Molybdenum Binding Site Models for the Molybdenum Cofactor. Synthesis, Spectroscopic Characterization, and EHMO Analysis of $(NBu^n_4)Na[Mo(O_2CC(S)Ph_2)_3]$[†]

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The reaction of the *cis*-dioxo Mo(VI) complex $[MoO_2(O_2CC(S)Ph_2)_2]^{2-}$ (**1**), having two coordinated thiobenzilate ligands, with an excess of thiobenzilic acid yields the monomeric monooxo Mo(V) complex $[MoO(O_2CC(S)Ph_2)_2]^-$ (**2**), which is stable under these acidic conditions. However, partial neutralization of the thiobenzilic acid results in the reduction of **2**, which, once formed, slowly yields the non-oxo tris-chelate Mo(IV) species $[Mo(O_2CC(S)Ph_2)_3]^{2-}$(**3**). The generation of such a monomeric Mo(V) intermediate mimics the redox behavior of molybdenum hydroxylase enzymes. The pH dependence of the above Mo(V)–Mo(IV) conversion reaction as well as its relationship to the molybdenum center in nitrate reductase is discussed. The Mo site in **3** was revealed to be trigonal prismatic by a previous X-ray structure study. This structure constitutes the first example of a trigonal-prismatic geometry in a Mo(IV) complex whose ligands have no extensive intraligand π-conjugation. The electronic structure as well as the spectroscopic and electrochemical properties is analyzed in terms of extended Hückel molecular orbital calculations which are consistent with previous molecular orbital calculations for tris(dithiolene) complexes. Compared to the case of the dithiolene complexes, a stabilization of the prismatic structure is observed in the present thiobenzilate complex (**3**) as a result of improved σ- and π-bonding interactions between the Mo(IV) center and the sulfurs of the thiobenzilate ligands. The role of the solid packing interactions is also considered.

Introduction

A common feature of oxomolybdoenzymes is their ability to carry out an oxo-transfer reaction between the molybdenum center and the substrate, with molybdenum cycling through the oxidation states VI, V, and IV. The catalytic reactions[1] are formally hydroxylations of a substrate X which may be represented by the two-electron redox reaction $X + H_2O \rightleftharpoons XO + 2H^+ + 2e^-$.

All three oxidation states have been studied by EXAFS, but only the paramagnetic Mo(V) state could be detected by EPR spectroscopy. The EPR signals observed upon reduction of the enzyme with substrates or dithionite are pH and anion dependent, and the concentration of this Mo(V) species is also usually in equilibrium with both Mo(VI) and Mo(IV).[2]

Our interest in models for the molybdenum centers of hydroxylases led us to develop the chemistry of thiobenzilate–molybdenum complexes because this sterically hindered ligand forms the only *cis*-dioxo Mo(VI) complex,[3] $[MoO_2(O_2CC(S)Ph_2)_2]^{2-}$ (**1**), chemically reducible by organic phosphines or aliphatic thiols to the monomeric monooxo Mo(V) complex $[MoO(O_2CC(S)Ph_2)_2]^-$ (**2**).[4] To our knowledge, all dioxo Mo(VI) complexes thus far reported containing bulky ligands yield upon chemical reduction monomeric $Mo^{IV}O^{2+}$ species while those containing ligands which allow a close approach between the $Mo^{VI}O_2^{2+}$ and $Mo^{IV}O^{2+}$ centers yield oxo-bridged Mo(V) dimers.[5]

Therefore, contrary to this general behavior, complex **1** shows the peculiarity of being reduced to the Mo(V) complex, **2**, instead of a Mo(IV) complex. This led us to obtain and characterize by X-ray crystallography the first mononuclear five-coordinated Mo(V) species possessing a $MoO(S_2O_2)$ donor set. Such an environment is consistent with the minimal coordination unit, $MoOS_{2,3}(N/O)$, of several molybdoenzymes in their reduced forms and possesses the cis coordination by two thiolate groups proposed for the molybdenum cofactor.

We herein report that **2** can be further reduced by thiobenzilate ions to give the non-oxo tris-chelate Mo(IV) species $[Mo(O_2CC(S)Ph_2)_3]^{2-}$ (**3**), in which the terminal oxo group in complex **2** has been replaced by another bidentate thiobenzilate moiety. Therefore, complexes **2** and **3** are the first pair of X-ray-characterized monomeric Mo(V) and Mo(IV) compounds having a common chelate ligand which is also biologically relevant. In this paper, we describe the full details of their chemical conversion reaction and their relationship to the molybdenum center in nitrate reductase. Besides this, there is a close structural relationship between **3** and other previously characterized tris-chelate complexes containing N,S and S,S donor ligands. Among them, tris(dithiolene) complexes are the oldest known members of this class whose structural, spectroscopic, and redox properties have been thoroughly investigated and reviewed.[6] Specially significant is the fact that these compounds can adopt a trigonal-prismatic (TP) geometry distorted toward octahedral to an extent which apparently depends on the formal oxidation state of the molybdenum atom and π-bonding donor ability of the ligands. Both factors can be rationalized if we take into account that in a TP structure there are two important π-bonding interactions to which Gray[7] attributed the prism stability: (a) between the metal d_{z^2} orbital and p_z orbital on each ligand; (b) between the metal d_{xy} and $d_{x^2-y^2}$ orbitals and p_x or p_y orbitals on each ligand. This second π-bonding interaction may be particularly favored if π ligand orbitals are extensively delocalized as a result of an intraligand conjugation as in the dithiolene ligand case.

[†] In this paper, compound numbers may refer to either the neutral salts or the negative coordination spheres.

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The HOMO for a 14-electron compound (Mo(IV)) is a π^* MO resulting from the d_{z^2}–p_z interaction mentioned above, while for a 12-electron compound (Mo^{VI}) this same π^* MO is the LUMO.[8] Therefore, the occupation of this orbital in monoanionic, and dianionic tris(dithiolene) complexes of the group 6 transition metals are expected to destabilize TP structures, favoring a distortion toward octahedral geometry. The X-ray crystal structure characterization of the dianionic Mo(IV) complex **3** revealed, however, a nearly perfect trigonal prism constrained by the geometric requirements of sulfur vs oxygen coordination (vide infra). Thus, although the MoS_3O_3 polyhedron is severely tapered, the twist angle between triangular faces has a value of 4.7°, much lower than those found in any other characterized trigonal-prismatic tris(dithiolene) complex.

