

SCF-MO-LCAO Calculation on the Peroxochromate Ion, CrO_8^{3-}

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The results of an *ab initio* MO-SCF-LCAO calculation on the ground state of the peroxochromate anion are presented. A minimal basis of Slater type orbitals expanded in terms of Gaussian functions was employed. Contracted orbitals consisting of two Gaussian functions were used for the chromium core orbitals and all oxygen orbitals, together with two uncontracted functions for the chromium 4s, 4p, and 3d orbitals. The results provide a basis for a detailed description of the bonding in the ion.

THERE exist a number of complex molecules which exhibit molecular oxygen or the peroxide ion bonded symmetrically (or nearly symmetrically) to a transition-metal atom. These include Vaska's complex $\text{Ir}(\text{O}_2)\text{Cl}(\text{CO})[\text{PPh}_3]_2$ ¹ and related synthetic molecular oxygen carriers, and a number of peroxo-complexes of the type CrO_5 ² and CrO_8^{3-} ³.

Ibers⁴ has discussed the mode of co-ordination of molecular oxygen to a number of d^8 Ir and Rh complexes in terms of the Chatt-Dewar π -bonding scheme.⁵ It is suggested that variation in the metal d -orbital energies in the complexes leads to different amounts of d -orbital back donation to the oxygen π^* -orbitals, thus accounting for the considerable range of O-O distances. These vary from 1.30 Å in $\text{Ir}(\text{O}_2)\text{Cl}(\text{CO})[\text{PPh}_3]_2$ ⁶ to 1.625 Å in $[\text{Ir}(\text{O}_2)(\text{diphos})_2][\text{PF}_6]$.⁴ Mason⁷ has discussed the bonding of molecular oxygen to transition metals and pointed out the resemblance between the co-ordinated oxygen molecules in the various systems and the excited states of the isolated molecule.

The peroxo-complexes have been studied in detail by Griffith.⁸ He describes a 'bent-bond' scheme for σ -bonds between Cr and O in CrO_5 , CrO_8^{3-} , and related complexes, based on the assumption that the Cr hybrid orbitals cannot subtend the 45° angle which is needed

if they are to point directly at the oxygen atoms.⁹ On the other hand Tuck and Walters¹⁰ have proposed a scheme whereby the peroxide ligands act as monodentate π -donors with the usual back donation to ligand π^* orbitals not taking place since the chromium atom in its formal oxidation states of VI in CrO_5 and V in CrO_8^{3-} has insufficient occupied d -orbitals. As Griffith has pointed out, this argument would predict lengthened O-O distances over that observed in the peroxide ion, through O-O π -bond weakening, whereas in CrO_8^{3-} the distance is shorter (1.40 Å) than in O_2^{2-} (1.49 Å). Swalen and Ibers,¹¹ who have performed a ligand-field calculation on CrO_8^{3-} based upon structural, magnetic and optical data, suggest that there is some π -bonding between Cr and one set of oxygens of the peroxide ligands, and that this accounts for the O-O bond shortening.

It is clear, then, that there is considerable ambiguity in the interpretation of the experimental results in terms of the bonding in such complexes. The nature of the bonding difference between the molecular oxygen complexes and the peroxides apparently derives from the different oxidation states of the metal atoms involved, but it is not certain whether there is a rigid demarcation between the two forms of O_2 co-ordination in these complexes. The calculation on CrO_8^{3-} in

¹ L. Vaska, *Science*, 1963, **140**, 809.

² R. Stomberg, *Arkiv Kemi*, 1964, **22**, 29.

³ R. Stomberg and C. Brosset, *Acta Chem. Scand.*, 1960, **14**, 441.

⁴ J. A. McGinnety, N. C. Payne, and J. Ibers, *J. Amer. Chem. Soc.*, 1969, **91**, 6301, and other related papers.

⁵ J. Chatt, *J. Chem. Soc.*, 1953, 2923; M. J. S. Dewar, *Bull. Soc. chim. France*, 1951, **18**, C71.

⁶ J. A. McGinnety, R. J. Doedens, and J. Ibers, *Inorg. Chem.*, 1967, **6**, 2243.

⁷ R. Mason, *Nature*, 1968, **217**, 543.

⁸ W. Griffith, *J. Chem. Soc.*, 1962, 3948 and following papers.

⁹ W. Griffith, *J. Chem. Soc.*, 1964, 5248.

¹⁰ D. G. Tuck and R. M. Walters, *Inorg. Chem.*, 1963, **2**, 428.

