and D_{2d} versions are related by a relatively simple breathing motion[11] shown in Figure 4. We suggest that a T_d ground state will be favored for phosphine or phosphite ligands where steric crowding is important. Diffraction data will be obtained for exemplary species to establish the solid-state geometries. It should be noted that the above-mentioned breathing motion may well be so rapid that the true limiting slow-exchange nmr spectra would not be obtained for a D_{2d} species.

Earlier we discussed[9,10,12,13] for H_xML_4 molecules a novel rearrangement mechanism which comprised an approach to a near regular tetrahedral ML_4 substructure in the ground or transition state, with concomitant hydrogen atom traverse of the ML_4 tetrahedral faces. This mechanism, given the trivial label of "tetrahedral tunneling," was demonstrated for six-[8,10,13] and suggested for five-coordinate[12] complexes. We anticipated that this same mechanism would also be operative in some seven (H_3ML_4) and eight (H_4ML_4) classes with the exchange barrier being higher in the latter case because hydrogen atom motion must be concerted. We propose that the H_4MoL_4 phosphine complexes have a D_{2d} tetrahedral or near regular tetrahedral MoP_4 substructure and that intramolecular rearrangement comprises a concerted hydrogen atom traverse of the tetrahedral faces. From an analysis of the molecular permutation group,[13] we find that there are four basic permutational sets plus the identity set which are potentially distinguishable on the basis of nmr line-shape studies. Simple physical mechanisms involving largely hydrogen motion would be pairwise exchange of the hydrogens, a concerted motion of three hydrogens, or a concerted motion of all four hydrogens. As yet we have not established whether mechanistic information can be qualitatively or quantitatively inferred from an analysis of the nmr line shapes, but of the possible mechanistic sets we believe that the most realistic one involves predominantly a concerted motion of three of the hydrogen nuclei.

We are presently attempting to obtain a more complete analysis of the low-temperature limit nmr data and mechanistic information from the line-shape data. Additionally, we are examining analogous eight-coordinate molybdenum and tungsten complexes to see whether the steric or electronic character of the ligand can have a profound effect upon the barrier to intramolecular rearrangement. Preliminary information for the complex $MoH_4[P(OC_2H_5)_2C_6H_5]_4$ has established that its nmr characteristics are qualitatively different from those of the above-described phosphine complexes. A full report on this study of stereochemically nonrigid eight-coordinate complexes will be presented shortly.

Acknowledgment. We are indebted to Mr. William Peet and Dr. D. H. Gerlach for substantial assistance in the preparation of these complexes.

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N-Fluoro-2,6-dimethylpiperidines. Conformational Behavior as Observed by ^{19}F Nuclear Magnetic Resonance

Sir:

Nitrogen inversions in amines are known to be fast, but generally get slower if nitrogen is substituted by at least one electronegative atom, such as oxygen or chlorine.[1] In recent work, nitrogen inversion in cyclic *N*-chloroamines was studied[2] and the authors concluded that for *N*-chloropiperidine, nitrogen inversion may be excluded as the rate-determining process; on the other hand they stated that "the observation of only one AB spectrum (for the α protons in *N*-chloropiperidine-*3,3,5,5-d*$_4$ at $-40°$) can be explained either by the presence of only one conformer, presumably with chlorine equatorial, or by a superposition of the AB spectra from the two conformers." [2]

It appears, therefore, that the proton nmr is not very satisfactory in this case as no clear demonstration can be drawn. It seemed interesting to us to use *N*-fluoro compounds for solving problems such as "six-membered ring reversal, *vs.* nitrogen inversion," this for two reasons: one is that fluorine will decrease as much as possible the rate of inversion of nitrogen; the other is that it will be easy to observe this nucleus by ^{19}F nmr technique with which large spectral differences between conformers are expected.[3]

We prepared separately the two *N*-fluoro derivatives of *cis*- and *trans*-2,6-dimethylpiperidine according to the expected reaction.[4] According to a described

$$2R_2NH + FClO_3 \longrightarrow R_2NF + R_2NH_2^+ClO_3^-$$

procedure, 2,6-dimethylpyridine was hydrogenated into *cis*- and *trans*-2,6-dimethylpiperidine which were separated on a spinning band column:[5] cis, bp 64° (100 mm); trans, bp 71° (100 mm). The fluorination can be carried out either in ether or in $CFCl_3$ solution (100 ml) at low temperature (between -60 and $-20°$) by an excess of perchloryl fluoride ($FClO_3$) diluted in nitrogen (15% vol). By this procedure 3.3 g of the *cis*-2,6-dimethylpiperidine (0.03 mol) gave 2.4 g of chlorate (0.0122 mol) which precipitated; from the solution the expected *N*-fluoro cis derivative was isolated by evaporation of the solvent at low temperature: a viscous oil, not distillable, but rather stable at room temperature; mass spectrum m^+/e M = 131 (0.09), M − CH_3 = 116 (1), M − NF = 98 (0.62).