With respect to the ligand π-bonding donor ability, we should point out that in **3** the average Mo–S distance of 2.291 Å is far shorter than those reported for molybdenum 1,2-dithiolene complexes, indicating considerable double-bond character. On a first analysis, this result does not seem to be consistent with both the "innocent" character of this ligand,[9] which has no extensive intraligand π conjugation as 1,2-dithiolene ligands do, and the π-donor carboxylate group nature which is weaker than that of a thiolate group. Hence, in order to determine the cause of these structural features as well as to rationalize the spectroscopic and electrochemical properties, an extended Hückel molecular orbital (EHMO) analysis has been carried out on **3** and the results have been compared to those obtained for an ideal tris(dithiolene)–Mo(IV) complex.

Experimental Section

Starting Materials and Methods. Reagent grade solvents, distilled and dried by standard methods, were used in all cases. The preparation and characterization of thiobenzilic acid, $(NH_4)_2[MoO_2(O_2CC(S)Ph_2)_2]$ (**1**), and $(Bu^n{}_4N)[MoO(O_2CC(S)Ph_2)_2]$ (**2**) have been reported previously.[3,4] $Na_2MoO_4{\cdot}2H_2O$, tetra-*n*-butylammonium hydroxide, and tetra-*n*-butylammonium tetrafluorophosphate were purchased from Aldrich Chemical Co.

^1H and ^{13}C NMR spectra were recorded on a Varian UNITY 300 spectrometer. The electronic spectra were recorded on an Perkin-Elmer Lambda 2 spectrophotometer using quartz cells. Cyclic voltammetric measurements were carried out by using an HQ-101 battery-powered potentiostat, a Newstronics 200P triangular-wave generator, and a Rinken-Denshi F-35 X-Y recorder. Potentials were measured versus a methanolic saturated calomel reference electrode (E = 0.00V vs aqueous SCE) using 0.1 M tetrabutylammonium hexafluorophosphate solutions as supporting electrolytes.

Synthesis. The synthesis of **3** was carried out under an argon atmosphere. Addition of $Na_2MoO_4{\cdot}2H_2O$ (0.121 g, 0.5 mmol) to a stirred solution of thiobenzilic acid (0.6 g, 2.5 mmol) and tetra-*n*-butylammonium hydroxide (0.26 g of MeOH solution, 12.5%, 0.125 mmol) in 3 mL of MeOH (degassed before use) produced an intensely red solution which was fully deaerated (by bubbling argon in an ultrasonic bath over 35–40 min), the flask being sealed with a septum stopper. Storage, for 10–12 h at room temperature and additionally 12 h at −15 °C, produced a red crystalline solid, which was collected to give 0.36 g (yield 64%). Anal. Calcd for $C_{60}H_{63}MoNNaO_8S_3$: C, 59.7; H, 6.6; S, 9.0; N, 1.3; Na, 2.1. Found: C, 60.6; H, 6.1; S, 8.8; N, 1.1; Na, 1.9.

EHMO Calculations. All calculations were performed by using a package of programs for molecular orbital analysis by Mealli,[10] based on CDNT (atom Cartesian coordinate calculations), ICON (extended Hückel method with the weighted H_{ij} formula), and FMO (fragment molecular orbital), including the drawing program CACAO (computer-aided composition of atomic orbitals).

The extended Hückel parameters are as follows. H_{ij}: Mo(5s), −8.34 eV; Mo(5p), −5.24 eV; Mo(4d), −10.50 eV; S(3s), −20.00 eV; S(3p), −13.30 eV; O(2s), −32.30 eV; O(2p), −14.80 eV; C(2s), −21.40 eV; C(2p), −11.40 eV; H(1s), −13.60 eV. Orbital exponents: Mo(5s), 1.96; Mo(5p), 1.92; Mo(4d), 4.54 (0.6097) + 1.90 (0.6097); S(3s, 3p), 1.817; O(2s, 2p), 2.275; C(2s, 2p), 1.625; H(1s), 1.300.

Geometrical parameters are as follows. $[Mo(SCH_2CO_2)_3]^{2-}$: Mo–S = 2.291 Å; S–C = 1.863 Å; Mo–O = 2.076 Å; O–C = 1.291 Å; O═C = 1.222 Å; C–C = 1.550 Å; S–Mo–S = 88.7°; O–Mo–O = 78.1°; Mo–S–C = 106°; Mo–O–C = 128°. $[Mo(SCHCHS)_3]^{2-}$: Mo–S = 2.393 Å; S–C = 1.740 Å; C═C = 1.336 Å; S–Mo–S(interligand) = 83.1°; Mo–S–C = 110°.

Results and Discussion

Preparation and Spectroscopic Characterization of the Complexes. It has been previously reported in a brief account of this research[4] that the reaction of **1** with an excess of thiobenzilic acid in dry deoxygenated methanol yields the monomeric molybdenum(V) complex **2** and dithiodibenzilic acid.

$$[MoO_2(O_2CC(S)Ph_2)_2]^{2-} + Ph_2C(SH)CO_2H \rightarrow [MoO(O_2CC(S)Ph_2)_2]^{-} + {}^1/{}_2[(O_2CC(Ph)_2S)_2]^{2-} + H_2O \quad (1)$$

The reaction can be followed spectrophotometrically by monitoring its optical spectrum. As the Mo(VI) complex concentration (λ_{max} = 370 nm) diminishes with time, three new maxima and two tight isosbestic points are observed. The reaction goes to completion and displays a final spectrum which does not change appreciably over a 24-h period, indicating that **2** is quite stable in the presence of the excess thiobenzilic acid. Under these conditions, the reaction is first order in the Mo(VI) complex as shown by linear plots of $\ln(A_t - A_\infty)$ vs time both at 370 nm, disappearance of **1**, and at 503 nm, appearance of **2**. For both wavelengths, a pseudo-first-order constant with respect to complex **1** concentration was determined by a least-squares analysis ($K_{obs} = 6.1 \times 10^{-5}\ s^{-1}$; T = 25 °C).

