

- (15) The yield was not optimized.  
 (16) Recovery of the starting material was 32% in this reaction.  
 (17) I. D. Jenkins, J. P. H. Verheyden, and J. G. Moffatt, *J. Am. Chem. Soc.*, **98**, 3346 (1976).  
 (18) The stereohomogeneity of this compound was supported by the consistent appearances of the NMR signals of H<sub>1</sub> and the triazole 5 proton.  
 (19) Direct coupling between protected sugar derivatives and polyaza heterocycles often gives positional isomers. For example, see F. A. Lehmkuhl, J. T. Witkowski, and R. K. Robins, *J. Heterocycl. Chem.*, **9**, 1195 (1972).  
 (20) The  $\beta$  configuration at the anomeric position of **9a, b** was supported by the singlet resonance of H<sub>1</sub>.  
 (21) (a) S. D. Bernardo and M. Weigle, *J. Org. Chem.*, **41**, 287 (1976); (b) G. Just and B. Chalard-Faure, *Can. J. Chem.*, **54**, 861 (1976); (c) D. B. Repke, H. P. Albrecht, and J. G. Moffatt, *J. Org. Chem.*, **40**, 2481 (1975); (d) H. P. Albrecht, D. B. Repke, and J. G. Moffatt, *ibid.*, **39**, 2176 (1974); (e) G. A. Ivanovics, R. J. Rousseau, M. Kawana, P. C. Srivastava, and R. K. Robins, *ibid.*, **39**, 3651 (1974); (f) the literature in ref 19; (g) J. T. Witkowski, and R. K. Robins, *J. Org. Chem.*, **35**, 2635 (1970).  
 (22) (a) K. Kobayashi and W. Pfeleiderer, *Chem. Ber.*, **109**, 3175 (1976); (b) M. Kawazu, T. Kanno, S. Yamamura, T. Mizoguchi, and S. Saito, *J. Org. Chem.*, **38**, 2887 (1973); (c) N. Takamura, N. Taga, T. Kanno, and M. Kawazu, *ibid.*, **38**, 2891 (1973); (d) G. Kowollik, P. Langen, and A. Holy, *J. Prakt. Chem.*, **312**, 145 (1970). For doubleheaded nucleosides, see (e) M. W. Logue and N. J. Leonard, *J. Am. Chem. Soc.*, **94**, 2842 (1972); (f) R. Fecher, K. H. Boswell, J. J. Wittick, and T. Y. Shen, *ibid.*, **92**, 1400 (1970); (g) J. J. Baker, P. Mellish, C. Riddler, A. R. Somerville, and J. R. Tittensor, *J. Med. Chem.*, **17**, 764 (1974); (h) N. J. Leonard and R. L. Cundal, *J. Am. Chem. Soc.*, **96**, 5904 (1974).

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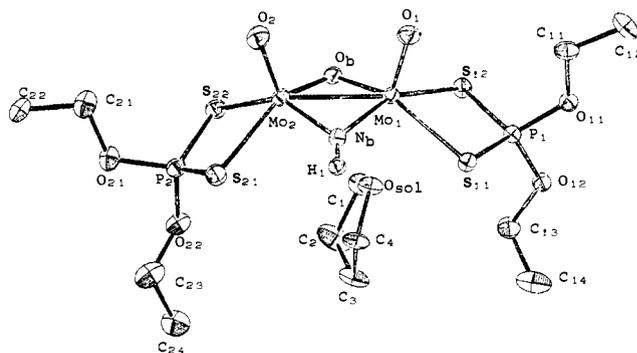
Received November 14, 1977

### Abstraction of NH from HN<sub>3</sub> by MoO[S<sub>2</sub>P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>. Structure of Mo<sub>2</sub>O<sub>3</sub>(NH)[S<sub>2</sub>P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>·THF

Sir:

