The $SO_2OH^-$ geometry achieved may be used to enlighten the complicated chemistry in the $SO_2$–$H_2O$–$O_2$ system, primarily for the design of synthetic work to isolate compounds containing the $SO_2OH^-$ ion.

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**Registry No.** $SO_3^{2-}$, 14265-45-3; $HSO_3^-$, 15181-46-1; S, 7704-34-9; $O_2$, 7782-44-7.

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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-carbethoxy-2,2-ethylenedithiolate (ced), and 1,1-dicarbethoxy-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) → Mo(V) and Mo(V) → 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constant spacings between one another and that move up or down in absolute energy in response to the charge donated or withdrawn by the ligands.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-carbethoxy-2,2-ethylenedithiolate (ced), and 1,1-dicarbethoxy-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 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 theory[4-6] 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.

**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 |

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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(1) (a) University of Strathclyde. (b) Florida Atlantic University. (c) Current address: Charles F. Kettering Research Laboratory, Yellow Springs, OH 45387.

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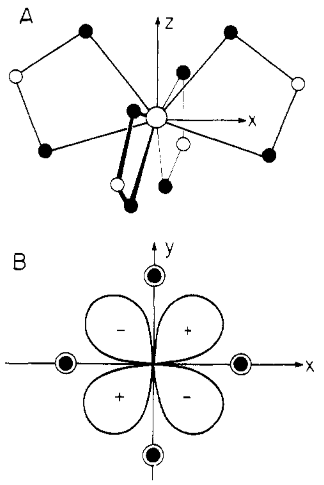

**Figure 1.** Geometry of the complexes (after ref 4a) illustrating (A) coordinating S atoms and (B) a Mo 4$d_{xy}$ orbital.

on the description of Nieuwpoort and Steggerda.[4a] Figure 1 illustrates this geometry for the dithiocarbamate case. The ligands present in the synthesized complexes contain ethyl groups substituted on nitrogen (in the case of dtc) and on COOH groups (in the cases of ced and ded). The sulfur of txn is substituted by a *tert*-butyl group. If these alkyl groups are included, the basis set for, e.g., the ded complex becomes unmanageably large; hence, in such cases we either have neglected the alkyl group altogether or have performed the calculation for the methyl derivative. The effects of these changes are discussed fully in context. We refer to the ligands as $R_2$dtc, Rtxn, Rced, and $R_2$ded, R being the relevant substituent.

A problem arises with molecular orbital calculations for charged species. The txn and dtc complexes are both positive ions (with Mo(V)) and neutral complexes (with Mo(IV)). However the ded, ced, and *i*-mnt complexes are 3– ions (with Mo(V)) and 4– ions (with Mo(IV)). Calculations on bare ions invariably yield eigenvalues that are linearly shifted in the energy scale because of the lack of counterion. This means that the eigenvalues of ions of different charge type cannot be directly compared. This can, in principle, be overcome by including appropriate counterions in the calculations, but in practice, unless the crystal structure is known, the inclusion of counterions is likely to be a somewhat arbitrary exercise. We have not pursued this course. We partially simulated the effect of the counterion by inclusion in the Hamiltonian of a spherically symmetrical potential—a Faraday cage—to shift the eigenvalues for the positive and negative ions in the appropriate directions in energy space. This is a valid procedure, but again, one cannot accurately reproduce the effect of different counterions (i.e., their geometrical extension in space and their symmetry), and in particular, the Faraday cage does not include any covalency effects. Thus, although eigenvalues for positive and negative ions are correctly shifted toward each other into the same energy range, results for the series of positive and negative ions cannot be completely brought together. In what follows we will compare the energy results for ions within their own particular subgroups and make reference from series to series in terms of differential results, e.g., the slope of a line on a graph etc. General trends can thus be correlated between the two series in a valid manner. Also, it should be stated that the charge distribution over the atoms is unaffected by the superimposition of the Faraday cage.

