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Ab Initio Calculations on the Sulfite Ion, SO_3^{2-} , and Hydrogen Sulfite Ion, HSO_3^- or SO_2OH^-

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Ab initio calculations on the sulfite and hydrogen sulfite ions (HSO_3^- and SO_2OH^-) are presented. Geometry optimizations have been performed on all the ions, and the surroundings of the ions, SO_3^{2-} and HSO_3^- , in the solid state have been accounted for by incorporating the crystal field in the calculations. The mechanism behind the shortening of the S-O bond in HSO_3^- as compared with SO_3^{2-} was confirmed to be a transformation of an antibonding into a nonbonding orbital upon protonation. The isomers HSO_3^- and SO_2OH^- were found to be of comparable energy. The very long S-OH bond (1.716 Å) found indicates the system to be assembled from comparatively weakly interacting species of SO_2 and OH^- .

Introduction

The $\text{H}_2\text{O}-\text{SO}_2-\text{O}_2$ system is of great interest for several important processes, e.g., SO_2 -induced steel corrosion, SO_2 removal from flue gas from coal and oil combustors, and atmospheric oxidation of SO_2 to H_2SO_4 with environmental acidification as a result. The reaction mechanisms involved are not well understood, especially the oxidation step S(IV)-S(VI), which is considered to be rate determining for processes such as mentioned above.

We believe that the polarization of the sulfur(IV) characteristic electron pair in different media is important for sulfite chemistry. Therefore, we have commenced a series of ab initio calculations, and this work comprises calculations on SO_3^{2-} , HSO_3^- , and *trans*- and *cis*- SO_2OH^- . For the first two ions crystal structure determinations are available and the influence of the crystal field has been evaluated.

During the course of this investigation a study comprising ab initio MO calculations for oxides, oxyacids, and oxyanions of S(IV) and S(VI) was published by Baird and Taylor.^{2a} In the present work, we have used more elaborate basis sets, and we have also investigated the electrostatic effects on the HSO_3^- ion of a surrounding crystal (when applicable). The agreement between the fully comparable species, i.e. free SO_3^{2-} and HSO_3^- , is however fairly good, although the aims of the two studies were somewhat different.

In the present study we have primarily addressed two problems concerning the hydrogen sulfite ion, the solutions of which are amenable with a restricted computational effort. The first concerns the difference in structure between the sulfite and the hydrogen sulfite ion. This specific problem has been addressed with semiempirical methods for the free ion,^{2b} and the tentative explanation is that an antibonding S-O orbital becomes H-S bonding as a result of the protonation. (Although Baird and Taylor^{2a} have carried out geometry optimizations on the system, their aim did not concern this particular problem.) One of our aims in the present work is to investigate this phenomenon in further detail with use of proper ab initio techniques and to account for the surroundings of the ion in the solid state by incorporating the crystal field in the calculations.

The second problem concerns possible isomers of the SO_2OH^- ion, i.e. *cis*- and *trans*- SO_2OH^- , and their stability with respect to HSO_3^- . IR and Raman studies of solid salts and solutions have indicated the form HSO_3^- to be the more stable one for the ion.^{3,4} However, there is also spectroscopic evidence that the two forms exist in equilibrium in aqueous solutions.^{5,6} The first single-crystal structure determination of a compound containing the HSO_3^- ion has recently been

made.^{7,8} There are hitherto no resolved structures containing the isomer SO_2OH^- .

We have approached these problems on an independent-particle SCF level. Geometry optimizations of SO_3^{2-} and HSO_3^- were made with and without a crystal field, with use of ordinary numerical grid methods, while for SO_2OH^- we used the force field technique. In the case of SO_2OH^- there are no calculations with a crystal field since there is no known crystal structure containing this compound. It is evident that such calculations are only capable of giving indications. When energy differences of the order of a few kcal/mol are sought (if the energy differences are larger, the equilibrium would be such that essentially only one of the species would be found), CI effects and interactions with the medium are far from negligible. It is equally clear that some possibilities could be ruled out on the basis of SCF calculations alone.

MC-SCF calculations were also performed on the HSO_3^- ion in order to make sure that a dissociation mechanism was not effective, which might have rendered the SCF calculations meaningless.

