$-2r(P) = 0.33$ Å),[23] and so this does not necessarily weaken the superexchange interaction. However, the small difference in the distances of the Cr(2)–O–Cr(1)–O–Cr(2) pathway will result in this interaction being weaker in α-$CrAsO_4$ than in α-$CrPO_4$. Hence, the differences in the magnetic structures of α-$CrPO_4$ and α-$CrAsO_4$ can be attributed to this indirect effect of the Cr–O distances being slightly longer in the latter material, rather than superexchange through the arsenate group being any stronger than that through phosphate.

The presence of antiferromagnetic and weaker ferromagnetic Cr–O–Cr interactions accounts for the magnetic susceptibility variations of these materials. The frustrations due to the competing superexchange pathways result in large $|\Theta/T_N|$ ratios although the magnetic ordering has three-dimensional characteristics. Antiferromagnetic Curie–Weiss behavior is observed when $T \gg T_N$, but as $T \rightarrow T_N$, there is a rise in the susceptibility due to short-range ferromagnetic order arising from the Cr(1)–O–Cr(2) interactions. Below T_N there is a rapid decrease in the short-range ferromagnetic order, and the system tends to antiferromagnetism as $T \rightarrow 0$. Thus, no field dependence develops below T_N, in contrast to β-$CrAsO_4$,[5] in which an ordered weak ferromagnetic component was observed by susceptibility measurements over the same field range. This difference may be explained by the magnetic symmetries of the ordered states; both α-$CrPO_4$ and α-$CrAsO_4$ belong to P_I magnetic groups that cannot allow a ferromagnetic component, whereas β-$CrAsO_4$ belongs to a primitive magnetic group that also permits a ferromagnetic component.[5]

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Registry No. α-$CrPO_4$, 7789-04-0; α-$CrAsO_4$, 15070-22-1.

Supplementary Material Available: A table of bond angles in α-$CrPO_4$ at 2 K and α-$CrAsO_4$ at 5 K (1 page). Ordering information is given on any current masthead page.

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Contribution from the Anorganisch-Chemisches Institut der Universität Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster, FRG, Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301, and School of Chemistry, University of Hyderabad, P.O. Central University, Hyderabad 500 134, India

The Richness of Structures Available to $CpMS_4MCp$ Complexes

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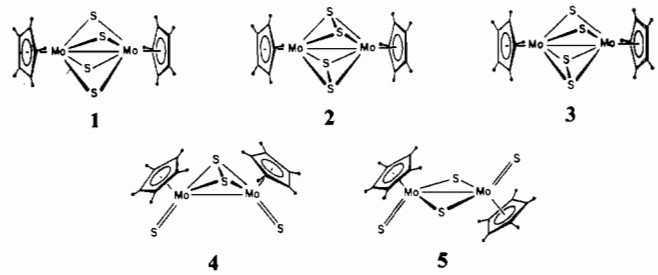
Compounds with the general formula $CpMS_4MCp$ display a remarkable variety in structure. By a detailed theoretical analysis of this class of complexes and related compounds such as NbX_2Y_6 (X = Se, Te; Y = Br, I) or $CpV(S_2)S_2VCp$, we are able to explain how the central S_4 unit traverses in many compounds a range in S–S bonding from a ring to isolated sulfide bridges. The isomer $CpMo(S_2)_2MoCp$ can undergo a symmetry-allowed transformation to form $CpMo(S)S_2(S)MoCp$. The bonding in the molecular compounds is compared to that in their solid-state analogues NbX_2Y_6. As in acetylene complexes, S_2 groups can enter the compounds under study in a parallel and a perpendicular orientation. The latter one is energetically preferred. The rearrangement of parallel- and perpendicular-oriented S_2 groups is symmetry forbidden.

Introduction

The strong affinity of chalcogenides for elements of the transition series is the basis for a variety of metal sulfur compounds. Metal sulfides are the most important class of naturally occuring metal ores.[1] Parallel to this, the chalcogenides display a broad range of capabilities as construction units in the design of stable transition-metal clusters.[2] Typical goals in this heavily investigated area of inorganic chemistry include the synthesis of models for important biological[3] and industrial[4] catalysts and the preparation of materials for energy storage and conversion.[5] A particular incentive is the prospect that discrete metal chalcogenide clusters may prove to be functional analogues of the active sites of nitrogenase[6] and hydrodesulfurization catalysts.[7]

Numerous complexes have been synthesized and structurally characterized, pointing to the extremely versatile ligand behavior of elemental sulfur. It can enter transition-metal compounds in many guises, as sulfide,[2] disulfide,[8] or polysulfide.[9] Each of these sulfur ligands can be linked to several metal atoms. Unsubstituted sulfur, for example, has been reported (besides its occurence in a terminal position) in doubly,[2] triply,[2,10] quadruply,[10a,11] 5-fold,[12] and 6-fold[13] bridging geometries.

Given this richness in coordination, it is not surprising that several isomers of the title compound are known. Some of them are shown in **1–5**.[14] In structures **1–3** two CpMo fragments are bridged by four S atoms, two of which have transformed into



1 **2** **3** **4** **5**

terminal ligands in **4**[14b] and **5**.[14d] Still more isomers can be thought of. Among those that exist **3**[14c] and **5**[14d] have been structurally

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Table I. Quadruply Bridged $L_mME_nML_m$ Complexes (n = 4; E = S, Cl, SR; M = Cr, Mo, V, Nb)

quadruply bridged compds	electron count	ref
$[CpMo(\mu\text{-}SC_3H_6S)_2MoCp]BF_4$	35	15
$[(S_2)_2Mo(\mu\text{-}S_2)_2Mo(S_2)_2]^{2-}$	34	16
$[X_4Mo(\mu\text{-}S_2)_2MoX_4]^{2-}$ (X = Cl, Br)	34	17
$(MeCp)Mo(S_2CH_2)(\mu\text{-}SMe)(\mu\text{-}SH)Mo(CpMe)$	34	7c
$[CpMo(\mu\text{-}S_2CH_2)(\mu\text{-}S)(\mu\text{-}SC(Ph)CH_2)]SO_3CF_3$	34	7b
$(MeCp)Mo(\mu\text{-}S_2CH_2)(SCH_2CH_2S)Mo(CpMe)$	34	18
$(MeCp)Mo(\mu\text{-}S_2CH_2)(SMe)_2Mo(CpMe)$	34	18
$[(MeCp)Mo(\mu\text{-}SMe)_4Mo(CpMe)]^{0,1+,2+}$	34, 33, 32	19
$CpMo(\mu\text{-}S_2C_6H_3Me)_2MoCp$	34	20
$CpMo(\mu\text{-}SCH_2CH_2S)_2MoCp$	34	20
$(i\text{-}BuCS_2)V(\mu\text{-}S_2)_2V(S_2C\text{-}i\text{-}Bu)_2$	34	21
VS_4	34	22
NbS_2Cl_2	34	23
$CpMo(\mu\text{-}S)(\mu\text{-}SMe)(S_2CH_2)MoCp$	33	7f
$[Cl_3Mo(\mu\text{-}S_2)Cl_2MoCl_3]^{2-}$	32	24
$Cp^*Cr(\mu\text{-}S_2)S(\eta'\text{-}S_2)CrCp^*$	32	25
$(Ph_2C_2S_2)Mo(\mu\text{-}S_2)_2Mo(S_2C_2Ph_2)$	32	26
$CpMo(\mu\text{-}S)_2(\mu\text{-}S_2)MoCp$	32	14c
$CpMo(\mu\text{-}S)_2(SMe)_2MoCp$	32	27
$[CpMo(\mu\text{-}SCH_2)(\mu\text{-}SCHC(Ph)H)]Br$	32	7a

characterized, and **2**[14a] and **4**[14d] have been described from spectroscopic data and reactivity patterns. **1** is not yet known. A list of some of the quadruply bridged complexes is given in Table I.

Considering the variety of possible structures, one may wonder why no isomers with rings of group 16 atoms are known. One simple reason may be that the combined constraints of M–L distance, L–L contacts in the bridge, and M–M separation leave only a small "window" for structures to be realized.