To determine the effect of pH on the rate of this reaction with thiobenzilic acid, a substrate that also acts as a proton source, variable amounts of sodium methoxide were added to the initial solution containing **1** and excess thiobenzilic acid. The result was that the reaction rate decreased rapidly with increasing pH and that the concentration of complex **2**, after reaching a maximum, decreased steadily with the changes in the corresponding visible bands, thereby suggesting further reduction of **2** by thiobenzilate ions. Therefore, as this second reaction proceeds, a bathochromic shift of the band at 503 nm is observed to give a final spectrum with an absorption maximum at 484 nm. On the basis of the distinctive colors of reactant, intermediate, and final product, it can be inferred that the overall reaction proceeds in two major stages. The first one involves the rapid disappearance of the yellow solution containing **1** and the formation of a purple intermediate **2**, while in the second stage, this latter complex disappears and a red-orange product **3** is formed.

To demonstrate that the second transformation involves the reduction of **2** by thiobenzilate ions, the course of the reaction between **2** and partially neutralized thiobenzilic acid was spectrophotometrically monitored. The initial band of **2** at 503 nm changed with time (Figure 1), giving a red-orange, EPR-silent solution with an absorption maximum at 485 nm. Although the small differences between these two chromophores did not allow kinetic treatment of the spectrophotometric data, it was possible to establish the reaction stoichiometry and to analyze the oxidation product of the thiobenzilate ions by ^{13}C and ^1H NMR spectroscopy. The final spectrum indicates that 1 mol of dithiodibenzilate ions is finally generated for each 2 mol of **2** reacted:

$$2[MoO(O_2CC(S)Ph_2)_2]^{-} + 4[Ph_2C(SH)CO_2]^{-} \rightarrow 2[Mo(O_2CC(S)Ph_2)_3]^{2-} + [(O_2CC(Ph)_2S)_2]^{2-} + 2H_2O \quad (2)$$

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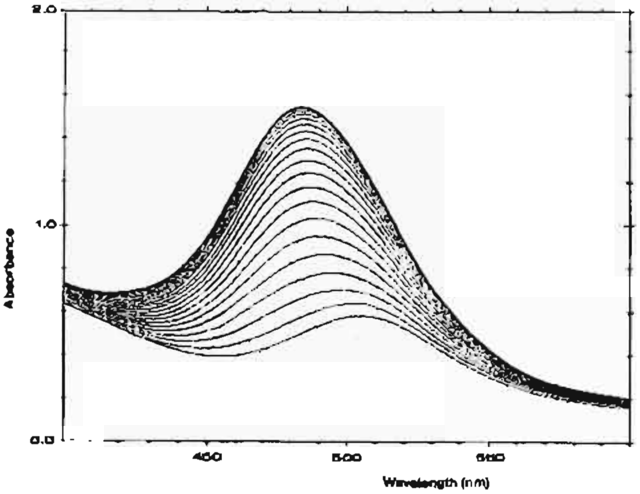

Figure 1. Spectral changes in the reaction of 2 (0.25 mM) with thiobenzilic acid (5 mM) neutralized with sodium methoxide (5 mM) in methanol solution at 25 °C. Spectra were recorded every 120 min at a scan rate of 120 nm min^{-1}.

On a preparative scale, attempts to isolate the red-orange product from this second reaction resulted in the obtention of a crystalline solid whose elemental analysis is in agreement with the formula $(Bu^n_4N)Na[Mo(O_2CC(S)Ph_2)_3]$. However, according to the procedure described in the Experimental Section, we favor the alternative method from molybdate and thiobenzilic acid, partially neutralized with n-butylammonium hydroxide, since it eliminates the need for crystallization of the highly air-sensitive intermediate 2. Upon redissolution in methanol, the UV-visible spectrum of 3 consists of two intense bands with λ_{max} (ϵ_M) = 485 (5900) and 307 (8000) nm (dm^3 mol^{-1} cm^{-1}).

The foregoing results demonstrate for the first time that thiols, which are considered as suitable physiological electron donors, effectively reduce Mo(VI), first to a monomeric Mo(V) species and then to a Mo(IV) species, with the second step being considerably slower than the first one. Prior to this work, other well-characterized dioxomolybdenum(VI) complexes, namely $MoO_2(S_2CNEt_2)_2$[11] and $MoO_2(LNS_2)$,[12] have been reported to undergo slow reduction by arenethiols in DMF. However, only the formation of a monooxo Mo(IV) complex has been reported in these latter systems, and apparently such monooxo Mo(IV) complexes decompose in excess thiol. Neither the reaction with aliphatic thiols nor the formation of stable monomeric monooxo Mo(V) or non-oxo tris-chelate Mo(IV) complexes has been previously reported.

The reactions (1) and (2), Mo(VI) → Mo(V) and Mo(V) → Mo(IV) in the present system, parallel the redox behavior of molybdenum enzymes and provide strong evidence that the local pH at the molybdenum center can play a major role in the overall catalytic reaction and in stabilizing the molybdenum cofactor structure. In this regard, EXAFS studies of the oxidized and the fully reduced samples of enzymes are consistent with the EPR work in indicating a pH- and anion-dependent change in structure. However, detailed interpretation of the EXAFS spectra of the reduced and oxidized samples of enzymes is difficult owing to the observation of nonstoichiometric amounts of M=O groups.