¹¹ J. D. Swalen and J. Ibers, *J. Chem. Phys.*, 1962, **37**, 17.

this paper is intended to provide some theoretical background for a description of the bonding in it and related peroxo-complexes and perhaps to serve as a comparison for any future calculations upon molecular oxygen complexes. *Ab initio* SCF-MO-LCAO calculations on CrO_4^{2-} and MnO_4^- have been reported¹² but this is the first such calculation on a peroxide complex.

Calculations.—The CrO_8^{3-} anion, as studied crystallographically in K_3CrO_8 ,^{3,11} exhibits $D_{2d} - 42m$ symmetry. The co-ordinates used in this calculation are those tabulated by Swalen and Ibers,¹¹ rotated by 45° about the z -axis such that one pair of peroxide groups lie in the xz -plane, the other pair in the yz -plane. The z -axis is the four-fold inversion axis which relates the four oxygen atoms, O_b , lying close to the xy -plane, with $\text{Cr}-\text{O}_b = 1.944 \text{ \AA}$, and the four atoms, O_a , which lie alternately above and beneath this plane, $\text{Cr}-\text{O}_a = 1.846 \text{ \AA}$. The O-O distance is 1.405 \AA .

The Gaussian orbital basis was constructed using two term Gaussian expansions of Slater orbitals, the Slater exponents being best free-atom values¹³ except for the $4p$ chromium orbital where an exponent of 1.04 was used.¹⁴ Klessinger's¹⁵ variationally chosen expansions were used for the $1s$, $2s$, and $2p$ orbitals and Stewart's¹⁶ least-squares expansions for the remaining Cr orbitals, $3s$, $3p$, $3d$, $4s$, and $4p$. All the basis functions were used as two term contracted Gaussian orbitals except for the Cr $3d$, $4s$, and $4p$ which were left uncontracted. There were thus 67 basis orbitals obtained from 116 Gaussian functions.

Atom SCF calculations on the ground states of the chromium and oxygen atoms, using the program of Roos *et al.*,¹⁷ were run with these basis orbitals. Total energies of -1018.734 and -72.431 a.u. compare poorly with Clementi's¹⁸ values of -1034.306 and -74.809 a.u. for Hartree-Fock wave functions for these atoms. However, the difference in, for example, the Cr $1s$ eigenvalue (6.5 a.u.) leads one to suppose that the major deficiency in the basis set will occur in the description of the core orbitals; the description of the valence orbitals should be in fair agreement with that obtained from an STO basis.¹⁹ This basis set is admittedly very limited but it is not unreasonable to expect that meaningful results can be obtained with it. Previous experience with calculations on SO_2 ²⁰ have shown that the use of two uncontracted Gaussian orbitals per atomic orbital yields results that agree well with much more accurate calculations and which are of comparable accuracy to those obtained with a minimal basis of atomic orbitals fitted by 3-GTO contracted functions. It would have been preferable to have left uncontracted the

oxygen valence orbitals, but the use of a basis set consisting of 99 functions would make prohibitive demands upon our present computational facilities. Calculations performed upon benzene and the allyl cation using minimal bases of contracted Gaussian functions showed no differences in the order of energy levels between 2-GTO calculations and 3- and 4-GTO calculations.²¹

Consideration of molecular symmetry in the calculation of the two-electron integrals²² reduced the number of unique integrals to about 400,000. SCF Convergence was obtained first for the closed-shell ion CrO_8^{2-} with 45 electron pairs. It was found necessary to employ a number of modifications in the standard iterative SCF procedure in order to obtain convergence. After the core orbitals had been occupied, electrons were introduced into the system four pairs at a time, and iterations carried out until approximate convergence had been obtained, before more electrons were added. In each cycle the new eigenvectors were compared with those from the previous cycle. For each eigenvector corresponding to an occupied molecular orbital in the previous cycle the eigenvector from the new set which had maximum overlap with it was selected for occupation in the next cycle. This prevents the wild oscillations that can occur when the ordering of the virtual levels alters after electrons are put into them. It was also found necessary to employ a fractional shift technique for the density matrix, using the formula

$$\mathbf{R}'_{\text{new}} = \mathbf{R}_{\text{old}} + \lambda(\mathbf{R}_{\text{new}} - \mathbf{R}_{\text{old}})$$

where the constant, λ , was *ca.* 0.2 in the initial cycles and was increased gradually to unity as convergence was obtained. \mathbf{R}_{new} is the conventional \mathbf{R} matrix obtained after a diagonalization cycle, and \mathbf{R}'_{new} the modified matrix actually used in the next cycle. Conventional extrapolation procedures¹⁷ were initially tried, but found to be ineffective.