As one further examines dinuclear complexes with bridging disulfide units, one is first struck by the various ways in which the S_2 group can bind. One very unexpected possibility has been observed in $CpCr(S_2)_2SCrCp$ (**6**),[25] where two metal atoms are

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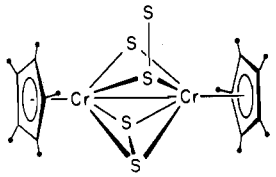

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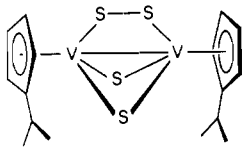
attached to the same sulfur atom of a S_2 ligand. Other S_2 coordination modes are known. In $(i\text{-PrCp})V(S_2)_2V(i\text{-PrCp})$ (**7**),[28]



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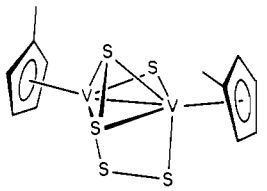
we encounter a bridging S_2 group in a parallel orientation; S_2 groups in parallel and perpendicular orientation occur in $MeCpV(S_2)_2SVCpMe$ (**8**).[29] This still does not exhaust the



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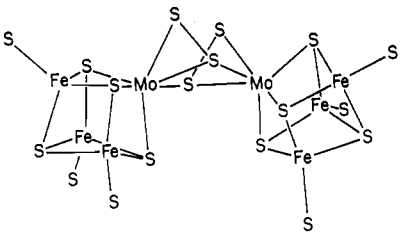
variety of S_2 coordination modes, as seen in $[Mo_2Fe_6S_8(S_2)_2(SC_6H_4Br)_6]^{4-}$ (**9**)[30] and $Me_5CpCo(S_2)_2CoCpMe_5$ (**10**),[31] where



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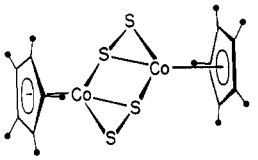
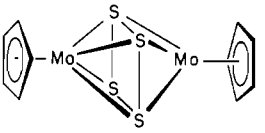


10

the η^1,η^2-S_2 ligands are in a steplike syn and anti arrangement, respectively. Many other ways of S_2-bonding are known, and numerous examples can be found in some recent reviews.[2,8-10]

One way to approach the bonding in the S_4-bridged compounds starts out from a cluster point of view by simply counting electrons. Let us assume $CpMoS_4MoCp$ to be a polyhedral molecule in which the central S_4 ring is sandwiched between two CpMo fragments. Applying the Wade–Mingos[32] rules, we find for a completely bonded octahedral M_2X_4 cluster a magic electron count of 46 electrons. This matches exactly the number of cluster electrons in $CpMoS_4MoCp$. None of the known $CpMoS_4MoCp$ isomers, however, has been reported in this structure type. Instead, the S_4 ring is cleaved in various ways, and the Mo–Mo distances in all structurally characterized isomers are indicative of metal–metal bonds.

In this article we want to explore some of the electronic requirements for stabilizing one or the other isomer of $CpMS_4MCp$ compounds. In particular, we are interested in the early-transition-metal species where M = Mo. We will start out from the hypothetical $CpMoS_4MoCp$ (**11**). In this model an S_4 ring with



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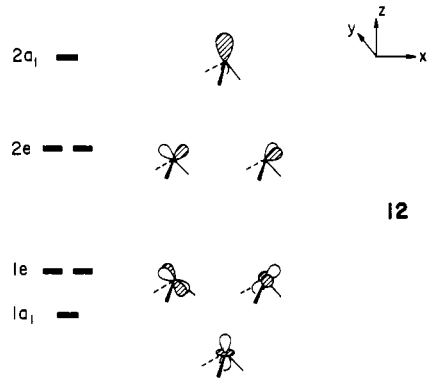
normal S–S single-bond distances is sandwiched between two CpMo fragments. It provides a convenient starting point for an analysis. As the S–S distance is stretched (and the Mo–Mo decreases), we will approach structure **1**. Further deformation will give **2** and **3**. Our conclusions are mainly based on symmetry and overlap arguments supplemented by extended Hückel[33] calculations. The technical details relevant to the computations may be found in the Appendix.

S_4 Rings in the Central Plane

A convenient starting point for the analysis is a fragment approach based on a $CpM(X_4)MCp$ partitioning of the molecule. The orbitals of the isolobal[34] conical fragments ML_3 and MCp have been discussed at length elsewhere.[35] The basic ordering in energy and the shape of the frontier orbitals of these fragments is shown in **12**. At relatively high energy there is an a_1 orbital,



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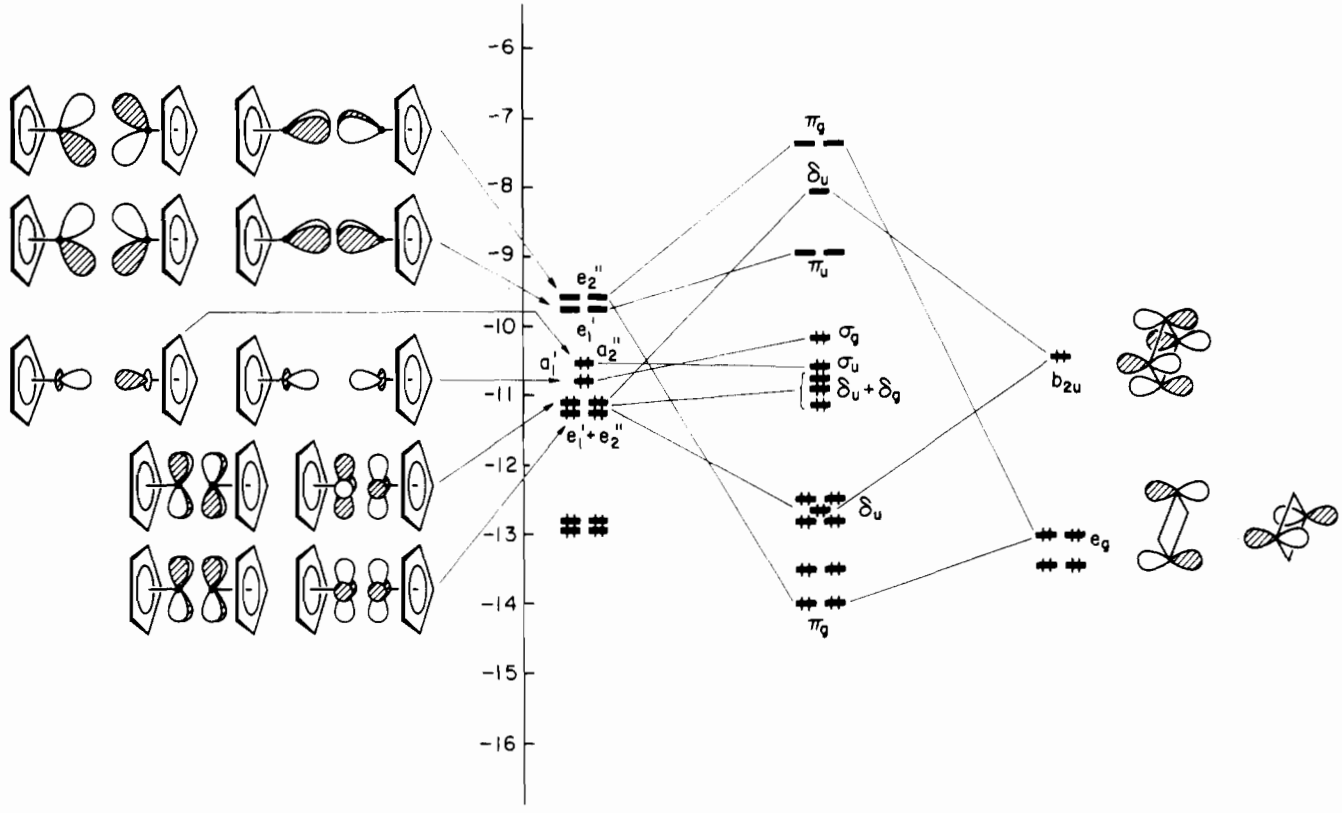

Figure 1. Interaction of two CpMo fragments and c-S_4 to form $CpMoS_4MoCp$.

$2a_1$, composed of metal s, p and a variable contribution of z^2 and a 2e set made up of a mixture of metal (xz,yz) and (x,y). These orbitals have the greatest interaction with the bridging ligands.

The lower set of orbitals, which would be the t_{2g} set of nonbonding orbitals in an octahedral metal complex, may be the major source of metal–metal interaction in a dinuclear metal complex of early transition metals. For CpMo the $a_1 + e$ triad is empty and the metal d block (a_1 and e_2) originating primarily from metal z^2,x^2-y^2, and xy is filled with five electrons. Figure 1 shows the assembly of a computed orbital diagram for the species $CpMoS_4MoCp$ in an idealized C_{2v} (pseudo-D_{4h}) symmetry. The S···S distance in the bridge is fixed at 2.1 Å. On the left are given the orbitals of a CpMo···MoCp dimer. For an Mo–Mo distance of 3.92 Å we find only very small level splittings. For cyclic S_4 we expect to see hydrocarbon-like orbitals interspersed with the sulfur lone pairs.

Our general expectations are fulfilled. The π_g and δ_u orbitals of the composite molecule ($D_{\infty h}$ symmetry assumed) are pushed up by the strong interaction between the e_1' and the e_2'' of the S_4 fragment with the symmetry-equivalent combination of the metal dimer. The a_1' and e_2'' orbitals of the metal fragment interact only slightly with the corresponding orbitals of the S_4 ring and stay at approximately the same energy. The result is a nice gap of approximately 1 eV for electron counts of 46 and 50 electrons. Note the high pseudosymmetry $D_{\infty h}$ (as indicated by the symmetry labels for the composite molecule in Figure 1); some orbitals are nearly degenerate. On the basis of these considerations, there seems to be nothing wrong with our model compound containing a cyclic S_4 bridging unit. There are, however, except for one recent example, $[(\eta^5\text{-}C_5Me_4Et)Rh(\mu,\eta^2\text{-}P_2)_2Rh(\eta^5\text{-}C_5Me_4Et)]$,[36] almost no reports of four-membered rings of group 15 or 16 elements sandwiched between metal fragments.

