15}$ Ω cm, and that the specific resistances of $[Re(S_2C_2H_2)_3]$, $[Re(S_2C_2Me_2)_3]$, and $[Re(S_2C_2Ph_2)_3]$ are 10^3, 4×10^5, and 6×10^7 Ω cm, respectively, then become natural consequences of this configuration.

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[9] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 143.