Once the closed-shell wavefunction has been obtained there remains the problem of finding the open-shell solution that gives minimum energy for the 91 electron problem, CrO_8^{3-} . The 20 occupied molecular orbitals of highest energy for the CrO_8^{2-} wave function could be conveniently classified into five groups of four orbitals of respectively σ , π , π , π^* , and π^* symmetry with respect to the peroxide groups. Thus the CrO_8^{2-} density matrix is a chemically reasonable trial closed-shell density matrix for CrO_8^{3-} . The virtual orbitals of lowest energy for the CrO_8^{2-} wave function are all predominantly either Cr $3d$ or $4p$ in character, and it should be one of these orbitals which holds the odd electron. It is worth noting here that the use of the lowest

¹² I. H. Hillier and V. R. Saunders, *Proc. Roy. Soc.*, 1971, **A320**, 161; *Chem. Phys. Letters*, 1971, **9**, 219.

¹³ E. Clementi and D. Raimondi, *J. Chem. Phys.*, 1963, **38**, 2686.

¹⁴ J. W. Richardson, R. R. Powell, and W. C. Nieuwpoort, *J. Chem. Phys.*, 1963, **38**, 796.

¹⁵ M. Klessinger, *Theoret. chim. Acta*, 1969, **15**, 353.

¹⁶ R. F. Stewart, *J. Chem. Phys.*, 1969, **50**, 2485.

¹⁷ B. Roos, C. Salez, A. Veillard, and E. Clementi, IBM Research, RJ518 (1968).

¹⁸ E. Clementi, *IBM J. of Res. and Develop.*, 1965, **9**, 2.

¹⁹ I. H. Hillier, and V. R. Saunders, *Internat. J. Quant. Chem.*, 1970, **4**, 203.

²⁰ P. D. Dacre and M. Elder, *Theoret. chim. Acta*, in the press.

²¹ D. B. Cook, P. D. Dacre, J. L. Dodds, and M. Elder, *Theoret. chim. Acta*, 1971, **22**, 167.

²² P. D. Dacre, *Chem. Phys. Letters*, 1970, **7**, 47.

eigenvalues technique for deciding upon the occupancy of the molecular orbitals in an open-shell SCF problem which is solved by repeated diagonalization carries with it no guarantee of finding the state of lowest energy for the system since these eigenvalues are not invariant quantities but vary with the values of the arbitrary, non-zero constants a , b , and c in the expression (1) for the Hamiltonian which is diagonalized.²³

$$\hat{h} = \frac{1}{2}[a(1 - \mathbf{R}_2)\mathbf{h}_1(1 - \mathbf{R}_2) + b(1 - \mathbf{R}_1)\mathbf{h}_2(1 - \mathbf{R}_1) + c(\mathbf{R}_1 + \mathbf{R}_2)(2\mathbf{h}_1 - \mathbf{h}_2)(\mathbf{R}_1 + \mathbf{R}_2)] \quad (1)$$

We performed three separate open-shell SCF calculations in each of which the trial closed-shell R matrix was the final CrO_8^{2-} density matrix. The trial open-shell R matrices were each given by $\mathbf{c}_x\mathbf{c}_x^\dagger$ where \mathbf{c}_x is a column eigenvector of a virtual MO from the CrO_8^{2-} calculation. The odd electron was constrained to remain in this orbital during the SCF iterations. The convergence criterion used was that no value in the open- and closed-shell density matrices should change by more than 10^{-3} in successive cycles. The final energies are given in Table 1.

TABLE 1

Total energies (a.u.) for various states of the CrO_8^{3-} ion

State	Energy	Dominant component of the open-shell MO
2B_1	-1598.188	Cr $3d_{xy}$
2B_2	-1598.129	Cr $4p_z$
2A_1	-1598.073	Cr $3d_{z^2}$

All programs used in this work were written by the authors for the Sheffield University ICL 1907 computer.

RESULTS AND DISCUSSION

The ground state of the CrO_8^{3-} ion is found to be 2B_1 with the unpaired electron occupying a molecular orbital which is predominantly Cr $3d_{xy}$ in character.* This is the ground state predicted by crystal-field theory¹¹ and by the angular overlap method if the amount of metal-ligand π -bonding is assumed to be small.²⁴ We did not perform a calculation using a degenerate open-shell orbital. The Cr atomic orbitals which have e symmetry are $3d_{xz, yz}$ which both crystal field and angular overlap methods predict to be less stable than the $3d_{xy}$ and $3d_{z^2}$ orbitals, and $4p_{x, y}$ which should be less stable than the $4p_z$ orbital. The computed total energy is -1598.188 a.u., 0.006 a.u. below the value for the isolated atoms calculated using the same basis set. However, it is not surprising that little binding energy is obtained for a calculation on a negative ion using a close to minimal basis set. More accurate calculations upon MnO_4^- ^{12, 25} using minimal basis sets