Anal. Calcd for $C_7H_{11}NF$: C, 64.08; H, 10.75; N, 10.67; F, 14.48. Found: C, 63.48; H, 11.4; N, 10.38; F, 11.5.

By the same procedure 2 g of *trans*-2,6-dimethylpiperidine (0.018 mol) gave 1.57 g of chlorate (0.008 mol) which precipitated; from the solution the expected *N*-fluoro trans derivative was isolated by evaporation of the solvent at low temperature: a viscous oil, not distillable, and rather unstable at room temperature; it may be kept for a long time under nitrogen at $-70°$; mass spectrum m^+/e M = 131 (0.12), M − CH_3 = 116 (1), M − NF = 98 (0.65).

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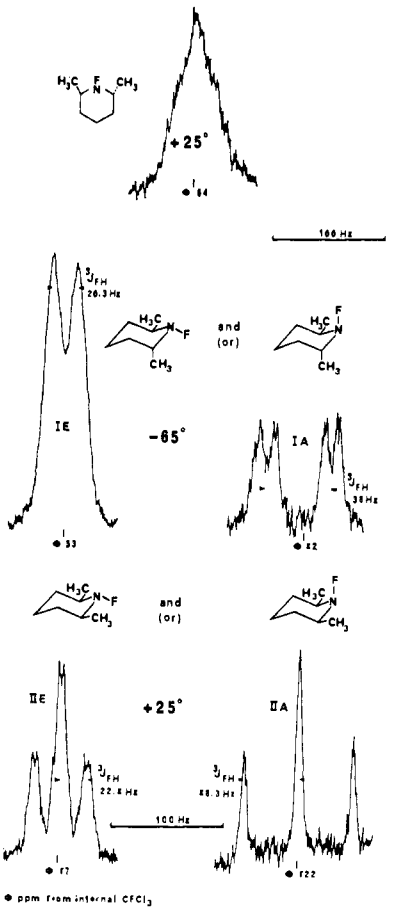

Figure 1. Fluorine nmr spectra (56.4 MHz $CFCl_3$) of *N*-fluoro-2,6-dimethylpiperidine [I (trans) and II (cis)]; no nitrogen inversion is observable at room temperature on II and the various coupling constants $^3J_{FH}$ are consistent with a Karplus-type law; if so, the N–F bond would be more stable when equatorial.

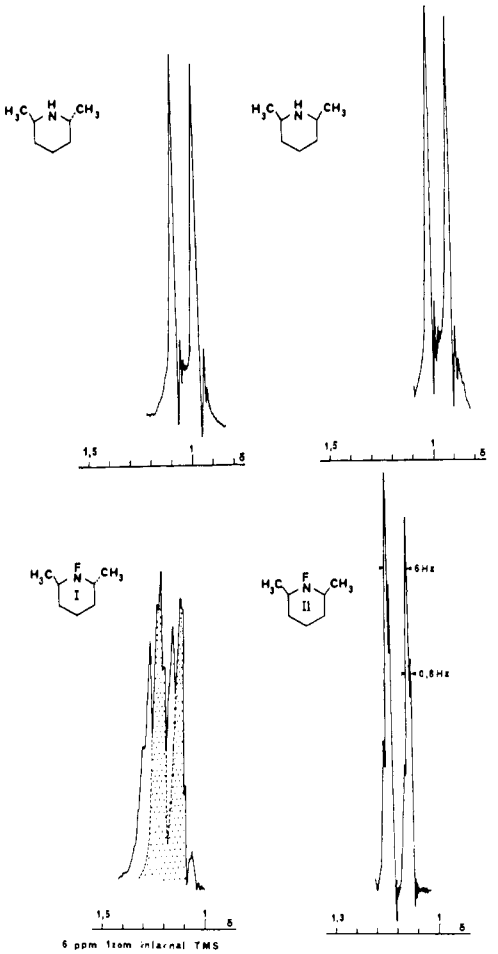

Figure 2. Room temperature proton nmr spectra (60 MHz, $CFCl_3$) of the methyl groups, showing the nonequivalence which appears on the *trans*-*N*-fluoro-2,6-dimethylpiperidine; nitrogen is a chiral center.

