Inorg. Chem. **1996,** *35,* 3285−3288

New Explanation for Ligand Bending in Transition Metal Tris(dithiolate) Complexes

Scott Campbell and Suzanne Harris*

Department of Chemistry, University of Wyoming, PO Box 3838, Laramie, Wyoming 82071-3838

Received October 27, 1995[⊗]

The results of Fenske−Hall molecular orbital calculations are reported for the trigonal prismatic complexes $Mo(S_2C_2H_2)_3$ and $Mo(S_2C_6H_4)_3$. Both complexes exhibit a bend of the S−C−C−S ligand plane away from the S−Mo−S plane. A series of calculations which systematically follow the changes in electronic structure as the bend angle α is varied between 0 and 30° indicates that the bend can be attributed to a second order Jahn−Teller distortion. The driving force for this distortion, which allows mixing between a set of ligand π orbitals and the metal d_{z^2} orbital, should be greatest for d^0 systems. In these systems the bent geometry leads to the stabilization of the doubly occupied HOMO. The driving force for ligand bending should be lower in systems having more or fewer electrons (e.g. $Re(S_2C_2Ph_2)_3$ or $V(S_2C_2Ph_2)_3$, respectively). While the steric bulk of the dithiolate ligands in the latter complexes may also influence the degree of ligand bending, this is probably a secondary effect.

Introduction

Six-coordinate molecular transition metal complexes that adopt trigonal prismatic geometry have received considerable attention. The factors which contribute to prism stability relative to octahedral stability have been extensively studied and are summarized in several recent articles.[3−6] A group of complexes often adopting trigonal prismatic geometry is the transition metal tris(dithiolates).[7] The earliest of these, $Re(S_2C_2Ph_2)_3$,[8] was used by Gray as a model for describing the bonding in these types of complexes. In addition to their tendency toward trigonal prismatic geometry, some of the tris(dithiolate) complexes possess another interesting structural feature. This is a bending of the S−C−C−S plane away from the S−Mo−S plane. The structures of both $Mo(S_2C_2H_2)_3$[1] and $Mo(S_2C_6H_4)_3$[2] display this bend (Figure 1). In $Mo(S_2C_2H_2)_3$ the ligand plane bend, denoted by α, is 18° for all three ligands, while in $Mo(S_2C_6H_4)_3$ the bend angles are 13.1, 21.1, and 30.0°. This characteristic bend is also present in $[Nb(S_2C_6H_4)_3]^-$ [9] and $Mo[Se_2C_2(CF_3)_2]_3$[10] but is absent in $[W(Se_2(COOCH_3)_2)_3]^{2-}$,[11] $Re(S_2C_2Ph_2)_3$, and $V(S_2C_2Ph_2)_3$.[12] Various authors have attributed this bend to both packing forces and the interaction of ligand π_v orbitals (π orbitals perpendicular to the plane of the dithiolate ligand) with metal d_{xy} and $d_{x^2-y^2}$ orbitals.[9] Schrauzer, using bond length and resonance arguments, has attributed this bending to intermediate sp^3-sp^2 hybridization of the sulfur atoms.[13] Other authors have suggested that a π interaction between the metal orbitals and the olefinic double bond causes the ligands to bend.[14] Although several authors have analyzed the electronic structure of this class of complexes, all of these analyses have been concerned primarily with the factors which stabilize the trigonal prismatic geometry and not with the cause of ligand bending. Consequently, none of these authors attempted to systematically compare the electronic structure of the complexes in D_{3h} (bend angle $\alpha = 0°$) vs C_{3h} (bend angle $\alpha > 0°$) geometries. The study reported here specifically addresses the issue of ligand bending, not the stability of trigonal prismatic vs octahedral structures.