An illustrative example is *Escherichia coli* nitrate reductase,[13] for which it has been postulated that reduction stops at a non-oxo Mo(IV) species whose EXAFS curve-fitting analysis indicates the presence of one or two non-terminal Mo–O (or Mo–N) bonds (2.11 Å) and two or three Mo–S bonds (2.34 Å). However, nonstoichiometric numbers (0.5) of Mo=O interactions (1.72 Å) were determined under certain circumstances (high-pH oxidized and reduced forms and low-pH reduced form) which were interpreted in terms of sample inhomogeneity. An interpretation seems consistent with monooxo and non-oxo molybdenum structures, for which few model compound data are available. Furthermore, this recent EXAFS study[13] clearly indicates an increase in the oxo content on decreasing the pH, which is contrary to a previous proposal[14] suggesting that (for the Mo(V) state) the high-pH → low-pH transition involves replacement of an oxo group in the high-pH species by a hydroxy group and an anion ligand in the low-pH species. This observation led Cramer et al.[15] to consider the possibility that the low-pH structure might involve a monooxo molybdenum species which is transformed, at high-pH or upon reduction, into a non-oxo species. Our present results are compatible with such an EXAFS data interpretation and enhance the viability of the postulated mechanism of this high-pH → low-pH transition. Thus, at high pH a NH (or SH) group becomes deprotonated, achieving sufficient π-electron-donor ability to displace the Mo=O group. Further, also consistent with the EXAFS data, it can be noted that the decrease in oxo content upon reduction of 2 to 3 is associated with a shortening in the average Mo–S bond distance (from 2.349 to 2.291 Å). Finally, it is worthwhile to mention that the calculated[4] g_i parameters for the monooxo Mo(V) complex, 2 (2.002, 1.961, 1.934), are similar to those reported for the nitrate reductase reduced form at low pH (1.995, 1.967, 1.954).[15] Therefore, on the basis of their structural properties, chemical reactivity, and pH stability, thiobenzilate–molybdenum complexes function as the most relevant chemical models of the active sites for certain oxomolybdoenzymes.

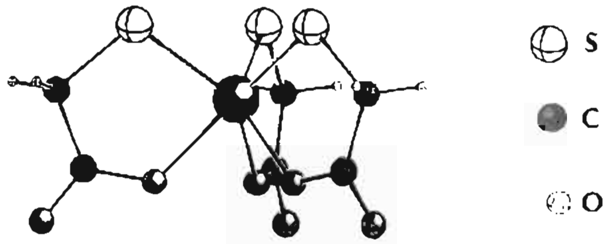

Figure 2. Ball-stick representation for $[Mo(O_2CC(S)Ph_2)_3]^{2-}$ (3), the phenyl rings having been substituted by H atoms.

Crystal and Molecular Structure of $(NBu_4)Na[Mo(O_2CC(S)Ph_2)_3]\cdot H_2O\cdot CH_3OH$ (3). To our knowledge, this molybdenum complex is the first compound with a TP structure containing both coordinated sulfur and oxygen atoms to be definitively characterized by X-ray crystallography. The detailed structural characterization of this complex has been previously reported.[16] The molecular structure consists of monomeric tris(thiobenzilate)–molybdenum(IV) anions in which the molybdenum atom is six-coordinated and bonded to both the sulfur and oxygen atoms from each one of the three thiobenzilate ligands, roughly forming a TP polyhedron with the two triangular faces defined by three sulfur atoms and three oxygen atoms, respectively. Figure 2 shows the molecular geometry of 3. The distortion from a regular TP geometry is demonstrated both by the average twist angle (4.7°) between the S_1–S_2–S_3 and O_1–O_2–O_3 planes and by the dihedral angle of 0.6° between these planes, which indicates that they are not perfectly parallel. Nevertheless, the approximate point symmetry of this tapered MoS_3O_3 coordination polyhedron is C_{3v}. The the phenyl rings from the ligands around each $Mo(S_3O_3)$ core do not appear to be constrained,[16] and in Figure 2, they have been replaced by hydrogen atoms for clarity.

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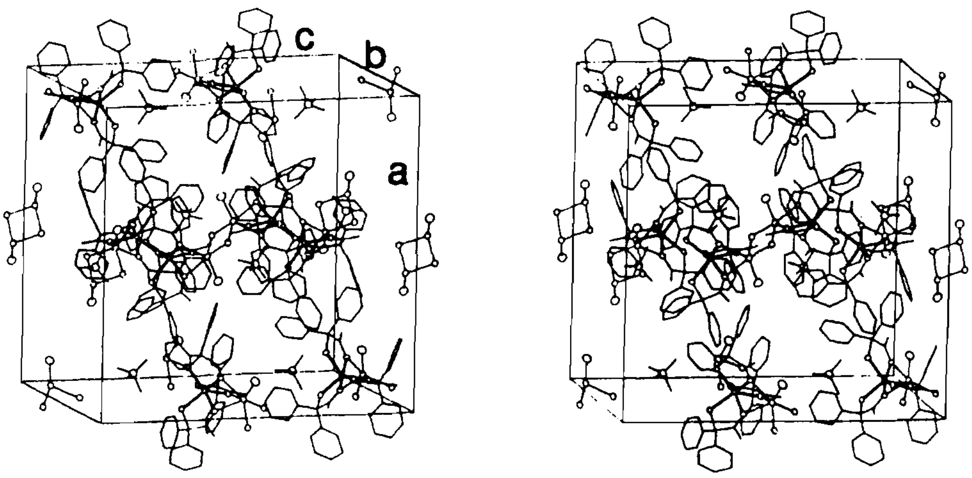

Figure 3. Stereoview of the unit cell for $(NBu^n_4)Na[Mo(O_2CC(S)Ph_2)_3]\cdot H_2O\cdot MeOH$.

For the present complex, the sulfur–metal distance (mean value 2.291(4) Å) is significantly shorter than those found in any other TP tris(dithiolene) Mo(IV) complex X-ray characterized, namely 2.374 Å for $[Mo(mnt)_3]^{2-}$ [8] and 2.393 Å for $[Mo(S_2C_2(CO_2Me)_2)_3]^{2-}$.[17] The latter longer Mo–S distances are also accompanied by a higher distortion toward an octahedral coordination as illustrated by the twist angles between trigonal planes of 28 and 10.6°, respectively. A plausible correlation of both features can be offered in terms of molecular orbital calculations previously used[18] to explain the stability of TP coordination in solid compounds of transition metals. From this MO treatment, it is found that TP coordination is most likely in predominantly covalent compounds of ions with configurations d^0, d^1, or d^2, yet an increase in the ionic contribution is expected to induce a departure from the TP geometry toward octahedral associated with an enlargement in the M–L bond.

