

On the Geometrical and Electronic Structure of the Hexahydroxochromate(III) Anion*

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Restricted Hartree–Fock and ligand-field configuration interaction calculations have been made on two structures of the $[\text{Cr}(\text{OH})_6]^{3-}$ anion. The bent structure (bond angle for the CrOH fragments 109°) was found in all circumstances to be significantly more stable than the O_h conformation (all CrOH fragments linear). The electronic effects within the anion are predominant and favour the bent structure, although the electrostatic repulsive interaction of the central cluster with the second co-ordination sphere favours the linear structure. The calculated ligand-field transitions predict a relatively small trigonal splitting of the T states (1500 cm^{-1}), the S_6 structure exhibiting a better agreement with the experimental transition energies.

In a recent paper Jacobs and Bock¹ reported the synthesis and structural characterization of $\text{K}_3[\text{Cr}(\text{OH})_6]$. Although the location of H atoms from X-ray measurements is notoriously difficult, the authors suggest a bent metal–ligand bond with a Cr–O–H angle of 109° , leading to an S_6 site symmetry for $[\text{Cr}(\text{OH})_6]^{3-}$. This angle was taken to be an indication of sp^3 hybridization of the oxygen atoms. The authors rationalized the overall stability of the S_6 structure, with respect to the alternative octahedral structure with linear bonds, in terms of interactions between $[\text{Cr}(\text{OH})_6]^{3-}$ and the second co-ordination sphere, whereas the intramolecular hydrogen bonds are thought to be weak and only of secondary importance. Although several groups^{2–5} have reported non-linear metal OH bonds, the experimental spectrum of $\text{K}_3[\text{Cr}(\text{OH})_6]$ does not reflect significant deviations from octahedral symmetry;⁶ it has to be conceded, however, that the reported spectra (KBr discs at room temperature) could hardly be expected to exhibit serious departures from O_h symmetry.

The purpose of the present report is three-fold: (i) to compare the relative stabilities of the O_h and S_6 structures on the basis of *ab initio* calculations; (ii) to determine the dominant factors favouring the most stable geometry; and (iii) to examine the influence of the Cr–O–H bond angle on the ligand-field spectrum.

Computational Procedure

The calculations were carried out both at the open-shell restricted Hartree–Fock (RHF) level and at a limited configuration interaction (CI) level. The Hartree–Fock orbitals were generated from Roothaan's double-Hamiltonian formalism⁷ for the ground state of $[\text{Cr}(\text{OH})_6]^{3-}$ and for the configuration average of all d^3 states.⁸ Using the latter (frozen) orbitals a configuration interaction was carried out for all ligand-field states (including the ground state). For ionic complexes these FRAV-LFCI (frozen average ligand-field configuration interaction) calculations yield transition energies that are comparable with a CASSCF (complete active space self-consistent field) calculation using three active electrons in the d shells.⁹

The basis set for chromium was obtained by a further contraction of the modified Wachters set proposed in a previous paper.¹⁰ In order to preserve the quality of the set, one s and two p primitives had to be duplicated in different contracted

gaussian-type functions, resulting in a non-segmented basis set. A well balanced description of the entire molecule requires a (9s5p/4s3p) basis set for oxygen and (4s/3s) for hydrogen. Due to the negative charge of the oxygen atom in the complex, primitives for the O^- anion were used,¹¹ while for the hydrogen atom the original Huzinaga basis set is appropriate.¹²

Since the O–Cr–O bond angles deviate by only 0.35° from 120 or 90° , the CrO_6 cluster was taken to be perfectly octahedral, with the experimental¹ Cr–O bond length of 2.005 \AA . The hydrogen atoms were located at 0.75 \AA from O, either in a linear CrOH arrangement (for the octahedron) or at a Cr–O–H bond angle of 109° as reported¹ and a dihedral $\text{HO}\cdots\text{CrO}$ angle of 26.09° (S_6 symmetry).¹ These (slightly) idealized O_h and S_6 structures were obtained from the average values of the reported bond angles and distances. The described procedure is somewhat similar to the method of Halpin and Hall¹³ for determining the hydride locations in transition-metal systems.

Results and Discussion

Geometry of the Ground State.—At the open-shell RHF level of approximation the $(d\pi)^3$ quartet ground state of the S_6 structure (with bent bonds) is found to be at $-1495.275\ 12\ E_h$, or 78 kcal mol^{-1} more stable than the ${}^4A_{2g}(d\pi^3)$ octahedral structure with linear CrOH bonds; this corresponds to a surprisingly large bending stabilization of 13 kcal mol^{-1} per metal–ligand bond.