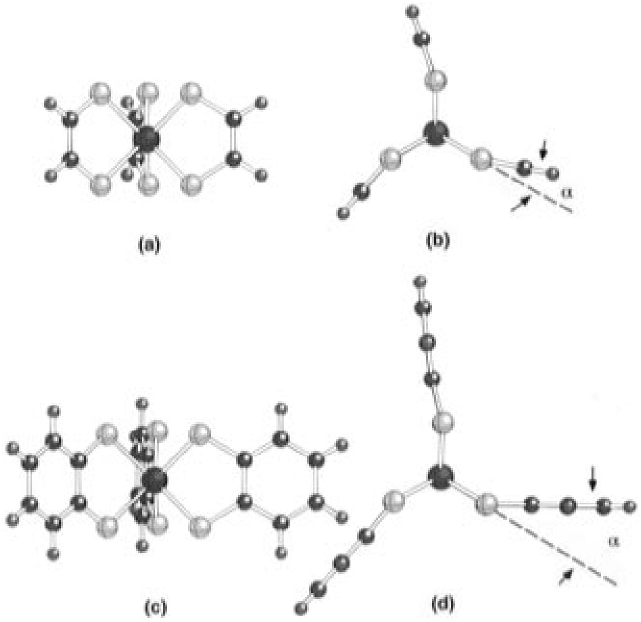

Figure 1. Structures of trigonal prismatic $Mo(S_2C_2H_2)_3$[1] and $Mo(S_2C_6H_4)_3$.[2] "Side" views of the complexes are shown in parts a and c while "top" views are illustrated in parts b and d. The angle α shown in the "top" views (b and d) measures the angle between the S−C−C−S plane of the ligand and the S−Mo−S plane.

In order to investigate possible causes for the ligand bending, we have carried out a series of Fenske−Hall[15] molecular orbital calculations on both $Mo(S_2C_2H_2)_3$ and $Mo(S_2C_6H_4)_3$. In these

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

(1) Smith, A. E.; Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. *J. Am. Chem. Soc.* **1965**, *87*, 5798.
(2) Cowie, M.; Bennet, M. J. *Inorg. Chem.* **1976**, *15*, 1584.
(3) Martin, J. L.; Takats, J. *Can. J. Chem.* **1989**, *67*, 1914.
(4) Karpishin, T. B.; Stack, T. D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 182.
(5) Kang, S. K.; Tang, J.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971.
(6) Cervilla, A.; Ramirez, J. A.; Llopis, E.; Palanca, P. *Inorg. Chem.* **1992**, *32*, 2085.
(7) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295.
(8) Stiefel, E. I.; Eisenberg, R.; Rosenberg, R. C.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 2956.
(9) Cowie, M.; Bennet, M. J. *Inorg. Chem.* **1976**, *15*, 1589.
(10) Pierpont, C. G.; Eisenberg, R. *J. Chem. Soc. A* **1971**, 2285.
(11) Ansari, M. A.; Mahler, C. H.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 2669.
(12) Eisenberg, R.; Gray, H. B. *Inorg. Chem.* **1967**, *6*, 1844.
(13) Schrauzer, G. N.; Mayweg, V. P. *J Am. Chem. Soc.* **1966**, *88*, 3225.
(14) Moriarty, R. E.; Ernst, R. D.; Bau, R. *J. Chem. Soc., Chem. Commun.* **1972**, 1242.
(15) Hall, M. B.; Fenske, R. F. *Inorg. Chem.* **1972**, *11*, 768.

S0020-1669(95)01390-5 CCC: $12.00

calculations the angle α between the S−C−C−S plane and the S−Mo−S plane was varied systematically between 0 and 30°. (This is obviously an idealized situation since the hypothetical D_{3h} structure would most likely include some change in the Mo−S bond lengths and some distortion within the dithiolate ligand.) At each angle we have examined the orbital energies and various Mo−S overlaps and overlap populations. Since the results of our calculations show that the orbital structures of both complexes are similar, we restrict our discussion to $Mo(S_2C_2H_2)_3$.