The structural preferences of our model compound can be probed by varying the Mo–Mo or S···S distances, respectively. Clearly, the variability in these structures and the focus of concern about M–M and S–S bonding lies in the inner octahedron in the bridging region. For this geometry it takes one distance (M–L, M–M, or L–L) and one angle (M–L–M, L–M–L, or M–M–L) or two distances to fix the bridging region. Our model calculations (using a constant Mo–S distance of 2.46 Å) gave a total energy curve as a function of the Mo–Mo distance, as shown in Figure 2. There is a local energy minimum for long Mo–Mo distances in a classic triple-decker type with completely bonded S_4. For increasing S–S and decreasing Mo–Mo distances the energy goes first uphill and then falls to a deep minimum at nonbonding S···S distances and very short Mo–Mo separations. We should point out that total energies cannot be realistically calculated using extended Hückel techniques, especially when there are several crossing orbitals. A good configuration interaction study would be required to establish reliably the existence of a small local minimum.

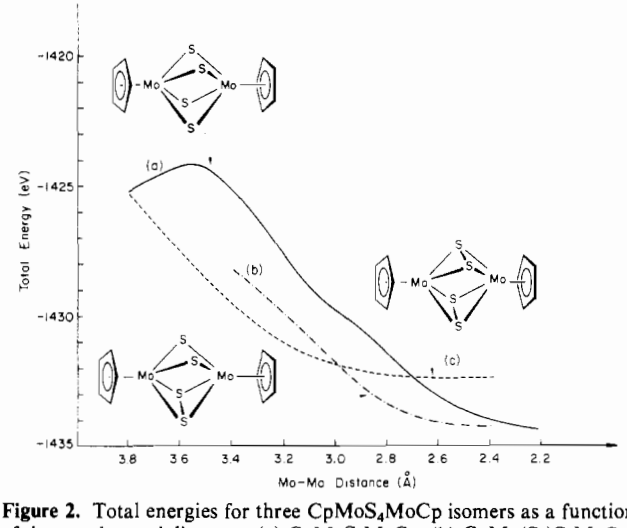

Figure 2. Total energies for three $CpMoS_4MoCp$ isomers as a function of the metal–metal distance: (a) $CpMoS_4MoCp$; (b) $CpMo(S_2)S_2MoCp$; (c) $CpMo(S_2)_2MoCp$.

As a general statement, all S lone-pair orbitals are in energy

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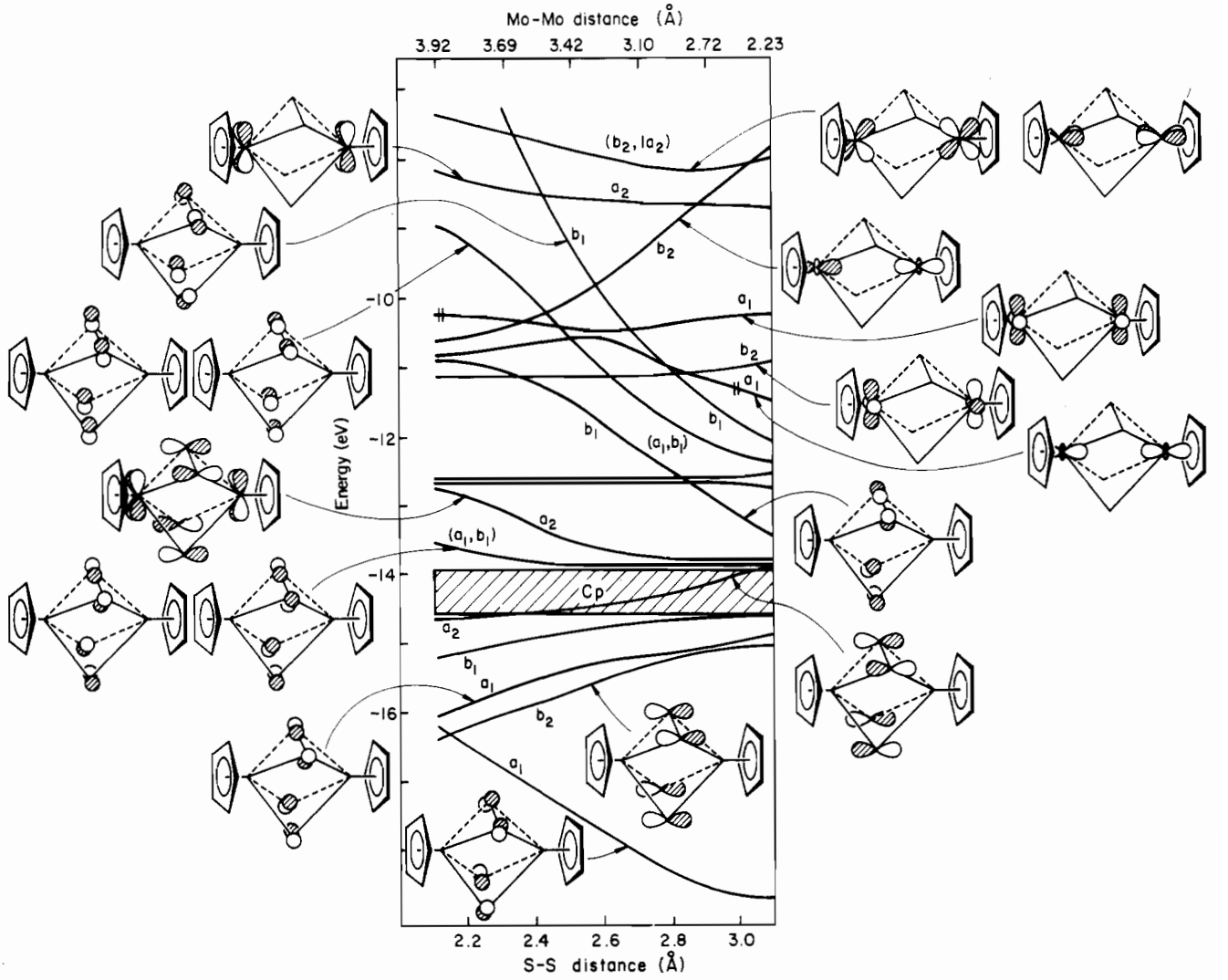
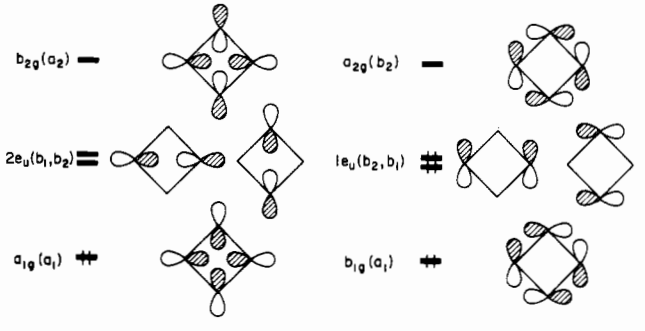


Figure 3. Energy levels of $CpMoS_4MoCp$ as a function of the Mo–Mo distance.

directly below the metal d block for short metal–metal distances. Lengthening the Mo–Mo bond (and decreasing the S···S distances) should stabilize all S–S bonding orbitals and destabilize all antibonding ones. The four-membered S_4 ring has eight in-plane σ orbitals, four radial and four tangential ones, as shown in **13**,



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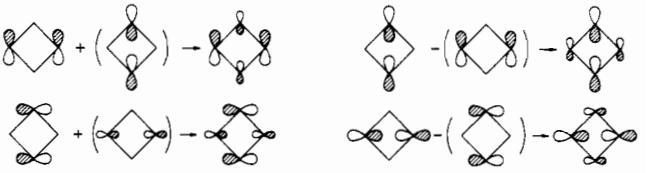
with symmetry labels in D_{4h} (C_{2v}) symmetry. The coordinate system in C_{2v} symmetry is chosen with the C_2 axis passing through two S atoms of the S_4 ring, as in Figure 3, in order to obtain a match in symmetry labels. Depending on the S–S separation, there is a variable amount of s,p-mixing, which is neglected in our schematic representation. For short S–S separations we expect the radial a_{1g} (a_1) and tangential b_{1g} (a_1) orbitals to be stabilized. In contrast, the S–S antibonding b_{2g} (b_1) and a_{2g} (b_1) orbitals should be substantially destabilized. The degenerate e_u orbitals can mix to form one slightly bonding and one slightly antibonding pair, as shown in **14** and **15**.