The mechanism behind the shortening of the S-O bond in HSO_3^- as compared with SO_3^{2-} was confirmed to be a transformation of an antibonding into a nonbonding orbital upon protonation. The isomers HSO_3^- and SO_2OH^- were found to be of comparable energy. For the latter a very long S-OH bond was found, indicating the system to be assembled from comparatively weakly interacting species of SO_2 and OH^- . A long S-OH bond was also found by Baird and Taylor,^{2a} who point out that it corresponds to "expected" single sulfur-oxygen bond lengths.²² This fact may have implications regarding the chemistry of SO_2 in aqueous surroundings.

Computational Details

Three different methods were used for the calculations on the complex. For the first set of geometry optimizations on the ion with hydrogen bound to sulfur (HSO_3^-) and on the sulfite ion (SO_3^{2-}) only RHF calculations were used and the geometry was found from a numerical grid. MC-SCF calculations were used in order to confirm the results obtained on the RHF level, and force field methods were used for the geometry optimizations of the ion with hydrogen bound to oxygen rather than to sulfur (SO_2OH^-).

The basis sets employed were of double- ζ quality with one diffuse s function and a polarizing diffuse d function added on sulfur. Basis

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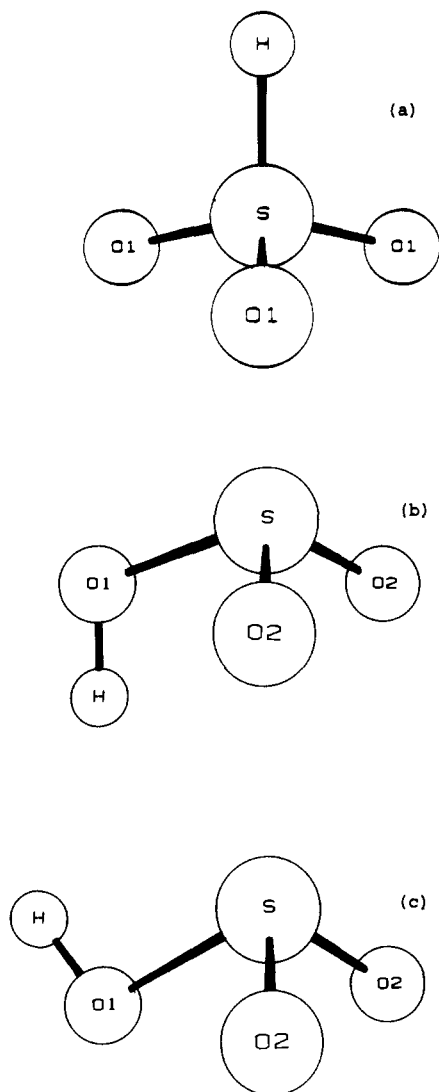


Figure 1. Molecular structure and labeling of atoms for the ions HSO_3^- (a), *cis*- SO_2OH^- (b), and *trans*- SO_2OH^- (c).

set parameters for sulfur were obtained from the 10s, 6p primitive set of Gaussians given by Roos and Siegbahn⁹ while van Duijneveldt's¹⁰ 7s, 3p, and 3s primitive sets were used for oxygen and hydrogen. The d exponent on sulfur was that recommended by Roos and Siegbahn.¹¹ The diffuse sulfur s exponent was chosen to be 0.064.

The MC-SCF calculations were carried out with two configurations corresponding to an occupied bonding S-H orbital (i.e. the ground state from the SCF calculations) and an occupied antibonding S-H orbital in order to obtain proper dissociation properties.

The effects of the crystalline surroundings on the binding of the ion were considered through the explicit inclusion of the electrostatic field produced by point charges in atomic positions throughout the (infinite) crystal.

The crystals selected for the present calculations were CsHSO_3 ,⁸ $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ ¹² (both structures have been solved with use of neutron diffraction techniques), and Na_2SO_3 .¹³ All atoms were included in the computation of the field, with charges on hydrogen, sulfur, and oxygen determined from SCF calculations (Cs and Na were assigned a charge of 1+). The field was calculated by using the Ewald technique,¹⁴ and the numerical potential thus obtained was approximated by a potential generated from a collection of point charges. This procedure, which has been successfully employed in several earlier

Table I. Computed and Experimental Geometries for SO_3^{2-} and HSO_3^-

	$r_{\text{S-O}}$, Å	$\alpha_{\text{O-S-O}}$, deg	$r_{\text{S-H}}$, Å
SO_3^{2-} , free ion	1.537	108.2	
Na_2SO_3	1.550	106.3	
Na_2SO_3^a (exptl)	1.504	105.69	
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$	1.562	105.2	
$\text{MgSO}_3 \cdot 6\text{H}_2\text{O}^b$ (exptl)	1.525	103.69	
HSO_3^- , free ion	1.468	114.2	1.364
CsHSO_3	1.473	112.9	1.341
CsHSO_3^c (exptl)	1.451	113.2	1.345

^a See ref 13. ^b See ref 12. ^c See ref 7 and 8.

