Electronic Structures of Model Molybdenum(VI) Complexes Having Terminal Oxygen Atoms

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A theoretical study by the all valence-electron SCMO method has been made of two molybdenum(VI) species containing two and three terminal oxygens respectively. The former is a model for the dimeric molybdenum(VI) oxalato-complex and the latter for the edta and diethylenetriamine complexes. In both cases the highest filled molecular orbitals arise mainly from the *p*-orbitals on the terminal oxygens. Results obtained from excited-state calculations with extensive configuration interaction are in general but not complete agreement with those from the experimental optical spectra.

MOLYBDENUM(VI) forms a wide range of complexes with oxygen donor ligands but for only a limited number of these are the structures known. Apart from the oxine and acetylacetonate complexes, where π-ring systems are probably involved, two main types of adduct have been described.[1-4] These involve a molybdenum(VI) ion in a basically octahedral environment, having attached ligand donor atoms, and either two or three terminal oxygens. These complexes yield similar u.v. spectra showing a strong peak situated at energies above 50,000 cm^{-1} and tailing into the near-u.v. and the visible region. (The edta complex shows a poorly defined shoulder at *ca.* 45,000 cm^{-1}.)

In addition to these complexes whose structure is known, a number of molybdenum(VI) complexes with sugars,[5] polyhydroxy-alcohols,[6] α-hydroxycarboxylic acids,[7] and amino-acids [8] have been described and their electronic spectra in solution recorded. The spectra

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[1] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

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[3] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.

[4] J. J. Park, M. D. Glick, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1969, **91**, 301; L. O. Atovmyan and O. N. Krasochka, *Chem. Comm.*, 1970, 1670; R. Stomberg, L. Trysberg, and I. Larkins, *Acta Chem. Scand.*, 1970, **24**, 2678.

[5] E. Bayer and W. Voelter, *Annalen*, 1966, **696**, 194.

[6] W. Voelter, E. Bayer, R. Records, E. Bunnenberg, and C. Djerassi, *Annalen*, 1968, **718**, 238.

[7] W. Voelter, E. Bayer, G. Barth, E. Bunnenberg, and C. Djerassi, *Chem. Ber.*, 1969, **102**, 2003.

[8] D. H. Brown and J. MacPherson, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1705.

are similar to those described above but for certain of the sugar complexes a further, poorly defined shoulder is observed near 36,000 cm^{-1}. Further information about the electronic excited states can be obtained from optical rotatory dispersion studies of molybdenum(VI) complexes with optically active ligands. The metal ions, when complexed with an optically active ligand, 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. 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. For the potentially bidentate ligands like mandelic and lactic acids, two Cotton effects are observed, at *ca.* 37,000 and 47,000 cm^{-1}. For the potentially polydentate ligands, up to five Cotton effects between 30,000 and 50,000 cm^{-1} are observed, with those at energies lower than 37,000 cm^{-1} being very weak.

The only previous molecular orbital calculations on molybdenum(VI) complexes have been carried out by the present authors.[9] These dealt with a hypothetical dimeric double-oxygen-bridged complex. The present work describes and interprets calculations of both the ground states and lower excited states of the two ions shown in Figure 1. The first complex (Figure 1,A) was taken as a model for the oxalato-complex [3] and the second (Figure 1,B) for the edta complex [4] with molybdenum(VI). The real complexes contain many atoms and the self-consistent field calculations of ground and excited states with configuration interaction would be heavy and would probably not reveal any new and different features.