14 **15**

We can identify almost all of these levels in the Walsh diagram in Figure 3. Note again the high cylindrical pseudosymmetry. The a_{1g} ($2a_1$ in Figure 3) and b_{1g} ($1a_1$) orbitals are stabilized for short S–S distances, just as expected. The b_{2g} ($1b_1$) combination of the sulfur s orbitals is raised and ends up right below the p block. One e combination ($3a_1$ and $2b_1$ in Figure 3) is essentially nonbonding and stays at approximately the same energy. The other e combination ($4a_1$ and $4b_1$ in Figure 3), which is antibonding with respect to S–S, is raised high in energy, along with the radial a_{2g} ($5b_1$) orbital. Besides the σ orbitals, for four S atoms we expect to see four π-type orbitals, which—according to the hierarchy of interaction—should be in the "intermediate" energy range and exhibit significantly less dependence on the S–S separation. The all-bonding combination $1b_2$ is lowest in energy (third from bottom). Next we find the nonbonding ($1a_2$, $2b_2$) orbitals. Due to the high pseudosymmetry of the complex they are nearly degenerate. The slight energy spread of the nonbonding pair is caused by mixing in a small amount of metal–metal π^* contribution. This leads to a slight increase in energy for small met-

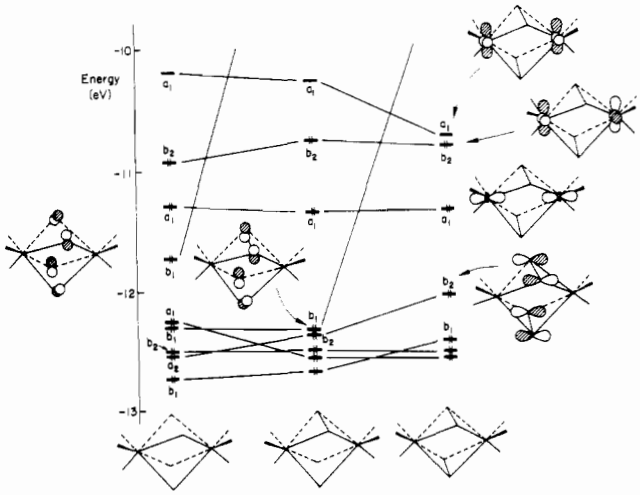
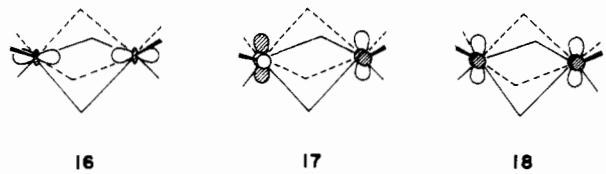


Figure 4. Molecular orbital correlation diagram for the interconversion of three $CpMoS_4MoCp$ isomers: (left) $CpMoS_4MoCp$; (middle) $CpMo(S_2)S_2MoCp$; (right) $CpMo(S_2)_2MoCp$.

al–metal distances. At highest energy is the all-antibonding π combination, $2a_2$. As expected, it rises slightly as the S–S distance decreases.

In addition, we have the metal 4d orbitals. For short M–M distances there is the (metal–metal) σ-bonding a_1 orbital **16** ($5a_1$ in Figure 3) at lowest energy. Next come the b_2 (δ^*) and a_1 (δ) orbitals **17**, **18** ($3b_2$ and $6a_1$). The other δ/δ^* and the π orbitals are raised higher in energy, due to Mo–Cp interactions. For longer metal–metal distances the metal–metal σ^*-bonding b_2 orbital comes down in energy.

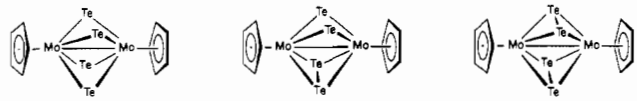


16 **17** **18**

Increasing the Mo–Mo distance (and decreasing the S–S distances) turns on substantial S–S repulsions. Following the Walsh diagram in Figure 3, all S–S antibonding orbitals are occupied up to a Mo–Mo distance of 3.3 Å. The structure, however, seeks to minimize S–S repulsions. As a consequence, a geometry with a short metal–metal bond and long S–S separations is preferred.

The situation is not much different for **2** and **3**. The total energy change for variation of metal–metal distances is shown in Figure 2b,c. Now we have energy minima at Mo–Mo distances around 2.6 Å, which is close to the observed geometry in **3**. The Walsh diagrams are qualitatively alike in all three cases, and we do not show all of them. We have to be careful about electron bookkeeping: replacing two S^{2-} by one S_2^{2-} without changing the charge on the complex results in a formal two-electron reduction of the metals. For **3** and **2**, one or two orbitals, respectively, are out of range in energy, because one or two S–S bonds are formed. **2**, **3**, and **1** are related by a sequence of two-electron reductions. The evolution of the frontier orbitals at a Mo–Mo distance of 2.6 Å for this series is shown schematically in Figure 4. Most of the orbitals experience only minor energy shifts. The b_1 orbitals, however, which are responsible for the bond breaking/making process, are very much affected by the structural change. For each bond formed the uppermost level is raised above the metal d block. Energetically, **3** is favored by approximately 0.5 eV (no geometry optimization); next comes **2** and then **1**. **3** is known, **1** has never been reported, and **2** has been suggested on the basis of spectroscopic data, as we pointed out before. The reason for the stability sequence is likely to be found in the reduced S···S repulsion.

What happens if we have higher group 16 homologues such as Te as bridging atoms? We did a set of calculations on the corresponding Te compounds **19**–**21** as well (Mo–Te: 2.75 Å).



19 **20** **21**

A Walsh diagram for the variation of the Mo–Mo distance in **19** is given in Figure 5. Replacing S by Te shifts all the formerly S-based levels to higher energies. This is a consequence of the Te 5p orbitals being much more diffuse than S 3p. The increased Te–Te interactions are evidenced by the appearance of the Te-based antibonding b_1 combination above the metal d block. Therefore, in the Te compounds some of the antibonding in-plane

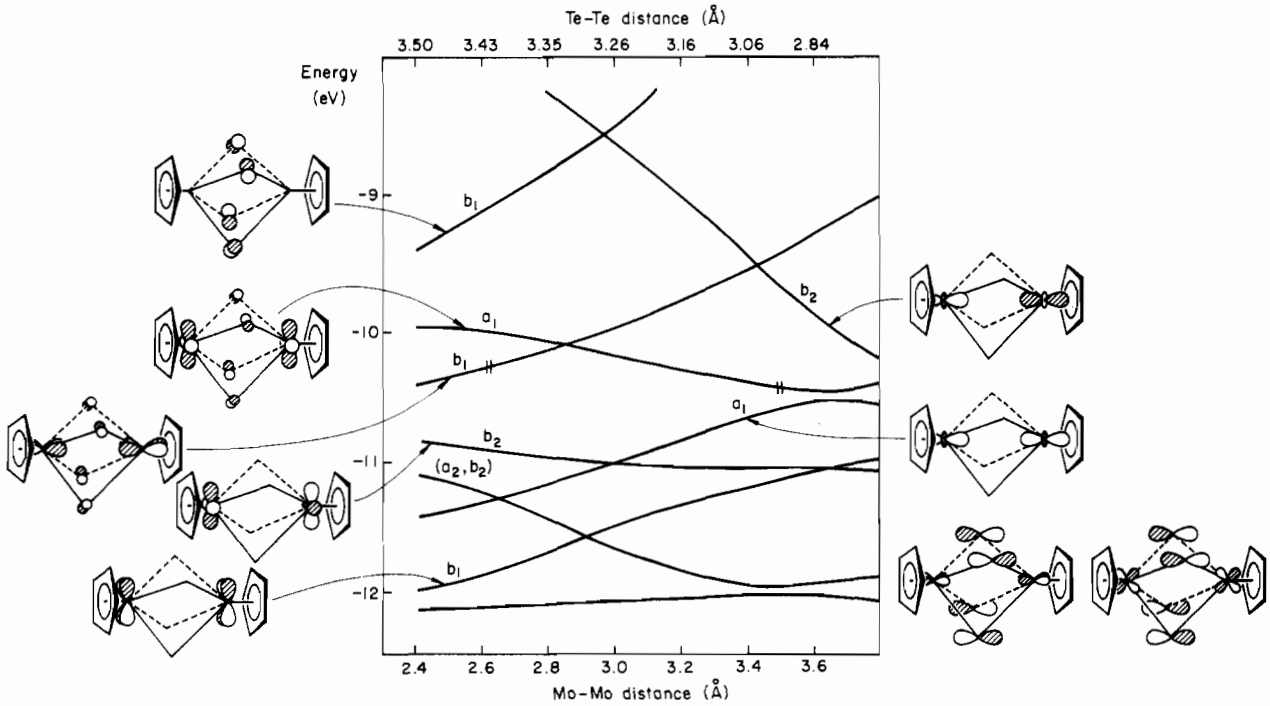


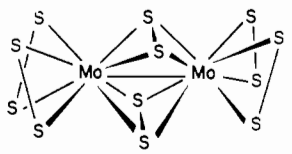
Figure 5. Energy levels of $CpMoTe_4MoCp$ as a function of the Mo–Mo distance.