In order to test the hypothesis advanced by Jacobs and Bock¹ the RHF calculation was also carried out in a point-charge field, simulating the crystal environment of the $[\text{Cr}(\text{OH})_6]^{3-}$ ion. The eighteen K^+ and the eight H^+ ions of the second co-ordination sphere were included. For both geometries point charges were placed at the experimentally determined positions.¹ The charge on the potassium ions was set equal to $+1$, for hydrogen to $+0.29$ (on the basis of a Mulliken population analysis). The incorporation of the counter ions confirms that the S_6 structure is the more stable molecule, but it reduces the energy difference between both geometries to 26 kcal mol^{-1} . This result clearly eliminates the crystal environment as the ultimate cause of the bond bending, since the introduction of the second co-ordination sphere apparently favours the linear structure by more than 8 kcal mol^{-1} and per bond.

Origin of Bond Bending.—From the above results, the origin of the bond bending apparently must lie in the electronic structure of the $[\text{Cr}(\text{OH})_6]^{3-}$ entity itself. Table 1 shows the result of a Mulliken population analysis of the ground states of

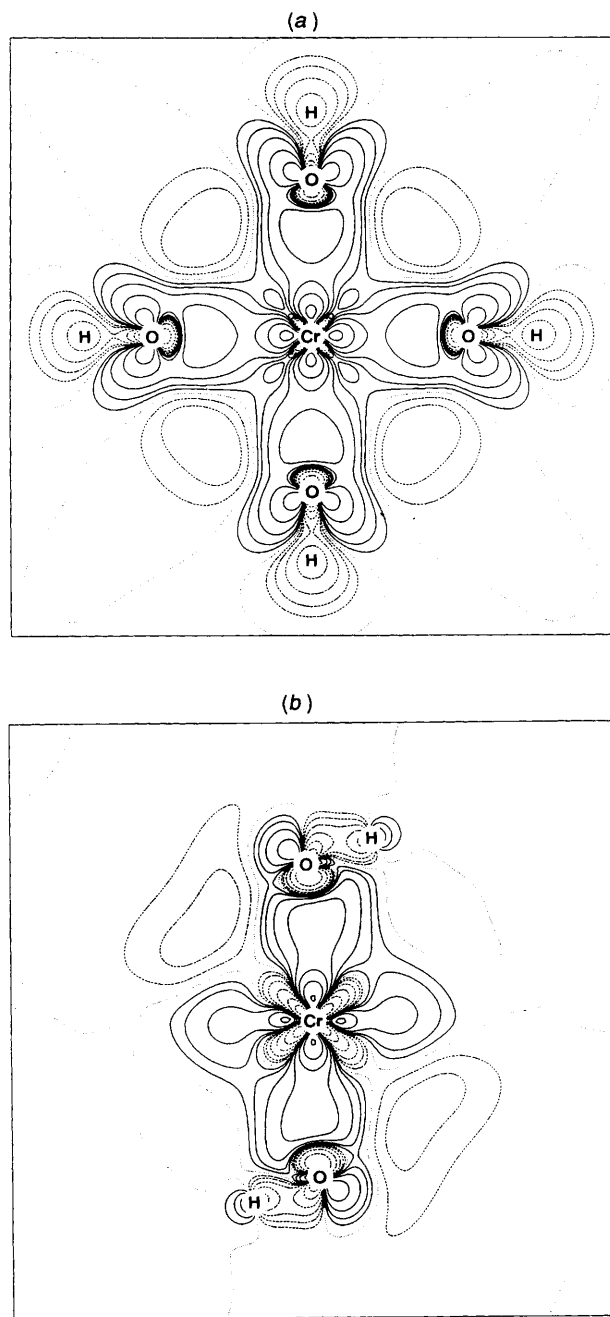
* Non-SI units employed: cal = 4.184 J , $E_h \approx 4.36 \times 10^{-18}\text{ J}$, au $\approx 5.291\ 77 \times 10^{-11}\text{ m}$.

Table 1 Atomic charges based on a Mulliken population analysis of $[\text{Cr}(\text{OH})_6]^{3-}$ in both geometries in their quartet ground states

	O_h		S_6	
Cr	+3.030		+2.380	
O	-1.240	} -1.007	-1.190	} -0.897
H	+0.233		+0.293	

Table 2 Comparison of the experimental and the calculated (RHF-LFCI) energies (in cm^{-1}) of the ligand-field transitions of $[\text{Cr}(\text{OH})_6]^{3-}$ in O_h and S_6 symmetries

