95/5. This behavior shows that up to +60° *nitrogen does not invert fast*, as compared to the nmr time scale.

In the case of the two compounds I and II we do not know exactly the conformation of fluorine in A and E conformers. From the experimental values of $^3J_{FH}$ we suppose that in IA the N–F bond (J = 58 Hz) is in the same conformation as in IIA (J = 48.3 Hz) and that in IE the N–F bond (J = 20.5 Hz) is in the same conformation as in IIE (J = 22.8 Hz). If we now suppose that the coupling constant ^3J(HCNF) follows a Karplus type law (as is the case for ^3J(HCCF)[8] and for ^3J(HCNH)[9]), then $^3J_{aa} > {}^3J_{ea}$. A corresponds to an axial conformation of the fluorine and E corresponds to an equatorial N–F bond, so the nitrogen–halogen bond seems in our case to be more stable in the equatorial conformation as was already stated by Lambert for the N–Cl bond.[2]

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Structure of Di-μ-sulfido-bis[oxo(L-histidinato)molybdenum(V)] Hydrate

Sir:

It is well established that molybdenum has an essential function in a number of sulfhydryl enzymes such as xanthine oxidase,[1] aldehyde oxidase,[2] and nitrogenase.[3] Of particular interest is the recent demonstration by Hardy, *et al.*, that in nitrogenase, the molybdenum atom is directly associated with the active site of the enzyme.[4] The importance of molybdenum–sulfur binding in these systems has been suggested by several workers, and it has also been proposed that at the active site the molybdenum is bound, at least in part, to a cysteine residue.

Recently, several sulfido-bridged complexes of Mo(V) and Mo(VI) have been isolated[5,6] and these support Spence's suggestion that the existence of a sulfido-bridged molybdenum species in these enzymes cannot be ruled out.[7] Support for this point of view can be drawn from the nonheme iron protein ferredoxin, where sulfido bridges are presumed to play a vital role.[8] The configuration of the M–S–M moiety in metal complexes is therefore of great interest, particularly for water-soluble ones which contain simple σ-donor ligands such as α-amino acids. In this communication we report the crystal and molecular structure of such a complex.

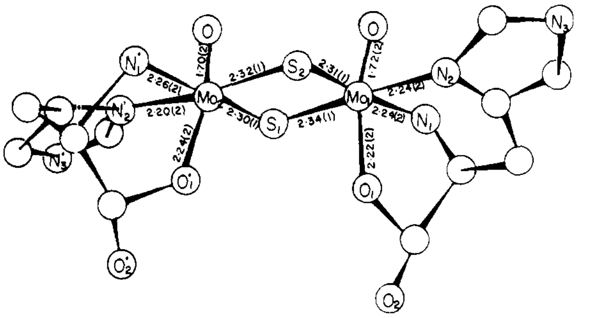

Figure 1. A perspective drawing of the [$Mo_2O_2S_2$(histidine)$_2$] complex.

The complex [$Mo_2O_2S_2$(histidine)$_2$] was synthesized as previously described,[6] and suitable crystals for X-ray study were obtained by slow evaporation of an aqueous solution maintained at pH 8 and at 45° in an oil bath. Precession and Weissenberg photographs showed the crystals to be tetragonal with extinctions 00l, $l \neq 4n$, and h00, $h \neq 2n$, indicating the space group $P4_12_12$ or $P4_32_12$. The unit cell dimensions are $a = b = 10.51$ (2), $c = 36.07$ (2) Å. The measured density of 2.02 (3) g/cm³ (flotation in a chloroform–bromoform mixture) compares favorably with the calculated 2.05 g/cm³ for $Z = 8$. Data were collected by the multiple-film integrated equiinclination Weissenberg technique using nickel-filtered Cu Kα radiation, and the intensities were estimated visually with a calibrated intensity strip prepared from the same crystal. The structure was solved by conventional Patterson and Fourier techniques. The space group was determined to be $P4_12_12$ based on the observation that appropriate transformations to space group $P4_32_12$ lead to the enantiomorphous D-histidine. At the present stage of full-matrix least-squares refinement, R = 0.094 for 980 observed reflections.