Table II. Triply Bridged $L_mME_nML_m$ Complexes (n = 3; E = S, Cl, SR; M = Cr, Mo, W, Nb)

tripley bridged compds	electron count	ref
$[Cl_4W(\mu\text{-}Se)(\mu\text{-}Se_2)WCl_4]^{2-}$	30	37
$[Br_4W(\mu\text{-}S)(\mu\text{-}S_2)WBr_4]^{2-}$	30	38
$[(C_4H_8S)Cl_3Mo(\mu\text{-}S_2)(\mu\text{-}SC_4H_8)MoCl_3(SC_4H_8)]^{2-}$	30	39
$CpCr(\mu\text{-}S\text{-}t\text{-}Bu)_2(\mu\text{-}S)CrCp$	30	40
$Nb_2X_2Y_2$ (X = Se, Te; Y = Br, I)	30	43
$Mo(S_2)Cl_3$	30	44
$(Me_2S)_2Cl_2Nb(\mu\text{-}S_2)SNbCl_2(SMe_2)_2$	30	45a
$(C_4H_8S)_2Cl_2Nb(\mu\text{-}S_2)SNbCl_2(SC_4H_8)_2$	30	45b

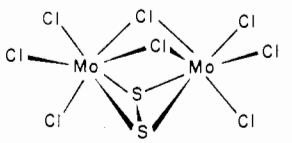
σ orbitals, which were always filled in the S-bridged compounds **1–3**, are not occupied. The all-antibonding tangential a_{2g} (b_2) orbitals, for example, which carried a major part of the destabilization for short S–S distances in **2**, are not occupied in **19**. In the same manner the e_1 set, which is pushed up for short Te–Te distances as well, is empty. Some metal orbitals (δ/δ^*) are occupied instead; these are essentially nonbonding for M–M distances of ~3.4 Å. From Figure 5 one would expect a (hypothetical) Te-bridged compound to prefer a structure having Te–Te bonds and long metal–metal separations.

A number of similar sulfur and/or halogen-bridged compounds—molecular as well as solid state examples—have been described. They are compiled in Table I. There is—surprisingly enough—a "magic electron count" for these compounds. Let us take $[(S_2)_2Mo(S_2)_2Mo(S_2)_2]^{2-}$ (**22**)[16] as an example. Taking the



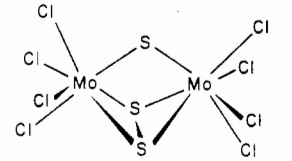
22

terminal S_2 groups as four-electron donors, the skeletal electron count is 34, and this electron count is good for many compounds in that group. Some other compounds, e.g. $[Cl_3Mo(\mu\text{-}S_2)Cl_2MoCl_3]^{2-}$ (**23**),[24] have an electron count of 32. This electron



23

count is easy to rationalize. We populate or depopulate the b_2 orbitals, which are almost purely metal–metal δ^* bonding. Since δ bonds tend to be weak, the Mo–Mo distance is not affected very much. Some related triply bridged compounds, such as $[Cl_4WSe_3WCl_4]^{2-}$ (**24**),[37] which are collected in Table II, have



24

been reported as well. Here one four-electron donor atom is missing compared to **23**, and the resulting electron count is 30. **23**, however, is reported to be paramagnetic, S = 1, which is difficult to understand if b_2 is the depopulated level. In order to clarify this discrepancy, we did a calculation on **23** using the experimental geometry. As in other related compounds, there is a HOMO–LUMO gap of approximately 0.6 eV. We are unable to explain the magnetic behavior of this complex from our computations.

Structurally, the quadruply and triply sulfur-bridged early-transition-metal compounds are not very selective. A unifying feature for all of them is a formal metal–metal σ bond. This precludes a fully bonded central ring for geometrical reasons. In comparison to the P_3-bridged compounds $L_3MP_3ML_3$ (M = Fe, Co, Ni, Pd, Pt),[47] there seems to be enough "stereochemical power" behind a M–M σ bond to dominate the structure for the early-transition-metal compounds.

We pause here for a moment to recall what we have learned so far. Four-membered rings of main-group atoms sandwiched between metal fragments are rare, and rings of group 16 atoms are—to our knowledge—not known at all. One can blame—as we did in the introduction—the combined constraints of M–L distance, L–L contacts in the bridge, and M–M separation to explain this fact. On the other hand, one can chose a slightly different point of view. As we have shown elsewhere,[41] the interactions of the e_1 hybrids (xz,yz) of the metal fragments with the "lone-pair" orbitals of the central ring becomes an important factor of bonding in inorganic "triple-decker" compounds. More specifically, for different sizes of the central ring there is a competition between a_2''/π (z^2/z) and e_1'/lone pair interaction of the metal fragment and the inorganic ring.[41c] For a six-membered ring the e_1'/lone pair interaction reaches a maximum, whereas the z^2/z interaction goes through a minimum. The overlap between the a_2'' combinations of the metal fragment and the inorganic ring, z^2 and z, respectively, is small, because the atoms of the central ring are situated in the node of the z^2 orbitals. If the ring size is reduced, then the main-group atoms are moving out of the node. As a result, the corresponding overlap increases. In contrast, the overlap of the e_1'' combinations with the lone-pair orbitals of the ring is diminished. For a three-membered ring, $\langle e_1'|\text{lone pair}\rangle$ reaches a minimum while $\langle z^2|z\rangle$ approaches its

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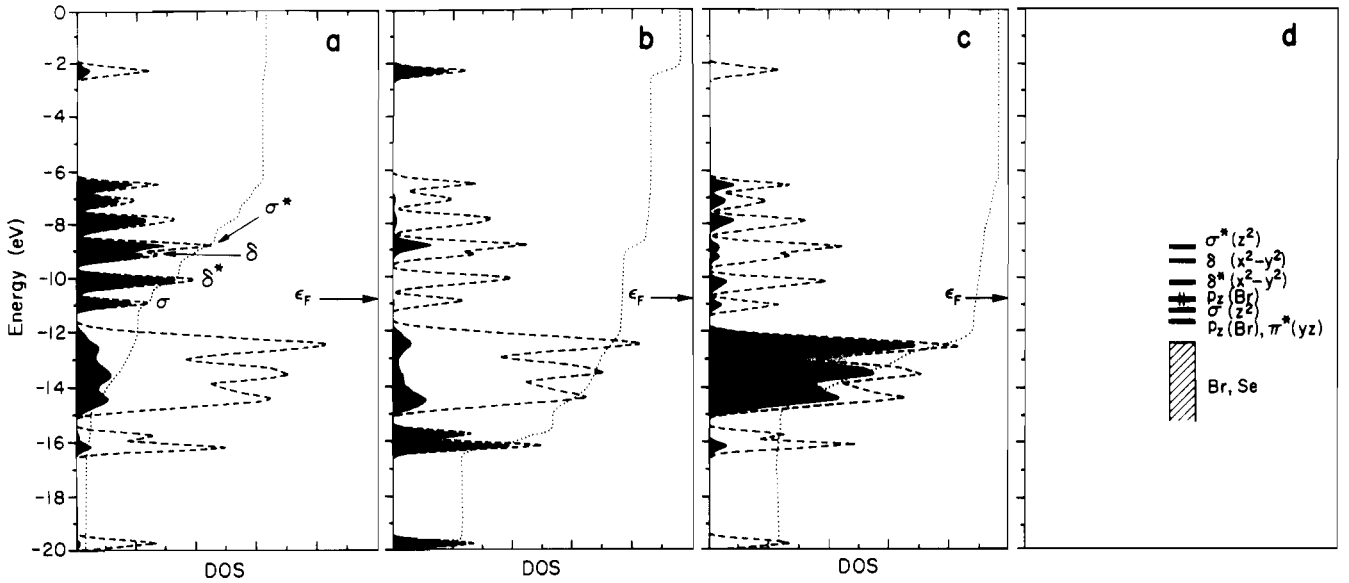
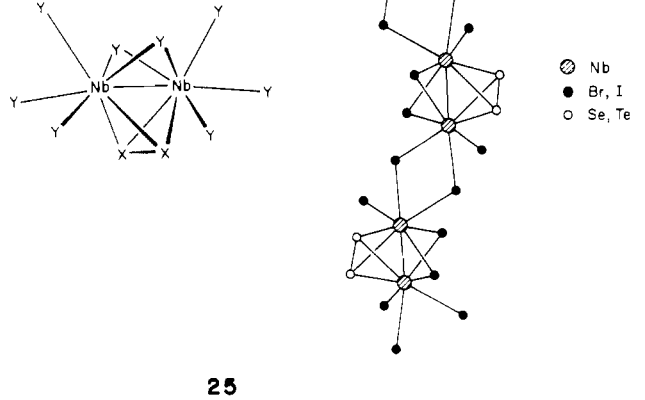


Figure 6. Total DOS (dashed line) and projected DOS (blackened area) for $NbSe_2Br_6$ giving (a) the Nb, (b) the Se, and (c) the Br contributions. The energy levels of a molecular $[Br_3NbSe_2Br_2NbBr_3]^{2-}$ unit are shown in (d).

maximum value. The combined overlaps have the smallest value for a four-membered ring, and—as we have seen—for this geometry nature prefers cleavage of the central ring as one possible structural alternative. Whether the central ring breaks or not should be mainly determined by the relative electronegativities of its constituents and the electron count. For S-based systems the electron count of the central ring is large enough that S–S σ bonds are broken. For many P and As type systems, however, the central ring can accommodate the imposed charge and stay intact. Interestingly, $[(CO)_4WTe_3]^{2+}$, a complex containing a Te_3 ring has recently been made.[42] This structure supports our hypothesis that Te rings may indeed be stabilized with appropriate metal fragments. In summary, we think that several factors are responsible for the cleavage of the central ring in the title compounds: the relatively small stability of the sandwiched four-membered rings, the electron count, and the presence of a very stable structural alternative, namely a metal–metal-bonded system such as **3**.