Recent studies have focused on the reactions of an oxomolybdenum(IV) compound, MoO(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>, with acetylene<sup>1</sup> and hydrazoic acid.<sup>2</sup> These reactions are of interest because the alkyne and azide ion are substrates for nitrogenase<sup>3,4</sup> and because Mo(IV) has been proposed as a portion of the active site of that enzyme.<sup>5-8</sup> The reaction of MoO(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub> with HN<sub>3</sub> in a mixture of CHCl<sub>3</sub> and aqueous HCl affords MoO<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>, N<sub>2</sub>, and NH<sub>3</sub> presumably by way of hydrolysis of the unstable intermediate, MoO(NH)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>. The hydrolysis would occur after abstraction of NH and liberation of N<sub>2</sub>. Since NH and O are isoelectronic, the mechanism of this reaction would be similar to that recently proposed<sup>5,7</sup> for nitrate reductase wherein coupling of Mo(IV) and Mo(VI) is achieved by oxygen atom transfer from the substrate to molybdenum.

A study of the reaction between MoO[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub> (**1**) and HN<sub>3</sub> has also been initiated with the anticipation that the products of the reaction as well as the intermediates should be distinctly different from those mentioned above. This difference should arise because MoO<sub>2</sub>[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>, unlike MoO<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>, does not appear to have an independent existence.<sup>9</sup> We have successfully isolated and characterized a yellow compound, Mo<sub>2</sub>O<sub>3</sub>(NH)[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>, from the reaction of **1** with HN<sub>3</sub> in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and aqueous HCl. The infrared spectrum of the compound in C<sub>2</sub>Cl<sub>4</sub> contains a sharp band at 3365 cm<sup>-1</sup> which can be attributed to  $\nu$ (NH). The <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) contains a broad resonance at  $\delta$  12.1 with the correct intensity for the hydrogen atom of the NH group and resonances due to two pairs of inequivalent ethyl groups. The proton-decoupled <sup>31</sup>P NMR spectrum, obtained in the same solvent, contains a single resonance even at -78 °C. Although a fluxional process of low activation energy could be responsible for the simplicity of the <sup>31</sup>P NMR spectrum, the collective spectra are in accord with a symmetric,



**Figure 1.** Drawing of Mo<sub>2</sub>O<sub>3</sub>(NH)[S<sub>2</sub>P(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O. The hydrogen atoms (except H<sub>1</sub>) have been omitted for clarity. Important bond distances (ångstroms) and angles (degrees) are listed: Mo<sub>1</sub>-Mo<sub>2</sub> = 2.589 (1), Mo<sub>1</sub>-N<sub>b</sub> = 1.944 (3), Mo<sub>1</sub>-O<sub>b</sub> = 1.947 (3), Mo<sub>1</sub>-O<sub>1</sub> = 1.678 (3), Mo<sub>1</sub>-S<sub>11</sub> = 2.506 (1), Mo<sub>1</sub>-S<sub>12</sub> = 2.547 (1), Mo<sub>2</sub>-N<sub>b</sub> = 1.936 (4), Mo<sub>2</sub>-O<sub>b</sub> = 1.940 (3), Mo<sub>2</sub>-O<sub>2</sub> = 1.678 (3), Mo<sub>2</sub>-S<sub>11</sub> = 2.489 (1), Mo<sub>2</sub>-S<sub>22</sub> = 2.522 (1), N<sub>b</sub>-H<sub>1</sub> = 0.82 (6); N<sub>b</sub>-Mo<sub>1</sub>-O<sub>b</sub> = 94.0 (1), N<sub>b</sub>-Mo<sub>2</sub>-O<sub>b</sub> = 94.5 (1), Mo<sub>1</sub>-N<sub>b</sub>-Mo<sub>2</sub> = 83.7 (1), Mo<sub>1</sub>-O<sub>b</sub>-Mo<sub>2</sub> = 83.5 (1), Mo<sub>1</sub>-N<sub>b</sub>-H<sub>1</sub> = 139 (4), Mo<sub>2</sub>-N<sub>b</sub>-H<sub>1</sub> = 135 (4), O<sub>1</sub>-Mo<sub>1</sub>-N<sub>b</sub> = 106.4 (1), O<sub>1</sub>-Mo<sub>1</sub>-Mo<sub>2</sub> = 103.6 (1), O<sub>1</sub>-Mo<sub>1</sub>-O<sub>b</sub> = 107.1 (1), O<sub>2</sub>-Mo<sub>2</sub>-N<sub>b</sub> = 109.5 (1), O<sub>2</sub>-Mo<sub>2</sub>-Mo<sub>1</sub> = 107.6 (1), O<sub>2</sub>-Mo<sub>2</sub>-O<sub>b</sub> = 109.1 (1).