As can be seen from Figure 1, each molybdenum atom is bound to an oxygen atom, two sulfur atoms, and a histidine molecule, resulting in a distorted octahedral configuration around each metal atom. The dimeric molecule consists of two octahedra sharing a common edge. The configuration and dimension of the histidine molecule, as well as the coordination sites it occupies, are very similar to those found in the oxo-bridged dimer Mo_2O_4(L-histidine)$_2 \cdot 3H_2O$, recently reported by Prout.[9] As expected, the average Mo–N(imidazole) bond length is somewhat shorter than the average Mo–N(amino) bond length. The Mo–O(carboxyl) distance of 2.23 (2) Å is the same as found by Prout[9] and is considerably shorter than that found by Knox[10] in $Na_2Mo_2O_4$[$SCH_2CH(NH_2)CO_2$]$_2 \cdot 5H_2O$, indicating (as pointed out by Prout[9]) the greater flexibility of the tridentate histidine ligand.

Of particular interest in this structure are the dimensions of the Mo_2S_2 bridge. The four Mo–S distances are not significantly different, having an average value of 2.32 (2) Å. This value is comparable to the Mo–S distances found in Mo_2S_6.[11] The S–S distance is

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3.64 (2) A. The Mo–Mo distance of 2.82 (1) Å, although longer than the value found for the analogous oxo-bridged dimer Mo_2O_4(histidine)$_2$, indicates considerable Mo–Mo interaction, which accounts for the diamagnetism of the complex. The Mo_2S_2 bridge is not planar, with a dihedral angle between the planes $Mo_1S_1S_2$ and $Mo_2S_1S_2$ of 160.9 (9°). Although it is difficult to forward an explanation for the nonplanarity of the Mo_2S_2 unit at this time, close examination of molecular models suggest that this is not a result of packing in the crystal. It is interesting to note that in the complex $[C_5H_5MoO]_2S_2$[12] where the Mo_2S_2 unit is strictly planar, the Mo–Mo distance of 2.89 (5) Å is considerably longer. Since in both structures the Mo–S distances and the S–Mo–S and the Mo–S–Mo bond angles are very similar, the nonplanarity of the Mo_2S_2 unit is probably dictated by the shorter Mo–Mo distance.

These results are of particular interest in view of the model proposed by Hardy, Burns, and Parshall for the configuration of molybdenum and iron in the active site of nitrogenase.[13] In this model, the two metal ions are held by a bridging atom in a manner which allows the nitrogen molecule to bind simultaneously to both metal ions. This model requires a relatively short Mo–Fe distance and an acute Mo–X–Fe angle (X = bridging atom). The Mo–Mo distance observed in this structure and, more important, the small Mo–S–Mo angle clearly suggest that one cannot rule out sulfur as the bridging atom (by sulfur we mean sulfide ion or a mercaptide).

A complete description of this structure and analysis of the hydrogen bonds will be presented in a subsequent publication.

