conformer is 490 ± 150 cm^{-1} lower in energy than II also support this conclusion.[5]

The results obtained here have a direct bearing on other studies. In particular, the higher energy form (II) of glycine has been sought unsuccessfully in interstellar molecular clouds.[10] Since the interstellar clouds are quite cool ($T < 100$ K), one anticipates that only the lowest energy states of a molecule will be populated. As a result, negative interstellar searches for conformer II may be much less significant than for conformer I.

Acknowledgment. L.S. and H.L.S. thank Drs. J. B. Shankle, J. W. Wilkes, B. Ashmore, and J. Swayze for their assistance and the University of Arkansas Computing Center for executing the calculations. L.S. also acknowledges partial support of this work by NSF Grant CHE-7920790.

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Received May 5, 1980

Molecular Structure of $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$. A Trigonal-Prismatic Electron-Deficient Molybdenum(II) Carbonyl Derivative

Sir:

Molybdenum carbonyl derivatives of both Mo(0) and Mo(II) adhere to the effective atomic number rule with great regularity.[1] In view of the premise that 16-electron species are common intermediates for reactions involving these and related compounds,[2] the properties of molybdenum carbonyl compounds which are formally electron deficient are of fundamental importance. We report a single-crystal X-ray study of $Mo(CO)_2(S_2CN\text{-}i\text{-}Pr_2)_2$ (**1**),[3] a 6-coordinate molybdenum(II) dicarbonyl monomer.[4] Previous reactivity studies have identified related compounds as reversible carbon monoxide carriers[5] and explored their addition chemistry.[6]

A trigonal-prismatic coordination geometry, unprecedented for metal carbonyl derivatives, is adopted by **1** in the solid state (Figure 1).[7] The complex is monomeric with a methylene chloride of solvation present. No unusual intermolecular distances are observed. Pertinent intramolecular distances and angles are listed in Table I while least-squares planes of interest and associated dihedral angles are tabulated in Table II. Although no crystallographic symmetry is imposed on the complex, the observed structure conforms to virtual C_{2v} symmetry with the C_2 axis passing through the metal directly between the two carbonyl ligands.

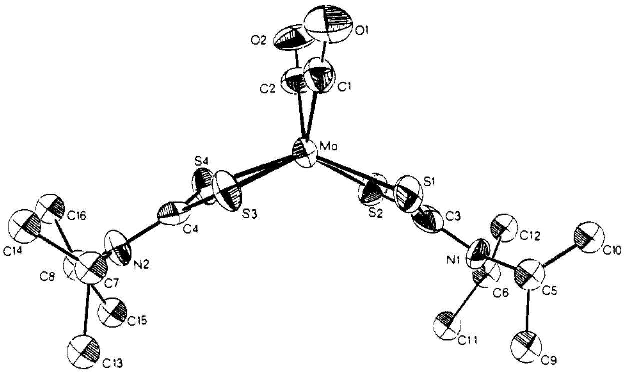

Figure 1. An ORTEP view of $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$ showing the atomic labeling scheme.

Table I. Selected Bond Distances and Angles for $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr_2]_2$

bond distances, Å		bond angles, deg	
Mo–C1	1.902 (8)	S1–Mo–S2	70.2 (1)
Mo–C2	1.919 (8)	S3–Mo–S4	70.6 (1)
Mo–S1	2.460 (2)	C1–Mo–C2	74.3 (3)
Mo–S2	2.456 (2)	S1–Mo–S3	98.7 (1)
Mo–S3	2.448 (2)	S2–Mo–S4	97.3 (1)
Mo–S4	2.451 (2)	S1–Mo–C1	85.7 (2)
C1–O1	1.180 (8)	S3–Mo–C1	84.3 (2)
C2–O2	1.175 (7)	S2–Mo–C2	83.7 (2)
N1–C3	1.329 (7)	S4–Mo–C2	83.9 (2)
N2–C4	1.309 (8)	Mo–C1–O1	177.4 (7)
		Mo–C2–O2	177.5 (6)