It is interesting to note that in the present complex containing a mixed hard–soft ligand both types of interactions are simultaneously present. Of these, the interaction with the low-lying oxygen donor orbitals from the carboxylate (hard) group is fundamentally ionic, while that associated with the high-lying orbitals from the thiolate (soft) group is fundamentally covalent. The actual TP geometry observed for this complex seems to indicate that the covalent interaction predominates, and therefore, the relative position of the carboxylate groups (trans to the sulfur atoms) would be determined mostly by the electrostatic interaction with the molybdenum d orbitals defined in the complex by the three S–Mo bonds which are positioned on a prismatic triangular face.

Obviously, the geometry of a particular complex is not governed only by electronic factors, and thus, the possibility that the observed molecular geometry is the result of the more stringent packing requirements of the sodium cation was raised.[19] The crystal structure of this mixed complex salt consists of monomeric tris(thiobenzilate)-molybdenum(IV) anions with sodium and tetrabutylammonium as the counterions and with one water and one methanol, per atom of molybdenum, as crystallization solvent molecules. A stereoview of the crystal structure is shown in Figure 3. The packing is mainly achieved by Coulombic interactions with sodium ions occupying the cavities between the complex anions which have a clear dipolar structure, favoring sodium coordination through the three carboxylate groups on one of the triangular faces of the prism. As a matter of fact, according to the MO calculations that we shall present later, a comparison of the negative charges on the sulfur atoms of a dithiolene–Mo(IV) complex and **3** reveals that in both complexes the S atoms have similar charges (−0.34 and −0.43 e, respectively) but the coordinated oxygen atom from the carboxylate is much more charged (−0.93 e). These differences in the negative charge distribution are also reflected in the positive charge supported by the Mo center, which is much higher in **3** (+1.18 e vs +0.20 e). As a result, the sodium coordination is clearly favored by the presence of the three carboxylate groups that form the base of a trigonal prism and two water and one methanol molecules that form the other (torsion angle 5.7°, dihedral angle 1.32°).

The role that this interaction may play in stabilizing the molecular structure of **3** has been properly noted by Kepert.[20] Thus, an interaction of this type was assumed to stabilize the exceptional structures found in several complexes containing β-diketones ligands attached to large metal atoms as, for example, in the $K[Cd(acac)_3]H_2O$ complex. For this latter complex, although an octahedron is preferred on the basis of all arguments concerning the interligand repulsion, its virtually TP geometry may be explained as a result of the strong interaction existing between the CdO_6^- unit and potassium ions which lie outside each of the triangular faces of the prism with the formation of an infinite linear polymer. Any twist toward octahedral geometry must enlarge these triangular faces, with a possible weakening of the potassium–oxygen bonding.

Clearly, a similar situation is also present in **3** where a "linear" stacking in the crystal lattice of the form $...Bu_4N^+(complex)Na^+(H_2O)_2(CH_3OH)Na^+(complex)Bu_4N^+...$ is observed. The stabilization of the crystal structure by an interaction of this type may also justify why attempts to crystallize other salts containing only ammonium, butylammonium, or tetraphenylphosphonium have been unsuccessful. We should finally mention that a similar dipolar interaction is also present in other tris-chelate Mo(VI) complexes containing three amine thiolate ligands and the S_3N_3 framework.[21] Their dipolar character can explain that they can be precipitated as a compound with the formula $(complex)\cdot 0.5Bu_4N^+Br^-$ after addition of tetrabutylammonium bromide.

Molecular Orbitals for the Anionic Complex $[Mo(O_2CC(S)Ph_2)_3]^{2-}$ (3). To substantiate the importance of the σ- and π-bonding interactions in stabilizing the TP structure of this complex, we have extended early qualitative molecular orbital (MO) analysis for tris(dithiolene) complexes[8,22] to the present case. Although in a TP coordination the σ and π bondings are not separable, from overlap considerations as well as extrapolation to octahedral limits, the a_1 (a_1') and e (e′) symmetry MO's in C_{3v} (D_{3h}) can be considered as π-type levels while e (e″) is predominantly a σ-type level.

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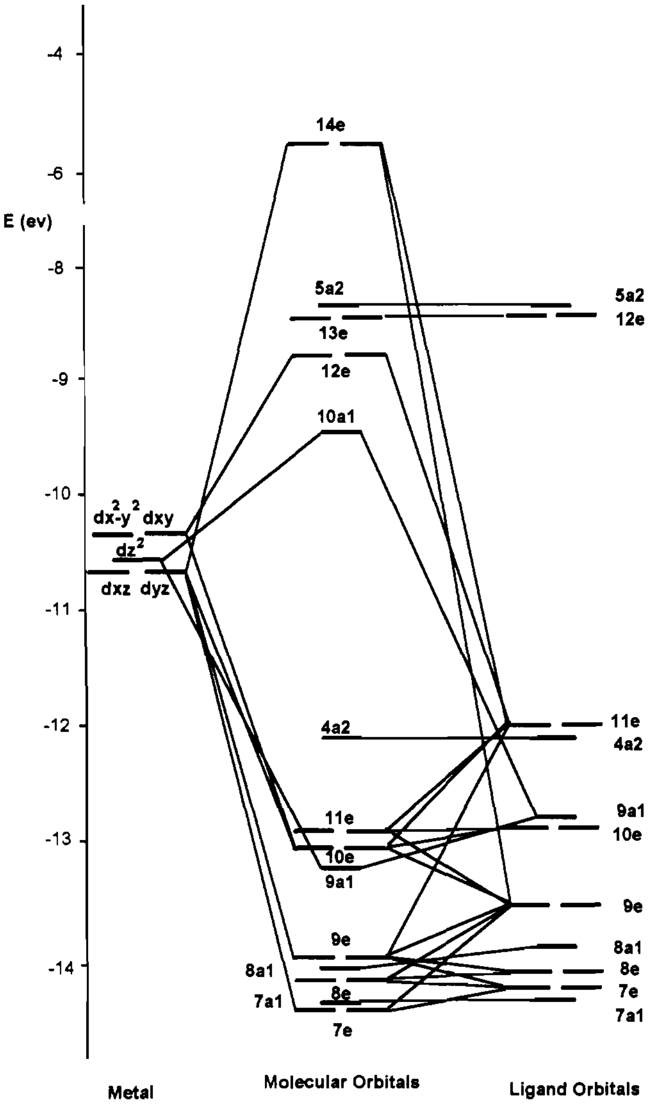

Figure 4. Complete molecular orbital energy level diagram for [Mo(O$_2$CCH$_2$S)$_3$]$^{2-}$.