Excited state	O_h	S_6	Experiment
${}^4\text{T}_{2g}$ ${}^4\text{A}_g$	9 353	14 209	16 900
${}^4\text{T}_{2g}$ ${}^4\text{E}_g$		15 402	
${}^4\text{T}_{1g}$ ${}^4\text{A}_g$	15 698	22 799	26 300
${}^4\text{T}_{1g}$ ${}^4\text{E}_g$		24 075	
${}^2\text{E}_g$ ${}^2\text{E}_g$	19 119	18 746	
${}^2\text{T}_{1g}$ ${}^2\text{A}_g$	20 093	20 177	
${}^2\text{T}_{1g}$ ${}^2\text{E}_g$		20 181	
${}^2\text{T}_{2g}$ ${}^2\text{A}_g$	25 706	27 780	
${}^2\text{T}_{2g}$ ${}^2\text{E}_g$		28 001	
${}^4\text{T}_{1g}$ ${}^4\text{A}_g$	28 609	35 618	
${}^4\text{T}_{1g}$ ${}^4\text{E}_g$		38 292	

**Fig. 1** Total density difference plots for the O_h (a) and S_6 (b) structures of $[\text{Cr}(\text{OH})_6]^{3-}$: $\Delta\rho = \rho(\text{complex; quartet ground state}) - \rho(\text{metal ion; } {}^4\text{A}_{2g}) - \rho(\text{non-interacting ligand cluster})$. The contour values are 0.0, ± 0.0025 , ± 0.005 , ± 0.01 , ± 0.02 , ± 0.04 and ± 0.08 au. In the octahedral case, the plane contains four hydroxyl ligands; in the S_6 case the plane of the section contains only two hydroxyl ligands (the latter section is more relevant than an alternative containing four oxygen atoms but no hydrogens). Full lines indicate regions where the electron density increases upon bond formation, dashed lines to an electron decrease and dotted lines correspond to nodal contours

the two structures. It follows that the S_6 stabilization can be thought of as being composed of an electrostatic contribution and of a charge-transfer contribution. From a purely electrostatic point of view the bending of the CrOH bonds is favoured as the positive hydrogen atoms are allowed to approach two of the neighbouring negative oxygen atoms, leading to incipient hydrogen bonds ($\text{H} \cdots \text{O}$ distances 2.65 and 2.89 Å).

The most obvious feature of Table 1, however, is the significant charge transfer from the ligands to the metal upon CrOH bending. At first sight this phenomenon appears somewhat counterintuitive, since the linearly co-ordinated ligand is supposed to be both a strong π donor and a stronger σ (sp) donor than the same ligand in a bent configuration, the latter usually being associated with sp^3 hybridization. Apparently however the bending mechanism, allowing a mixed σ and π interaction between metal and ligands, represents a more efficient electron-transfer channel; both the d_σ and the d_π orbitals of chromium are characterized by increased population. In S_6 the chromium d_σ orbitals contain 0.2 electrons more than in O_h , whereas the d_π population increases by more than 0.4 electrons.

Fig. 1 shows total density difference plots upon bond formation in the O_h and the S_6 structures. The density build-up in the Cr–O region is definitely more pronounced in Fig. 1(b) representing the S_6 molecule. As a consequence of the enhanced electron population on the metal, the d_π orbitals will tend to reduce the increased interelectronic repulsion by expanding, as witnessed by the negative density contours of the d_π region close to the chromium nucleus; in Fig. 1(a), describing the bonding phenomenon in the octahedral complex, the corresponding negative density contours are much less pronounced.

Ligand-field Spectrum.—The ligand-field spectrum for both structures has been calculated at the FRAV-LFCI level of approximation. This is the minimum level of sophistication that allows a meaningful comparison with experiment. Indeed, at the Hartree–Fock level, one is forced to use specific configuration specifications, which, at least in S_6 , neglect the interaction between very close-lying excited states; neglecting these interactions would not allow for a correct correlation between S_6 and O_h states. Even if one includes LFCI, the results cannot be expected to be quantitatively correct, but at least the qualitative features of the different states should be described properly. The remaining correlation errors can be expected to be quite comparable in the two structures, and a semiquantitative comparison with experiment should be possible.

Fig. 2 shows the state correlation diagram for the two relevant structures, while Table 2 details the numerical values of the different transitions. The most salient point is the different behaviour of the spin-forbidden and the -allowed transitions. In the octahedron the doublet states arise from the same predominant t_{2g}^3 configuration as the ground state, and to the extent that a one-electron configuration picture is appropriate, each of the three t_{2g} orbitals being occupied by precisely one