The irregular ligand bending in $Mo(S_2C_6H_4)_3$ and the fact that there is no ligand bending in $Re(S_2C_2Ph_2)_3$ and $V(S_2C_2Ph_2)_3$ suggest that crystal packing forces may also contribute to the observed structures of these complexes. Therefore, in addition to examining the electronic factors related to ligand bending, we have also compared the crystal structures of several tris(dithiolates) and considered the effect of ligand bulk on the structures of the complexes.

The first section of this report provides a brief description of the calculational details. This is followed by a discussion of the results of the molecular orbital calculations. These results suggest an electronic explanation for the ligand bending that is different from any of those previously proposed. Finally, the relative importance of electronic factors vs the bulk of the ligands is considered.

Calculational Details

Calculations were carried out using the Fenske−Hall approximate molecular orbital method.[15] Atomic charges, orbital populations, and overlap populations were arrived at by Mulliken population analysis.[16] All basis functions were generated by the numerical Xα atomic orbital program of Herman and Skillman,[17] used in conjunction with the Xα-to-Slater basis program of Bursten and Fenske.[18] Ground state atomic configurations were used for C and S; a +1 cationic configuration was used for Mo. This choice was justified by the resulting calculated atomic charges. The Mo 5s and 5p exponents were fixed at 2.2. The hydrogen exponent chosen was 1.2. Since adding d valence functions to sulfur had no effect on the qualitative features of the results, these d orbitals were omitted. The local coordinate systems for each of the sulfur atoms were chosen such that each sulfur p_z orbital points at the Mo atom and each sulfur p_x orbital is perpendicular to the plane of the ligand when the ligand is in the D_{3h} limit.

In order to clarify certain points it is useful to examine some of the interactions in terms of fragment molecular orbitals (FMO's). The FMO's chosen for the basis set transformation are each of the three sets of isolated dithiolate ligand MO's plus the metal AO's.

Discussion

The bonding in $Mo(S_2C_2H_2)_3$ is similar to the bonding in $Re(S_2C_2Ph_2)_3$. Although the electronic structure of $Re(S_2C_2Ph_2)_3$ has been described thoroughly by Gray and co-workers,[8] a short review is useful. Trigonal prismatic geometry with the metal coordinate system defined as in Figure 2a splits the metal d orbitals into a_1' (d_{z^2}), e' ($d_{x^2-y^2}$, d_{xy}), and e'' (d_{xz}, d_{yz}) sets. In the D_{3h} limit there are sets of ligand σ orbitals which have the correct symmetry to interact with each of the metal d orbitals and sets of ligand π orbitals which have the correct symmetry to interact with the e' and e'' metal d orbitals. In addition, there are two sets of ligand π orbitals, a_2'' and a_2', which are nonbonding with respect to the metal orbitals. This results in a complicated set of interactions of which the following four are typical.

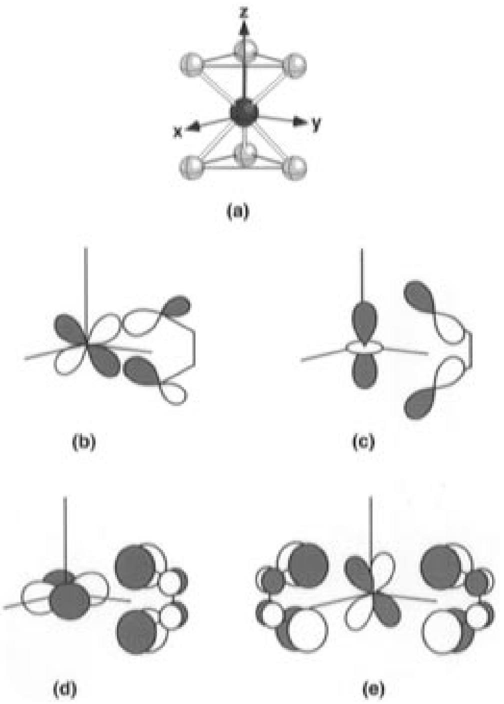

Figure 2. Illustrations of the central coordinate system (a) and typical metal−ligand orbital interactions in trigonal prismatic trisdithiolates. See text for detailed descriptions of the interactions.