Our analysis is based on extended Hückel calculations using the computational and geometrical parameters given in the Experimental Section. Three independent symmetric glycolate in place of three thiobenzilate ligands were considered since this simplification does not appreciably alter the bonding capabilities of the chelating ligand with regard to the molybdenum atom. A molecular orbital correlation diagram showing all the levels as well as the starting ligand and metal orbitals is shown in Figure 4.

We have also calculated the molecular energy levels for a hypothetical complex [Mo(S$_2$C$_2$H$_2$)$_3$]$^{2-}$ containing three ethylene-1,2-dithiolate ligands, assuming a regular TP coordination (D_{3h}) with appropriate parameters (see Experimental Section). Such a comparative study may help to elucidate whether or not intraligand conjugation and/or the number of sulfur atoms bonded to the molybdenum are essential features to stabilize this type of TP coordination. Figure 5 shows a comparative level pattern obtained for both model compounds. In both diagrams, only the levels of spectroscopic interest derived from the metal 4d orbitals are illustrated, even though the extent of mixing with other ligand orbitals is often so great that such an identification is difficult to make. Although the results indicate reversals in the order of certain of the lowest filled MO's it may be concluded that both level diagrams are qualitatively similar to that reported by Gray et al.[7] for Re(S$_2$C$_2$Ph$_2$)$_3$, the first TP complex proven as such.

For both complexes, 3 and [Mo(S$_2$C$_2$H$_2$)$_3$]$^{2-}$, the HOMO assigned to 4a$_1'$ (D_{3h}) or to 10a$_1$ (C_{3v}) consists of mostly a metal d$_{z^2}$ orbital which overlaps with a set of ligand orbitals from only sulfur p_z orbitals. It appears that the more compact oxygen p$_z$ orbitals have a negligible overlap with the Mo d$_{z^2}$ orbital and consequently an unsubstantial interaction.

An important outcome of our calculations is that the size of the interaction with the three sulfur atoms of the thiocarboxylate ligands, at the observed distance 2.291 Å, is comparable to the interaction with the six sulfur atoms of the dithiolene ligands at the longer bond length of 2.393 Å. Thus, the energy of the HOMO is approximately the same in both complexes, which may have important structural implications. In fact, considering that this HOMO orbital is antibonding in nature, as we have already mentioned, its occupancy has been postulated[7] as a possible destabilization factor for the TP coordination. In support of this argument, the structures of the neutral complexes [Mo(S$_2$C$_2$H$_2$)$_3$],[23] [Mo(Se$_2$C$_2$(CF$_3$)$_2$)$_3$],[24] and [Mo(S$_2$C$_6$H$_4$)$_3$],[25] which are formally d^0 complexes, exhibit regular TP geometry around the Mo atom, while the dianionic complexes[7] [Mo(mnt)$_3$]$^{2-}$and [W(mnt)$_3$]$^{2-}$, formally d^2 complexes, exhibit an intermediate structure between octahedral and trigonal-prismatic types.

The next level in the diagram obtained for both complexes is of a$_2'$ (D_{3h}) or a_2 (C_{3v}) symmetry and thus does not combine with any of the metal orbitals (Figure 4). These orbitals are, therefore, nonbonding π MO's in both complexes, but it should be noted that while 4a$_2$ represents a combination of only p$_y$ and p$_x$ orbitals of the three thiobenzilate sulfur atoms, 2a$_2'$ contains an asymmetric contribution from the olefin π orbitals that significantly increases its energy with respect to nonbonding a$_2$.

Taking into account the first bonding orbital, we have already mentioned that for tris(dithiolene) complexes a strong contributing factor to the stability of TP coordination has been assumed to be the optimum interaction between d$_{xy}$ and d$_{x^2-y^2}$ orbitals and the extensively delocalized p$_{x,y}$ orbitals from sulfur and olefinic carbon atoms. This leads to a particularly stable 7e$'$ MO and an antibonding level 8e$'$ localized primarily on the metal d orbitals. However, in view of the proximity in energy existing between these d orbitals and the above mentioned p$_{x,y}$ ligand orbitals, it has been pointed out[8] that the energy of this MO 7e$'$ must be more sensitive to changes in metal d orbital energies than other more stabilized MO's. In fact, the role of the energy of the d orbitals has been noted by Bennett et al.,[26] who determined the structures of the isoelectronic tris(benzenedithiolato) complexes [Mo(S$_2$C$_6$H$_4$)$_3$], [Nb(S$_2$C$_6$H$_4$)$_3$]$^-$, and [Zr(S$_2$C$_6$H$_4$)$_3$]$^{2-}$. Of these, the Mo complex has a TP geometry and the Nb analogue is closer to that geometry, while the Zr complex is closer to octahedral. That is, the M–S distances increase and the stability of the prism decreases along the series as one moves from Mo to Zr, increasing the d-orbital energy.

In a similar way, some enhancement of this π interaction must occur when the energy difference between d and ligand π orbitals is increased by a stabilization of the latter. For the present compound, the 11e ligand π orbital (C_{3v}) contains only p$_x$ and p$_y$ sulfur orbitals while the 7e$'$ ligand orbital (D_{3h}), its counterpart in the dithiolene complex, contains a mixture of sulfur p$_x$ and p$_y$ orbitals and olefin π orbitals. The asymmetric character of the latter combination raises the energy (the 7e$'$ level is 0.5 eV higher in energy than the 11e level of the thiocarboxylate ligand), decreasing the stability of the resulting MO.

