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The Electronic Structure of a Model Molybdenum(V) Complex with Ligands of the Type RCS_2^-

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A theoretical study of a model molybdenum(V) complex with RCS_2^- ligands, by the all valence-electron SCMO method is presented. In the models used here, one molybdenum atom is complexed octahedrally to two HCS_2^- groups, one terminal oxygen, and one bridging oxygen. The second molybdenum atom is complexed to the bridging oxygen, a terminal oxygen, two hydroxyl groups, and two water molecules. It is found that there is a strong Mo–Mo π bond, and this may account for the diamagnetic properties of molybdenum(V) complexes with dithiocarbamates and dithiocarbonates. The calculated electronic transitions are in good agreement with the experimental electronic spectra for complexes with the above ligands.

Introduction

Molybdenum(V) forms a number of complexes with ligands containing the bidentate group RCS_2^-. These include dithiocarbamates and dithiocarbonates.[1] The structure of the dithiocarbonate complex $M_2O_3(S_2COEt)_4$ has been determined,[2] and has been shown to be a dimer with a linear Mo–O–Mo bridge, a terminal oxygen, and two ligands attached to each molybdenum. The structure of an analogous phosphorothiolothionate complex, $M_2O_3[S_2P(OEt)_2]_4$, has also been determined,[3] and turns out to be similar to the dithiocarbonate complex, the difference being that the terminal oxygens in the latter are mutually *cis* and in the former, mutually *trans*. The dithiocarbamate complexes are considered from infrared and ultraviolet spectroscopic evidence to have similar structures to the dithiocarbonate complexes.[1] The three complexes are all diamagnetic. Thus, in continuing the theoretical study of molybdenum complexes,[4,5] we now examine systems involving the RCS_2^- group. Unfortunately the known complex contains rather too many atoms for full calculation of ground and excited states with configuration interaction, hence we considered the model system shown in Fig. 1, the bond lengths and angles of the sulphur-containing moiety being taken from the dithiocarbonate structure[2] whilst those involving MoO were taken as normal molybdenum–oxygen bond lengths. The site symmetry around each Mo atom is essentially octahedral.

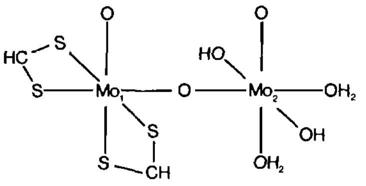

Figure 1. Model system.

The dithiocarbamate ligand itself exhibits several absorption peaks in the region 29,000–40,000 cm^{-1}, and these peaks suffer little change in wavelength when the ligand is complexed. A previous calculation,[6] using singly excited configurations, has suggested that the two peaks at about 33,000 and 39,000 cm^{-1} stem from $\pi \rightarrow \pi^*$ transitions and the one at 29,000 cm^{-1} from an $n \rightarrow \pi^*$ excitation. The electronic spectrum of the molybdenum(V) dithiocarbamate complex shows peaks in this region as well as two below it. Thus, it is of clear interest to ascertain whether this spectrum is understandable in terms of separate transitions located either on the ligand or on the molybdenum.

When metal ions are complexed to an optically active ligand, they become associated with the symmetry of the ligand and Cotton Effects related to the electronic transitions of the complex ion as a whole are observed. Cotton Effects associated with transitions located mainly on the metal are generally weak, unless the asymmetric atom is complexed directly to the metal or involved with the metal in a chelate ring system. Hence, a ligand of particular interest is the optically active dithiocarbamate (+)-*N*-1-phenylethyldithiocarbamate. Here the asymmetric atom cannot be categorised in either of these two ways and so the more intense Cotton Effects are likely to be associated with electronic transitions located mainly on the ligand. Measurements were therefore carried out using complexes of this ligand.

The present work sets out to interpret calculations of both the ground and lower excited states of the model system shown in Fig. 1 and to compare the results with those obtained experimentally for molybdenum(V) complexes of ligands of the type RCS_2^-.

Calculational Methods

The methods used were similar to those which have been previously described.[4]

Results and Discussion

Orbital Energy Levels and Charge Distribution

In Table I are listed the energies of the five filled molecular orbitals of highest energy and the five virtual orbitals of lowest energy for the molecule. Also specified, where of interest, are the main contributing atomic orbitals. Strictly speaking, because of the lack of symmetry of the system studied, every molecular orbital incorporates contributions from all the atomic orbitals of the basis set. However, some molecular orbitals are mainly localised on one or only a few atoms. In fact, these ten orbitals are located mainly on the molybdenum atoms and the surrounding CS_2 groups. It is of particular interest that the highest filled molecular orbital is mainly associated with molybdenum orbitals. This is consistent with the diamagnetic character of both the dithiocarbamate and dithiocarbonate complexes and represents the 'pairing-up' of the odd electrons in a metal–metal bond.

In Table II are listed the orbital occupancies of some of the constituent atoms. For a free Mo^V ion the formal orbital occupancy is $(5s)^0(5p)^0(4d)^1$, whilst that calculated for Mo_1 in the complex is $(5s)^{0.56}(5p)^{0.16}(5d)^{2.41}$. This indicates that there is substantial orbital mixing in the ligand–molybdenum bonding. The d-orbital occupancy of the sulphur atoms is surprisingly low.