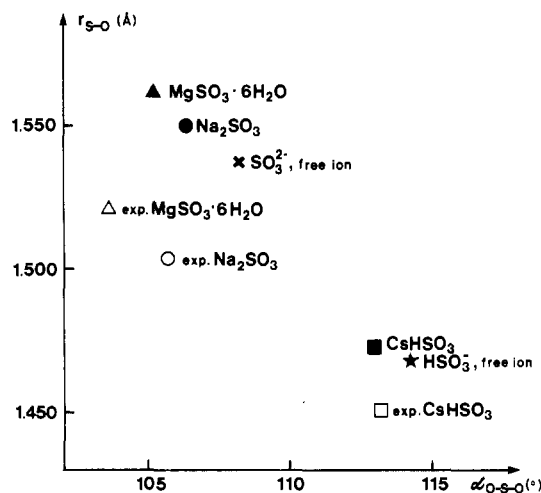


Figure 2. Comparison between calculated and experimental geometries for SO_3^{2-} and HSO_3^- .

studies,^{15,16} is described in detail in ref 17.

The calculations were, except for SO_2OH^- , carried out both with and without the stabilizing electrostatic field from the remaining crystal.

The geometry optimizations on SO_3^{2-} and HSO_3^- (with H attached to sulfur) were made with use of ordinary grid techniques, which were easy enough considering the limited number of degrees of freedom involved. For SO_2OH^- , however, the situation is different since even for the case of a symmetric species (one plane of symmetry containing S, one O, and H) there are seven degrees of freedom. For such a problem the force field approach is very convenient. One plane of symmetry containing the S and H and one oxygen atom was kept during these geometry optimizations. Two alternative geometries were investigated, one with the hydrogen in the *cis* and one with the hydrogen in the *trans* position relative to the two out-of-plane oxygen atoms (Figure 1). The stability of the lowest symmetrical state was investigated by calculating the energy generated by small symmetry-breaking nuclear displacements of the hydrogen and of the two out-of-plane oxygens.

Results and Discussion

A. SCF Results on SO_3^{2-} and HSO_3^- . Computed bond distances and angles of SO_3^{2-} and HSO_3^- with and without a stabilizing crystal field are shown in Table I and Figure 2 together with experimentally determined geometries of HSO_3^- and SO_3^{2-} from the appropriate crystals chosen.

Our calculations yield significantly longer bonds in SO_3^{2-} than in HSO_3^- in accordance with experimental results.

An orbital energy level diagram for SO_3^{2-} and for HSO_3^- is shown in Figure 3. The orbital energies are normalized such that the energies of the a_2 orbitals are made to coincide (an absolute comparison of the orbital energies is not meaningful because of the different total charges of the ions). From

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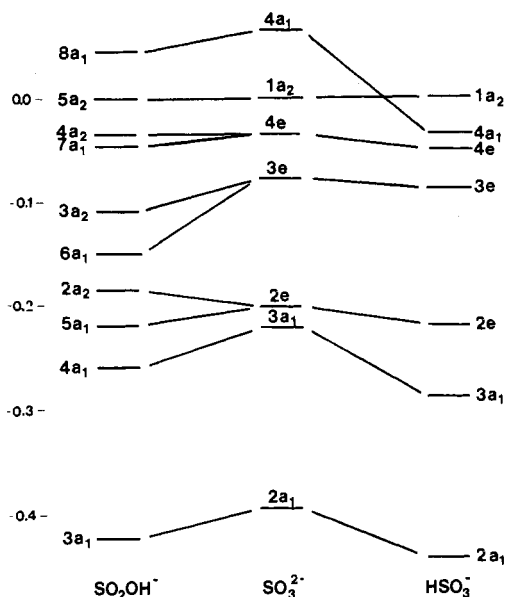


Figure 3. Orbital energy diagram for SO_2OH^- , SO_3^{2-} , and HSO_3^- . The energies (in au) are in both cases given relative to that for the a_2 orbital, which has been assigned zero energy.