In addition, there are two other important factors contributing to this π-bonding interaction, namely the Mo–S distance and the

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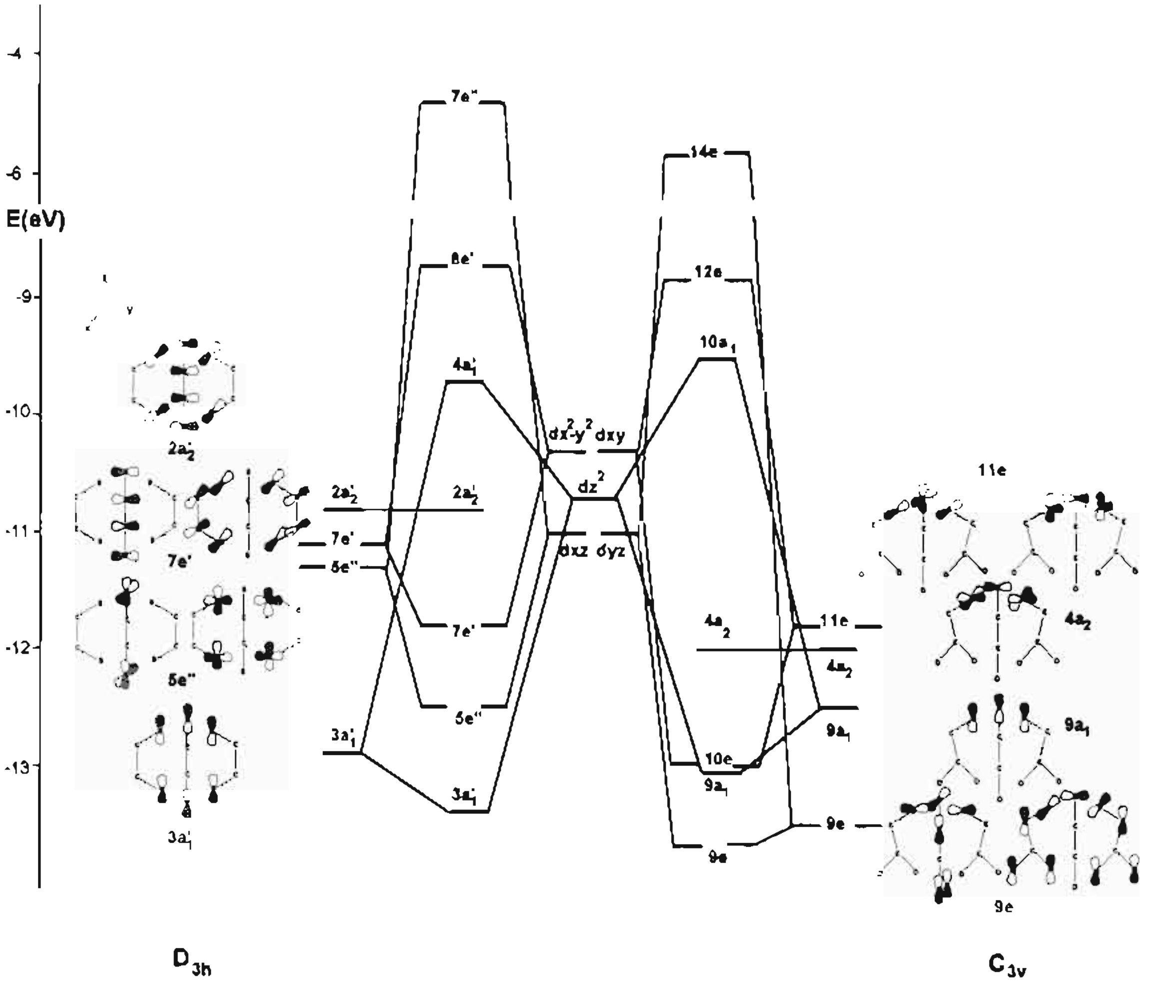

Figure 5. Comparative partial MO diagram showing the major d-orbital interactions for $[Mo(SCH_2CH_2S)_3]^{2-}$ (left) and $[Mo(O_2CCH_2S)_3]^{2-}$ (right).

angle between this bond and the *z* axis. When the value of this angle is increased and the Mo–S bond length is decreased, a more favorable d_z–p_z interaction can be expected. The higher value of this angle in 3 may be reasonably associated with the different hybridization (sp^3) at the carbon atom attached to the coordinated thiolate group while its shorter Mo–S bond length should be related to the lesser ability of the carboxylate group to compete for the available empty d orbitals as compared to thiolate group. Furthermore, the shortening in the Mo–S distance implicates a stronger repulsion among these three bonds, which yields a flatter TP structure with longer S···S interligand distances.

Extended Hückel calculations confirm our analysis since a glance at the diagrams in Figure 5 shows that a larger splitting of the Mo d_{xy}, $d_{x^2-y^2}$ orbitals results in the thiocarboxylate complex than in the dithiolene one. As a matter of fact, the interaction of these d orbitals with the fragment molecular orbital 7e′ in the dithiolene complex, having six interacting sulfur atoms, is equivalent to that observed with the fragment 11e in the thiobenzilate complex 3, which only has three interacting sulfur atoms.

Finally, if σ bonding is taken into account, the ligand orbitals which are oriented to interact with the empty $4d_{xz}$ and $4d_{yz}$ orbitals of the molybdenum atom have e (e″) symmetry in the C_{3v} (D_{3h}) point group. However, we must note that the 9e level is at considerably lower energy (−14.593 eV) than the 5e″ level of the $[Mo(S_2C_2H_2)_3]^{2-}$ complex (−12.875 eV). The reason for such an energetic difference lies in the fact that the 9e ligand set orbital is made up of the sulfur p_x and p_y orbitals with some admixture of p_z lower-lying orbitals of the oxygen atoms from the carboxylate groups. Thus, the important point is that the presence of the carboxylic groups on the ligand stabilizes this interaction, inverting the MO order ($3a_1'$ more stable than 5e″ in the dithiolene complex) by pushing the e levels down in energy (9e more stable than $9a_1$ in the thiocarboxylate complex).

Although, from the present results, it would be difficult to draw a conclusion about the relative strength of σ and π bondings, one can easily see that the structures of these complexes are significantly dependent upon the nature of the donor atoms of the chelating ligand. For the title thiobenzilate–molybdenum complex, both σ- and π-bonding effects cooperate to create a strong and short Mo–S bond that increases the separation between filled bonding and antibonding levels, which obviously represents a contributing factor to the stability of its TP structure.