## Results and Discussion

Table II summarizes some of the calculated data. In this table are given the eigenvalues of the highest occupied molecular orbital (HOMO) and of those orbitals immediately adjacent to it, the Mo 4$d_{xy}$ atomic orbital coefficient appertaining to the HOMO, and the calculated formal charge on the molybdenum atom. As stated before, we included the empty 3d orbitals on sulfur in all the calculations. The result of this is not very marked in the HOMO region, as may be seen by comparing results for the *i*-mnt complex with and without S 3d orbitals (entries V and VI in Table II). The orbital energies of V and VI differ very little from one another, as do the formal atomic charges. However, it is necessary to include the sulfur 3d orbitals to obtain quantitative comparisons.

**Table II.** Calculated Data for Molybdenum Complexes

| no. | complex | orbital energies, eV: 2nd HOMO | HOMO | LUMO | $d_{xy}$ coeff | formal charge on Mo |
|---|---|---|---|---|---|---|
| | | Mo(V) Complexes | | | | |
| I | Mo($Me_2$dtc)$_4{}^+$ | −4.42 | −1.01 | 2.68 | 0.971 | 0.635+ |
| II | Mo(Ettxn)$_4{}^+$ | −5.01 | −1.66 | 2.02 | 0.967 | 0.698+ |
| III | Mo($H_2$ded)$_4{}^{3-}$ | −5.37 | −2.02 | 1.68 | 0.969 | 0.353+ |
| IV | Mo(Hced)$_4{}^{3-}$ | −5.42 | −2.07 | 1.63 | 0.968 | 0.324+ |
| V | Mo(*i*-mnt)$_4{}^{3-}$ | −5.54 | −2.20 | 1.49 | 0.967 | 0.280+ |
| VI | Mo(*i*-mnt)$_4{}^{3-\,a}$ | −5.69 | −2.46 | 1.14 | 0.973 | 0.324+ |
| | | Mo(IV) Complexes | | | | |
| VII | Mo($Me_2$dtc)$_4$ | −3.97 | −3.42 | 3.26 | 0.963 | 0.450+ |
| VIII | Mo(Ettxn)$_4$ | −4.50 | −3.94 | 2.71 | 0.956 | 0.521+ |
| IX | Mo($H_2$ded)$_4{}^{4-}$ | −4.94 | −4.45 | 2.21 | 0.960 | 0.201+ |
| X | Mo(Hced)$_4{}^{4-}$ | −5.11 | −4.62 | 2.03 | 0.959 | 0.166+ |
| XI | Mo(*i*-mnt)$_4{}^{4-}$ | −5.39 | −4.90 | 1.73 | 0.956 | 0.119+ |

[a] No d on S.

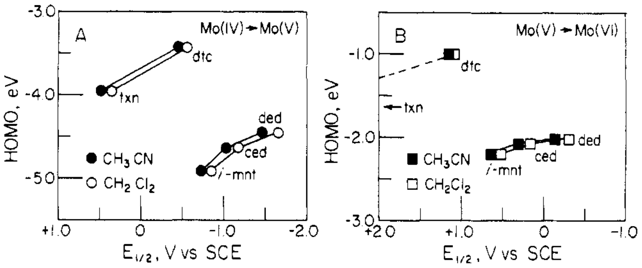

**Figure 2.** Plots of highest occupied orbital energy vs. $E_{1/2}$ for (A) Mo(IV) → Mo(V) oxidations and (B) Mo(V) → Mo(VI) oxidations.

**Correlations with Electrochemical Data.** Figure 2 shows graphs relating the energy of the HOMO in a particular complex to $E_{1/2}$, its electrochemical half-wave potential. Results for both Mo(IV) → Mo(V) and Mo(V) → Mo(VI) oxidations are shown. The two different lines in each case relate to experimental data measured in $CH_2Cl_2$ and $CH_3CN$.[2,3]

The results in Figure 2 illustrate a clear trend in orbital energies, which follows the expectation that greater electron-binding energies would cause $E_{1/2}$ values to become more positive. In Figure 2A (the Mo(V)/Mo(IV) couple), we also note that the slopes of the lines for the neutral complexes and the 4– ions are similar. However, the points for the *i*-mnt, ced, and ded complexes in Figure 2A,B, although following a consistent pattern, do not define a good straight line in either case. A straight-line plot for these points really is not expected since neither of our ded and ced model ligands contain ethyl groups substituted on the –COOH moieties, whereas the experimental data arise from the ethyl ester complexes. We expect that inclusion of alkyl groups on the –COOH moieties in the calculations would shift the energies of the highest occupied orbitals to lower absolute (i.e., more positive) values, and this may be checked by comparing the calculation for the Meced complex with that for Mo(Hced)$_4{}^{4-}$ itself. The highest occupied orbital of the latter is shifted from about −4.6 eV (for Hced) to about −4.0 eV for Meced. The methyl-substituted ded complex was too large for our calculational scheme, and hence, we do not have direct data for this, but clearly the energy of the HOMO would be shifted in the same sense as for Meced; moreover, the shifting will be more pronounced since there are more alkyl groups. Overall, we would expect a straight-line relationship to emerge.

