The Electronic States of the Dioxo-di-μ-oxo-dimolybdate(V) Group

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A theoretical study of the dioxodi-μ-oxo-dimolybdate(V) group by the all valence-electron SCMO method is presented. In the calculations described here, one molybdenum atom is complexed to the tridentate ligand L-cysteine and the other to two hydroxy-groups and one water molecule. It is found that there is considerable Mo–Mo bonding which is principally of σ type and four electronic transitions, all involving the Mo–Mo bond, are calculated to occur in the region 18,000—40,000 cm^{-1}. These agree well with those found in the spectra of the di-μ-oxo-bis[oxo-(L-cysteinato)molybdate(V)] ion.

MOLYBDENUM(V) forms a wide range of diamagnetic complexes which have been shown to incorporate a common dimeric oxygen bridged structure[1-6] in which ligands may either be complexed separately to the molybdenum atoms or may form a further bridge in the case of some which are polydentate. Experimental spectroscopic evidence (discussed later) indicates that the nature of the complexed group exerts little influence on the form of the electronic spectra of the species in the 18,000—40,000 cm^{-1} region, *e.g.* the L-cysteine complex (Figure 1) yields

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[1] D. H. Brown and J. MacPherson, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3309.

[2] D. H. Brown and J. MacPherson, *J. Inorg. Nuclear Chem.*, 1971, **33**, 4203.

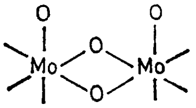
[3] D. H. Brown and J. MacPherson, *J. Inorg. Nuclear Chem.*, in the press.

[4] J. R. Knox and C. K. Prout, *Acta Cryst.*, 1969, **B25**, 1857.

[5] R. M. Wing and K. P. Callahan, *Inorg. Chem.*, 1969, **8**, 2303.

[6] A. Kay and P. C. H. Mitchell, *J. Chem. Soc. (A)*, 1970, 2421.

a single intense peak in the electronic spectrum at 35,000 cm^{-1} which extends into the visible region and imparts a yellow colour to the complex. This is typical of a wide range of complexes of this type. Furthermore, transition-metal ions, when complexed to an optically active ligand, become associated with the symmetry of the ligand and Cotton effects, related to the electronic transitions of the ion as a whole, are observed. Hence, since the intensities of optical rotation depend on magnetic as well as electric factors, electronic transitions which are masked in the electronic spectra can give rise to distinct Cotton effects. Again, the o.r.d. spectra and many Mo^{V} complexes with optically active ligands exhibit marked similarities.



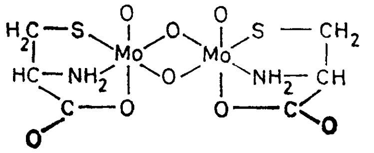


FIGURE 1 Geometry of the di-μ-oxo-bis[oxo(L-cysteinato)-molybdate(V)] ion

Gray and Hare [7] have published a molecular orbital treatment of the MoOCl$_5^{2-}$ ion and a modified version of this has been invoked [5] to interpret the spectrum of the molybdenum(V) complexes. As far as we are aware, no previous molecular orbital calculations on transition-metal complexes have obtained excited-state energies with inclusion of configuration interaction. In most previous work in the field, observed spectral band energies have been correlated with one-electron orbital–orbital gaps. This is inadequate and, indeed, in the context of the high symmetry of many transition-metal complexes, may lead even to the wrong qualitative answer, since adjacent sets of degenerate orbitals give rise to several electronic states and these are only separated in energy by the inclusion of the coulomb (J) and exchange (K) integrals resulting from electronic interaction.

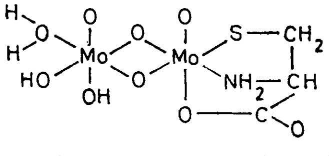


FIGURE 2 Assumed geometry of complex ion

Hence, since the excited states of the system are of particular interest, we decided to investigate, in as rigorous and sophisticated a manner as possible, the ground and lower excited states of the L-cysteine complex mentioned above. Unfortunately, the known complex contains rather too many atoms for self-consistent field calculations of ground and excited states with configuration interaction to be readily carried through and a representative system, in which one cysteine was replaced by two hydroxy-groups and a water molecule (Figure 2) was studied.

One major difference in the chemistry of Mo^{VI} and Mo^{V} in aqueous solution is that species containing the former polymerise rapidly *via* an unstable dimer (a one- or two-oxygen bridged structure) to moieties containing seven or eight molybdenum atoms: Mo^{V} species, however, form only dimers.[8] This contrast in chemical behaviour should be directly traceable to the electronic structures of the compounds (particularly that of the Mo–O–Mo bridge). Hence the corresponding hypothetical Mo^{VI} compound was also investigated.