The main conclusions to be drawn from the foregoing MO calculations can be summarized as follows: (1) delocalization of π orbitals of the sulfur atoms in unsaturated ligands decreases the stability of the interaction with the metal $d_{x^2-y^2}$ and d_{xy} orbitals, obtained for a TP coordination; (2) the contribution of the carboxylate groups to the interaction with d_{xz} and d_{yz} orbitals cannot be ignored and appears to contribute significantly to the stability of the Mo–S σ bonds of complex 3; (3) compared to the case of previously characterized tris(dithiolene)–Mo(IV) complexes containing the trigonally twisted MoS_6 coordination polyhedron, the smaller deviation from a TP geometry observed for the MoO_3S_3 unit in 3 very likely reflects differences in covalence in the Mo–S bonds that stem from differences in the relative energies of the Mo(IV) d orbitals and the σ and π ligand orbitals; (4) For both thiocarboxylate and dithiolene complexes, our Hückel calculations indicate that the nature of the HOMO is the same and consists of mostly a metal d_{z^2} orbital and a totally symmetric combination of sulfur p_z orbitals.

Spectroscopic and Electrochemical Properties. The UV–visible spectrum of 3 in methanol is essentially characterized by two absorption bands in the visible region which does not change on going from solid state to solution. The first of these bands occurs around 485 nm (ϵ = 5939 dm^3 cm^{-1} mol^{-1}) and the second around 307 nm (ϵ = 8000 dm^3 cm^{-1} mol^{-1}). The overall spectrum is, therefore, similar to those observed for previous tris(dithiolene)–Mo(IV) complexes, namely $[Mo(qdt)_3]^{2-}$ (396 (4700), 561 (5500)),[27] $[Mo(S_2C_2(CO_2Me)_2)_3]^{2-}$ (356 (11 500), 650 (5800)),[17] and $[Mo(S_2C_2(CN)_2)_3]^{2-}$ (389 (9900), 667 (5800)),[7] whose structures only show light distortions from ideal TP coordination (vide infra). Despite this spectral gross similarity, which is believed characteristic of TP coordination, the main feature of interest is that both bands are more shifted to higher energy in complex 3 than in any other dithiolene complex, suggesting that they are essentially ligand to metal charge transfer in character, as proposed by Enemark et al.[28] That these bands are found at higher energy in 3 than in any other characterized dithiolene complex is also consistent with the above MO calculations that support a higher stabilization in 3 of all the ligand-based MO's relative to metal-based MO's. Specifically, if these two bands are assigned to the transitions $^1A'_1 \rightarrow {}^1E'$ ($2a_2' \rightarrow 8e'$) and $^1A'_1 \rightarrow {}^1E'$ ($7e' \rightarrow 8e'$), an assignment proposed for the dithiolene chromophore by Gray et al.,[7] a stabilization of the π nonbonding ligand orbital ($2a_2'$) and sulfur π orbitals interacting with metal d orbitals d_{xy}, $d_{x^2-y^2}$ ($7e'$), respectively, leads one expect the observed blue (hypsochromic) shift of both bands in complex 3

Cyclic voltammograms of 3, in DMF or CH_3OH, show an oxidation peak when scanned in the anodic direction coupled to a reduction peak which only appears in the cathodic direction after anodic scanning. The formal potential ($E^{\circ\prime} = (E_{pa} + E_{pc})/2$) has a value of –0.260 V vs SCE at the glassy carbon electrode and remains independent of scan rate. Values of the current function ($I_{pa} = i_{pa}/Acv^{1/2}$) are close to 375 A mol^{-1} s$^{-1/2}$ V$^{-1/2}$, suggesting a one-electron process. This electron stoichiometry was confirmed by potential step chronoamperometry with a potential step of 0.0 to –0.6. V The resulting chronoamperograms show a linear dependence of current i vs $t^{-1/2}$, implying that the Cottrell equation[29] is valid. We can conclude that no chemical complications occur at the electrode process, which allows an estimation for the diffusion coefficient of complex 3 ($D = 3.4 \times 10^{-6}$ cm^2 s^{-1}).

We shall now briefly attempt to compare the oxidation potential of 3 with those reported for tris(dithiolene)–Mo(IV) complexes and correlate their values with the above extended MO calculations. In principle, a relationship between the oxidation potential and the energy of the HOMO, the participating orbital in the oxidation reaction, has been reported for many systems.[30] For similar complexes, under similar experimental conditions, both parameters must be linearly correlated.

A comparison of their half-wave potentials reveals that dithiolene complexes have lower reduction potentials than that found for the tris(thiobenzilate) complex 3. Thus, the only well-characterized $[Mo(S_2C_2(CO_2Me)_2)_3]^{2-}$,[17] $[Mo(S_2C_2(CN)_2)_3]^{2-}$,[31] and $[Mo(qdt)_3]^{2-}$ [28] complexes exhibit half-wave potentials of 0.026, 0.49, and 0.265 V, respectively. This finding is unexpected since, according to Figure 5, both types of complexes have similar HOMO energies, or the energy is even somewhat higher for complex 3. It remains possible, however, that destabilization of the HOMO occurs by enhanced d_{z^2}–p_π interactions favored by the twist angle between of the upper and lower triangular faces of the complex. Such a lowering of the molecular symmetry allows sulfur π orbitals to interact with the HOMO[19,32] and thereby pushes this energy level up. The larger the d_{z^2}–p_π interaction, the more the HOMO will be destabilized and the easier it becomes to oxidize the complex. The twist angle of 28° for $[Mo(S_2C_2(CN)_2)_3]^{2-}$ and 10.28° for $[Mo(S_2C_2(CO_2Me)_2)_3]^{2-}$ agree with these MO considerations since the former complex has a higher potential than the latter and both are in turn higher than that obtained for complex 3, whose twist angle is only of 4.7°. However, this argument predicts that $[Mo(qdt)_3]^{2-}$, with a twist angle of 4.5°, should have a potential comparable to that observed for complex 3. The reported value[28] of 0.265 V is unexpected and may be a consequence of a difference between solution and solid geometries. Indeed, the observation of a nearly perfect TP structure for the $[Mo(qdt)_3]^{2-}$ complex has been considered unexpected[33] since its oxidized monoanionic Mo(V) derivative has a structure significantly distorted from the ideal TP geometry (twist angle of 14.6°).

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