Table II. Gross and (Pertinent) Overlap Populations for SO_3^{2-} and HSO_3^-

orbital or charge	SO_3^{2-}		HSO_3^-		HSO_3^-	
	(free) S-O	(in Na_2SO_3) S-O	(free) S-O	S-H	(in CsHSO_3) S-O	S-H
$1a_1$	0.184	0.183	0.198	0.016	0.196	0.013
$2a_1$	-0.060	-0.043	-0.058	0.416	-0.056	0.370
$3a_1$	0.143	0.136	0.083	0.106	0.091	0.094
$4a_1$	-0.250	-0.243	0.072	0.058	0.032	0.207
e	0.264	0.251	0.319		0.311	
e	0.064	0.084	0.013		0.027	
e	0.118	0.108	0.180		0.171	
e	0.100	0.095	0.126		0.121	
total	0.566	0.570	0.934	0.596	0.895	0.684
$q(\text{S})$	0.603+	0.741+	1.024+		0.991+	
$q(\text{O})$	0.868-	0.914-	0.670-		0.717-	
$q(\text{H})$			0.013-		0.161+	

Figure 3 it is clear that the orbitals of a_1 symmetry behave differently from those of a_2 and of e symmetry. While the latter retain their internal spacing almost exactly, the a_1 orbitals are shifted down, with different amounts relative to the a_2 and e orbitals. This is consistent with the fact that the orbitals of a_1 symmetry show substantial H character in several orbitals, notably $2a_1$ and $4a_1$.

The mechanism behind the shortening of the S-O bonds in HSO_3^- as compared with SO_3^{2-} is illustrated by the calculated gross and overlap populations presented in Table II. The $4a_1$ orbital, i.e. the highest occupied orbital in the a_1 symmetry, has for SO_3^{2-} a strongly antibonding character. When the ion gets protonated at the sulfur site, charge is withdrawn from S onto the H through the $2a_1$ orbital, which almost entirely describes the S-H bonding. As a result $4a_1$ turns into a nonbonding orbital of mixed O lone-pair and H character. This result is presumably caused by the LUMO (1s) of H^+ being very low in energy compared with the orbitals in SO_3^{2-} , the highest of which are positive in the absence of a stabilizing field. No unique H-S bonding orbital results from the calculations; it is however well-known that the invariance of RHF closed-shell wave functions in cases like the present (i.e. the low energy of the LUMO of H^+) often yields a delocalized description of bonds (localized bonds are usually obtained in MC-SCF calculations, where this invariance is removed). The remaining variations in overlap populations are essentially

insignificant, particularly since the calculations refer to slightly different geometries.

The effects of the crystal field on the system are a slight lengthening of the S-O bonds and a shortening of the S-H bond. This brings the computed S-H bond distance almost entirely in agreement with experiment. Computed angles come out satisfactorily, whereas the S-O bond distances do not, particularly for the SO_3^{2-} case. We find it somewhat surprising that the bond length in the latter system comes out as much as 0.05 Å too long from a one-determinantal SCF calculation of the present quality; e.g., the investigation by Carlsen¹⁸ on SO_2 would indicate that somewhat too short bond distances are to be expected from calculations of comparable quality.

From Table I and Figure 2 it follows that, although the error in the computed S-O bond distances is large for both $\text{MgSO}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_3 , the calculations correctly predict the relative importance of the crystal field in the two cases. This result makes it unlikely that the source of the error is to be found in the approximative treatment of the crystals. We have furthermore undertaken a series of calculations using much larger basis sets on both the oxygen and the sulfur centers. No significant changes of the computed S-O bond distances resulted from these calculations, and it thus seems unlikely that the error is caused by insufficient basis sets. A likely explanation is thus that correlation effects are important in this case, and this problem is now being further investigated.^{18b} At any rate, the deviations are not of any consequences as far as the conclusions of the present paper are concerned.

The effects of the field on the charge distribution and orbital energies are for the most part minor. There is a general shift in all orbital energies, but the internal spacing remain largely unaffected. The populations are somewhat more sensitive; the S-H bonding seems to become more shared between the $2a_1$ and the $4a_1$ orbitals in the crystal, and in general the charge distribution becomes more polarized. The rotations in occupied space, which generate the changes in the S-H bond characteristics, reveal little information, however, since closed SCF orbitals are free to rotate among themselves (see the discussion above).