We have already mentioned that in the Nb compounds in Tables I and II the (metal–metal) δ^*-bonding orbitals are not occupied. $Nb_2Se_2I_6$ (**25**), an interesting solid-state example, was reported



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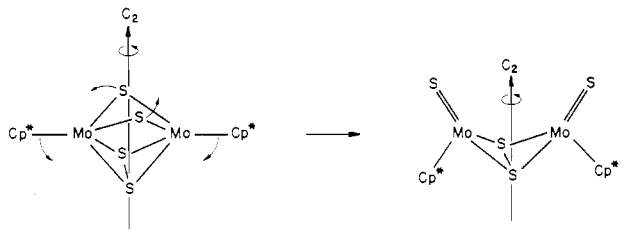
by Franzen, Hönle, and Schnering.[43] From the composition one might have expected a Nb^{5+} compound. One finds, however, infinite chains of halogen-bridged $Nb_2Se_2I_4$ units containing Se_2 dumbbells bridging a Nb–Nb bond in a side-on fashion. A number of homologous compounds, $Nb_2Se_2Br_6$, $Nb_2Te_2Br_6$, and $Nb_2Te_2I_6$, could be prepared. Although we find isolated Nb_2 pairs in the structure, all of these compounds exhibit metallic luster and undergo reversible thermal transitions with temperature. Franzen et al.[43] speculate that the existence of Nb in a formal 4+ oxidation state and of a chalcogen in an 1− oxidation state permits a simultaneous redox reaction leaving us with niobium(5+) and chalcogen(2−), respectively. This case is in fact closely related to the examples we discussed before, i.e. the transitions between **2** and **3**. From Figure 4 we can see that the reaction is symmetry forbidden. Experimentally, there is no tendency for thermal anisotropy within the Nb_2Y_2 unit.

Since we observe a pairing distortion in this structure, the bonding can be expected to be very localized within the Nb_2Y_2 tetrahedra. We have computed a band structure for the polymer, and it supports this picture. The actual bands are not shown, only the contributions of individual orbitals to the DOS in Figure 6. At −16 eV are—very localized—the Se–Se-bonding states; next come, spread out over some 3–4 eV, the halogen states, mostly lone pairs. Around −11 eV we find the metal states. First is the Nb–Nb σ bond; the next two peaks are the δ and δ^* levels, followed by σ^*. The other δ and the π states are raised by interactions with the other ligands. The DOS projections may be compared with the levels of a $Br_3Nb(Se_2)Br_2NbBr_3$ unit in Figure 6d. There is a reasonable match. From our band structure calculations we find in fact a small DOS at the Fermi level (marked with an arrow), indicating (semi)metallic behavior. Substituting Se by Te brings more chalcogen states close to the Fermi level, but the general bonding pattern remains unchanged.

There are still other interesting features of the Mo_2S_4 cores. Wachter and co-workers[14c] reported the thermal conversion of **3** into **4**. A correlation diagram that we construct for this reaction (assuming the persistence of a 2-fold axis, **26**) shows it to be



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allowed. So is the interconversion of **2** and **5**. DuBois et al.[27a] used the same line of thought to explain the different structural

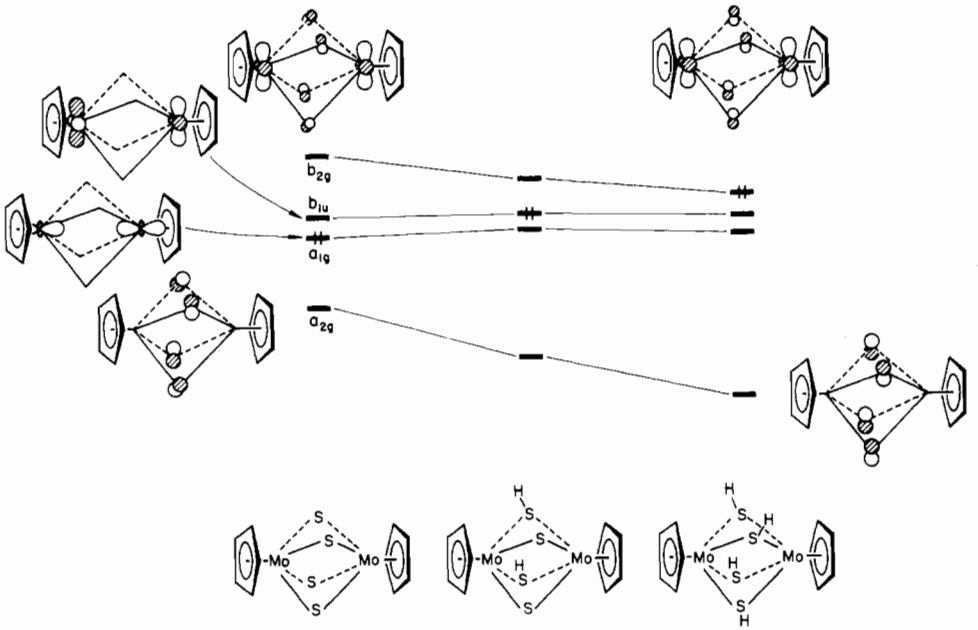
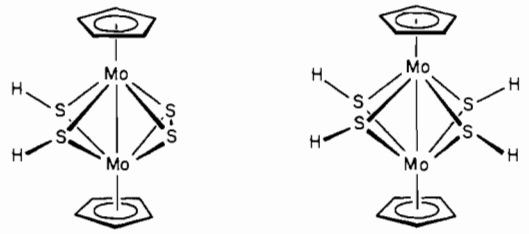


Figure 7. Comparison of the orbital occupancy in $CpMoS_4MoCp$, $CpMo(S)_2(SR)_2MoCp$, and $CpMo(SR)_4MoCp$.

features for the Mo_2S_4 and other known dimers containing different bridging ligands, e.g. **27** and **28**.

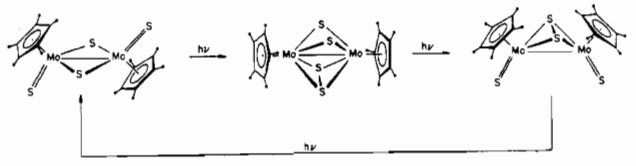


27 **28**

Perhaps it is worthwhile here to remark on what may be obvious, namely the essential similarity of S^{2-} and SR^-. SR^- is the result, formally (and sometimes actually), of the addition of R^+ to S^{2-}. S^{2-} has four lone pairs, and two are used in bonding to the metals. The third lone pair of S^{2-} is "taken care of" by this maneuver of R^+ addition. One other one remains, a frontier orbital active in repulsion or further bonding.

That nothing much happens may be seen in the comparison of the frontier orbitals of **1**, **27**, and **28** in Figure 7. One must be careful about electron counting: replacing a S by SR without changing the charge on the complex results in a one-electron reduction of the two metals. Therefore, the change in the electron count in Figure 7 results.

It may be interesting to note that a photochemical conversion between structures **3** → **4** → **5** has been reported.[48] The reaction sequence is given in **29**. The isomerization was suggested to result



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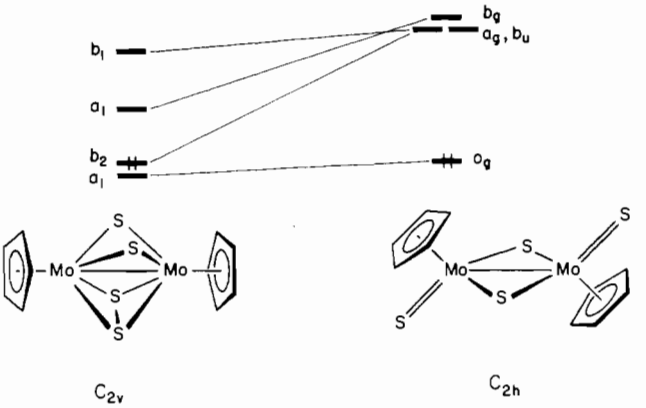
from a LMCT excited state involving terminal sulfur atoms: Mo is reduced from Mo^{5+} to Mo^{4+} and S is oxidized from S^{2-} to S_2^{2-}. In this process—which is formally a two-electron reduction of the metal—two S^{2-} are transformed into a S_2^{2-} group. One bonding MO is formed; the corresponding antibonding combination is raised in energy. As a result, the b_2 orbital is populated in **3**, and in **5** the two electrons are located in a sulfur lone pair. An explanation for the isomerization **3**–**5** may be gathered from the correlation diagram **30**.[49] The HOMO in **3** is the b_2 orbital. After



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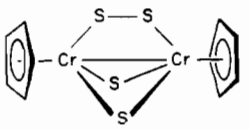
the opening process—which is symmetry allowed—a_g is the HOMO of **5**. According to our calculations, **5** is preferred for the present electron count.

