Inorganica Chimica Acta, 8 (1974) 285–287

The Electronic Structures of the Oxodiperoxooxalatomolybdate(VI) and Tetraperoxomolybdate(VI) Ions

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Received May 30, 1973

A theoretical study by the all valence-electron SCMO method has been made of the oxodiperoxo-oxalatomolybdate (VI) and the tetraperoxomolybdate (VI) ions. In both cases the highest filled molecular orbitals are located mainly on the surrounding oxygen atoms and the lowest virtual orbitals mainly on the central molybdenum atom. The energies obtained from excited state calculations with extensive configuration interaction are in reasonable agreement with experimental spectral results.

Introduction

In general molybdenum does not form peroxomolybdate complexes with organic ligands as readily as does chromium. However the structures of at least three such peroxomolybdates have been described – two with hexamethylenephosphorustriamide[1] and one with oxalate as ligand.[2] These all contain, as well as the organic ligand, bidentate peroxo-groups and terminal oxygens. The oxodiperoxooxalatomolybdate(VI) ion is the simplest of these and so is a convenient species for self-consistent field calculational purposes. Hence we have examined its electronic structure and excited states and for comparison, we have also examined the tetraperoxomolybdate(VI) ion.

Peroxomolybdates are of importance as industrial oxidising agents and catalysts and are also thought to participate directly in oxygen transfer reactions in some naturally occurring oxidases, although the latter mechanisms are as yet a matter of conjecture. Thus a study of these two peroxomolybdate ions is of clear interest in any study of the electronic structures of molybdenum complexes. The present paper therefore describes calculations on both the ground and lowei excited states of the two ions.

Calculational Methods

The methods used were similar to those previously described.[3] The geometries of the two ions were as published.[2,4]

Results and Discussion

Ground States

Due to the lack of symmetry in the oxodiperoxo–oxalatomolybdate(VI) ion, every atom contributes to all the molecular orbitals. 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. In the more symmetrical tetraperoxomolybdate(VI) ion there is less orbital mixing and so the localised descriptions of the orbitals are more appropriate. In Table I are listed 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 cases the five highest filled orbitals are mainly located on the surrounding oxygen atoms and the five lowest virtual orbitals on the central molybdenum atom. Thus the lower energy electronic transitions will be mainly of charge transfer type and originate in oxygen molybdenum movement.

The nett atomic charges for the two ions are shown in Figure 1. The charges on the oxygens of the peroxide ions are comparable to those of the'complexing'

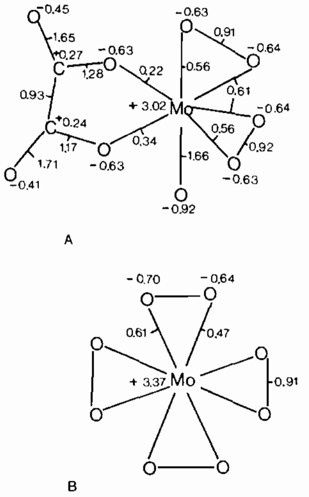

TABLE I. Energies (eV) and character of highest bonding and lowest virtual orbitals ψ_n.

n	E_n	
$[MoO_2(O_2)_2(C_2O_4)]^{2-}$		
1	4.23	mainly COO groups
2	3.51	mainly O–O groups and O(terminal)
3	3.34	mainly O–O groups and O(terminal)
4	3.04	mainly O–O groups
5	2.89	mainly O–O groups
–1	15.39	mainly Mo and O(terminal)
–2	15.45	mainly Mo and COO groups
–3	15.91	mainly Mo and O–O groups
–4	16.10	mainly Mo
–5	16.84	mainly Mo
$[Mo(O_2)_4]^{2-}$		
1	4.57	mainly O–O groups
2	4.57	mainly O–O groups
3	4.09	mainly O–O groups
4	4.00	mainly O–O groups
5	3.74	mainly O–O groups
–1	16.98	mainly Mo
–2	17.32	mainly Mo
–3	17.35	mainly Mo
–4	17.35	mainly Mo
–5	17.51	mainly Mo

oxygens of the oxalate ion and about two thirds that of the terminal oxygen. The charges on both molybdenum atoms are as expected for ions of similar overall formal charge.