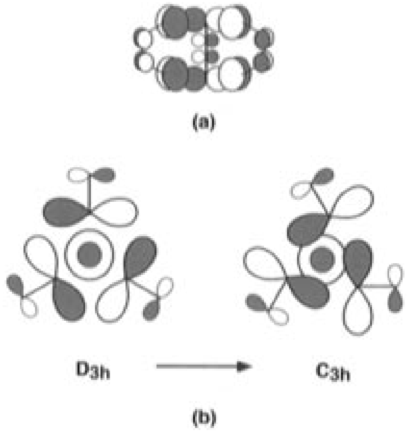

Figure 3. (a) Illustration of the nonbonding a_2' HOMO in a D_{3h} model of $Mo(S_2C_2H_2)_3$. (b) Development of overlap and bonding between the a_2' combination of ligand π_v orbitals and the metal d_{z^2} orbital as the symmetry changes from D_{3h} to C_{3h}.

I. σ bonding between ligand σ orbitals that point toward the metal and metal d_{xz} and d_{yz} orbitals. (Figure 2b).

II. Bonding between ligand σ orbitals and metal d_{z^2} orbitals. These are a mixture of σ and π interactions (Figure 2c).

III. Donation from ligand π_v orbitals perpendicular to the ligand plane into metal d_{xy} and $d_{x^2-y^2}$ orbitals. These are purely π interactions. (Figure 2d).

IV. Donation from ligand π_v orbitals into metal d_{xz} and d_{yz} orbitals. These are π and δ type interactions (Figure 2e).

The results of Fenske−Hall calculations for $Mo(S_2C_2H_2)_3$ show that in the D_{3h} limit the HOMO is a nonbonding a_2' combination of ligand π_v orbitals and the LUMO (a_1') consists primarily of the metal d_{z^2} orbital. The a_2' nonbonding HOMO is shown in Figure 3a. This level ordering is consistent with a description of the complex in which each dithiolate ligand carries a 2− charge and the Mo center is formally Mo(VI)-d^0. In this description, all of the metal d orbitals are unoccupied. The calculated energy difference between the HOMO and LUMO

---

(16) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.
(17) Herman, F.; Skillman, S. *Atomic Structure Calculations;* Prentice-Hall: Englewood Cliffs, NJ, 1963.
(18) Bursten, B. E.; Jensen, R. J.; Fenske, R. F. *J. Chem. Phys.* **1978**, *68*, 3320.

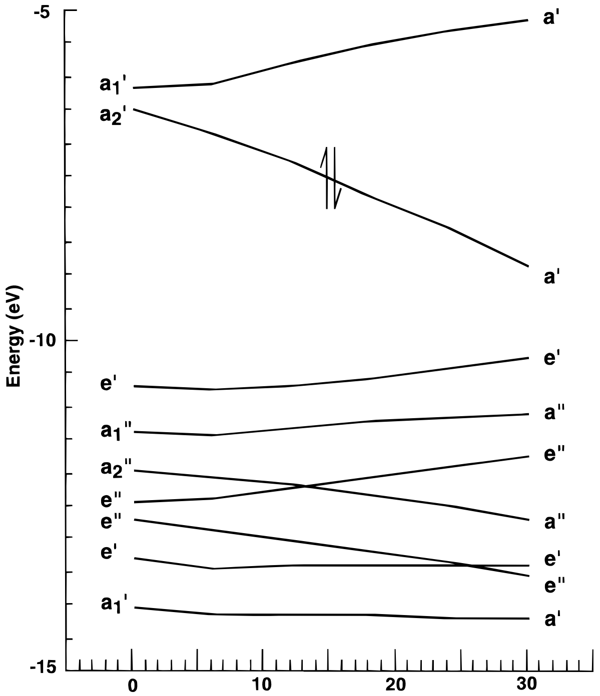

Figure 4. Variations in the energies of the LUMO and the 12 highest energy occupied orbitals of $Mo(S_2C_2H_2)_3$ as a function of the twist angle α.

is very small, however, and the orbitals are nearly degenerate. This orbital arrangement is also consistent with the results of Gray and co-workers[8] for $Re(S_2C_2Ph_2)_3$.