B. MC-SCF Results on HSO_3^- . MC-SCF calculations were undertaken in order to investigate possible strong dissociated interactions involving configurations containing an occupied antibonding S-H orbital. SCF calculations may give good results for the wrong reasons, so to speak, when it comes to such quantities as bond lengths, due to forced dissociation limits.

In the present case such effects turn out to be unimportant both with and without the field. For the two-configurational calculation there is a lengthening of the S-H bond distance, 1.37 and 1.40 Å with and without the crystal field, respectively, pulling the calculated results somewhat away from the experimental result for the ion in the crystal. This was of course to be expected since inclusion of an antibonding configuration by necessity must lengthen the bonds in question if there is an effect at all. The effect in the crystal is somewhat smaller than in the free-ion case, which of course is due to a stabilizing effect of the field, which favors the ionic dissociation path. All effects are, however, minor.

C. Force Field Calculations on SO_2OH^- . The problem at hand was to compare the energetics of the two isomers (HSO_3^- and SO_2OH^-) on the SCF level in order to get an idea if the two ions are likely to exist in equilibrium or not.

The geometries of SO_2OH^- were determined only for the two symmetric cases with hydrogen cis and trans relative to

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Table III. Calculated Bond Distances (Å) and Angles (deg) for SO_2OH^- ^a

	$r_{\text{S-O}_1}$	$r_{\text{S-O}_2}$	$r_{\text{O}_1\text{-H}}$	$\alpha_{\text{S-O}_1\text{-H}}$	$\alpha_{\text{O}_2\text{-S-O}_1}$	$\alpha_{\text{O}_2\text{-S-O}_3}$
<i>cis</i> - SO_2OH^-	1.716	1.485	0.9814	109.8	102.2	112.0
<i>trans</i> - SO_2OH^-	1.732	1.482	0.9760	109.1	101.8	112.9

^a O_1 is the oxygen that has been protonated.

Table IV. Gross and Overlap Populations for SO_2OH^-

orbital	S-O ₁	S-O _{2,3}	O ₁ -H
1a ₁	0.116	0.186	0.048
2a ₁	0.066	0.087	0.151
3a ₁	0.161	-0.086	0.133
4a ₁	0.117	0.013	0.157
5a ₁	0.091	0.131	-0.014
6a ₁	-0.126	0.122	0.023
7a ₁	-0.014	0.105	0.002
8a ₁	-0.270	-0.183	-0.068
1a ₂	0.228	0.001	
2a ₂	0.102	-0.034	
3a ₂	0.004	0.052	
4a ₂	0.005	0.062	
5a ₂	-0.030	0.053	
total	0.225	0.736	0.428
q(S)	0.858+	q(O ₂)	0.713-
q(O ₁)	0.732-	q(H)	0.300+

the two oxygens on the opposite of the sulfur atom (see Figure 1). The possibility of nonsymmetric low-energy states was probed by making SCF calculations with the proton moved slightly out of plane and with the out-of-plane oxygens displaced asymmetrically. The results of the geometry optimizations are shown in Table III. We found no indications of lower energy configurations of the ion.

The *cis* form of the ion is found to be slightly more stable than the *trans* form. The energy difference, 7 kcal/mol, between the two isomers is too small to be conclusive. The lowest state of SO_2OH^- is calculated to be 4 kcal/mol lower than that of HSO_3^- , which indicates the existence of the equilibrium $\text{HSO}_3^-(\text{aq}) \rightleftharpoons \text{SO}_2\text{OH}^-(\text{aq})$. The crystallization of HSO_3^- in CsHSO_3 indicates that HSO_3^- is less soluble than SO_2OH^- in the polar aqueous solution. However, precautions are necessary; correlation might well contribute several kcal/mol to the computed energy difference and the solvent might stabilize either HSO_3^- or SO_2OH^- .

Baird and Taylor^{2a} found the SO_2OH^- ion to be higher in energy by 5 kcal/mol compared with the energy for HSO_3^- . These authors made, however, only geometry optimizations in a smaller basis set, and furthermore, their large basis set is inferior to ours. We thus conclude that our results are closer to a "correct" SCF result than theirs, although as pointed out above these small energy differences are at any rate of no consequence for the conclusions in this work.