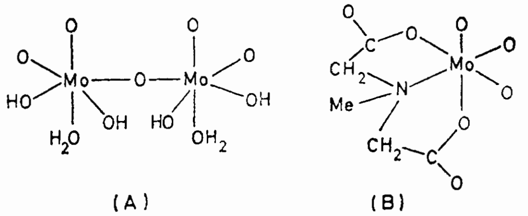

FIGURE 1

Calculational Methods.—The methods used were similar to those previously described.[9] The geometries of the species examined were based on the known structures of the molybdenum(VI) oxalato- [3] and edta complexes.[4]

RESULTS AND DISCUSSION

Orbital Levels and Charge Distribution.—Because of the lack of symmetry in these systems, every molecular orbital incorporates contributions from all the atomic orbitals of the basis set. However, some molecular orbitals are mainly localised on a few atoms so that they describe, to a good approximation, certain isolated parts of the bonding. Table 1 lists the energies of the five filled orbitals of highest energy and the five virtual orbitals of lowest energy for both the molybdenum(VI) ions. In both species, the five filled orbitals are associated with the terminal oxygen atoms. The virtual orbitals are more delocalised, the main contributions arising from the molybdenum atoms and from the water molecule and the carboxyl groups in complexes A and B respectively.

TABLE 1

Energies (eV) and character of highest bonding and lowest virtual orbitals, ψ_n

Complex A		
n	E_n	
1	4·57	Lone pair on O of Mo=O
2	4·02	Lone pair on O of Mo=O
3	3·54	Lone pair on O of Mo=O
4	3·40	Lone pair on O of Mo=O
5	3·26	Lone pair on O of Mo=O
−1	13·66	p on Mo + lone pair on O of H_2O
−2	13·71	s on Mo + lone pair on O of H_2O
−3	14·34	p on Mo + lone pair on O of H_2O
−4	14·55	Lone pair on H_2O
−5	15·44	s and p on Mo
Complex B		
1	6·55	Lone pair on O of Mo=O
2	6·30	Lone pair on O of Mo=O
3	4·50	Lone pair on O of Mo=O
4	4·42	Lone pair on O of Mo=O
5	3·17	Lone pair on O of Mo=O
−1	15·65	s on Mo + carboxyl group
−2	15·73	s and p on Mo
−3	15·95	Delocalised
−4	16·40	p on Mo
−5	16·41	s and p on Mo

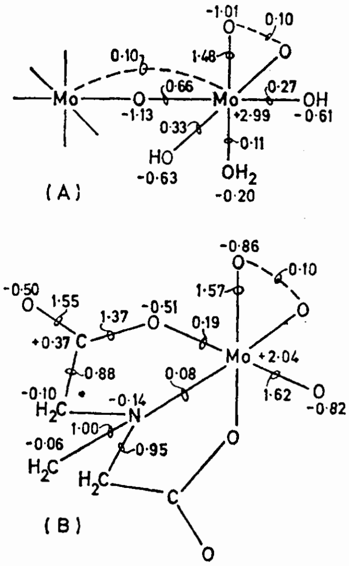

FIGURE 2

The bond orders and atomic charges for the two ions are shown in Figure 2. The bond orders are defined so that they afford a measure of the covalent character of

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[9] D. H. Brown, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1972, 1105.

the bond.[10] Thus, where there is considerable charge separation in the bond with resulting high ionic character, the bond order will be small. A C–N or C–C bond, therefore, should show a bond order close to 1·0, whereas an Mo–O bond order would be expected to be considerably lower. ' Dative ' bonds to the molybdenum also exhibit relatively low bond orders and high charge separation, for example, the Mo–H_2O bond in complex A and the Mo–N bond in complex B. These reflect the weak contributions from molybdenum to the molecular orbitals in which the oxygen or nitrogen atoms figure. This means that a large charge transfer from the ligand to molybdenum would be required to give a high bond order, at the same time balancing the charge distribution. This result indicates the predominantly ionic character of dative bonds in these complexes and is consistent with the basic tenets of ligand-field theory. Higher bond orders are found in the molybdenum–terminal oxygen bonds and the C–O bonds of the carboxylic acid groups: in both cases there is considerable double-bond character. The bonding between molybdenum and the terminal oxygens is, in fact, mainly of $d_\pi p_\pi$ type. In compound A the high charge separation on the Mo–O–Mo bridge suggests a strong ionic bonding component superimposed on the basic strong covalent bond, the whole accounting for the stability of the linear bridge. The molybdenum–molybdenum bond order (0·10) is small but still significant, being some ten times greater than would normally be expected for a ' non-bonding ' interaction.