For the trans *N*-fluoro derivative (I) ring reversal is allowed. Its ^{19}F nmr spectrum (Figure 1) has a broad signal at room temperature at ϕ 64 ppm from $CFCl_3$ (solvent and reference); this signal is clearly split into two parts at $-65°$: a doublet (called E) at ϕ 57 ppm (J = 20.5 Hz) and a doublet of doublets (called A) at 82 ppm (J_1 = 11.8 Hz; J_2 = 58 Hz). The proportion of these two diastereoisomeric forms of I is IE/IA = 85/15 as obtained by integration of nmr signals. As the ring shape of such a trans system is unique, the diastereoisomerism is due to the N–F bond; one signal (E or A) is due to an equatorial fluorine, and the other is due to an axial fluorine. This figure clearly indicates that at $-65°$, ring reversal *and* nitrogen inversion are slow as compared to the nmr time scale;[6] from this ^{19}F nmr spectrum it cannot be concluded whether at 25° nitrogen inversion is slow or not but the ^1H nmr spectrum of I gives the answer (Figure 2); at room temperature the two methyl groups of this trans *N*-fluoro compound are not equivalent ($\Delta\nu$ = 3 Hz at 60 MHz in $CFCl_3$). This is due either to a ring rigidity or to a nitrogen rigidity. Such rings ordinarily reverse rapidly[7] but let us suppose that fluorine, like the bulky *tert*-butyl group for instance, induces a ring rigidity; in this case nitrogen inverts rapidly at room temperature (as seen in ^{19}F nmr, Figure 1) and the ring has no more reason to be rigid since the fluorine atom oscillates; therefore, the two methyl groups of I should be equivalent, which is not the case. If we suppose now that at 25° the ring rapidly reverses but that nitrogen does not invert, the spectral data become clear. Fluorine is always trans relative to one of the methyl groups, and always cis relative to the other; when the temperature is lowered, the ring reversal is slowed and the two conformations E and A of the ring appear clearly at $-65°$ in ^{19}F nmr (but resolution is too poor in ^1H nmr to see these phenomena on the methyl groups at low temperature).

The spectral behavior of the cis *N*-fluoro derivative II confirms this interpretation; in this case ring reversal is not allowed and methyl groups are always equatorial and equivalent. If at +25° nitrogen inversion is fast, one signal will be observed, but if this inversion is slow, we have a chance to observe two signals: one due to an equatorial fluorine and the other due to an axial fluorine. In fact, one observes in the pure liquid (Figure 1) two signals at room temperature: one (E) is a relatively narrow triplet (J = 22.8 Hz) whose shape is unchanged from -50 to $+60°$; the other signal (A) is a broad triplet (J = 48.3 Hz). The proportion of these two diastereoisomeric forms of II is IIE/IIA =

(6) Jeol C60H apparatus; ^1H nmr (60 MHz) internal reference TMS ($CFCl_3$); ^{19}F nmr (56.4 MHz) internal reference $CFCl_3$.

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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

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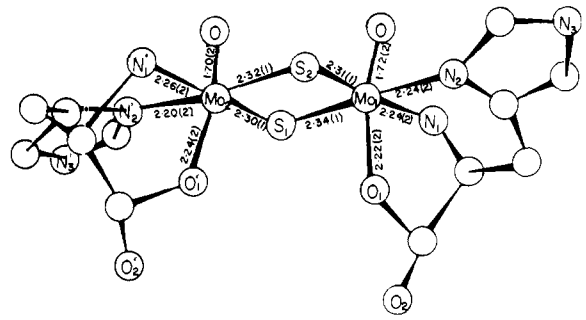

Figure 1. A perspective drawing of the $[Mo_2O_2S_2(histidine)_2]$ complex.

σ-donor ligands such as α-amino acids. In this communication we report the crystal and molecular structure of such a 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_3(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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