described by eq 5. It is interesting to note that in acetonitrile

$$[\mathrm{LMoOX_2}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{LMoOX_2}] \qquad X = \mathrm{Cl, Br} \qquad (5)$$

as solvent further oxidation to Mo(VI) or reduction to Mo(III) is not observed. This behavior has been observed previously.[23-25]

The cyclic voltammogram of $[\mathrm{LMoO_2Br}]\mathrm{PF_6}$ in acetonitrile exhibits one reversible electron transfer, which is assigned to the couple $[\mathrm{LMoO_2Br}]^+/[\mathrm{LMoO_2Br}]^0$. Excess of bromide ions of the supporting electrolyte affects the peak current ratio, $I_p(\mathrm{ox})/I_p(\mathrm{red})$ at scan rates smaller than 0.05 V $\mathrm{s^{-1}}$. This indicates slow decomposition of the reduced species (most probably loss of $\mathrm{Br^-}$) according to eq 6.

$$[\mathrm{LMoO_2Br}]^+ \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{LMoO_2Br}]^0 \rightleftharpoons \mathrm{Br^-} + \text{products} \qquad (6)$$

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der chemischen Industrie. We wish to thank Professor J. H. Enemark and Dr. M. Minelli (University of Arizona) for measuring the ^{95}Mo NMR spectrum.

Supplementary Material Available: Listings of thermal parameters, positional parameters of hydrogen atoms, observed and calculated structure factors, and elemental analyses of complexes (10 pages). Ordering information is given on any current masthead page.

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(23) Isbell, A. F.; Sawyer, D. T. *Inorg. Chem.* **1971**, *10*, 2499.

(24) Taylor, R. D.; Street, J. P.; Minelli, M.; Spence, J. T. *Inorg. Chem.* **1978**, *17*, 3207.

(25) Spence, J. T.; Minelli, M.; Kroneck, P. *J. Am. Chem. Soc.* **1980**, *102*, 4538.

(26) Experimental details have been reported elsewhere: Minelli, M.; Enemark, J. H.; Wieghardt, K.; Hahn, M. *Inorg. Chem.* **1983**, *22*, 3952.

(27) LeGall, J. Y.; Kubicki, M. M.; Petillon, F. Y. *J. Organomet. Chem.* **1981**, *221*, 287.

Contribution from Exxon Research and Engineering Company,
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Steric Effects in $[\mathrm{CpMoS}(\mu\text{-S})]_2$ Dimers Studied by Interactive Molecular Graphics

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Interactive molecular graphics (IMG) has been applied to modeling steric effects in the sulfido-bridged molybdenum dimers, $[(\mathrm{C_5H_{5-n}Me_n})\mathrm{MoS}(\mu\text{-S})]_2$ (n = 0 and 5). This technique, which is already well established in other areas, proves to be a convenient means of probing steric effects in such organometallic complexes. It is shown that the intramolecular van der Waals energies of the syn isomers of these cyclopentadienyl derivatives are higher than those of the corresponding anti isomers for configurations that have been previously indicated to be electronically the most favorable.

Introduction

Systematic studies of the synthesis, structure, and reactivity of molybdenum(V) coordination complexes with sulfur-containing ligands are important in the search for an understanding of the active sites in molybdoenzymes[1] and in heterogeneous hydrotreating catalysts.[2] Among the more widely studied classes of such complexes is that containing the dinuclear $[\mathrm{MoS}(\mu\text{-S})]_2^{2+}$ core. A variety of well-characterized examples are known, in which the ligands L (L′) that complete the coordination about each molybdenum are a pair of monodentate S ligands, a chelating S,S or N,S ligand, or a cyclopentadienyl group.[3-12] Full structural details for a number of these complexes have been obtained by single-crystal X-ray diffraction. In each case, the molecular structure corresponds to one of the two geometric isomers shown in Figure 1, designated syn and anti. The "closed" form shown in Figure 1 has been suggested as a third possible isomer, but it has not yet been observed experimentally. The syn isomer is the more common, having been found for L = L′ = diethyldithiocarbamate,[4,5] dibutyldithiocarbamate,[6] tetrasulfide ($\mathrm{S_4}^{2-}$),[8] disulfide ($\mathrm{S_2}^{2-}$),[7] and 1,2-ethanedithiolate[9,10] and for L = disulfide and L′ = tetrasulfide.[8,11] The anti configuration was observed for L = 1,2-ethanedithiolate,[9,10] methylcyclopentadienyl,[12] and pentamethylcyclopentadienyl.[12] Only the 1,2-ethanedithiolate complex has been characterized in both configurations. The anti isomer was prepared in low yield (3%) from a complex reaction involving $\mathrm{MoCl_3}$, NaHS, NaOMe, and 1,2-ethanedithiol. The syn isomer was isolated (6% yield) from a mixture of the same reagents having a slightly different composition. Three higher yielding procedures that have been developed for synthesis of the complex[13] invariably result in the syn isomer. This is in keeping with the molecular orbital calculations of Lichtenberger et al.[16] that predicted relative stabilities in the order syn > closed > anti.