The geometry of SO_2OH^- (see Table III) compared with that of SO_3^{2-} is notable, the distance between the sulfur and the protonated oxygen being markedly increased while the other two S-O bonds are shortened. Figure 3 shows the orbital energy diagram of SO_2OH^- as compared to the orbital energies of SO_3^{2-} (and HSO_3^-). The orbital that is most affected is an a₁ orbital, formerly a member of a degenerated e set on SO_3^{2-} . From Table IV it follows that this orbital is now antibonding (between the sulfur and the protonated oxygen), which is reflected in a lengthening of the S-OH bond. The O-H bond is described by the orbitals 2a₁, 3a₁, and 4a₁. The shortening of the two other S-O bonds is mainly due to less antibonding character in the HOMO. It should be noted that this orbital still has substantial antibonding character. The correlation of 4a₁ and 5a₁ is somewhat ambiguous since these orbitals correspond to a mixture of their pure components.

The chemical implications of the SO_2OH^- geometry are considerable. In an early Raman spectroscopic investigation

of aqueous sulfite solutions, Simon and Kriegsmann⁵ ascribed a line at 709 cm⁻¹ to a symmetric S-OH stretch frequency in SO_2OH^- . Nyberg and Larsson¹⁹ have plotted $\nu_{\text{S-O}}$ (900-1400 cm⁻¹) against $r_{\text{S-O}}$ (1.40-1.55 Å) for different sulfites, and although the S-OH bond in SO_2OH^- falls outside this range, their curve can be nicely extrapolated to $\nu_{\text{S-OH}} = 709$ cm⁻¹ and $r_{\text{S-OH}} = 1.72$ Å.

The S-OH bond is surprisingly long in SO_2OH^- , compared to Se-OH in SeO_2OH^- ²⁰ (Se-O = 1.66 Å, Se-OH = 1.75 Å, $\Delta = 0.1$ Å) and to S-OH in SO_3OH^- ²¹ (S-O = 1.45 Å, S-OH = 1.60 Å, $\Delta = 0.15$ Å). This implies that SO_2OH^- should be a reactive component in aqueous sulfite solutions. It is, for example, reasonable to assume that the dimerization to $\text{S}_2\text{O}_5^{2-}$ takes place via SO_2OH^- . Further, the important aqueous oxidation of SO_2 to SO_4^{2-} may well be dependent on SO_2OH^- . On the basis of the knowledge of the SO_2OH^- structure a variety of interesting theoretical and experimental investigations may be initiated.

Conclusions

Concerning the result of protonation of SO_3^{2-} at the sulfur center, the shortening of the S-O bonds stems from an antibonding S-O orbital becoming nonbonding. The hydrogen-sulfur bond is described in the RHF calculations by several orbitals in the a₁ symmetry because of the low energy of the LUMO of H⁺.

The implementation of the crystal field did provoke some movement of charges, yielding more "polar" ions (the hydrogen becomes positively charged and the negative charge on the oxygen increases), and the bonding properties of the orbital did change somewhat as concerns the sulfur-hydrogen bond. The orbital energies are almost uniformly shifted downward, and the bond distances and bond angles shift on the order of 0.02-0.03 Å and 2°, respectively. The angles and particularly the H-S bond distance were improved compared to the experimental values, while the S-O distances for SO_3^{2-} in particular becomes worse. The reason is probably correlation effects, and this is the subject of another study.

Two-configuration MC SCF calculations on HSO_3^- essentially confirmed that the SCF approximation is satisfactory for this system. The S-H bond distances became, not surprisingly, longer by 0.03 Å (which in fact makes agreement with experiment somewhat worse) and were completely described by a single MO.

Force field calculations on SO_2OH^- , i.e. SO_3^{2-} protonated at an oxygen center, indicated that HSO_3^- and SO_2OH^- might well exist in some equilibrium state with appreciable concentrations of both ions in the solution state. We find, contrary to Baird and Taylor,^{2a} the SO_2OH^- ion to be lower in energy than HSO_3^- . Although our calculations are somewhat more accurate than theirs, the energy differences are too small to be of significance considering possible CI and solution effects. The lowest energy configuration of SO_2OH^- was found to possess a plane of symmetry and have the proton in a *cis* position relative to the two out-of-plane oxygens.

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The SO_2OH^- geometry achieved may be used to enlighten the complicated chemistry in the $\text{SO}_2\text{-H}_2\text{O-O}_2$ system, primarily for the design of synthetic work to isolate compounds containing the SO_2OH^- ion.