In D_{3h} symmetry, no mixing is possible between the HOMO (a_2' ligand π_v orbitals) and the LUMO (a_1' metal d_{z^2} orbital). In complexes where the ligand is bent ($\alpha > 0$), however, this restriction is removed. The symmetry of the complex becomes C_{3h}, and both the HOMO and LUMO now transform as a′. In addition, the ligand π_v orbitals are no longer perpendicular to the metal d_{z^2} orbital; instead they twist in toward the metal d_{z^2}. The change in orientation of the ligand π_v orbitals together with the lowering of the symmetry allows overlap between the ligand π_v and metal d_{z^2} orbitals and mixing of the "a_2'" and "a_1'" sets of orbitals. This leads to the formation of a bonding a′ orbital and an antibonding a′ orbital. Figure 3b illustrates how the bonding interaction develops as the ligand planes bend away from the S−Mo−S planes. This bonding interaction should result in a lowering of the HOMO energy and an increase in the Mo−S bond strengths.

Although it is not strictly true that changes in the total energy are proportionally reflected in changes in the sum of the orbital energies, it is often a good approximation. Therefore an examination of orbital energy dependence on the twist angle α is useful. The variations in the energies of the LUMO and the 12 highest occupied orbitals as a function of the twist angle α are shown in Figure 4. It is apparent that as the complex distorts toward C_{3h} symmetry there is a significant decrease in the energy of the a′ HOMO. There is also a corresponding increase in the energy of the unoccupied a′ LUMO. In addition to the energy changes in the HOMO−LUMO a′ orbitals there are four sets of lower energy orbitals whose energies are affected by the geometry change. These include two sets of e″ orbitals, one a_2'' orbital, and one a_1'' orbital. Qualitatively, however, the energy increases and decreases for these lower lying orbitals are similar, and this suggests that the driving force for the ligand twist is the stabilization of the a′ HOMO. This type of geometrical distortion involving HOMO-LUMO mixing is a second-order Jahn−Teller distortion,[19] i.e. a distortion which allows two orbitals having similar energies to mix together in the distorted structure with the result that one orbital is stabilized and one is destabilized.

Table 1. Total Mo−S Overlap Populations as a Function of α in $Mo(S_2C_2H_2)_3$

angle (α), deg	0	6	12	18	24	30
overlap pop.[a]	1.491	1.555	1.564	1.576	1.587	1.588

[a] This is the sum of the overlap populations between all sulfur orbitals and all metal orbitals.

Table 2. Individual Metal Orbital−Sulfur Overlap Populations in $Mo(S_2C_2H_2)_3$

	metal orbital				
	z^2	x^2-y^2	xy	xz	yz
D_{3h} geometry	0.017	0.217	0.217	0.256	0.256
C_{3h} geometry	0.088	0.215	0.215	0.256	0.256
net change ($D_{3h} \rightarrow C_{3h}$)	0.071	−0.003	−0.003	0.000	0.000

A description of the ligand twist as a second-order Jahn−Teller distortion is consistent with the observation that the maximum twist angle is observed in the tris(dithiolate) complexes where only two electrons are available to occupy the nearly degenerate a_2' and a_1' orbitals. In complexes having fewer electrons (i.e. $V(S_2C_2Ph_2)_3$) or, in particular, additional electrons (i.e. $Re(S_2C_2Ph_2)_3$) the driving energy for the distortion will be considerably less.