* In CrO_8^{3-} , point group D_{2d} , an orbital with b_1 symmetry is antisymmetric with respect to the dihedral mirror planes which each pass through two peroxide groups and relate the other two. The Cr $3d$ orbital which lies in the xy -plane and is directed between the peroxide groups has b_1 symmetry. This orbital is either $3d_{xy}$ (present work) or $3d_{z^2-y^2}$ (ref. 11, 24) depending upon the choice of orientation of the x and y axes.

have yielded total energies 0.5 to 0.7 a.u. above the corresponding free atom values. The calculated orbital energies and population analyses²⁶ of all the occupied molecular orbitals are listed in Tables 2 and 3. It can

TABLE 2
Inner shell orbitals of CrO_8^{3-} *

Symmetry	Orbital energy (a.u.)	Population analysis (%)						
		Cr			O _a	O _b		
		1s	2s	3s	2p	3p	1s	1s
$1a_1$	-214.238	97.7	2.3					
$2a_1$	-25.840	1.9	96.7	1.5				
$1b_2$	-21.865				96.6	3.4		
$1e$	-21.854				96.6	3.4		
$2b_2$	-19.324						54.8	43.6
$2e$	-19.322						7.0	91.4
$3a_1$	-19.321						4.0	94.4
$4a_1$	-19.317						94.4	4.0
$3e$	-19.314						91.6	7.0
$3b_2$	-19.312						43.6	54.8
$5a_1$	-3.156	0.2	1.1	96.1				
$4b_2$	-1.966				3.3	95.2		
$4e$	-1.900				3.2	95.1		

* Small contributions from valence shell orbitals have been ignored, which accounts for the unnormalized percentages. The maximum value ignored is a contribution of 2.4% of Cr $4s$ to $5a_1$.

be seen that 37 of the 91 electrons occupy orbitals which have positive orbital energies. The maximum orbital energy is 0.268 a.u. The results of other workers on similar negatively charged systems indicate that this is a predictable result and should not necessarily be regarded as an artifact of the basis set. In a calculation on NiF_6^{4-} , Moskowitz *et al.*²⁷ used 216 GTO's contracted to a larger than minimal basis set of 74 GTF's and found 44 out of 86 electrons occupying levels of positive energy with a maximum orbital energy of 0.252 a.u. A calculation on SO_4^{2-} (ref. 19) using 112 GTO's contracted to 39 GTF's found 16 out of 50 electrons in levels of positive energy, whilst in an extended basis calculation on CrO_4^{2-} (ref. 12) (141 GTO's contracted to 43 GTF's) the relative numbers were 14 out of 58. Only in the cases of the neutral Ni (π -allyl)₂²⁸ and the strongly-bound singly-charged MnO_4^- have basis sets of comparable accuracy led to all negative orbital energies. It is quite probable that if the K^+ ions that surround the CrO_8^{3-} ion in the crystal were included in the calculation then the energies of the valence orbitals would be lowered considerably. The energies of the highest occupied orbitals are very similar and it is almost certain that the inclusion of the K^+ ions in the calculation or the use of a more accurate basis set would change the relative ordering of these levels. However,

²³ R. McWeeny, Reprint No. 98, Uppsala University Quantum Chemistry Group (unpublished, 1963); also in *Molecular Orbitals in Physics, Chemistry, and Biology*, Academic Press, New York, 1964, p. 305.

²⁴ D. W. Smith, *J. Chem. Soc. (A)*, 1971, 1024.

²⁵ P. D. Dacre and M. Elder, *Chem. Phys. Letters*, 1971, **11**, 377.

²⁶ R. S. Mulliken, *J. Chem. Phys.*, 1955, **23**, 1833; 1841.

²⁷ J. W. Moskowitz, C. Hollister, C. J. Hornback, and H. Basch, *J. Chem. Phys.*, 1970, **53**, 2570.

²⁸ A. Veillard, *Chem. Comm.*, 1969, 1022; 1427.

we have sufficient confidence in the present basis set to expect that the qualitative description of the molecular orbitals that it allows would not differ significantly from that obtained from a more accurate calculation, and we can thus embark on an analysis of the bonding in the ion.