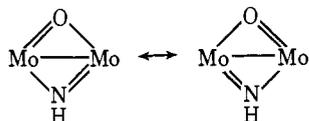
dinuclear complex containing five-coordinate Mo atoms with NH and oxo ligands occupying the bridging sites.

Recrystallization of this compound from THF-heptane at -20 °C afforded yellow solvated prisms. A complete structural determination<sup>10</sup> at -150 °C showed the presence of a dinuclear complex, Mo<sub>2</sub>O<sub>3</sub>(NH)[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>, and THF in a 1:1 ratio. The quality of this structure is remarkably good and all 29 hydrogen atoms, including the NH hydrogen atom, were located and refined as individual atoms. The important feature of this structure is the authenticated presence of the NH ligand at a bridging site (Figure 1). The nitrogen atom (N<sub>b</sub>) was unequivocally identified in the diffraction experiment since attempts to refine it as if it were an oxygen atom resulted in an unreasonably large thermal parameter. The N<sub>b</sub>-H<sub>1</sub> distance is 0.86 (6) Å.

The basic structural aspects of the dinuclear complex are in agreement with those deduced from the spectroscopic data. The coordination geometries about the molybdenum atoms within the complex are similar to, but not identical with, each other as shown in Figure 1. Excluding the nearby molybdenum atom, each is a square pyramid with a terminal oxygen atom in the axial site. The remaining sites are occupied by the sulfur atoms from a chelating dithiophosphate ligand, the symmetric bridging NH group, and the symmetric bridging oxygen atom. The two molybdenum atoms and two bridging atoms are not coplanar but rather O<sub>b</sub> and N<sub>b</sub> are symmetrically displaced away from the terminal oxo ligands. The angle between the plane defined by Mo<sub>1</sub>, O<sub>b</sub>, and Mo<sub>2</sub> and the one defined by Mo<sub>1</sub>, N<sub>b</sub>, and Mo<sub>2</sub> is 159.0°. The terminal oxygen atoms are eclipsed while the Mo<sub>1</sub>-Mo<sub>2</sub> distance of 2.589 (1) Å indicates the presence of a metal-metal single bond. This bond causes the Mo<sub>1</sub>-O<sub>b</sub>-Mo<sub>2</sub> and Mo<sub>1</sub>-N<sub>b</sub>-Mo<sub>2</sub> angles to be significantly smaller than would be expected in its absence, while the O<sub>b</sub>-Mo<sub>1</sub>-N<sub>b</sub> and O<sub>b</sub>-Mo<sub>2</sub>-N<sub>b</sub> angles are larger.<sup>11</sup> The portion of the structure which has been discussed to this point resembles that of the unsymmetrically bridged compound, Mo<sub>2</sub>O<sub>3</sub>S(S<sub>2</sub>CNPr<sub>2</sub>)<sub>2</sub>,<sup>12</sup> as well as those of the symmetrically bridged complexes, Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>,<sup>13</sup> Mo<sub>2</sub>O<sub>4</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>,<sup>14</sup> and Mo<sub>2</sub>S<sub>4</sub>(S<sub>2</sub>CNBu<sub>2</sub>)<sub>2</sub>.<sup>15</sup> The solvent molecule in Mo<sub>2</sub>O<sub>3</sub>(NH)[S<sub>2</sub>P(OEt)<sub>2</sub>]<sub>2</sub>·THF occupies a unique "hole" in the lattice with its oxygen atom directed toward Mo<sub>1</sub>. The distance between these atoms is 2.633 (3) Å. Although the presence of THF exerts a small but observable steric influence on the equatorial ligands around Mo<sub>1</sub>, the interaction between THF and Mo<sub>1</sub> must be very weak since crystals readily lose

THF on standing at room temperature. Furthermore, the two independent Mo-terminal oxygen atom distances are identical.