Figure 1 also shows the bond orders (or bond indices). These are so defined[5] that they afford a measure of the covalent character of the bond. Thus the unit C–C bond index in the oxalate ion correlates with the classical view of this bond. So also do the O–O bonds in the peroxo groups, in contrast to the Mo–O bonds where the charge separations suggest considerable ionic character in the bonding. Double-bond character is indicated to the three terminal oxygens of which two lie on the oxalate ion and one on the molybdenum and to a lesser extent in the carbon oxygen bonds of the C–O–Mo link. The non-equal Mo–O bond lengths in the tetraperoxomolybdate(VI) ion are also reflected in the bond indices.

The individual orbital occupancies are listed in Table II. For an isolated molybdenum(VI) ion the formal electronic configuration is $(5s)^0$ $(5p)^0$ $(4d)^0$ whilst that calculated for the complexes shows that all three orbital sets are occupied to some extent. This is indicative of considerable orbital mixing in the bonding of the ligands to the molybdenum atom.

Excited States

The results of the excited state and configuration interaction treatment for both systems are given in Table III. For brevity only states having energies below 50,000 cm^{-1} are included. Also in the Table are the experimental bands for the two complexes. These were obtained both in reflectance and transmittance using an aqueous solution. The experimental spectra were ill-defined, rising in the ultraviolet region with shoulders occurring at 32,700 and 41,000 cm^{-1} for the oxodiperoxo–oxalatomolybdate(VI) ion and at 44,000 cm^{-1} for the tetraperoxomolybdate ion. The calculations for the former ion suggest a weak peak around 17,100 cm^{-1} (probably too weak to observe), two

TABLE II. Orbital occupancies.

	ns	np	$4d$
$[MoO(O_2)_2C_2O_4]^{2-}$			
Mo	0.34	0.41	2.22
O (peroxide)	1.77	4.87	–
O (terminal)	1.79	5.13	–
O (C–O–Mo)	1.58	5.05	–
O (C–O)	1.60	4.80	–
$[Mo(O_2)_4]^{2-}$			
Mo	0.34	0.38	1.90
O	1.80	4.83	–
O peroxo	1.77	4.93	–

TABLE III. Calculated electronic spectra.

Main contributing configurations $\psi_n{}^m$		Energy, cm^{-1}	Oscillator strength $\times 10^3$	Experimental uv spectra, cm^{-1}
n m	*n m*			
$[MoO(O_2)_2C_2O_4]^{2-}$				
$1\rightarrow2$	$1\rightarrow1$	17,100	0	
$1\rightarrow3$	$1\rightarrow1$	34,670	8.5	32,700 (sh)
$2\rightarrow1$	–	41,050	12.0	41,000 (sh)
$3\rightarrow4$	$3\rightarrow5$	43,300	1.0	
$3\rightarrow3$	$1\rightarrow3$	44,170	5.0	
$4\rightarrow1$	$2\rightarrow3$	45,080	2.0	
$5\rightarrow1$	$4\rightarrow1$	45,540	3.0	
$2\rightarrow3$	$3\rightarrow3$	46,020	5.0	
$2\rightarrow4$	$2\rightarrow2$	47,000	6.0	
$3\rightarrow5$	$3\rightarrow4$	48,570	14.9	
$4\rightarrow3$	$5\rightarrow3$	49,630	5.0	
$[Mo(O_2)_4]^{2-}$				
$1\rightarrow1$	$2\rightarrow1$	44,100	18.6	44,000 (sh)
$2\rightarrow1$	$1\rightarrow1$	45,250	19.6	
$1\rightarrow2$	$2\rightarrow2$	46,800	0.6	
$2\rightarrow2$	$1\rightarrow2$	46,850	0.8	
$2\rightarrow3$	$1\rightarrow4$	47,100	0.1	
$1\rightarrow4$	$2\rightarrow3$	48,200	6.2	
$1\rightarrow3$	$2\rightarrow4$	49,150	0.1	
$2\rightarrow4$	$1\rightarrow3$	49,850	0.1	

peaks, at 34,670 and 41,050 cm^{-1} followed by a succession of peaks from 43,300 cm^{-1} – probably too close together to give discrete peaks experimentally. Thus the experimental and theoretical results are in reasonable agreement. For the tetraperoxomolybdate (VI) ion, calculation predicts a number of peaks starting above 44,000 cm^{-1}, again probably occuring too close together to give discrete peaks. This is in agreement with the experimental results.

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