The bond orders and atomic charges of the sulphur-containing half of the molecule are shown in Figure 2. The bond orders are so defined that they give a measure of the covalent character of the bond.[7] Thus, the bond order between the molybdenum and the terminal oxygen is almost double that to the bridging oxygens, and shows that the former approximates to a 'double bond'. The Mo–Mo bond (overall order 1.06) superimposed on the Mo–O–Mo bridge bonds helps to account for the stability of molybdenum(V) complexes such as these with linear oxygen bridges. (The comparable molybdenum(VI) linear oxygen bridge has a bond order contribution from the Mo–Mo bond of only 0.10[5]). The high charge separation on the Mo–O–Mo bridge suggests that, in addition, there will be a strong ionic contribution to the overall stability of the bridge system.

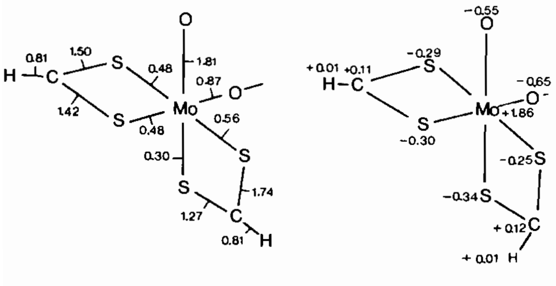

Figure 2. Bond orders and atomic charges.

TABLE I. Energies and character of highest bonding and lowest virtual orbitals, ψ_n.

n	E_n (eV)	
1	–2.61	p and d on molybdenums
2	–6.37	CS_2 groups
3	–6.65	p on sulphurs
4	–7.02	p on sulphurs
5	–7.16	p on sulphurs
–1	2.58	d on molybdenums (mainly antibonding)
–2	3.05	diffuse – mainly on CS_2 groups
–3	3.35	diffuse
–4	3.68	s, p, and d on molybdenums
–5	3.97	CS_2 groups (mainly antibonding)

TABLE II. Orbital Occupancies.

	ns	np	nd
Mo	0.56	1.16	2.41
O (bridge)	1.66	4.99	–
O (terminal)	1.75	4.81	–
S_1	1.51	4.44	0.32
S_2	1.54	4.45	0.30
S_3	1.56	4.49	0.28
S_4	1.49	4.40	0.34

Structural evidence[8] indicates that, in molybdenum(V) complexes, the Mo–S bond length depends on the nature of the atom *trans* to the sulphur. The order is Mo–S (*trans* to O terminal) ≫ Mo–S (*trans* to O bridge) > Mo–S (*trans* to S). This order of bond lengths is reflected in the calculated bond orders, to the extent that the Mo–S bond opposite the terminal oxygen is the longest bond and has the lowest bond order. The bond from molybdenum to the other sulphur of the same chelated CS_2 group shows the highest bond order and implies, firstly, that, where there is a significantly longer Mo–S bond, there is a correspondingly lower bond order, and, secondly, this appears to cause the donor properties of the chelate CS_2 group to become more concentrated on its other sulphur atom.

TABLE III. Calculated excited states and experimental spectra.

Main contributing$_m$ configurations ψ_n n m	Oscillator strength $\times 10^3$	Energy cm^{-1}	U.V. Spectra[a]			Cotton Effects
			A	B	C	D
1→−1	0.0	4,030				
1→−4 > 1→−3	0.0	10,300				
1→−3 > 1→−4 > 1→−5	5.7	16,800	15,050	16,100	17,900	
1→−2 > 1→−5	165.5	21,800	20,100	19,450	19,700	−21,000
1→−2 > 1→−5 > 1→−4	1000.8	25,400	27,100	26,300	29,400	−28,500
4→−5 > 2→−5 > 2→−1	40.0	32,890	35,000	33,300	31,700	+33,500
2→−1 > 2→−5 > 4→−5 > 2→−3	7.0	36,100				
2→−2	96.0	39,060				
3→−1	111.8	40,080				
5→−2	408.8	43,120				
2→−1 > 2→−5	79.6	43,350				
4→−1 > 5→−1	15.5	45,650				
5→−1 > 3→−2	28.1	46,690				
3→−2 > 3→−3 > 5→−2	28.3	48,800				
3→−2 > 2→−4 > 2→−3	55.3	50,100				

A = $Mo_2O_3[S_2P(OEt)_2]_4$
B = $Mo_2O_3(S_2CNEt_2)_4$
C = $Mo_2O_3(S_2COEt)_4$
D = $Mo_2O_3[S_2CNHCH(Me)(Ph)]_4$

[a] References 1 and 9.

Excited States

Table III lists the results of the excited state and configuration interaction calculations. For brevity, only states with energies below 50,000 cm^{-1} are included. Also included in Table III are the experimental spectra for the molybdenum(V) complexes of diethyldithiocarbamate, O-ethyldithiocarbonate, diethylphosphorothiolothionate, and the o.r.d. results from the molybdenum(V) complex of (+)-*N*-1-phenylethyldithiocarbamate. (Between 16,000 and 33,000 cm^{-1} the u.v. spectrum of the latter complex is similar to that of diethyldithiocarbamate complex.) The calculated energies for the model and experimental values for the real complexes are in satisfactory agreement – even when, as in the phosphorothiolothionate complex, PS_2 groups replace the CS_2 groups of the ligands. A study of the main contributing configurations to the calculated states shows that the peaks at about 33,000 and 39,000 cm^{-1} possess strong ligand character, whereas those below 30,000 cm^{-1} have a greater contribution from molybdenum orbitals, and could be loosely described as charge-transfer states. The most intense Cotton Effect, at 33,500 cm^{-1}, corresponds to the mainly internal ligand transition.

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