Methods of Calculation

Ground State.—The SCFMO method employed to calculate ground-state properties and its method of parameterisation has been described fully previously.[9,10] Input data for all atoms but molybdenum have been given previously.[9] The diagonal Hamiltonian matrix elements for molybdenum were I_{5s}, 7·10; I_{5p}, 3·92; I_{4d}, 4·30 eV; and a single value for all the two-electron repulsion integrals for this atom was employed. The most reasonable value for this quantity is the arithmetic mean of γ_{5s5s}, γ_{5p5p}, and γ_{4d4d} and, after calculating these separately,[9] γ_{Mo} was set at 6·37 eV. In computing the inter-orbital overlap integrals Burns orbitals [11] were employed, since they avoid the difficulty of the non-integral effective principal quantum number which appears in the Slater representation for 4*d* orbitals.

The geometries of both the derived Mo^{V} and Mo^{VI} complexes were based on the published structure [4] for the known cysteine complex.

Excited States.—The lower excited states of the systems were calculated by allowing configuration interaction between the 25 states generated from all the one electron transitions from the five highest filled molecular orbitals to the first five virtual orbitals. There is complete mixing between these states, as all the excited electronic states have identical symmetry. With reference to the ground state as zero energy, the eigenvalues of the configuration interaction matrix are the required transition energies. The computed value of the oscillator strength for each band can be correlated directly with the experimental peak areas but, since a simplified model complex was studied, we can only use the oscillator strengths as a differential measure of the intensities of the peaks in the electronic spectrum of the authentic cysteine complex.

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[7] H. B. Gray and C. R. Hare, *Inorg. Chem.*, 1962, **1**, 363.

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[9] K. A. Levison and P. G. Perkins, *Theor. Chim. Acta*, 1969, **14**, 206; 1970, **17**, 1.

[10] (*a*) D. R. Armstrong, P. G. Perkins, and J. J. Stewart, *J. Chem. Soc.* (*A*), 1971, 3674; (*b*) P. G. Perkins, I. C. Robertson, and J. M. Scott, *Theor. Chim. Acta*, 1971, **22**, 299.

[11] G. Burns, *J. Chem. Phys.*, 1964, **41**, 1521.

RESULTS AND DISCUSSION

Ground-state Properties.—Owing to the lack of symmetry of the systems, every molecular orbital contains contributions from all the atomic orbitals of every atom: nevertheless, some molecular orbitals are mainly located on a few atoms so that they describe, to a good approximation, certain isolated areas of the bond system. In Table 1 are listed the energies of the five filled orbitals of highest energy and the five empty molecular orbitals of lowest energy for both the molybdenum-(v) and -(vi) complexes, together with the chief contributing atomic orbitals. For the Mo^V complex all the five bonding orbitals given have positive eigenvalues, and this effect stems from the crystal-field effect of the ' extra ' electrons on the ion.[12] It is of striking significance that the highest filled orbital of the Mo^V complex is mainly associated with the Mo–Mo $d_\sigma d_\sigma$ bond. This is satisfyingly consistent with the diamagnetic character of the complex and the qualitative viewpoint that diamagnetism is achieved by ' pairing up ' the two odd electrons on the molybdenum atoms in a metal–metal bond. It is also noteworthy that for a free Mo^V ion the formal orbital occupancy is $(5s)^0(5p)^0(4d)^1$, whilst that calculated for the complex is $(5s)^{0\cdot43}(5p)^{0\cdot87}(4d)^{4\cdot01}$. This indicates, as would be expected, that substantial orbital mixing (covalency) occurs in the bonding of ligand atoms to the molybdenum. The total bond orders between the atoms of the dimer (defined as in ref. 10*a*) are shown in Figure 3(a). This shows, for the molybdenum(v) complex, that the bond order between molybdenum and the terminal oxygen is almost double that to the bridging oxygens and approximates to a ' double bond '. In fact, this atom is mainly bonded through $d_\pi p_\pi$ interaction together with a modicum of *ps* and *ds* bonding. The molybdenum–molybdenum bonds are effectively single and σ in character, although theoretically there could be both π and δ components. The O–O cross-ring bonding, on the other hand, is virtually negligible. Of great interest is the presence of a significant, bonding interaction between the terminal oxygens and the ' opposite ' molybdenum atoms. Although small, the order of this bond is some ten times greater than would be normally expected for a ' non-bonding ' interaction. The gain in molecular stability due to this bond could account for the observed displacement of the molybdenum atoms out of the O–O–S–N planes by 0·38 Å in the direction of the terminal oxygen ligands.[4] [This distortion is also reported[13] for the similar dimeric molybdenum(v)-oxalato complex, $BaMo_2O_4(C_2O_4)_2(H_2O)_2$]. The molybdenum–carboxyl oxygen bond is unusually long in the cysteine complex (2·30 Å) and this is reflected in the low calculated bond order (0·33). Since the molybdenum atom is in a quasioctahedral environment with the carboxyl oxygen of cysteine *trans* to the strongly bonded terminal oxygen, it is not surprising that the latter atom withdraws electron density. This accounts for the weak bond formed between the carboxyl oxygen and the molybdenum atom.