The orbital energies of Tables 2 and 3 are not the eigenvalues that result from diagonalizing the matrix \mathbf{h}

electron is in a more stable orbital than most of the other valence electrons. Similar observations have been made for SO_3F^{30} and for the benzene dication.^{31,32} We have considered the possibility that the ground state of the ion might have double occupancy of the, at present, singly-occupied orbital, with one of the now doubly-occupied orbitals being singly occupied. The energy required to promote one of the electrons from a

TABLE 3
Valence-shell orbitals of CrO_3^{3-} *

Symmetry	Orbital energy (a.u.)	Population analysis (%)										
		Cr			O_a				O_b			
		4s	4p	3d	2s	2p _r	2p _t	2p _z	2s	2p _r	2p _t	2p _z
6a ₁	-0.875	9.7			42.0			3.2	40.0	1.6		1.6
5b ₂	-0.851		1.8	1.0	45.2			3.2	43.2	1.6		2.0
5e	-0.847		4.8	0.5	44.4	0.2		3.4	41.6	1.2		2.2
6b ₂	-0.511		9.1	0.2	37.6	1.6		1.6	46.4			2.0
7a ₁	-0.497			2.6	44.4	2.4		1.2	47.2			2.0
6e	-0.491		1.3	1.1	45.8	1.6		0.8	45.4	0.2		2.6
8a ₁	-0.009	17.1		0.5	1.2	44.8				8.0		27.6
7e	{0.003		13.8	1.4			0.6	40.0			33.8	
								5.0	0.2			5.0
1b ₁	0.038			1.8				47.6			50.8	
7b ₂	0.040		3.9	11.4	0.8	13.2		24.0	2.4	43.2		0.4
9a ₁	0.055	5.6		1.4	2.0			41.6	3.2	34.4		11.6
8e	{0.057		8.9	6.3	2.8	14.6		36.4	1.2	26.2		0.2
											2.4	
1a ₂	0.068							52.4			47.6	
8b ₂	0.079		2.4	0.4	0.4	33.6		14.8	3.2	0.4		44.4
9e	{0.096		0.9	1.5	1.0	36.2		7.8	1.2			41.6
											4.4	
10a ₁	0.218	0.7		29.1	0.4	16.0		17.2	0.8	27.2		8.4
10e	{0.228		5.7	5.9				26.6			46.0	
								2.6	0.8	0.2	11.2	0.8
2a ₂	0.239							47.6			52.4	
2b ₁	0.243							51.6			43.4	
9b ₂	0.256		33.8	4.1	1.2	16.8		12.0	0.4	24.4		6.8
11e	{0.268		12.5	9.8				20.2			8.6	
					0.2	12.8		6.2	0.2	26.4		3.2
3b ₁	0.014			98.2				0.8			0.8	

* The oxygen p -orbital that lies in the plane of the CrO_2 group involved is designated $2p_r$. The p -orbital perpendicular to this plane is $2p_t$. Where two lines are assigned to an e species, the first gives populations for the Cr and the two ligands in the xz -plane, the second concerns the two ligands in the yz -plane.

defined in (1), but are calculated from the formulae $\mathbf{c}_x^\dagger(2\mathbf{h}_1 - \mathbf{h}_2)\mathbf{c}_x$ for a doubly-occupied molecular orbital with eigenvector \mathbf{c}_x , and $\mathbf{c}_y^\dagger\mathbf{h}_2\mathbf{c}_y$ for a singly-occupied orbital, \mathbf{c}_y . The negatives of these orbital energies, which are invariant to the choice of constants in (1), are the open-shell analogues of the Koopmans' theorem ionization potentials,²⁹ and have been used as such by previous workers.^{30,31} We note that the orbital energies for the doubly-occupied orbitals closely resemble the corresponding eigenvalues obtained by diagonalization of \mathbf{h} with $a = b = c = 1$ in (1). The greatest difference is 0.04 a.u. However, there is no such resemblance for the open-shell orbital where the eigenvalue is 0.451 a.u. and the orbital energy 0.014 a.u. It is apparent that the open-shell ionization potential is not a very reliable value since it seems to indicate that the unpaired

doubly-occupied orbital, \mathbf{c}_x , pairing it in the singly-occupied orbital, \mathbf{c}_y , is given by

$$E_{\text{promotion}} = \mathbf{c}_y^\dagger(2\mathbf{h}_1 - \mathbf{h}_2)\mathbf{c}_y - \mathbf{c}_x^\dagger(2\mathbf{h}_1 - \mathbf{h}_2)\mathbf{c}_x - \mathbf{c}_x^\dagger[\mathbf{J}(\mathbf{R}_y) - \mathbf{K}(\mathbf{R}_y)]\mathbf{c}_x$$

where $\mathbf{R}_y = \mathbf{c}_y\mathbf{c}_y^\dagger$ is the density matrix for the initially singly-occupied orbital and the notation is that of McWeeny.²³ This quantity turns out to be always positive for electron promotion from any of the doubly-occupied orbitals, with a minimum value of 0.267 a.u. for promotion from the orbital $10a_1$. Thus the orbital $3b_1$ is correctly assigned as the open-shell orbital, despite the indications of the orbital energies. The error in ionization potentials computed by Koopmans' theorem and the analogous open-shell formulae derives from neglect of the reorganization energy, and the differences

²⁹ T. Koopmans, *Physica*, 1934, **1**, 104.