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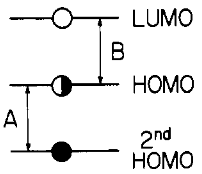

**Figure 3.** Pattern of orbital energies in the HOMO region.

Turning to Figure 2B (the Mo(VI)/Mo(V) couple), we note that the ethylenedithiolate complexes exhibit a relationship that is approximately linear and is arranged in the same sense as that for the Mo(V)/Mo(IV) couple. No comparison of slopes for 3− ions and 1+ species can be made because it has not been possible to observe electrochemical oxidation of a Mo(V)–txn complex.[2,3,10] However, this Mo(V) → Mo(VI) redox potential can be estimated from the difference in HOMO energies of $\mathrm{Mo(Ettxn)_4{}^+}$ and $\mathrm{Mo(Me_2dtc)_4{}^+}$ (Table II) and the slope of the line observed for the 3− ions in Figure 2B. Thus, we estimate the $E_{1/2}$ value for $\mathrm{Mo(txn)_4{}^+}$ oxidation to lie near 3.5 V vs. SCE.

**Properties of the Highest Occupied Orbital.** A remarkable property of the highest occupied orbital in all the cases considered is that it is almost exclusively metal centered, being constituted in all cases principally by the $d_{xy}$ orbital on molybdenum. This is a remarkable feature of a complex in which all orbitals of the central atom can be, from symmetry, involved in the bonding, and we believe it has considerable significance in explaining the properties of molybdenum in such site symmetries. To examine to what extent localization of the metal $d_{xy}$ orbital is peculiar to molybdenum, we carried out calculations based on complexes of similar geometry where the central atom lies in the same site symmetry, replacing molybdenum first with chromium and then with tungsten. Of course, there is no such chromium complex with which to make experimental comparisons, but our test aimed to discover whether the $d_{xy}$ orbital was similarly isolated in a chromium complex involving eight-coordinate site symmetry. On the other hand, tungsten complexes do exist that incorporate this site symmetry.[4,11] For brevity the results are not detailed here, but essentially, we found that for such a chromium complex the highest occupied orbital, although metal centered, involved linear combinations of the d orbitals and not one unique basis. For the tungsten complex, although the $d_{xy}$ orbital did lie as the highest occupied, the degree of localization on the metal was less than in the related molybdenum complex (the coefficient of the $d_{xy}$ orbital in the highest occupied orbital was 0.88). Hence, it seems that this virtually totally metal-centered orbital is a property most marked with molybdenum complexes.

The general pattern of orbital energies around the "central area" in the molybdenum complexes is shown in Figure 3. It is remarkable that the separations $A$ and $B$ in Figure 3, for both the molybdenum(IV) and molybdenum(V) complexes, remain sensibly constant over the entire series for a given Mo oxidation state. For molybdenum(IV), $A$ varies from 0.49 to 0.56 eV and $B$ from 6.63 to 6.68 eV, while for molybdenum(V) these separations encompass the range $A$ = 3.25–3.41 eV and $B$ = 3.68–3.70 eV. This does not mean, of course, that the levels lie at the same *absolute* energies in each complex; it already has been shown that the energy of the highest occupied orbital varies quite strongly with the type of chelating agent. Rather, it is found that the whole *manifold* of important orbital levels moves up or down in energy in response to the type of ligand; i.e., the manifold responds to whether the ligand tends to withdraw or supply electron density to the molybdenum atom.[12] A glance at Table II confirms that the charge on molybdenum varies quite strongly over the series, being in general more positive for the molybdenum(V) complexes. The orbital energy levels also show that it is the HOMO that is most affected in energy by the change from the Mo(V) to Mo(IV) complex. This is to be expected, since it is the most localized on molybdenum.