The individual orbital occupancies are listed in Table 2. For the isolated molybdenum(VI) ion the formal orbital configuration is $(5s)^0(5p)^0(4d)^0$, whilst that calculated for the complexes shows that all three orbital sets are to some extent occupied. This is indicative of considerable orbital mixing in the bonding of the ligands to the molybdenum atom. The relatively high p-orbital population for the bridging oxygen atom in complex A breaks down into fairly symmetrical occupancy of each p orbital (p_x 1·795, p_y 1·784, p_z 1·851), again suggesting a strong ionic contribution to the bridging bonds. In the limited context of two molybdenum(VI) species, this is consistent with chemical evidence: the oxalato-complex (with a linear bridge) is prepared by solid-state oxidation of the dimeric oxygen-bridged molybdenum(V) oxalate complex. On attempted recrystallisation from water a polymeric molybdenum(VI) oxalato-complex is obtained. Clearly the bridging system is unstable in aqueous solution, unlike the essentially covalent bridge structure of the molybdenum(V) complex,[9] which is stable.

TABLE 2

Orbital occupancies

Complex A

	$n\,s$	$n\,p$	$4d$
Mo	0·284	0·469	2·261
O(terminal)	1·756	5·252	
O(terminal)	1·766	5·218	
O(bridge)	1·696	5·430	
O(hydroxyl)	1·701	4·908	
O(hydroxyl)	1·699	4·926	
O(water)	1·561	4·628	

Complex B

	$n\,s$	$n\,p$	$4d$
Mo	0·312	0·512	3·135
O(terminal)	1·782	5·075	
O(terminal)	1·787	5·060	
O(terminal)	1·770	5·048	
O(carbonyl)	1·592	4·916	
O(carbonyl)	1·602	4·900	
O(acidic)	1·633	4·766	
O(acidic)	1·631	4·867	
N	1·219	3·920	
C(carboxyl)	1·032	2·600	
C(carboxyl)	1·039	2·597	
C	0·907	3·195	
C	0·908	3·195	

Excited States.—The results of the excited-state and configuration interaction treatment for both systems are in Table 3. For brevity, only states having energies below 50,000 cm^{-1} are included. The actual appearance of the spectra of the complexes predicted by these results will depend critically on the breadth of the

TABLE 3

Calculated electronic spectra

Complex A

Main contributing configurations ψ_n^m $n \rightarrow m$	Energy/cm^{-1}	Oscillator strength $\times 10^3$
$1 \rightarrow -1$	37,600	0
$1 \rightarrow -2$	38,000	85·5
$2 \rightarrow -2$	42,300	0
$3 \rightarrow -2$	42,500	43·3
$3 \rightarrow -1$	43,700	0
$2 \rightarrow -1$	44,000	12·0
$3 \rightarrow -1$	45,000	0
$4 \rightarrow -2$	45,530	48·9
$1 \rightarrow -3$	46,360	0
$4 \rightarrow -1$	47,540	0
$1 \rightarrow -5$	49,160	0
$2 \rightarrow -3$	49,200	50·9
$1 \rightarrow -4$	49,210	59·7
$5 \rightarrow -1$	51,000	62·8