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Molecular Orbital Study of Some Eight-Coordinate Sulfur Chelate Complexes of Molybdenum

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A number of molybdenum complexes involving the formal oxidation states Mo(IV) and Mo(V) have been studied by a self-consistent-field molecular orbital technique. All the complexes were of dodecahedral geometry and had eight sulfurs chelated to the central metal atom. In all, a series of five tetrakis complexes was studied, including the ligands dithiocarbamate (dtc), thioxanthate (txn), 1,1-dicyano-2,2-ethylenedithiolate (*i*-mnt), 1-cyano-1-carbomethoxy-2,2-ethylenedithiolate (ced), and 1,1-dicarbomethoxy-2,2-ethylenedithiolate (ded). The 4d orbitals were included on molybdenum, and the empty 3d levels on all sulfur atoms. The results show that the highest occupied molecular orbital in each case has over 90% metal d_{xy} character. Further, the energy of this orbital is linearly related to the reversible half-wave potentials for Mo(IV) \rightarrow Mo(V) and Mo(V) \rightarrow Mo(VI) oxidations of the complexes. A further irreversible oxidation observed experimentally also is closely related to the calculated energy levels. Relationships between the calculated results and Mo $3d_{5/2}$ X-ray photoelectron binding energies, EPR parameters, and charge-transfer absorption energies are discussed. Electrochemical and spectroscopic properties of these MoS_8 complexes can be understood in terms of a manifold of orbital energies that retain approximately constant spacings between one another and that move up or down in absolute energy in response to the charge donated or withdrawn by the ligands.

Introduction

Previous electrochemical and spectroscopic studies^{2,3} on the eight-coordinate molybdenum complexes formed with dithiocarbamate (dtc), thioxanthate (txn), 1,1-dicyano-2,2-ethylenedithiolate (*i*-mnt), 1-cyano-1-carbomethoxy-2,2-ethylenedithiolate (ced), and 1,1-dicarbomethoxy-2,2-ethylenedithiolate (ded) have revealed a large range and a regular trend in half-wave potentials for these compounds, which are strongly dependent on the nature of the ligand. Molybdenum 3d and sulfur 2p X-ray photoelectron (XPE) binding energies, measured for four of the complexes, also experience large shifts with changes in ligand structure and correlate well with $E_{1/2}$ values. On the other hand, charge-transfer absorption energies and Mo(V) EPR spectral properties change very little across this series of compounds. To rationalize, substantiate, and throw more light on these effects and their origins, we have carried out molecular orbital calculations on a series of such compounds. We have calculated the energy levels in the species, the eigenvectors that reveal the nature of the bonding and antibonding orbitals, and the electron population in each orbital and on each atom of the complex. From these results, we suggest a rationale of all the observed experimental trends in this series of complexes.

Method of Calculations

The complexes described contain a heavy metal (molybdenum) and ligands, which themselves contain many atoms. Overall, such calculations must encompass very large basis sets, even if the calculations are restricted to valence orbitals. Clearly, such complexes are beyond the scope of ab initio calculations, and we have considered it necessary

Table I. Input Data for Atoms

	exponents			VSIP, eV			repulsion integral, eV
	s	p	d	s	p	d	
H	1.000						17.00
C	1.550	1.325		19.44	10.67		15.60
N	1.875	1.650		25.58	13.19		18.87
O	2.200	1.975		32.38	15.85		22.14
S	1.967	1.517	0.833	20.52	10.78	1.80	13.81
Mo	1.060	0.560	2.290	7.10	3.92	4.30	6.37

and sufficient to carry out our calculations at the CNDO/INDO level. There have been one or two calculations on isolated complexes of this type at the extended Hückel level of theory⁴⁻⁶ but no systematic study of a series of compounds at the level that we have employed. The basic method of calculation follows closely that described previously.^{7,8} In our basis set we included 4d orbitals on molybdenum and empty 3d orbitals on all sulfur atoms. The basis sets for the other first-row atoms were the usual s and p groups. The input data for the calculations for all atoms are given in Table I. Since we were interested in the energetics of electron removal from both Mo(IV) and Mo(V) species, we have carried out separate calculations on each of these oxidation states for each ligand. Because of the size of the basis sets, we found it necessary to perform a larger-than-usual number of iterations to obtain self-consistency, and each of the calculations described extended to 30 evaluations and iterations of the density matrix. This ensured a satisfactory degree of self-consistency in the formal atomic charges.

The geometry around the molybdenum site was taken basically as dodecahedral,⁹ and the geometries of the complexes were all based

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