³⁰ I. H. Hillier and V. R. Saunders, *Internat. J. Quant. Chem.*, 1970, **4**, 503.

³¹ J. L. Dodds and R. McWeeny, *Chem. Phys. Letters*, 1971, **13**, 9.

³² J. L. Dodds, Ph.D. Thesis, University of Sheffield, 1971.

in relativistic and correlation energy between the two states before and after ionization.³³ The relativistic contribution to the ionization energy should not be large, and Clementi has shown that the change in correlation energy when a single electron is added to a closed-shell system is not large,³⁴ so the dominant contribution to the error in the ionization energy will be the neglect of the reorganization energy that results from the ionization. The change in correlation energy when an electron pair is formed or broken is much greater, however, so it is possible that the reorganization energy and the correlation energy difference cancel approximately for ionization from a closed-shell system. Thus

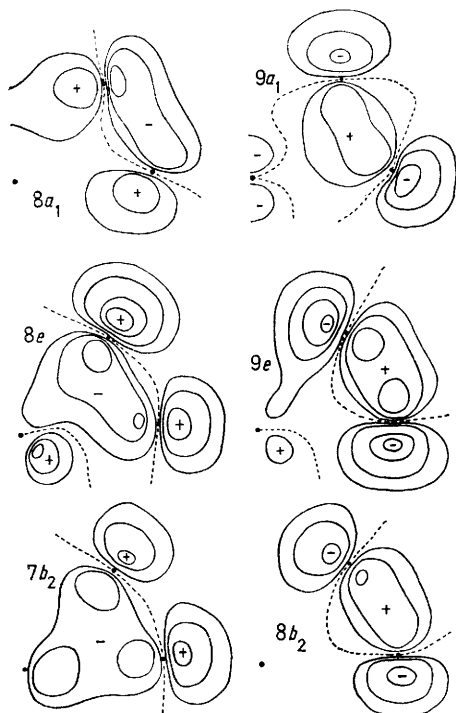


FIGURE 1 Contour diagrams of the CrO_8^{3-} molecular orbitals which are predominantly O-O π -bonding (left) and σ -bonding (right). Contours are plotted in the xz -plane with the x -axis horizontal. The Cr atom position is marked by a point at the extreme left of each diagram, with O_b to the right and O_a to the right and above. Plotted contours are ± 0.05 , ± 0.1 , ± 0.2 , and ± 0.3

Koopmans' theorem for a closed-shell system would give a more reliable ionization energy than would the analogous formula for an open-shell system. In the latter case a better estimate would be obtained by taking the difference between the SCF total energies before and after ionization and thus taking account of the reorganization energy. For the CrO_8^{3-} and CrO_8^{2-} ions, this leads to a value of 0.294 a.u. for the ionization energy of the unpaired electron, which value is rather satisfactorily 0.026 a.u. above the least-stable doubly-occupied orbital.

Contour diagrams for the valence molecular orbitals

³³ E. Clementi, *J. Chem. Phys.*, 1960, **36**, 33.

³⁴ E. Clementi, *J. Chem. Phys.*, 1963, **33**, 2248.

are presented in Figures 1—3. The eight valence orbitals of lowest energy, which are predominantly

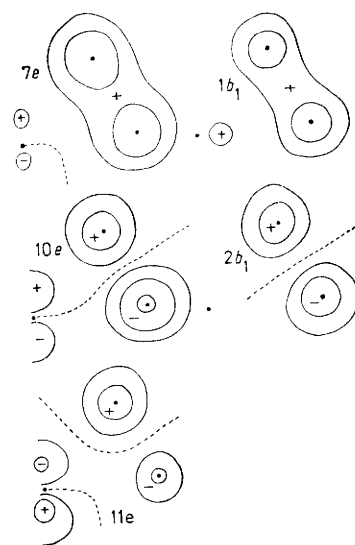


FIGURE 2 The CrO_8^{3-} molecular orbitals which are predominantly O-O π -bonding (above) and π -antibonding (below) perpendicular to the xz -plane. Contours are plotted at ± 0.5 , ± 0.1 , and ± 0.2 in a plane parallel to and 1 a.u. above the xz -plane. The projections of the atomic sites are marked as in Figure 1

O 2s in character, and the orbitals $1a_2$ and $2a_2$ which are respectively pure O-O π -bonding and π -antibonding perpendicular to the CrO_2 groups, are not shown. Contours are plotted either in the xz -plane or 1 a.u. above this plane. Since the molecular symmetry makes the four O_2 groups equivalent, contours are only plotted for one half of the xz -plane. The valence orbitals