Complex B

Main contributing configurations ψ_n^m $n \rightarrow m$	Energy/cm^{-1}	Oscillator strength $\times 10^3$
$1 \rightarrow -2$	19,000	13·1
$2 \rightarrow -2$	21,000	17·1
$1 \rightarrow -5$	29,000	3·8
$2 \rightarrow -5$	31,000	0·7
$3 \rightarrow -2$	32,500	1·0
$1 \rightarrow -4$	33,800	4·7
$2 \rightarrow -4$	35,100	8·4
$4 \rightarrow -2$	36,700	5·2
$1 \rightarrow -1$	42,200	4·1
$2 \rightarrow -1$	44,500	9·3
$5 \rightarrow -2$	45,100	1·0
$5 \rightarrow -2$	46,000	11·1
$3 \rightarrow -5$	46,100	17·3
$4 \rightarrow -5$	47,400	1·5
$2 \rightarrow -3$	48,000	8·1
$3 \rightarrow -4$	50,100	15·3

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

different electronic bands. Examination of the experimental u.v. spectra of molybdenum(VI) with non-π-bonding oxygen donors shows that there is a steady build-up of intensity as energy increases throughout the near-u.v. region, with the appearance in a few cases of indistinct shoulders. In fact, in the oxalato-complex, no *isolated* peak is observed below 50,000 cm^{-1} whilst in the edta complex a weak shoulder appears at *ca.* 45,000 cm^{-1}. These results suggest that the absorptions either are associated with a large natural line-width, are strongly vibronically coupled with one or more quanta, or there are a number of allowed transitions occurring close together in the energy scale.

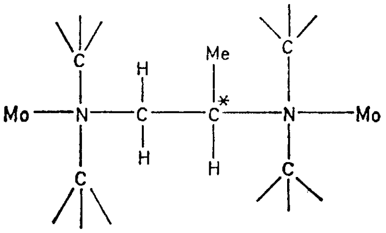

FIGURE 3

In the absence of any further calculated data on the shapes of the absorption peaks, we are not able to correlate our results more closely with observation. However, it may be said that there is general agreement between the observed electronic spectra and the calculated quantities. Further progress must await better resolution of the experimental spectra or calculation of the band contours. Neither of these advances is likely to be easy.

Of particular interest is the optical activity of the (+)-propylenediaminetetra-acetic acid complex which, from its spectroscopic, analytical, and chemical properties, is likely to be isostructural with the edta complex. In this complex there is only one asymmetric carbon atom and this is not involved in the chelate rings of the complex ion (Figure 3). It has been suggested that such a situation is necessary for significant optical activity associated with the complexed metal ion.[11] Now, the molecular orbitals involved in certain of the electronic transitions contain appreciable contributions from the atomic orbitals of the asymmetric carbon atom. This is particularly true of the virtual orbitals associated with the calculated electronic transitions at 33,800 and 35,100 cm^{-1}. This correlates well with the experimental evidence, since a strong Cotton effect is observed at 36,000 cm^{-1}.

Other orbitals involved in the excited states contain much smaller contributions from the basis set on the asymmetric carbon atom but there will be an additive effect associated with six transitions occurring in the $46,000 \pm 2000$ cm^{-1} region to account for the weak Cotton effect found at 46,000 cm^{-1}. At present, because of the lack of a suitably defined magnetic dipole operator, we cannot comment quantitatively on the Cotton effects in these complexes.

Although one must be cautious in extrapolating from the information relevant to the complexes examined above to molybdenum(VI) complexes in general, it is significant that the u.v. spectra of the molybdenum(VI) complexes with α-hydroxycarboxylic acids, polyhydroxy-alcohols, sugars, and amino-acids (except sulphur-containing cysteine) are similar in general form. Some polyhydroxy-alcohols and sugars, however, afford up to five Cotton effects between 30,000 and 50,000 cm^{-1}.[12] The greater sensitivity of the o.r.d. of these complexes is probably due to the several asymmetric carbon atoms present and their closer proximity to the complexed molybdenum. Thus in all these complexes the same general electronic transition pattern may hold for the low-energy electronic bands, *i.e.*, promotion of electrons from orbitals associated mainly with terminal oxygens to those centred chiefly on the molybdenum atom, together with contributions from the complexed ligands.

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[11] E. Larssen and I. Olsen, *Acta Chem. Scand.*, 1964, **18**, 1025.

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