Given these relative stabilities, it is then somewhat intriguing that the cyclopentadienyl complexes have only been characterized

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(1) Coughlan, M. P., Ed. "Molybdenum and Molybdenum-Containing Enzymes"; Pergamon Press: New York, 1980.

(2) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979; pp 390–445.

(3) Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

(4) Muller, A.; Bhattacharyya, R. G.; Mohan, N.; Pfefferkorn, B. *Z. Anorg. Allg. Chem.* **1979**, *454*, 118–124.

(5) Huneke, J. T.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 3698.

(6) Spivack, B.; Dori, Z.; Stiefel, E. I. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 501.

(7) Pan, W.-H.; Harmer, M. A.; Halbert, T. R.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 459.

(8) Draganjac, M.; Simhon, E.; Chan, L. T.; Kanatzidis, M.; Baezinger, N. C.; Coucouvanis, D. *Inorg. Chem.* **1982**, *21*, 3321–3332.

(9) Bunzey, G.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 682.

(10) Bunzey, G.; Enemark, J. H.; Howie, J. K.; Sawyer, D. T. *J. Am. Chem. Soc.* **1977**, *99*, 4168.

(11) Clegg, W.; Christou, G.; Garner, C. D.; Sheldrick, G. M. *Inorg. Chem.* **1981**, *20*, 1562.

(12) Rakowski Dubois, M.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064–3071.

(13) $\mathrm{Mo_2S_4}(1,2\text{-ethanedithiolate})_2^{2-}$ has been prepared from the reaction of 1,2-ethanedithiol with $\mathrm{(NH_4)_2MoS_4}$,[14] with $\mathrm{(TEA)_2Mo_2S_8}$,[15] and with $\mathrm{(NH_4)_2Mo_2S_{12}}$.[3] In each case, yields of better than 50% could be obtained.

(14) Pan, W.-H.; Leonowicz, M. E.; Stiefel, E. I., unpublished work.

(15) Halbert, T. R., unpublished work.

(16) Chandler, T.; Lichtenberger, D. L.; Enemark, J. H. *Inorg. Chem.* **1981**, *20*, 75–77.

(17) Gelder, J. I.; Enemark, J. H. *Inorg. Chem.* **1976**, *15*, 1839–1843.

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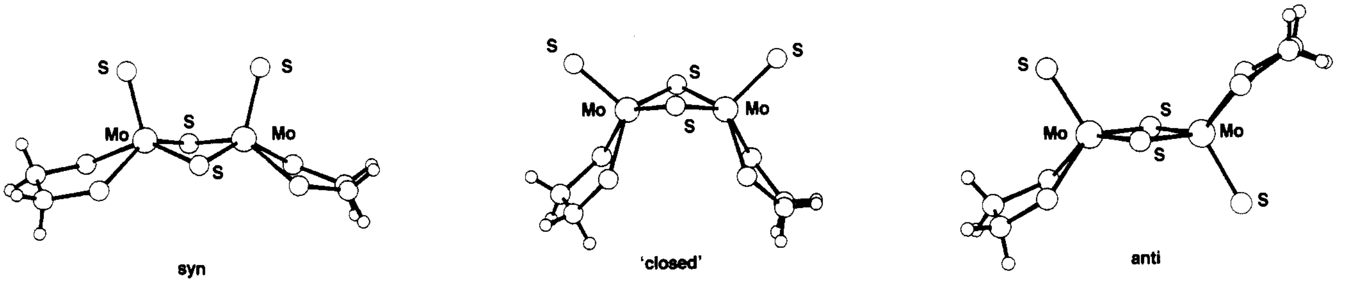

Figure 1. Three forms of the bis(μ-sulfido)bis(sulfido(1,2-ethanedithiolato)molybdate(V)) anion, $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2^{2-}$. The closed form differs from the syn isomer only in the value of the Mo–S–S–Mo torsion angle.