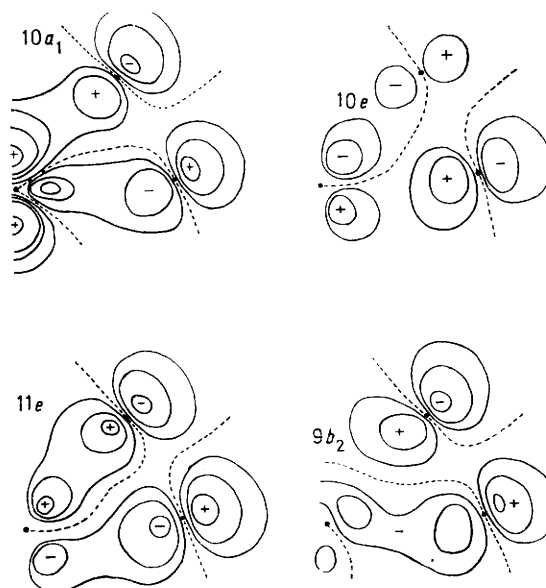


FIGURE 3 The CrO_8^{3-} molecular orbitals which are predominantly O-O π -antibonding and lie in the xz -plane. Contours are plotted at ± 0.5 , ± 0.1 , ± 0.2 , and ± 0.3 in the xz -plane, with the atomic sites marked as in Figure 1

can be conveniently classified by the contribution each makes to the O-O bonding.

(a) O-O σ -Bonds. These are orbitals $9a_1$, $8b_2$, and $9e$. They are not pure σ -orbitals because there is a small amount of mixing with the O-O π -bonding orbitals which have the same symmetry. Orbital $9a_1$ is the most stable, containing some Cr $4s$ and $3d_{z^2}$ components contributing to a small amount of Cr-O_a π -overlap and Cr-O_b σ -overlap. The orbital $8b_2$ has negligible Cr components, whilst $9e$ has a Cr $3d_{xz}$ component which allows some Cr-O_a σ -bonding.

(b) O-O π -Bonds, in the CrO₂ plane. These are orbitals $8a_1$, $7b_2$, and $8e$. These orbitals all have large Cr components and make considerable contributions to the Cr-O σ -bonding. The metal orbitals contributing the most to this bonding are respectively $4s(8a_1)$, $3d_{x^2-y^2}(7b_2)$, and $3d_{xz}(8e)$. The bonding most closely resembles the Chatt-Dewar⁵ scheme of σ donation from a filled π -orbital to a vacant metal orbital proposed by Tuck and Walters,¹⁰ although in the $8e$ orbital the overlap regions lies mainly between Cr and O_a. The slight admixture of the O-O σ -bonding orbitals of the same symmetry has apparently facilitated Cr-O overlap, and this overlap has made the π -orbitals more stable than the σ -orbitals, contrary to the ordering in the oxygen molecule.

(c) O-O π -Bonds, perpendicular to the CrO₂ plane. These are orbitals $7e$, $1b_1$, and $1a_2$. There are no metal orbitals of a_2 symmetry, but small contributions of the Cr orbitals $4p_x$ and $3d_{xz}$ to $7e$ and of $3d_{xy}$ to $1b_1$ lead to some delocalization of these π -orbitals towards the chromium atom. In addition the orbital $7e$ is stabilized by the small amount of O-O and Cr-O_a σ -bonding and Cr-O_b π -bonding that it exhibits in the xz -plane, involving the Cr $3d_{xz}$ orbital.

(d) O-O π^* In the CrO₂ plane. These are orbitals $10a_1$, $10e$, $11e$, and $9b_2$. The orbital $10e$ is predominantly O-O π -antibonding perpendicular to the CrO₂ plane, but it does have a significant in-plane π^* component, while $11e$ is predominantly π -antibonding in the CrO₂ plane, with a smaller π^* component perpendicular to this plane. The molecular orbitals $10a_1$, $10e$, and $11e$ each exhibit considerable Cr-O σ -bonding character, occurring through overlap of the Cr $3d_{z^2}$ ($10a_1$) and $3d_{xz}$ and $4p_x$ ($10e$ and $11e$) orbitals. This is the overlap of metal orbitals of π -symmetry with ligand π -antibonding orbitals that supplements the ligand-metal σ -bond in the Chatt-Dewar model.⁵ Of course, in the Chatt-Dewar model for metal-olefin complexes the ligand π^* orbitals are initially empty, and on complex formation there is back donation from filled orbitals of π -symmetry on the metal atom. In the CrO₈³⁻, considered as a peroxide complex of Cr^V, both the ligand π and π^* orbitals are initially occupied and all the bonding electrons apparently originate on the ligands. However, this formalistic view of the bonding should not be allowed to obscure the fact that, regardless of the origin of the bonding electrons, both components of a Chatt-Dewar bonding scheme are present in the

molecular ion, and the metal atom, far from carrying a charge of +5, is revealed as being fractionally negatively charged by the population analysis (Table 4). The