Table II. Dihedral Angles between Selected Least-Squares Planes

defining planes	dihedral angle, deg
MoS1S2:MoS3S4	135
MoS1S2:MoC1O1C2O2	113
MoS3S4:MoC1O1C2O2	112
MoC1O1C2O2:S1S2S3S4	91

Previous trigonal-prismatic monomers have been identified only for unusual complexes[8] involving severe ligand steric constraints[9] or tris(1,2-dithiolato)metal derivatives where interligand S···S interactions may play a unique role.[10] Note that the interligand S···S distances in **1** range from 3.68 to 4.66 Å and substantially exceed the sum of van der Waals radii (3.60 Å).[11] Indeed, the

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[4] Suitable single crystals were obtained by slow recrystallization of **1** from a saturated methylene chloride solution. The dark blue-green solid exhibits two strong infrared absorptions attributable to cis-carbonyl ligands at 1934 and 1842 cm^{-1}. Note that a KBr pellet prepared under aerobic conditions was purple in color and displayed intense infrared absorptions at 2015, 1938, and 1900 cm^{-1} attributable to $Mo(CO)_3[S_2CN\text{-}i\text{-}Pr_2]_2$ and a very strong absorption at 968 cm^{-1} attributable to $Mo(O)[S_2CN\text{-}i\text{-}Pr_2]_2$.

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[7] The crystal selected was monoclinic, space group $P2_1/n$, with unit-cell dimensions $a = 10.287$ (4), $b = 13.204$ (3), $c = 19.410$ (5) Å, $\beta = 101.99$ (6)°, and $Z = 4$. Of the 5013 reflections monitored, 2366 independent reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement which converged to 0.048 and 0.049 for R and R_w, respectively. The final difference Fourier map was featureless with the largest residual electron density only 0.31 e/Å^3.

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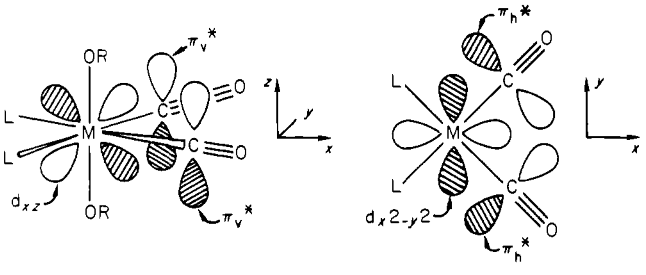
dihedral angle between the MoS1S2 and MoS3S4 chelate planes has opened to 134.8° relative to the 120° angle associated with an idealized D_{3h} prism.

The linear molybdenum carbonyl units exhibit bond distances typical of Mo(II) and W(II) complexes.[12] The acute C1–Mo–C2 coordination angle of 74.3 (3)° is not sterically imposed. A related 6-coordinate molybdenum(II) dicarbonyl structure, $Mo(CO)_2(py)_2(O\text{-}t\text{-}Bu)_2$ (**2**),[13] displays a distorted octahedral geometry in which the C–Mo–C angle is 72°. We believe that optimization of retrodative metal-to-carbonyl π bonding for these d^4 cases is responsible for the similar values of the C–Mo–C angle in both complexes in spite of the surprising gross structural differences (vide infra).

The Mo–S distances of 2.45 and 2.46 Å are typical of dithiocarbamate Mo–S distances.[14] Longer Mo–S bond distances of 2.6–2.8 Å have been reported for dithiocarbamate complexes with sulfur trans to such high trans influence ligands as oxo or nitrene.[15]

We have performed extended Hückel calculations[16] in an effort to identify the electronic factors which favor the trigonal-prismatic coordination geometry observed for **1**. Our calculations indicate that the 18-electron dinitrosyl analogue of **1**, $Mo(NO)_2(S_2CNR_2)_2$,[17] should adopt an octahedral geometry, and, indeed, precedent exists for such a result since the isoelectronic $Fe(CO)_2(S_2CNR_2)_2$[18] and related $MoCl_2L_2(NO)_2$[19] are indeed octahedral.