Moving out of the Central Plane

In the last section we have seen a number of ways in which the sulfur-bridged compounds avoid the formation of a closed *n*-membered ring. The possibilities we found were the breaking of S–S bonds by forming S_2^{2-} groups and S^{2-} ligands or even an η^1-bonding mode of a S_2^{2-} group, as encountered in $CpCrS_5CrCp$ (**6**).[25] Yet there are still other possibilities to escape the ring formation, one of which is realized in $CpCr(\mu\text{-}S)_2(\mu\text{-}S_2)CrCp$ (**31**)[50] or $(i\text{-}PrCp)V(S_2)_2V(i\text{-}PrCp)$ (**7**).[28] The obvious question



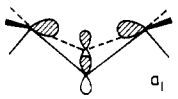
31

(48) Bruce, A. E.; Tyler, D. R. *Inorg. Chem.* **1984**, *23*, 3433.

(49) A similar argument has been used to explain the semibridging carbonyls in $[CpMo(CO)_2]$ dimers (M = Cr, Mo): Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2575.

is whether there is an electronic reason for this. The point we address here is related to parallel and perpendicular bonding in acetylene complexes, which has been analyzed by D. M. Hoffman and one of us earlier.[51]

In our analysis we can start from the orbitals of a CpV fragment, which were given at the beginning of this paper. Two of these fragments interact. The dimeric CpV···VCp unit will develop into two face-sharing octahedra with the bridging ligands, one S_2^{2-} and two S^{2-}. The fragment symmetry is now C_{2v}. We have four filled orbitals on the bridging ligands, which can donate charge into empty orbitals of CpV···VCp. The bonding combinations are shown in **32–35**. The frontier orbitals of the



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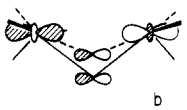

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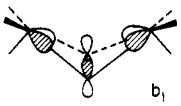

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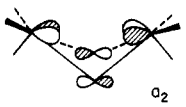

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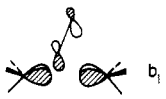
$CpVS_2VCp^{2+}$ fragment are given on the left side of Figure 8. The interaction is illustrated for a S_2^{2-} group in the parallel geometry. The S_2^{2-} group has two π and two π^* frontier orbitals. The interaction of the metal fragment with the π orbitals turns out to be not very important, and we focus on the π^* metal fragment interactions only. The bonding interactions between π^* orbitals of S_2^{2-} and the metal fragment are shown in **36** and **37**. From



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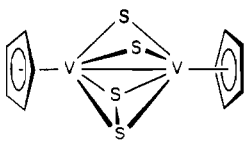
the interaction diagram in Figure 8 we see a gap of approximately 1 eV for a compound with two electrons less. This indicates that species such as $CpTiS_4TiCp$ or $CpVAs_2S_2VCp$ might be kinetically stable. These compounds may be attractive synthetic goals.

For comparison we did a calculation on the "perpendicular" isomer **38**. The interaction diagram is not shown here, but in



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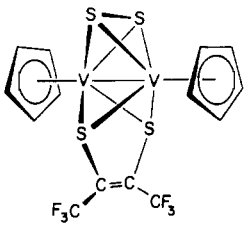
general terms it is not very different from the parallel alternative. The HOMO in both cases represents a M–M σ bond; the LUMO, which is approximately 0.5 eV higher in energy for the parallel geometry, has δ^* character. This energy difference for the LUMO could be one reason why—except for **31**—compounds with formally two more electrons, i.e. the corresponding Mo compounds or $CpV(S_2)(S_2C_2F_6)VCp$ (**39**),[28a] prefer the perpendicular ori-



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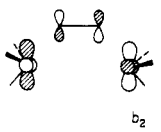
entation. There are some differences in overlap between both structures. By symmetry, in the parallel structure the b_2 orbital can interact with the δ^* and σ^* combinations of the metal fragment **40** and **41**. The a_2 orbital interacts with another δ^* com-



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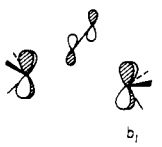

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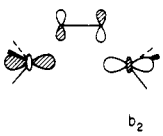

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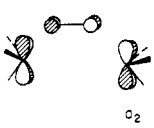

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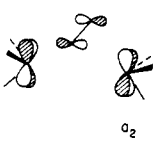


44

bination of the metal fragment **42**. The interactions of the π^* orbitals in the perpendicular orientation are with the $\delta(b_1)$ and $\delta^*(a_2)$ combinations of the metal fragment **43** and **44**.

Our calculations make the perpendicular orientation approximately 0.95 eV more stable than the parallel one. Since the energy matches between the orbitals of bridging S_2^{2-} and the metal fragment are similar, the difference must be caused by the overlap factor. There are two different overlaps to consider in the perpendicular case and three for the parallel bonding mode. Although there are more interacting orbitals in the parallel geometry, the individual overlaps are considerably bigger for the perpendicular S_2 orientation. These differences in overlap are responsible for the energy difference between structures **7** and **38**.

If the parallel geometry is less stable by 0.95 eV, why do we not observe the perpendicular geometry, or why do we not have an interconversion between the two structures? As in the case of the acetylene complexes, the reaction is symmetry forbidden. But, given the poor performance of the extended Hückel method in finding a reasonable minimum for the different $CpMo_4MoCo$ isomers **1–3** in Figure 2, is the 0.95-eV energy difference at all credible? As we mentioned above, the main problem in calculating a reliable minimum for **1–3** lies in the presence of several level crossings that make the problem hard to tackle within the framework of the one-electron model. For the conversion **7** → **38** the situation is less complicated. There is a level crossing between the a_2 orbitals, though an avoided one. This leaves us with a diamagnetic species all along the isomerization pathway. Moreover, the interactions responsible for the stability of **7** and **38**, the fragment overlaps shown in **40–44** overlayed by a small amount of S···S repulsion, are quite transparent. We think that the energy difference between **7** and **38**—even though its absolute numerical value may be not reliable—is significant.

We just mentioned that during the rotation of the S_2^{2-} there is a level crossing between the a_2 orbitals, though an avoided one. If we rotate the S_2 unit in **7**, the a_2 orbitals cross-correlate with

(50) Goh, L. Y.; Mac, T. C. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1474.
(51) (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858. (b) Hoffman, D. M.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1982**, 1471.

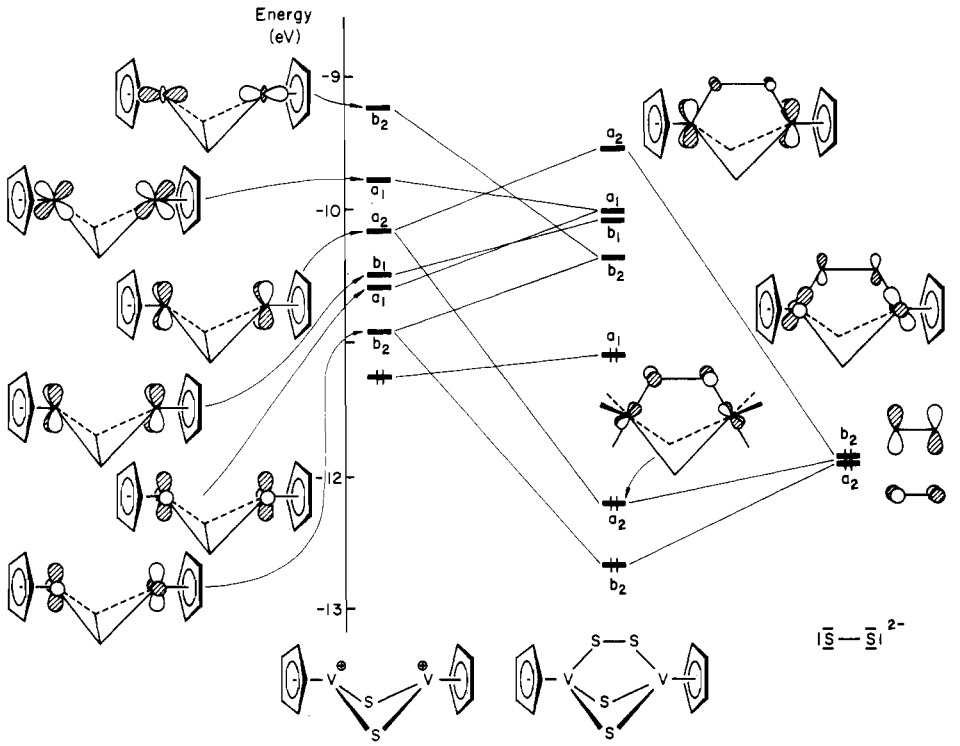
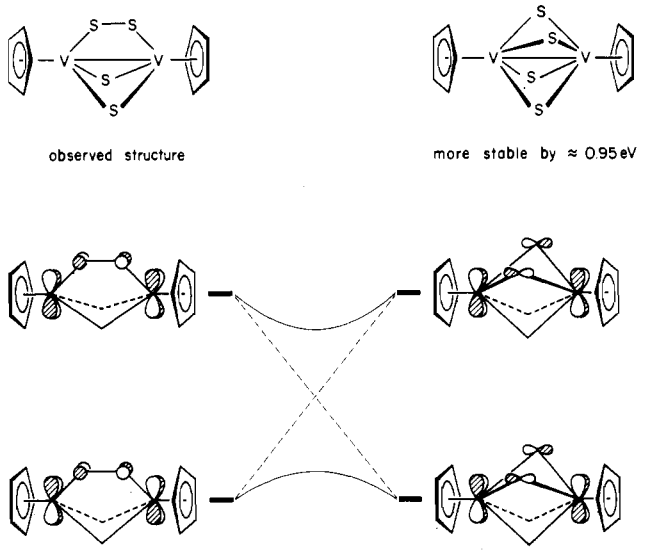