Table I. Bond Angles Around the Coordination Sphere of the Molybdenums

Atoms	Angle	Atoms	Angle
Mo_1–S_1–Mo_2	74.8 (5)	Mo_1–S_2–Mo_2	75.0 (5)
S_1–Mo_1–S_2	103.5 (5)	S_1–Mo_2–S_2	104.1 (5)
S_1–Mo_1–O	96.3 (6)	S_1–Mo_2–O	106.1 (7)
S_1–Mo_1–O_1	84.2 (6)	S_1–Mo_2–O_1'	94.0 (6)
S_1–Mo_1–N_1	86.6 (7)	S_1–Mo_2–N_1'	161.2 (7)
S_1–Mo_1–N_2	162.0 (7)	S_1–Mo_2–N_2'	84.7 (8)
S_2–Mo_1–O	102.5 (7)	S_2–Mo_2–O	103.5 (6)
S_2–Mo_1–O_1	91.2 (6)	S_2–Mo_2–O_1'	90.8 (6)
S_2–Mo_1–N_1	158.1 (8)	S_2–Mo_2–N_1'	87.7 (7)
S_2–Mo_1–N_2	86.0 (7)	S_2–Mo_2–N_2'	164.8 (6)
O–Mo_1–O_1	165.7 (7)	O–Mo_2–O_1'	151.3 (7)
O–Mo_1–N_1	95.4 (8)	O–Mo_2–N_1'	84.8 (7)
O–Mo_1–N_2	96.4 (8)	O–Mo_2–M_2'	85.6 (8)
O_1–Mo_1–N_1	70.3 (7)	O_1–Mo_2–N_1'	70.9 (7)
O_1–Mo_1–N_2	80.4 (8)	O_1–Mo_2–N_2'	76.0 (8)
N_1–Mo_1–N_2	79.6 (8)	N_1'–Mo_2–N_2'	80.9 (8)

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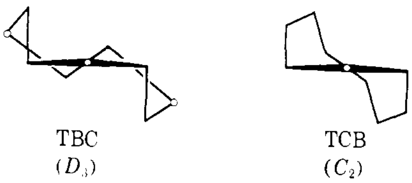
The Conformation of Cyclononane. Evidence from 251-MHz ^1H Nuclear Magnetic Resonance and 63-MHz ^{13}C Fourier Transform Nuclear Magnetic Resonance

Sir:

Hitherto, knowledge about the conformation of cyclononane has come largely from X-ray diffraction studies on derivatives of cyclononane and from semiempirical strain-energy calculations on cyclononane itself. Thus, X-ray work has shown that the nine-membered skeletons of cyclononylamine hydrobromide[1] and cyclononanone–mercuric chloride[2] have approximately C_2 symmetry and are essentially twist chair-boats (TCB). In contrast, trimeric acetone peroxide[3] exists in the twist boat-chair (TBC) of D_3 symmetry; the presence of three *gem*-dimethyl moieties in this compound, however, introduces large steric strains in other possible conformations, such as the TCB. The TBC form has also been assigned to 1,1,4,4-tetramethylcyclononane and related derivatives on the basis of low-temperature nmr measurements and steric strain considerations.[4] The strain-energy calculations of Hendrickson[5] show that the TBC is 2.2 kcal/mol more stable than the TCB. Bixon and Lifson[6] come to similar conclusions and also suggest that the occurrence of the TCB in cyclononylamine hydrobromide may reflect lattice forces rather than any inherent conformational stability of this form over the TBC. However, Allinger, *et al.*, in a very recent paper give results of calculations showing that the TCB is of lower energy than the TBC form[7] (in the structures circles represent carbon atoms lying on C_2 axes).



We now report that cyclononane shows both ^1H and ^{13}C temperature-dependent spectra,[8] and that an analysis of these spectra, together with nmr measure-

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[7] N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, **93**, 1637 (1971). Professor Allinger has informed us that in view of the strong evidence for the TBC given in the present paper, he and his coworkers have reexamined the calculations reported in the above reference, and they have found that by error no calculation had been carried out for the TBC conformation. They have now made such a calculation and find that the TBC (D_3) form has a calculated heat of formation of −32.20 kcal/mol, as compared with −30.08 kcal/mol for the TCB (C_2) and −31.8 kcal/mol determined experimentally for cyclononane. Thus, these calculations are now in agreement with previous ones[5,6] in showing that the TBC is more stable than the TCB.

[8] At 60 MHz, the single line given by cyclononane in its proton spectrum has been reported to remain unsplit at low temperatures (J. D. Roberts, Abstracts, Nineteenth National Organic Chemistry Symposium of the American Chemical Society, Tempe, Ariz., June 1965). Even at 100 MHz, only broadening of the cyclononane line was observed by us down to −165°.