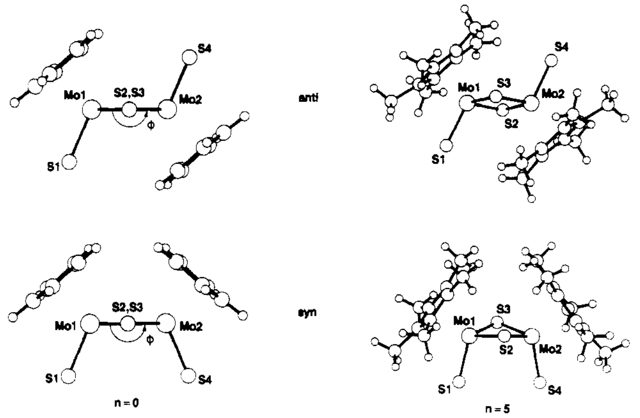

Figure 2. Configurations of the cyclopentadienyl derivatives, $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ (n = 0 and 5). For the n = 0 materials, both syn and anti forms are shown in the planar configuration corresponding to a Mo1–S2–S3–Mo2 torsion angle of ϕ = 180°. The pentamethyl derivatives, n = 5, are shown as ϕ_{anti} = 180° (observed crystallographically) and ϕ_{syn} = 154°.

in the anti configurations. This observation is all the more interesting in light of the surprising reactivity of these complexes toward H_2, acetylene, and ethylene.[12] Such reactivity has not been found to occur in the syn complexes with L = S,S or N,S ligands.[15] Two possible explanations might initially be considered to account for the apparent difficulty in isolating the syn isomers. First, differences in the electronic structure resulting from the change of an S,S type ligand to a cyclopentadienyl group might favor the anti isomer. Second, the greater steric bulk of the cyclopentadienyl functions might act to destabilize the syn (and closed) forms. Indeed, the possible importance of steric effects in determining the geometries of compounds based on the related $[MoO(\mu\text{-}S)]_2^{2+}$ core was recognized earlier by Gelder and Enemark.[16]

The steric possibility is one that lends itself very readily to modeling by routines that are incorporated in many interactive molecular graphics packages. First, precise atomic coordinates are available from published crystal structure analyses, and, secondly, in order to model such steric effects it is necessary not to calculate absolute interaction energies but merely to map out changes in relative energy with conformation. The present report then describes the application of interactive molecular graphics to the study of steric effects in $[MoS(\mu\text{-}S)]_2^{2+}$ dinuclear complexes.

Methods

Crystallographic coordinates of the $(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)$ (n = 1 and 5) moieties were taken from the structural work of Rakowski DuBois et al.[12] The centroids (CT) of the C_5 rings were first computed by a least-squares process using the CRYSTALS system.[18] These centroids provide a useful point for maintaining connectivity and suitable centers about which changes in energy with ring rotation could be monitored.

For the n = 1 material, the methyl group was first deleted and hydrogens were added geometrically (at a distance of 1.00 Å) to each of the ring carbons. The complete anti dimer was generated by application of the center of inversion at the crystallographic origin. The syn form was derived by an addition π rotation of one C_5H_5MoS fragment about the Mo–Mo vector.

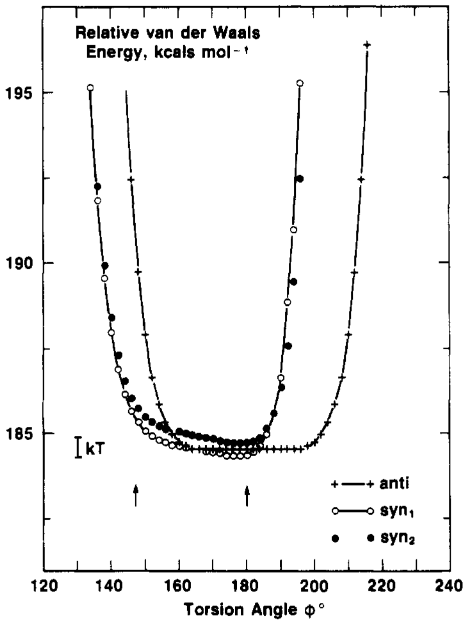

Figure 3. Intramolecular van der Waals energies of the syn and anti isomers of the unsubstituted cyclopentadienyl derivative, $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ (n = 0), calculated as a function of the Mo1–S2–S3–Mo2 torsion angle, ϕ. The syn$_2$ form has one of the cyclopentadienyl ligands rotated by 36° from the eclipsed position of the syn$_1$ form (see text). The torsion angles, ϕ_{anti} = 180° and ϕ_{syn} = 147°, that are observed crystallographically for the related 1,2-ethanedithiolato derivatives are indicated by arrows.