Figure 8. The interaction of $[CpVS_2VCp]^{2+}$ with S_2^{2-} in the parallel geometry.

the corresponding orbitals in **38**. We calculated a correlation diagram for the rotation **45**, keeping the V–S distance constant



45

during the motion. No energy barrier was found. We still think it is justified to call the reaction forbidden, because there is an intended level crossing.

If **7** is less stable than **38**, why is it formed at all? The formation of **7** is determined kinetically. Presumably **7** is formed from $(i\text{-PrCp})_2V_2S_5$ (**8**)[28a] via S abstraction from the μ-η^2-S_2 unit, **46**.[52]

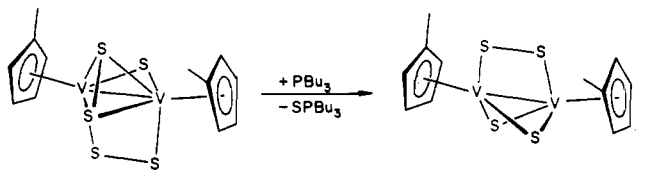


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Table III. Parameters Used in Extended Hückel Calculations

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	C_1[a]	C_2[a]
S	3s	−20.00	1.817			
	3p	−13.30	1.817			
Te	5s	−20.80	2.51			
	5p	−14.80	2.16			
Cl	3s	−30.00	2.033			
	3p	−15.00	2.033			
Br	4s	−27.01	2.588			
	4p	−12.44	2.131			
I	5s	−23.30	2.681			
	5p	−14.00	2.322			
V	3d	−11.00	4.75	1.70	0.4755	0.7052
	4s	−8.81	1.30			
	4p	−5.52	1.30			
Cr	3d	−11.22	4.95	1.80	0.5060	0.6750
	4s	−8.66	1.70			
	4p	−5.24	1.70			
Nb	4d	−12.10	4.08	1.64	0.6401	0.5516
	5s	−10.10	1.89			
	5p	−6.86	1.85			
Mo	4d	−11.06	4.54	1.90	0.5899	0.5899
	5s	−8.77	1.96			
	5p	−5.60	1.90			

[a] These are the coefficients in the double-ζ expansion.

In general, synthetic rationales for most of the compounds we discussed in this paper are hard to give. A typical synthesis starts out from an organometallic precursor that is reacted with elementary sulfur, phosphorus, or arsenic. The product distribution seems to be determined by those fragments of main-group atoms, which are initially cut out of these molecular units (e.g. S_8 rings or P_4 tetrahedra). The energy barriers to excising or abstracting such E_n units must be small. Some day we will understand the mechanisms of formation of these compounds, but for the moment

(52) Similar reactions have been reported, e.g. for the conversion of $(MeCp)_2V_2Fe(CO)_3S_4$ to $(MeCp)_2V_2Fe(CO)_3S_3$, and $[Mo_3S_7(SCH_2CH_2S)_3]^{2-}$ to $[Mo_3S_4(SCH_2CH_2S)_3]^{2-}$, respectively. Bolinger, M. C.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313. Halbert, T. R.; McGauley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849. Keck, H.; Kuchen, W.; Mathow, J.; Wunderlich, H. *Angew. Chem.* **1982**, *94*, 927; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 929.

we must be satisfied with the partial understanding of the structures themselves, which we think we have attained.

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Appendix

All the calculations were performed by using the extended Hückel method[33a,b] with weighted H_{ij}'s.[33c] Unless otherwise mentioned, the experimental bond lengths were used. The values for the H_{ii}'s and the orbital exponents are listed in Table III. The parameters for C and H are the standard ones.[33a,b]

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Dependence of Bond Angles upon Bond Distances in Simple Covalent Hydrides, Halides, and Oxides[1]

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Ab initio molecular orbital calculations for a variety of hydrides, fluorides, and oxides of first- and second-row elements show that the optimum bond angle subtended by a pair of ligands increases significantly as the internuclear separation between the ligand and the central atom is decreased. This dependence is interpreted in terms of a directed valence theory of bonding, with departures from ideal bond angles arising from steric clashes among ligands. Some of the apparent anomalies of bond angles in simple hydrides and halides are resolved by the discovery that the steric size of a ligand depends significantly upon the length of its bond to the central atom.

For many years, chemists have attempted to elucidate the principal factors that determine the three-dimensional arrangement of ligands X about a central atom A in common molecules. The most successful simple theory of structure is the well-known VSEPR (valence shell electron pair repulsion) method elaborated by Gillespie,[2] in which repulsion between electron pairs on A is considered to be the dominant factor. In VSEPR, the number of electron pairs at A determines the "ideal" geometry, and the electronegativity of the ligands controls minor deviations from this structure.

We wish to report *ab initio* molecular orbital calculations which indicate that the bond distance R_{AX} is a major factor in determining the optimum XAX bond angle in AX_n molecules, particularly if A is a first-row element.

The variation in HOH angle with changes to the OH bond distance in H_2O is illustrated in Figure 1.[3] The MO calculations here use the 6-31G* basis set,[4,5] i.e., one that includes d orbitals on oxygen, in which inner-shell atomic orbitals are expanded by a fixed linear combination of six Gaussian orbitals and the valence-shell atomic orbitals are expanded as a combination of two sets of Gaussians, one with three components and one with one. The HOH angle widens appreciably as the OH distance is reduced, becoming greater than the tetrahedral value (109.5°) for OH separations of 0.83 Å or less. As the bond is stretched, the angle closes down toward 90°.[6] Similar results are obtained[3] for NH_3 (not shown) and for the singlet state of CH_2 (Figure 1). Although the trend of increasing bond angle with decreasing XH atomic separation is also obtained when X is a second-row atom, the rate of change is only about one-third of that obtained when X is from the first row (see Figure 1 results for H_2S). Again the limiting angle is near 90° for long bond distances but stays well under the tetrahedral value even at short separations. This behavior is not related significantly to the ligand's electronegativity or to the number of lone pairs on A, as the variation for CH_2 is similar to that for H_2O and is very different from that for PH_3 (not shown).

The substantial dependence of bond angle upon interatomic separation and the limiting values of about 90° for bond angles at long separations for the hydrides are unanticipated by VSEPR theory. To explore this point further and to discover the actual reasons for bond angle variations, the ab initio MO calculations were extended to a variety of other molecules. For reasons of economy, smaller basis sets were employed.[7] The basis set used

(1) Research supported by the Natural Sciences and Engineering Research Council of Canada.
(2) Gillespie, R. J., *Molecular Geometry*; Van Nostrand Reinhold: Company: London, 1972.
(3) The detailed values of the predicted bond angles and energies as a function of the varied separations are reported in Tables 1-4, available as supplementary data.
(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; Chapter 4.
(5) Calculations were performed on a VAX 8600 using the GAUSSIAN 86 program (release C) from Carnegie-Mellon University, by M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, R. Martin, J. J. P. Stewart, F. Bobrowicz, D. Defrees, R. Seeger, R. Whiteside, D. Fox, E. Fluder, and J. A. Pople.
(6) Calculations with the 6-31G* basis set which include correction for the more substantive effects of electron correlation have been performed by second-order Moller-Plesset perturbation theory. The bond angle–bond length curves are virtually identical with those without correlation when the distances are short. (This applies even to the results for CH_2, for which there is a doubly excited configuration that lies close to the lowest singlet state.) For long AX separations, the optimum XAX angles are smaller than those obtained by the Hartree–Fock calculations, due to incipient bonding between the ligands themselves that is introduced by incorporating doubly excited configurations into the wave function. For example, as the OH bond in H_2O becomes very long, the best electronic structure eventually becomes an oxygen atom separated from an H_2 molecule. To avoid these difficulties, and because there is no significant effect of correlation upon angle at short AX separations (the area of prime importance here), these 6-31G*/MP2 calculations are not discussed further herein.

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