Bending of the ligands should also decrease anti-bonding interactions between adjacent sulfur atoms. It can be seen from Figure 3 that although in the D_{3h} geometry the a_2' orbital is nonbonding with respect to the metal d_{z^2}, it is antibonding with respect to adjacent sulfur atoms in the trigonal planes. Bending of the ligands to the C_{3h} geometry decreases the overlap between adjacent sulfur atoms which in turn should lower the energy of this antibonding orbital. It appears that this is a minor factor in the observed bend, however, since the decrease in overlap between adjacent sulfur atoms is minimal until the distortion angle, α, is quite large.

Since the ligand twist is expected to increase the strength of the metal−ligand bonds and since orbital overlap populations provide a measure of the strength of a particular bond, it is also useful to analyze the metal−ligand orbital overlap populations. Table 1 lists the total Mo−S overlap populations as a function of α. These show that there is an increase in the total Mo−S overlap population as the molecule distorts from D_{3h} symmetry. To determine the specific metal orbitals involved in this increase in bond strength it is helpful to examine the overlap populations between the sulfurs and each metal d orbital. These quantities are shown in Table 2 for both the idealized D_{3h} geometry and the C_{3h} structure. It is apparent that most of the increase in Mo−S overlap population can be attributed to the increased d_{z^2}-S interaction. This provides further evidence that it is the interaction between the ligand π_v orbitals and the metal d_{z^2} orbital that promotes ligand bending. The earlier suggestion[9,14] that the ligand π_v−($d_{x^2-y^2}$, d_{xy}) interaction is responsible for ligand bending is not supported by our results; the S−$d_{x^2-y^2}$ and S−d_{xy} overlap populations are actually smaller in the bent geometry. To further illustrate this point, it is useful to examine the interaction between the three ligand π_v orbitals and the metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals. As illustrated in Figure 2d, it is these ligand π_v orbitals which interact most strongly with the metal $d_{x^2-y^2}$ and d_{xy} orbitals. It is also a positive combination of these three orbitals which forms the a_2' nonbonding orbital

---

(19) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry, 1*; John Wiley and Sons, Inc.: New York, 1985.

Table 3. Ligand π_v Orbital−Metal Orbital Overlap Populations

	metal orbital		
	z^2	$x^2 - y^2$	xy
D_{3h} Geometry			
π_v ligand 1	0.000	0.000	0.068
π_v ligand 2	0.000	0.051	0.017
π_v ligand 3	0.000	0.051	0.017
tot.	0.000	0.103	0.103
C_{3h} Geometry			
π_v ligand 1	0.027	0.000	0.064
π_v ligand 2	0.027	0.041	0.023
π_v ligand 3	0.027	0.054	0.010
tot.	0.080	0.096	0.096

that interacts with the metal d_{z^2} as the ligand planes bend. The overlap populations between the three ligand π_v orbitals and the metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals are shown in Table 3. Again, it is apparent that twisting of the ligands results primarily in increased bonding between the sulfurs and the metal d_{z^2} orbital. The effects of ligand bending on the interaction between the sulfurs and the metal $d_{x^2-y^2}$, and d_{xy} orbitals are much smaller and tend to weaken rather than strengthen the metal−sulfur interaction.