Adjacent complexes are connected by one-dimensional hydrogen bonds ( $N_b-H\cdots O_b$ ) along the  $x$  axis. The  $H\cdots O_b$  distance is 2.24 (6) Å while the  $N_b-H\cdots O_b$  angle is 176 (5)°. Since  $Mo_1$ ,  $Mo_2$ , and both atoms of the NH ligand are coplanar within experimental error, there is no evidence for a stereochemically active lone pair on  $N_b$ , and its hybridization must be approximately  $sp^2$ . Furthermore, the hybridization at  $O_b$  must be the same if it is assumed that the NH proton is engaged in linear hydrogen bonding to a lone pair of electrons on  $O_b$ . It is worth noting that the NH moiety has all the structural properties one would expect of either a bridging nitrene or a multiply bonded imide which is shown below.



Further aspects of this structure and the implications that can be drawn from it will be described in a subsequent publication.

The isolation of a compound which contains an NH ligand from a reaction medium in which water is abundantly available is surprising in view of the well-known proclivity of molybdenum in its higher oxidation states to form bonds to both terminal and bridging oxo ligands. This stability toward hydrolysis and protonation may be due to the location of the NH group at a bridging site. However, the recent isolation<sup>16</sup> of  $Mo(NH)X_2(dppe)_2$  ( $X = Cl$  or  $Br$ ;  $dppe = Ph_2PCH_2CH_2PPh_2$ ), which survives in  $CH_3OH$ -containing  $HX$ , suggests that even a terminal NH group can have an appreciable stability to protonation. In any event, these structural results confirm the belief that abstraction of NH from  $HN_3$  by  $Mo(IV)$  is a feasible process.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant No. MPS 75-08188) and the Marshall H. Wrubel Computing Center.

**Supplementary Material Available:** Tables of fractional atomic coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

## References and Notes

- E. A. Maatta, R. A. D. Wentworth, W. E. Newton, J. W. McDonald, and G. D. Watt, *J. Am. Chem. Soc.*, **100**, 1320 (1978).
- E. A. Maatta and R. A. D. Wentworth, unpublished work.
- R. Schöllhorn and R. H. Burris, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 213 (1967); M. J. Dilworth, *Biochim. Biophys. Acta*, **127**, 285 (1966).
- R. W. F. Hardy and E. Knight, *Biochim. Biophys. Acta*, **130**, 69 (1967).
- P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Am. Chem. Soc.*, **94**, 8640 (1972).
- E. L. Moorehead, B. J. Weathers, E. A. Ufkes, P. R. Robinson, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **99**, 6089 (1977), and references therein.
- R. A. D. Wentworth, *Coord. Chem. Rev.*, **18**, 1 (1976).
- W. E. Newton, J. L. Corbin, and J. W. McDonald, *Proc. Conf. N<sub>2</sub> Fixation*, 1st, 1976, 53 (1976).
- G. J.-J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Nucl. Chem. Lett.*, **12**, 697 (1976).
- The orthorhombic space group is  $P_{bca}$  with eight molybdenum dimers per unit cell. Using 3100 reflections with  $I > 3\sigma(I)$ , the current values of  $R(F)$  and  $R_w(F)$  are 2.6 and 4.0%, respectively. All atoms were refined anisotropically except hydrogen atoms. The unit cell dimensions (ångstroms) are  $a = 11.636$  (6),  $b = 18.290$  (8), and  $c = 23.904$  (11).  $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$  and  $R_w(F) = [\sum w(|F_o| - |F_c|)^2 \sum w F_o^2]^{1/2}$ .
- In dinuclear complexes, such as  $[Nb(OMe)_5]_2$  (A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, and J. G. Riess, *Inorg. Chem.*, **15**, 1196 (1976)) and  $[Mo(O)_2(OH)]_2^{2-}$  (J.-M. LeCarpentier, A. Mitschler, and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1288 (1972)), which contain two bridging oxygen atoms per dimer but do not contain metal-metal bonds, metal-bridging oxygen-metal angles are 109–110° and metal-metal distances are 3.5–3.6 Å.
- J. Diran-Collin, L. Ricard, and R. Weiss, *Inorg. Chim. Acta*, **18**, L-21 (1976).
- J. Diran-Collin, M. Schappacher, L. Ricard, and R. Weiss, *J. Less-Common Metals*, **54**, 91 (1977).
- L. Ricard, C. Martin, R. Wiest, and R. Weiss, *Inorg. Chem.*, **14**, 2300 (1975).
- B. Splvack, Z. Dori, and E. Steifel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975).
- M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalle, *J. Less-Common Metals*, **54**, 487 (1977).