TABLE 1

Energies and character of highest bonding and lowest virtual orbitals of Mo^V and Mo^{VI} complexes

Molybdenum(v) complex		
ψ_1	9·35 $d_\sigma d_\sigma$	Mo–Mo bonding with trace on O (bridge)
ψ_2	4·26	Cysteine S and COO group
ψ_3	3·04	Lone pair on S and ' ketonic ' O of COO group
ψ_4	2·84	Lone pair on S and ' ketonic ' O of COO group
ψ_5	2·63 π bond	COO group
ψ_{-1}	16·27 $p_\pi p_\pi$	Mo–Mo bonding
ψ_{-2}	17·26 $p_\pi p_\pi$	Mo–Mo bonding
ψ_{-3}	18·02 $d_\pi d_\pi$	Mo–Mo bonding
ψ_{-4}	18·39 $d_\sigma{}^* d_\sigma{}^*$	Mo–Mo antibonding
ψ_{-5}	18·78 $d_\delta d_\delta$	Mo–Mo bonding
Molybdenum(iv) complex		
ψ_1	−3·53	Cysteine S and COO group
ψ_2	−5·18	Lone pair on S and COO group
ψ_3	−5·57	Lone pair on S and ' ketonic ' O of COO group
ψ_4	−6·32 π bond	COO group
ψ_5	−6·51	O atoms of COO group
ψ_{-1}	5·52 $d_\sigma d_\sigma$	Mo–Mo bonding
ψ_{-2}	6·92 $p_\pi p_\pi$	Mo–Mo bonding
ψ_{-3}	7·81 $p_\pi p_\pi$	Mo–Mo bonding
ψ_{-4}	8·65 $d_\pi d_\pi$	Mo–Mo bonding
ψ_{-5}	8·99 $d_\sigma{}^* d_\sigma{}^*$	Mo–Mo antibonding

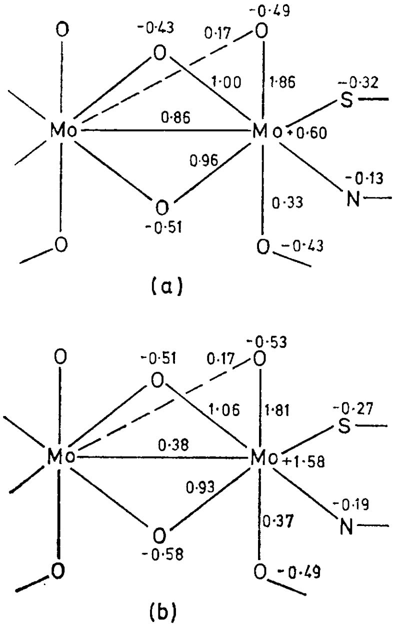

FIGURE 3 Atomic charges and bond orders of the bridging region

The results suggest that, in solution, the sulphur and

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[12] D. R. Armstrong, P. G. Perkins, and J. J. Stewart, to be published.

[13] F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, 1965, **4**, 1377.

amino-groups which are the stronger σ donors are most likely to co-ordinate first, thus leaving the carboxyl group to compete with water molecules for the vacant site on molybdenum. On acidification, however, protonation of the carboxy-group will modify its donor properties to the molybdenum site. This should not destroy the complex, since the methyl ester of cysteine forms a stable complex.[6] Experimentally it is found that the o.r.d. spectrum of the cysteine complex does change in weak acid (pH *ca.* 3) giving a five-fold decrease in the intensity of rotation. This is consistent with the optically active cysteine now acting as a bidentate ligand, thus cutting down the already small contribution of the orbitals on the cysteine to the excited states and giving rise to the observed Cotton effects.