An analysis of Chisholm's electron-deficient complex **2** illustrates the role ligand π donation can play in Mo(II) complexes with a formal electron count of 16 and indirectly provides insight into the electronic structure of **1**. An octahedral σ-bonding scheme for **2** leaves three metal $d\pi$ orbitals. For a d^4 configuration, only two of the three $d\pi$ levels need be occupied, and for the C_{2v} symmetry of **2** (oriented as shown below) the $d\pi - \pi^*(CO)$ bonding leads easily to the realization that $d_{x^2-y^2}$ will overlap most effectively with both carbonyl π_h* orbitals while d_{xz} will be stabilized by mixing with both π_v* orbitals. Particularly noteworthy is the observation that decreasing the C–M–C angle from 90° increases overlap for both of these $d\pi$ stabilizing interactions. Clearly, d_{yz} is left as the $d\pi$ orbital with decreased π* overlap relative to d_{xz} as the coordination angle of the two cis π-acceptor ligands tends toward 70°. The key feature of the analysis of this electron-deficient complex is that the d_{yz} orbital need not contain electrons; i.e., the HOMO of electron-precise analogues becomes the new LUMO. As such, this vacant orbital can be "sacrificed" to higher energy in order to achieve extra stability for lower lying filled orbitals. For **2**, the trans alkoxides can be thought of as sp^2 hybridized with a filled oxygen p orbital perpendicular to the Mo–O–R plane which is of the proper symmetry to interact with (and be stabilized by) d_{yz} if the alkyl group resides in the xz plane. This is indeed the observed geometry and suggests that $d_{x^2-y^2}$ and d_{xz} are stabilized by CO π* orbitals and filled with the four metal electrons while d_{yz} is vacant due to destabilization by the filled oxygen $p_\perp$ orbital.[20]



The critical orbital in assessing the electronic structure of **1** is also the LUMO, largely of $d\pi$ character, which increases substantially in energy as the coordination geometry changes from octahedral to trigonal prismatic. We calculate an energy gap of less than 0.2 eV between the HOMO and LUMO orbitals among the nest of three $d\pi$ levels for an idealized octahedral $Mo(CO)_2(S_2CNR_2)_2$ geometry while the observed geometry produces a separation of greater than 1.2 eV between the HOMO and LUMO, consistent with the observed diamagnetic behavior of **1**. Although the concomitant stabilization realized in lower lying orbitals which accompanies destabilization of this vacant metal $d\pi$ orbital is not localized in a single molecular orbital, we believe mixing of filled dithiocarbamate π orbitals with this orbital is optimized in the trigonal prism. This feature provides the electronic driving force responsible for the observed structure. The two carbonyl ligands stabilize two of the three $d\pi$ orbitals equally well in either the trigonal or the octahedral case, and both of these orbitals are filled for a d^4 configuration. The crux of the geometrical preference stems from the planar nature of the dithiocarbamate ligands. This fixes the orientation of the filled ligand π orbitals perpendicular to the bite of the ligand and limits overlap of the $d\pi$ LUMO with filled S π-type orbitals in the octahedral case. In order to effectively interact with the single vacant $d\pi$ level, a trigonal-prismatic geometry is adopted.[21]

These results and hypotheses have implications for organometallic mechanisms involving 6-coordinate 16-electron intermediates. The potential π-donor properties of the dithiocarbamate ligands are of importance in the isolation and geometry of **1**. We suggest that the alkoxy groups of **2** provide π-electron density to the metal which allows isolation of this 16-electron complex. Furthermore, the highly reactive species $(\pi\text{-}C_5H_5)Mo(CO)_2R$[22] and $[(\pi\text{-}C_5H_5)Mo(CO)_3]^{+}$[23] fit into this scheme in that none of the ligands have π-electron density available to raise the LUMO energy, and as a result, these are very electrophilic reagents.

Acknowledgment. This work was supported by a Cottrell Research Grant from Research Corporation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Stimulating discussions with Professor R. Hoffmann during the course of this work were very beneficial. Expert crystallographic assistance was generously provided by Scott Wilson.

Supplementary Material Available: A listing of positional and thermal parameters is available (4 pages). Ordering information is given on any current masthead page.

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Received May 12, 1980