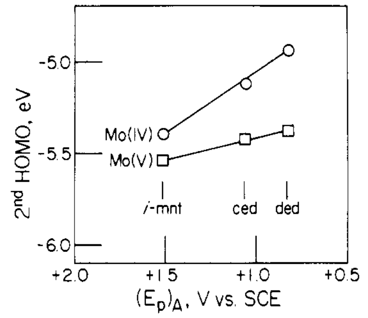

**Figure 4.** Plots of second highest occupied orbital energy vs. voltammetric peak potential for irreversible oxidation of $\mathrm{MoS_8}$ complexes in $\mathrm{CH_2Cl_2}$ (wave $A^2$): (○) Mo(IV) energies; (□) Mo(V) energies.

Electrochemical studies show that continuation of the voltammetric sweep to potentials more positive than the reversible Mo(IV) → Mo(V) and Mo(V) → Mo(VI) oxidations affords an additional irreversible oxidation of the ded, ced, and *i*-mnt complexes.[2,3] Figure 4 shows a plot of the potential for this oxidation (wave $A^2$) vs. the energy of the *second*-highest occupied orbital for each complex. The lines in Figure 4 show the correct trend of orbital energy with change in electrochemical parameter. However, the energy of the orbital that participates in this irreversible redox processes is far less sensitive to the formal oxidation state of the central atom. This result is consistent with this orbital having mixed metal–ligand character, a property that also rationalizes the chemical instability of the further oxidized species.

**Correlations with XPE Binding Energies.** It has previously been shown that the molybdenum core-electron binding energies in the isolable $\mathrm{Mo^VS_8}$ complexes correlate well with the $E_{1/2}$ values for these complexes.[3] Since the binding energy for a core electron in a given atom can be related empirically to the formal charge on that atom, we might expect that these XPE results should be directly relatable to the calculated formal charges on the molybdenum atom in the complexes. We have not, as yet, found such a direct correlation for the entire series of complexes (Table II) but believe this stems from our (necessary) noninclusion of all the alkyl groups on the ligands. The molybdenum charge is particularly sensitive to this feature, and small differences are involved. However, we do expect that the charge on the molybdenum atom, in general, controls both the $E_{1/2}$ values and the energies of the core electrons in the orbitals of the complex. This is completely consistent with the pattern we have established of there being a manifold of levels around the barycenter of the orbital series in which the orbitals retain an approximately constant relationship to each other while the entire manifold moves up and down in energy in response to the charge withdrawn or donated by the ligands.

**EPR Spectra.** The EPR spectra for this series of complexes can be interpreted on the basis that each Mo(V) complex has a free electron localized in a metal-centered orbital. It already has been shown that the highest occupied orbital in the Mo(V) complexes is localized on the molybdenum atom; this fits well

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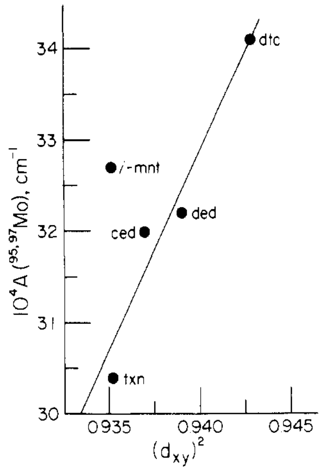

**Figure 5.** $^{95,97}$Mo hyperfine splitting constant vs. the square of the $d_{xy}$ coefficient.

qualitatively with the EPR observations. However, we may proceed further and compare the coefficients for the $d_{xy}$ orbital from complex to complex with the hyperfine splittings in the EPR spectral lines stemming from the $^{95}$Mo and $^{97}$Mo nuclei. The magnitudes of these splittings have been determined.[2,3] We would expect the splittings to increase in magnitude with increase in metal d character of the highest occupied orbital. Since the character of the highest occupied orbital is determined in each calculation, we can plot the *square* of the $d_{xy}$ coefficient (which determines the percentage d contribution) against the observed splitting constants. Figure 5 shows such a plot, and it can be seen that there is effectively a straight-line relationship between the splitting constant and the square of the $d_{xy}$ coefficient. Only the case of the *i*-mnt complex appears to be anomalous, and at present we can advance no reason for this deviation.