In the hypothetical Mo^{VI} compound, two points are of primary interest. First, the configuration of the bonded Mo atom is $(5s)^{0\cdot43}(5p)^{0\cdot96}(4d)^{2\cdot4}$. This shows that the two electrons added to give the Mo^{V} oxidation state are accommodated almost entirely in the $4d$ orbitals and principally go to build up the metal–metal bond. This is confirmed by the calculation of a low Mo–Mo σ bond order (0·38) in the Mo^{VI} compound [Figure 3(b)].

This low bond order could account to some extent for the experimental observation that molybdenum(V) compounds are mainly dimeric in weakly acid solution,[8] whereas corresponding species containing molybdenum(VI) polymerise rapidly through the dimer stage to give polyanions containing seven or eight molybdenum atoms. In these, presumably, more extensive metal–metal bonding occurs.

Excited States.—The results of the configuration interaction treatment are listed in Table 2. In this compilation, only states with energies below 40,000 cm^{-1} are given. These calculated states are in satisfactory agreement with the experimental results (Table 2) for the peaks in the ultraviolet spectra and the Cotton effects in the o.r.d. spectra appertaining to the L-cysteine complex. This suggests that the treatment of the excited states is appropriate. In the region discussed, the electronic transitions all involve orbitals which are mainly located on the two molybdenum atoms. This means that they should be only slightly affected in intensity or energy by changing the ligands. The latter conclusion agrees with the experimental evidence: a number of diamagnetic Mo^{V} complexes containing the dimeric oxygen-bridged fragment have been described, and these all exhibit a strong peak in the u.v. region near 33,000 cm^{-1} and, in some cases, a shoulder situated at a lower frequency. The exact positions and extinction coefficients of both peaks are somewhat difficult to measure, as they appear as shoulders on the side of a larger band with a maximum above 50,000 cm^{-1}. Thus, we are not at present able to make a valuable comparison with the oscillator strengths calculated in the present work. The o.r.d. spectra of different complexes show greater variation, within certain limits. The majority of the complexes give two strong Cotton effects in the regions 33,000—35,000 and 25,000—27,000 cm^{-1} and sometimes up to two other weaker Cotton effects (see Table 3). O.r.d. spectra are more susceptible to the configuration and conformation of the ligands than are u.v. spectra, therefore variations in chelation could also account for the greater differences in the o.r.d. spectra. However, no more than the calculated four transitions have been identified between 20,000 and 40,000 cm^{-1} in any of the complexes examined.

TABLE 2

Calculated excited states and experimental data

	State	f(calc)	^1E_n (cm^{-1})	Experimental data (cm^{-1}) U.v. spectra		Experimental data (cm^{-1}) Cotton effect
$^1\Psi_1$	ψ_1^{-1}	0·01	13,250			
$^1\Psi_2$	ψ_1^{-2}	0·00	20,320			
$^1\Psi_3$	ψ_1^{-3}	0·01	27,390			25,500 *
$^1\Psi_4$	ψ_1^{-4}, ψ_1^{-5}	0·08	30,870	29,300 †	32,000 *	31,000 *
$^1\Psi_5$	ψ_1^{-4}, ψ_1^{-5}	0·55	35,700	35,000 †		36,000 *

* Measurements carried out in aqueous solution (ref. 3).
† Measurements carried out in solid state (ref. 6).

TABLE 3

Experimental data for various ligands

Ligand	Cotton effect (cm^{-1} × 10^{-3})	Electronic spectra (cm^{-1} × 10^{-3})
L-Cysteine [a] pH 7·0	−25·5, +31·0, +36·0	32·0
L-Cysteine [a] pH 3·5	−27·0, +36·0	32·0
D-Tartaric acid [b]	−25·0, +28·5, −32·0, +35·0	33·5
D-Galactonic acid [b]	−23·8, +27·5, −28·5, + 32·0	33·0
L-Histidine [a]	−26·5, +33·0	33·3
L-Serine [a]	−25·5, +33·0	33·0
D-Sorbitol [a]	+24·0, −30·0, +35·0	33·5
L-Arabitol [a]	−24·0, +29·0, −34·0	33·5
D-Mannose [c]	+26·0, −33·5	32·4
D-Fructose [c]	+23·0, −33·0	32·2
L-Rhamnose	−26·0, +35·0	32·2
D-PDTA * [d]	−21·0, −26·0, +33·0	26·0, 33·0

* D-1,2-propylenediaminetetra-acetic acid.

[a] ref. 3; [b] ref. 2; [c] ref. 1; [d] ref. 5.

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