The intramolecular van der Waals repulsion energy was calculated as a function of the Mo1–S2–S3–Mo2 torsion angle, ϕ (Figure 2), according to the formula and parameters given by Del Re et al.[19] The summation was made over all nonbonded atom pairs, save for the contributions from the molybdenum atoms that were not included. Although for manipulation of the dimer the connectivity was arranged as Mo1–S2–S3–Mo2, for the energy calculations the bonding scheme indicated in Figure 2 was reconstructed. The results of these calculations are shown in Figure 3.

The available structural data on the *anti*-$[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ dimers (n = 1 or 5) indicate that an apex of the cyclopentadienyl ring eclipses the terminal sulfido ligand in projection. To probe the effects of possible ring rotations about the Mo–CT vector, the calculation for the syn form was repeated for a configuration in which the ring was rotated by 36° from this eclipsed position. Although inspection of a ball and stick model might suggest that this adjustment would improve the meshing of the two rings as they approach each other, the energy calculations show that this does not reduce the steric constraints (Figure 3).

The pentamethyl derivatives provide somewhat more of a challenge. The atomic coordinates for the $[(C_5C_5)MoS(\mu\text{-}S)]$ fragment were again taken from Rakowski DuBois et al.[12] Protons were added geometrically to each methyl carbon such that tetrahedral geometry and C–H distances of 1.00 Å would result. The anti dimer was then generated by application of the inversion center at the origin. In this starting configuration,

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[18] Watkin, D. J.; Carruthers, J. R. "CRYSTALS User Guide"; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1981.

[19] Del Re, G.; Gavuzzo, E.; Giglio, E.; Lelj, F.; Mazza, F.; Zappia, V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 3289–3296.

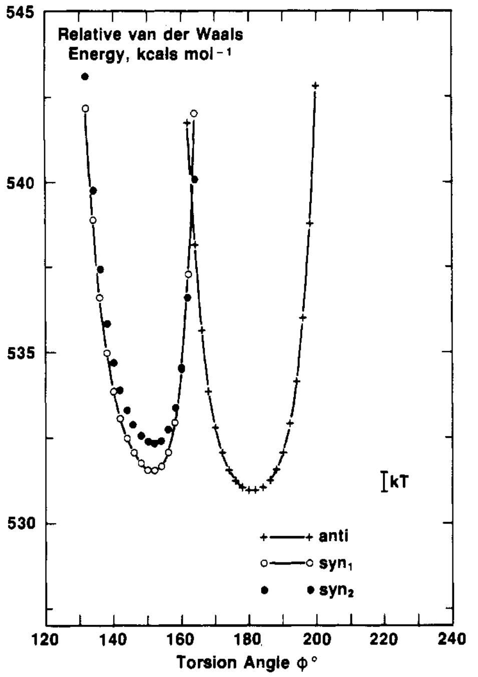

Figure 4. Intramolecular van der Waals energies of the syn and anti isomers of the pentamethyl derivative, $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ (n = 5), calculated as a function of the Mo1–S2–S3–Mo2 torsion angle, ϕ (legend as for Figure 3).

rotations about the C(ring)–C(methyl) bonds in each cyclopentadienyl fragment were automatically adjusted in an incremental fashion so as to minimize the total van der Waals energy sum.[20] This energy was then again plotted as a function of torsion angle, ϕ (Figure 4). For the syn form, generated as above by a π rotation of the C_5Me_5MoS moiety about the Mo–Mo vector, the energy was first similarly minimized at $\phi = 160°$. In an additional set of calculations, one ring was rotated 36° about the Mo–CT vector and the process repeated. The results of all of these computations are displayed in Figure 4.