In summary, our results indicate that the driving force for the observed bend in the ditholate ligands is a second-order Jahn−Teller distortion which stabilizes (for d^0 metals) the HOMO. Since it has been proposed, however, that ligand bending in these complexes may be attributed to crystal packing forces, we also examined and compared the crystal structures of several of these complexes. The crystal structures of complexes such as $Mo(S_2C_6H_4)_3$, $[Ph_3As][Nb(S_2C_6H_4)_3]$, $V(S_2C_2Ph_2)_3$, and $Re(S_2C_2Ph_2)_3$ (particularly when viewed utilizing van der Waals spheres on each atom) show, not surprisingly, that packing of the complexes does vary as the steric bulk of the ligand changes. The structures support the idea that ligand movement is hindered by the presence of the bulky phenyl substituents, since ligand bending is generally observed in complexes which incorporate less bulky (or even flat) dithiolate ligands (e.g. $[Nb(S_2C_6H_4)_3]^-$ or $Mo(S_2C_6H_4)_3$), while the bend is generally absent or greatly decreased in complexes having much bulkier ditholate ligands (e.g. $V(S_2C_2Ph_2)_3$ or $Re(S_2C_2Ph_2)_3$). At the same time, however, the bent ligands are always observed in the complexes containing d^0 metals (where bending will lead to the maximum electronic stabilization) while the planar ligands occur in complexes containing fewer or more electrons (where the electronic driving force for bending should be smaller). Taken together, these observations suggest that while the bulk of the ligand may be a secondary factor in determining whether the ditholate bends, it is actually the number of ligand and metal electrons and thus the occupation of the a_2' and a_1' orbitals which is the major factor affecting the bend angle.

Conclusions

In conclusion, the results presented here indicate that any electronic preference toward C_{3h} geometry results primarily from HOMO−LUMO mixing which lowers the energy of the HOMO. The suggestion by previous workers[9] that the ligand bend is caused by increased π_v−metal (xy, $x^2 - y^2$) interactions is not supported in this study; in fact, the e′ orbitals involved in this interaction are the most insensitive to ligand bending.

In general, complexes of transition metal tris(dithiolates) have similar molecular orbital schemes and are characterized, in the D_{3h} limit, by a small gap between the nonbonding a_2' and metal a_1' orbitals. A distortion toward C_{3h} geometry leads to mixing of the ligand a_2' and metal a_1' pair which in turn results in the formation of bonding and antibonding a′ orbitals which are lowered and raised respectively in energy. The bend of the ligands may be viewed as a second-order Jahn−Teller distortion, and the magnitude of the driving force for this distortion will depend on orbital occupation. The distortion should be most favored for complexes such as $Mo(S_2C_6H_4)_3$ or $[Nb(S_2C_6H_4)_3]^-$ where the a_2' orbital is doubly occupied but the a_1' orbital is empty. For complexes such as $Re(S_2C_2Ph_2)_3$, ligand bending should be less favorable since an extra electron would then occupy the antibonding a′ orbital. We would expect a bend to still be favored for $V(S_2C_2Ph_2)_3$, but now only one electron occupies the a_2' orbital and the driving force for the bend will be smaller. The smaller driving force combined with the bulkier dithiolate ligands in the vanadium and rhenium complexes may account for the absence of the bend in these complexes. It is interesting to observe that the structures of the similar selenium containing complexes $Mo[Se_2C_2(CF_3)_2]_3$ and $[W(Se_2(COOCH_3)_2)_3]^{2-}$ suggest that the same factors are responsible for the geometries of these complexes. A ligand bend of 18° is observed in the d^0 $Mo[Se_2C_2(CF_3)_2]_3$ complex, while the ligand bend is absent in the d^2 $[W(Se_2(COOCH_3)_2)_3]^{2-}$. Thus, while electronic factors (i.e. orbital occupations) appear to provide the principle driving force for the observed ligand bends (particularly in d^0 systems), the bulk of the dithiolate ligand probably also plays a role in determining the structures of these complexes. A systematic study of the structures of a series of tris(dithiolate) complexes incorporating both metals having different d orbital populations and ligands of different bulkiness would aid greatly in determining the role played by the ligand. It would be very informative to know, for example, not only whether a bend is still observed in a d^0 Mo complex when a bulkier ligand is introduced but also whether the ligands begin to bend in the vanadium and rhenium complexes when less bulky dithiolate ligands are used. In addition, as suggested by a reviewer, it would be extremely informative to know whether the structures observed in the solid state are maintained in solution.

Acknowledgment. We thank the National Science Foundation for partial support of this work (Grant 9421784). S.C. acknowledges support through a DOE/EPSCoR Traineeship.

IC9513907