**Electronic Spectra.** The electronic absorption spectra of the complexes depend on the energy level sequences around the highest occupied and lowest unoccupied orbital regions; thus, it is germane to inquire whether any correlation should exist between these properties and $E_{1/2}$ values. Orbital levels alone are not sufficient to determine absorption energies, but where there is no orbital degeneracy and localization is strong (and hence configuration interaction is reduced), a qualitative result is reliable. The latter conditions apply to these complexes. One sees that the energy gaps are little changed from complex to complex, and hence, the electronic absorption spectra will not be as sensitive to ligand structure as are $E_{1/2}$ values and core-electron binding energies. This expectation is demonstrated by the charge-transfer absorptions of the ethylenedithiolate complexes, which correspond to the almost constant spacings *A* (for ligand → metal charge transfer) or *B* (for metal → ligand charge transfer) in Figure 3. Experimentally, the charge-transfer energies observed for Mo(V)- and Mo(VI)-ethylenedithiolate complexes[2,3] cover a range of $\leq 0.12$ eV, in agreement with the prediction that these properties are not highly sensitive to ligand structure. There are other recent observations,[13,14] which have been rationalized qualitatively on a similar basis, of families of structurally related transition-metal complexes exhibiting a large range in $E_{1/2}$ values but only small changes in electronic absorption energies.

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**Registry No.** I, 60120-38-9; II, 84623-25-6; III, 81642-89-9; IV, 81642-87-7; V, 81643-66-5; VII, 33850-23-6; VIII, 84623-26-7; IX, 82614-52-6; X, 81643-62-1; XI, 81643-61-0.

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# Some Reactions of Tetrakis($\mu$-acetato)dichromium(II) with Potentially Chelating Ligands: Two Unexpected Products

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Reactions of $Cr_2(O_2CCH_3)_4$, under mild conditions, with $NaOCH_2CH_2N(CH_3)_2$ and with $Na[B(C_2H_5)_2(2\text{-pyrazolyl})_2]$ have been examined, and crystalline products, **1** and **2**, respectively, have been isolated in good yields. In neither case did we find a simple substitution product. Compound **1** consists of $Cr_4(O_2CCH_3)_4(OCH_2CH_2NMe_2)_4$ molecules, which have crystallographic $\bar{4}$ ($S_4$) symmetry. Two $Cr_2(\mu\text{-}O_2CCH_3)_2$ units, in which the $O_2CC$ planes are approximately orthogonal and Cr–Cr = 2.531 (2) Å, form a bisphenoid of Cr atoms, and there is a square set of oxygen atoms (from $OCH_2CH_2NMe_2$ groups) between the upper and lower $Cr_2$ units. The N atoms are coordinated to the Cr atoms along the extensions of the Cr–Cr bonds. This compound crystallizes in space group $P4_2/n$ with two tetranuclear formula units in a unit cell of dimensions $a$ = 13.269 (2) Å, $c$ = 10.611 (2) Å, and $V$ = 1868 (1) Å$^3$. Compound **2** contains mononuclear $Cr((pz)_2BEt_2)_2$ molecules residing on crystallographic inversion centers. This bright orange, square-planar Cr(II) complex is air stable and crystallizes in space group $P2_1/c$ with the following unit cell parameters: $a$ = 10.154 (4) Å, $b$ = 8.507 (1) Å, $c$ = 13.624 (4) Å, $\beta$ = 93.30 (3)°, and $V$ = 1175 (1) Å$^3$. The Cr–N distances are identical within experimental error: 2.058 (4) and 2.061 (4) Å. The stability of the compound may be in part due to the fact that one ethyl group from each ligand is positioned above and below the $CrN_4$ coordination plane.

## Introduction

It is true generally that the reactions of compounds containing M$\equiv$M (triple) and M$\overset{4}{-}$M (quadruple) bonds may proceed either in conservative ways, i.e., with retention of the initial multiple bond, or in various nonconservative ways, i.e., with modification or outright loss of the initial M–M multiple bond.[1,2] The tendency for nonconservative reactions to occur

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