To complete the picture, a similar set of calculations were performed for the 1,2-ethanedithiolato complexes in which steric effects are expected to be less pronounced. Coordinates for syn form were taken from Bunzey and Enemark.[9] As there is an error in the published coordinates for the anti form,[20] this was generated from the syn form by a π rotation about the Mo–Mo vector after the Mo1–S2–S3–Mo2 torsion angle, ϕ, had been set to 180°. Following geometrical addition of hydrogens to the carbon atoms, the energy calculations were performed as above. The results are plotted in Figure 5.

All of these calculations were performed interactively with the CHEMGRAF package[21] as implemented without modification on a VAX 11/780 system.

Results and Discussion

The ethanedithiolato derivatives of the $Mo_2S_4^{2+}$ core will be considered first, in order to establish the torsion angles observed in a system with minimal steric constraint. As seen in Figure 5, steric effects are indeed small for a wide range of torsion angles, ϕ, in both isomers. In the anti isomer, steric effects should be minimal from 130 to 230°. The torsion angle observed crystallographically is 180°.[9] In the two other known anti structures[12] the torsion angles have also been 180°, suggesting that for the anti form 180° is the preferred angle for electronic structural and bonding reasons. We have made no allowance for the role of "crystal-packing" forces in determining the torsion angle that is observed crystallographically. The observation of similar central geometries in the crystal structures of such dimers containing a variety of ligands does, however, suggest that such effects are not dominant. Also ignored were possible changes in strain energy[22] over the range of torsion angles considered.

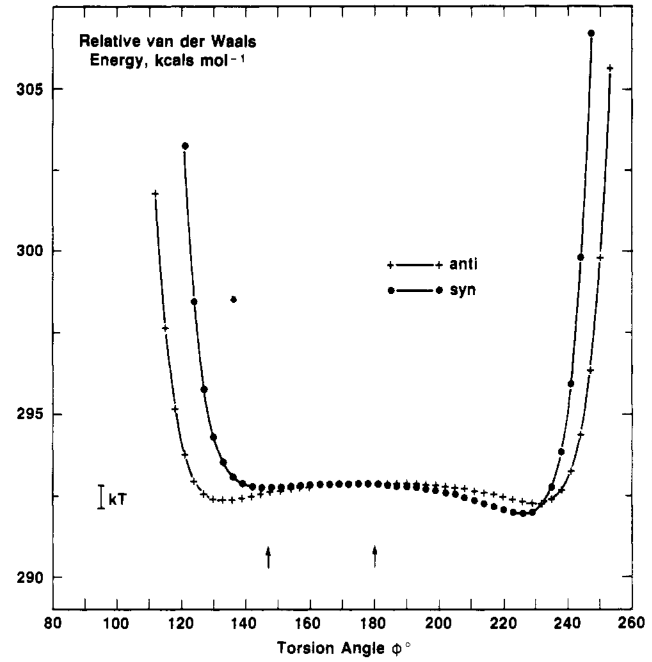

Figure 5. Intramolecular van der Waals energies of the syn and anti isomers of the 1,2-ethanedithiolato derivatives, $[(C_2H_4S_2)MoS(\mu\text{-}S)]_2$, plotted as a function of the Mo1–S2–S3–Mo2 torsion angle, ϕ (S2 and S3 are labeled S1 and S2 (syn), and S2 and S2′ (anti) in ref 9). The torsion angles observed in the corresponding crystal structures are ϕ_{anti} = 180° and ϕ_{syn} = 147° (indicated by arrows). The closed form would correspond to ϕ_{syn} = 213°.

In the syn form of the ethanedithiolato complex steric effects should be minimal between 140 and 230° (Figure 5). The crystallographically observed torsion angle is 147°.[9] In the syn configuration electronic structural and bonding factors apparently favor an angle near this value. In four other syn structures investigated crystallographically, the torsion angle has varied between 143 and 154°.[5,7,8] By comparison of the two isomers of the ethanedithiolato complex, it is also noteworthy that the energy of the anti isomer at ϕ_{anti} = 180° is slightly higher than that of the syn isomer with ϕ_{syn} = 147°. This is consistent with the observation that several different synthetic approaches tried recently have led to the isolation only of the syn isomer.[13] As noted previously, the syn isomer has also been predicted to be the more stable form on the basis of theoretical studies of the electronic structure and bonding in this system.[16]