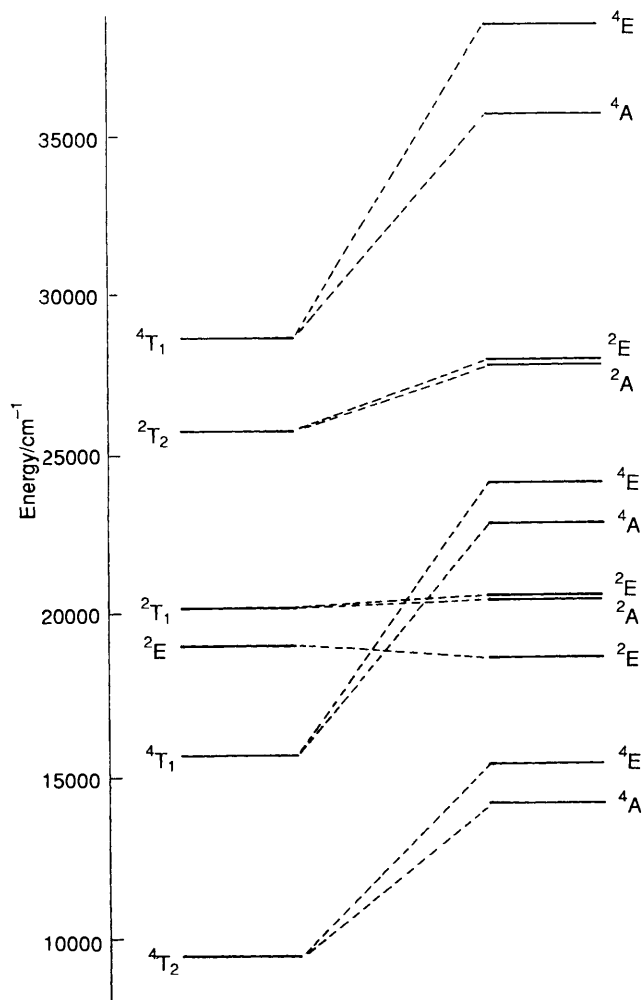


Fig. 2 State correlation diagram showing the effect of bond bending on the FRAV-LFCI energies of all t^3 and quartet states. The energies of the quartet ground states of both structures were set equal to zero. All g subscripts have been omitted

electron.¹⁴ The configuration interaction within the ligand-field manifold (LFCI) will impose very nearly the same properties on the S_6 doublets as on the O_h doublets. As a consequence, the trigonal splitting of the doublet states is predicted to be very small, since the t_{2g} orbital splitting (calculated at $\approx 2500 \text{ cm}^{-1}$) can be expected to be essentially irrelevant; this is exactly the situation described by Fig. 2 and Table 2. Also the overall position of the doublets does not change very much upon bond bending.

This is in marked contrast to the behaviour of the quartet states, characterized by rather large energy shifts and correspondingly larger trigonal splittings in going from O_h to S_6 . This behaviour is obviously related to the fact that all quartet-quartet transitions correspond to $d_\pi \rightarrow d_\sigma$ transitions. At the orbital level, the $d_\sigma-d_\pi$ splitting increases from $\approx 9400 \text{ cm}^{-1}$ in O_h to 14 650 and 17 150 cm^{-1} . Comparable energy differences are found at the state level (Fig. 2, Table 2).

The calculated trigonal-state splittings of the relevant excited quartets are too small to be observable in the broad d-d bands of the spectrum. The *ab initio* results do suggest, however, that the observed bands are definitely more compatible with the S_6 bent structure than with the octahedron. This fact should be

regarded as an indirect confirmation of the bent structure of the $[\text{Cr}(\text{OH})_6]^{3-}$ molecule in the crystal.

Conclusion

In agreement with the X-ray study, our present RHF and FRAV-LFCI calculations point to a bent structure for the $[\text{Cr}(\text{OH})_6]^{3-}$ complex. This follows directly from the comparison of the total energies of the ground states of both conformations, and indirectly from a comparison of the experimental band position and the calculated transition energies for the O_h and S_6 structure respectively. In order to obtain an exact structure for $[\text{Cr}(\text{OH})_6]^{3-}$ a complete optimization, including the second co-ordination sphere, at a higher level of approximation (CASSCF-MRCI) would be needed. For the present, these calculations are hardly feasible.

As for the origin of the S_6 geometry of the anion, our conclusions differ from those of ref. 1. Only the electronic effects within the $[\text{Cr}(\text{OH})_6]^{3-}$ entity are to be held responsible for the bent structure of the molecule. The repulsive interactions among the first and second co-ordination spheres, the latter represented as point charges, favour the O_h structure, but are not large enough to overcome the electronic effects.

In spite of the rather large shifts of the quartet transitions, the electronic structure of the chromium(III) ion in this highly ionic molecule can fairly well be considered as octahedral, the trigonal splitting of the T levels amounting only to about 1500 cm^{-1} , justifying the usage of the O_h microsymmetry to describe the ligand-field spectrum. Even if one takes into account the limitations of the FRAV-LFCI method, our calculations suggest that the ${}^4T_{1g}(\text{F})$ transition may not be situated at 26 300 cm^{-1} as previously proposed on the basis of the appearance of a weak shoulder in the experimental spectrum, but at a somewhat lower energy. This would also lead to a less extreme Racah parameter B .

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