TABLE 4
Valence orbital populations

Cr		O _a	
$3d_{xy}$	1.020	$2s$	1.853
$3d_{yz}$	0.525	$2p_r$	1.333
$3d_{xz}$	0.525	$2p_i$	1.927
$3d_{x^2-y^2}$	0.346	$2p_z$	1.202
$3d_{z^2}$	0.655	O _b	
$4s$	0.709	$2s$	1.865
$4p_x$	0.968	$2p_r$	1.359
$4p_y$	0.968	$2p_i$	1.951
$4p_z$	1.032	$2p_z$	1.089
		Total Populations	
Cr	24.716	O _a	8.311
		O _b	8.260

orbital $9b_2$ shows only Cr-O_b σ -bonding involving the metal $3d_{x^2-y^2}$ atomic orbital. We note that, as could be

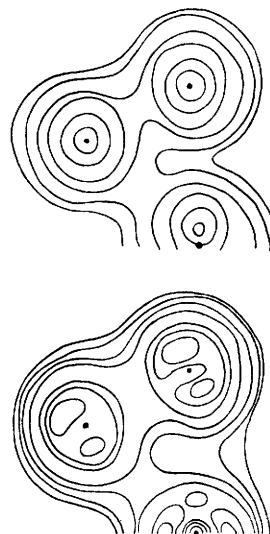


FIGURE 4 Total density diagrams for the CrO₈³⁻ valence molecular orbitals $8a_1$ through $3b_1$. Contours are plotted at 0.01, 0.02, 0.06, 0.1, 0.2, 0.3, 0.5 electrons in the xz -plane (right) and in a plane 1 a.u. above this (left)

predicted from the directional character of the O-O π -antibonding orbitals, the maximum overlap density for these Cr-O σ -bonds lies outside the CrO₂ triangle, making these bonds effectively slightly bent.

(e) O-O π^* Perpendicular to the CrO₂ plane. These are the orbitals $10e$, $2a_2$, $2b_1$, and $11e$, the components of the e orbitals formed from atomic orbitals antisymmetric with respect to the CrO₂ plane being involved in each case. The $10e$ orbital is weakly Cr-O π -bonding through participation of the Cr $3d_{xy}$ orbital, and $11e$ is antibonding in the same way. There is no Cr atomic orbital component in either the $2a_2$ or $2b_1$ orbitals.

In Figure 4 are shown the total valence orbital density contours both in the plane of a CrO₂ group and 1 a.u. above this plane. These diagrams sum the contribution to the bonding made by the molecular orbitals $8a_1$ to $3b_1$. It can be seen that there is slightly more

electron density in the overlap region between Cr and O_a than between Cr and O_b (as predicted by Ibers and Swalen¹¹). This agrees with the crystal structure data which show Cr-O_a to be significantly shorter than Cr-O_b.

The bonding in the O₂ part of the molecule is clearly based on that in the peroxide ion, for it is possible to identify molecular orbitals with major components which are respectively the σ , the two π , and the two π^* orbitals of the peroxide ion. However, the population analysis indicates that each O₂ group carries a negative charge of only *ca.* 0.6 electrons so there is obviously a considerable Cr atomic orbital component in some of these molecular orbitals. Inspection of the figures suggests that the bulk of the Cr-O bonding arises from overlap of Cr atomic orbitals with the O-O in-plane π -bonding density, and with the in-plane π -antibonding density. These are the two modes of metal-ligand bonding that constitute the Chatt-Dewar scheme. Additionally, there is a small amount of π -overlap between the Cr orbitals and the O-O out-of-plane

π -density. It is not possible to assess the effect upon the O-O bond strength of the withdrawal of both π and π^* electron density from the oxygen atoms towards the Cr. The O-O bond length in CrO₈³⁻ should be something like that observed in the peroxide ion, and the value of 1.405 (± 0.039) Å observed by Swalen and Ibers suggests that the O-O π -antibonding electrons are more strongly involved in Cr-O bonding than the π -bonding electrons. A comparison of Figures 1 and 3 suggests that this might be true, but no quantitative estimate of the difference is available. In any event, the O-O length in the peroxide ion (1.49 Å) is scarcely significantly greater than the observed value in CrO₈³⁻ in view of the estimated error on the latter value.

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