Turning to the unsubstituted cyclopentadienyl system, $[(C_5H_5)Mo(\mu\text{-}S)]_2$, Figure 3 illustrates that there is again an extended region ϕ = 160–200° within which steric effects are small for the anti configuration. The complex can thus adopt the ϕ = 180° configuration, which is apparently preferred from a bonding standpoint. In the monomethyl derivative, $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ (n = 1), in which the single methyl group has little steric significance with respect to ϕ_{anti}, the central Mo1–S2–S3–Mo2 fragment is indeed planar.[12] This observation also indicates that although there appears to be a difference in molybdenum coordination number between the 1,2-ethanedithiolato and cyclopentadienyl derivatives, the core geometries are comparable.

In the syn configuration, there is also a large region of minimal steric interaction from ϕ = 155 to 185°. However, the flexing required to attain the presumably more desirable ϕ = 147° is sufficient for steric effects to have already become appreciable (Figure 3). The two configurations represented by ϕ_{anti} = 180° and ϕ_{syn} = 147° differ in van der Waals energy by some 0.9 kcal mol^{-1}. At this point we do not have a quantitative description

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(20) Examination of the published coordinates for the anti isomer of ref 9 revealed that the z parameter for atom S(4) (0.0159 (3)) is physically unreasonable. J. H. Enemark has recently informed us that the correct value should be 0.3043 (*Inorg. Chem.* **1984**, *23*, 3430).

(21) Davies, E. K. "CHEMGRAF Program suite"; Chemical Crystallography Laboratory: University of Oxford, Oxford, 1982.

(22) Brubaker, G. R.; Johnson, D. W. *Inorg. Chem.* **1984**, *23*, 1591–1595.

of how the electronic structure and bonding interactions in detail vary with ϕ, but clearly, unless such factors permit the syn isomer to adopt a more planar geometry, then the syn form will only be accessible via synthetic routes that lead directly to this configuration and do not permit kinetically facile interconversion. Such routes have not yet been demonstrated.

The situation becomes more acute in the case of the pentamethyl derivatives, as illustrated in Figure 4. The energy minimum for the syn form, at $\phi = 152°$, is conveniently close to 147°. Nevertheless, it is already 0.6 kcal mol^{-1} above that of the minimum in the anti form. Although this energy difference of approximately kT ($kT = 0.59$ kcal mol^{-1} at 298 K) might possibly be overcome by propitious crystal-packing or solvation effects, it could well be enough to greatly favor the anti configuration under conditions that permit interconversion. In light of these results it is understandable that the syn forms of the $[(C_5H_{5-n}Me_n)MoS(\mu\text{-}S)]_2$ complexes have not yet been isolated and characterized structurally.

Conclusion

Interactive molecular graphics can provide a rapid means of probing steric effects in organometallic complexes. Such modeling is thus a valuable complement to the information provided by molecular orbital energy or molecular mechanics calculations. The efficacy of the method has been demonstrated in monitoring intramolecular steric constraints on the conformations of bis(μ-sulfido)bis(sulfidocyclopentadienylmolybdenum) complexes. It has been shown that the intramolecular van der Waals energies of the syn forms of the $[(C_5R_5)MoS(\mu\text{-}S)]_2$ (R = H, Me) dimers are somewhat higher than those of the corresponding anti forms for configurations that have been previously indicated to be electronically the most favorable.

Acknowledgment. The authors thank Dr. E. I. Stiefel for numerous stimulating discussions and for his valuable insight regarding the chemistry of the Mo/S clusters referred to in this work. We also thank Prof. J. H. Enemark for several helpful comments.

Contribution from Ames Laboratory—DOE[1] and the Department of Chemistry,
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Low-Temperature Routes to New Structures for Yttrium, Holmium, Erbium, and Thulium Oxychlorides

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The pyrohydrolysis of $(NH_4)_3RCl_6$ (R = Y, Dy, Ho, Er, Tm, Yb) has been studied at 270–550 °C. This produces in part the YOF form of YOCl near 500 °C and $R\bar{3}m$ (disordered SmSI + YOF) phases for YOCl, HoOCl, ErOCl, TmOCl and YbOCl at 270–400 °C. Fluxed transformations of the disordered materials yield the new SmSI form of HoOCl (from LiCl-KCl) and YOF-type TmOCl, ErOCl (LiCl-KCl or RCl_3), YOCl, and HoOCl (KCl). No new structures are found for Dy and Yb. Reactions with LiCl-KCl or KCl melts also produce R_3O_4Cl phases for R = Y, Yb, Dy, and Ho, the last two being new. The $R\bar{3}m$ oxychlorides of Y, Ho, Er, and Yb are intercalated by sodium in liquid ammonia at room temperature to yield 3R-Na_xROCl. The relationship of these new structure types to the previously known (PbFCl or SmSI) forms of the rare-earth-metal oxychlorides are considered. Different preparative routes are observed to exercise some kinetic control over the structures of the ROCl products even for reactions run at the same temperature. ScOCl has the FeOCl-type layered structure.