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Received December 16, 1977

## Structure and Absolute Configuration of Tris(*N*-methylthioformohydroxamato)iron(III), an Antibacterial Metal Chelate and Potential Iron Siderochrome

Sir:

Microbial iron transport compounds generally contain oxygen-donor chelating groups such as hydroxamates (e.g., ferrichromes) or catecholates (e.g., enterochelin). These groups bind Fe(III) very strongly but have a much weaker affinity for Fe(II).<sup>1,2</sup> Recently a potentially new class of siderochromes has been isolated from bacteria such as *Pseudomonas Fluorescens*. The parent compound is a thiohydroxamic acid,  $HC(=S)N(Me)OH$  (called fluopsin<sup>3</sup> or thioformin<sup>4</sup>), which forms very stable Cu(II) and Fe(III) complexes. The metal chelates and the parent acid all show potent antibiotic activity. Despite the importance of finding sulfur bonded to iron in such species, there have been no detailed studies on these compounds. We report here the determination of the molecular structure and absolute configuration of synthetic tris(*N*-methylthioformohydroxamato)iron(III), fluopsin F.

$Fe[HC(S)N(Me)O]_3$  was prepared by reacting an ethanolic solution of the ligand and aqueous iron(II) sulfate in air, as described by Egawa et al.,<sup>4</sup> the atmospheric oxidation to Fe(III) occurring very rapidly. It was also prepared by a ligand displacement reaction using  $Fe(acac)_3$ , as has been successfully used for the synthesis of other tris(thiohydroxamato)iron(III) compounds.<sup>5</sup> The complex dissolves to a small extent in solvents such as chloroform, acetone, acetonitrile, and methanol to yield stable purple solutions which display a characteristic double-peak visible absorption spectrum:  $\lambda_{max}$  600 nm ( $\epsilon$  1262), 505 (1465). Well-formed single crystals of the complex were grown from  $CHCl_3/MeOH$  or  $MeCN/CHCl_3$  mixtures. High-spin Curie-Weiss behavior was observed over the range 300–80 K:  $\mu_{eff} = 5.84 \mu_B$  at 295 K,  $\theta = 4^\circ$ . The ESR spectrum of the complex in a frozen  $CHCl_3/MeCN$  glass showed an isotropic line at  $g = 4.3$ . Though signals in this position are predicted only for rhombically distorted Fe(III) species, they do occur in this and other trigonally distorted siderochromes. The dilemma between rhombic spin Hamiltonians and trigonal molecular structure in iron transport compounds has recently been discussed by Oosterhuis and explained, in part, by use of fourth-order terms in the crystal-field potential.<sup>6</sup>

Tris(*N*-methylthioformohydroxamato)iron(III) can potentially exist in two isomeric forms, cis(fac) and trans(mer), by virtue of the different donor atoms in the ligand, and each geometrical isomer can have two optical isomers,  $\Lambda$  and  $\Delta$ . To provide a definitive structural basis for chemical and biochemical studies, we have determined the molecular structure of the title complex. To our knowledge this is the first report of the structural details of a tris(thiohydroxamato) metal chelate. Crystal data:  $C_6H_{12}N_3O_3S_3Fe$ ,  $M$  326.2, rhombohedral,  $a = 7.094$  (2) Å,  $\alpha = 102.00$  (1)°,  $V = 329.6$  Å<sup>3</sup>, space group  $R3$ ,  $D_{measd} = 1.64$  g cm<sup>-3</sup>,  $D_{calcd} = 1.64$  g cm<sup>-3</sup> for  $Z = 1$ . The crystallographic symmetry necessarily requires a cis arrangement of the ligands. Reflection data were collected on