Introduction

The majority of the rare-earth-metal oxychlorides, bromides, and iodides exist in the tetragonal PbFCl structure while the heavier chlorides have the rhombohedral (3R) SmSI structure at ambient pressure.[2,3] Erbium at the crossover point is dimorphic, the higher temperature form being the SmSI type. The structure of ScOCl is unknown, but an FeOCl type has been suggested.[2] The situation is summarized as follows:

Sc Y La ... Dy Ho Er Tm Yb Lu
FeOCl |←— PbFCl —→|
(?) |←SmSI—→|

In addition, an obscure work by Ward et al.[4] reported the preparation of a YOCl composition that could be indexed on a large tetragonal cell, although they noted at the same time that the pattern resembled those of the then structurally unknown ErOCl–LuOCl series.

Our interest in other structural types of YOCl was stimulated by the observation that the oxidative deintercalation of the layered 3R-M^1_xYClO[5] at room temperature led directly to well-crystallized 3R-YOCl in the YOF-type structure,[6] a form hitherto known only for oxyfluorides. This structure in fact is an alternate stacking order of the same slabs or sheets found in the SmSI type. In an attempt to reach this product by a more direct route we discovered that the generation of YOCl by NH_4Cl–Y_2O_3 reactions in air at 300–550 °C, similar to the route used by Ward et al.,[4] also led to the YOF-type structure mixed with the normal PbFCl form. We have subsequently made a more thorough study of this synthesis route to the oxychlorides of yttrium and a number of the heavier lanthanides and have found that a number of new examples of YOF- or SmSI-type structures can be so obtained.

Experimental Section

The R_2O_3 (R = rare-earth element) starting materials were produced at Ames Laboratory and were generally better than 99.95% in the specified metal. KCl was dried at 500 °C while LiCl was slowly sublimed, both under high vacuum. RCl_3 compounds of sufficient purity were obtained from the hexahydrates by slow drying under high vacuum. Powder pattern data were secured for samples mounted on cellophane tape by utilizing an Enraf-Nonius Guinier camera with silicon as an internal standard, the 2θ values of the latter being fit to a quadratic in line position. Lattice constants for known structures were calculated by a least-squares fit to indexed 2θ values. Powder patterns were calculated with the program POWD 5.[7] Both the SmSI and YOF structures occur in space group $R\bar{3}m$ with all atoms in special positions 6c (hexagonal cell). The SmSI-type patterns were calculated by using the fractional coordinates reported for YbOCl[8] while those for the YOF form were obtained by adjusting the reported z positional parameters[6] so as to give interatomic distances very similar to those calculated for the SmSI form

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(1) Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

(2) Hulliger, F. *Phys. Chem. Mater. Layered Struct.* **1976**, *5*, 254.

(3) Beck, H. P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1976**, *31B*, 1562.

(4) Ward, R.; Orr, W. C.; Katz, L.; Looky, J. T.; Valleta, R. M.; Burgess, T. E. *NYO*-6652, **1956**, 4; *Nucl. Sci. Abstr.* **1961**, *15*, 12903.

(5) Ford, J. E.; Corbett, J. D.; Hwu, S.-J. *Inorg. Chem.* **1983**, *22*, 2789.

(6) Mann, A. W.; Bevan, D. J. N. *Acta Crystallogr., Sect. B* **1970**, *B26*, 2129.

(7) Clark, C. M.; Smith, D. K.; Johnson, G. J. "A Fortran IV Program for Calculating X-Ray Powder Diffraction Patterns—Version V"; Department of Geosciences, The Pennsylvania State University: University Park, PA, 1973.

(8) Brandt, G.; Diehl, R. *Mater. Res. Bull.* **1974**, *9*, 411.

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