

- (15) The yield was not optimized.
 (16) Recovery of the starting material was 32% in this reaction.
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Tadashi Sasaki,* Katsumaro Minamoto,
 Toshimichi Suzuki, Toyoyuki Sugiura
 Institute of Applied Organic Chemistry
 Faculty of Engineering, Nagoya University
 Furo-cho, Chikusa-ku, Nagoya, Japan

Received November 14, 1977

Abstraction of NH from HN₃ by MoO[S₂P(OC₂H₅)₂]₂. Structure of Mo₂O₃(NH)[S₂P(OC₂H₅)₂]₂·THF

Sir:

Recent studies have focused on the reactions of an oxomolybdenum(IV) compound, MoO(S₂CNEt₂)₂, with acetylene¹ and hydrazoic acid.² These reactions are of interest because the alkyne and azide ion are substrates for nitrogenase^{3,4} and because Mo(IV) has been proposed as a portion of the active site of that enzyme.⁵⁻⁸ The reaction of MoO(S₂CNEt₂)₂ with HN₃ in a mixture of CHCl₃ and aqueous HCl affords MoO₂(S₂CNEt₂)₂, N₂, and NH₃ presumably by way of hydrolysis of the unstable intermediate, MoO(NH)(S₂CNEt₂)₂. The hydrolysis would occur after abstraction of NH and liberation of N₂. Since NH and O are isoelectronic, the mechanism of this reaction would be similar to that recently proposed^{5,7} 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[S₂P(OEt)₂]₂ (**1**) and HN₃ 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 MoO₂[S₂P(OEt)₂]₂, unlike MoO₂(S₂CNEt₂)₂, does not appear to have an independent existence.⁹ We have successfully isolated and characterized a yellow compound, Mo₂O₃(NH)[S₂P(OEt)₂]₂, from the reaction of **1** with HN₃ in a mixture of CH₂Cl₂ and aqueous HCl. The infrared spectrum of the compound in C₂Cl₄ contains a sharp band at 3365 cm⁻¹ which can be attributed to ν(NH). The ¹H NMR spectrum (CD₂Cl₂) contains a broad resonance at δ 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 ³¹P 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 ³¹P NMR spectrum, the collective spectra are in accord with a symmetric,

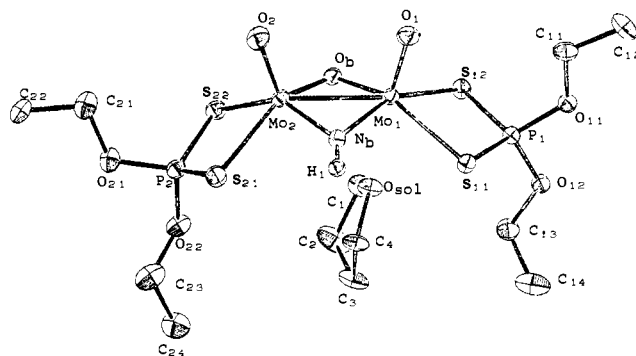


Figure 1. Drawing of Mo₂O₃(NH)[S₂P(OC₂H₅)₂]₂·C₄H₈O. The hydrogen atoms (except H₁) have been omitted for clarity. Important bond distances (ångstroms) and angles (degrees) are listed: Mo₁-Mo₂ = 2.589 (1), Mo₁-N_b = 1.944 (3), Mo₁-O_b = 1.947 (3), Mo₁-O₁ = 1.678 (3), Mo₁-S₁₁ = 2.506 (1), Mo₁-S₁₂ = 2.547 (1), Mo₂-N_b = 1.936 (4), Mo₂-O_b = 1.940 (3), Mo₂-O₂ = 1.678 (3), Mo₂-S₁₁ = 2.489 (1), Mo₂-S₂₂ = 2.522 (1), N_b-H₁ = 0.82 (6); N_b-Mo₁-O_b = 94.0 (1), N_b-Mo₂-O_b = 94.5 (1), Mo₁-N_b-Mo₂ = 83.7 (1), Mo₁-O_b-Mo₂ = 83.5 (1), Mo₁-N_b-H₁ = 139 (4), Mo₂-N_b-H₁ = 135 (4), O₁-Mo₁-N_b = 106.4 (1), O₁-Mo₁-Mo₂ = 103.6 (1), O₁-Mo₁-O_b = 107.1 (1), O₂-Mo₂-N_b = 109.5 (1), O₂-Mo₂-Mo₁ = 107.6 (1), O₂-Mo₂-O_b = 109.1 (1).

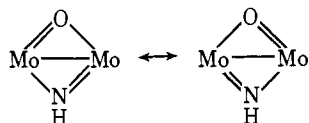
dinuclear complex containing five-coordinate Mo atoms with NH and oxo ligands occupying the bridging sites.

Recrystallization of this compound from THF-heptane at -20 °C afforded yellow solvated prisms. A complete structural determination¹⁰ at -150 °C showed the presence of a dinuclear complex, Mo₂O₃(NH)[S₂P(OEt)₂]₂, 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_b) 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_b-H₁ 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_b and N_b are symmetrically displaced away from the terminal oxo ligands. The angle between the plane defined by Mo₁, O_b, and Mo₂ and the one defined by Mo₁, N_b, and Mo₂ is 159.0°. The terminal oxygen atoms are eclipsed while the Mo₁-Mo₂ distance of 2.589 (1) Å indicates the presence of a metal-metal single bond. This bond causes the Mo₁-O_b-Mo₂ and Mo₁-N_b-Mo₂ angles to be significantly smaller than would be expected in its absence, while the O_b-Mo₁-N_b and O_b-Mo₂-N_b angles are larger.¹¹ The portion of the structure which has been discussed to this point resembles that of the unsymmetrically bridged compound, Mo₂O₃S(S₂CNPr₂)₂,¹² as well as those of the symmetrically bridged complexes, Mo₂O₂S₂[S₂P(OEt)₂]₂,¹³ Mo₂O₄(S₂CNEt₂)₂,¹⁴ and Mo₂S₄(S₂CNBu₂)₂.¹⁵ The solvent molecule in Mo₂O₃(NH)[S₂P(OEt)₂]₂·THF occupies a unique "hole" in the lattice with its oxygen atom directed toward Mo₁. 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 Mo₁, the interaction between THF and Mo₁ 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 isolation¹⁶ 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.

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A. W. Edelblut, Barry L. Haymore*
R. A. D. Wentworth*

Contribution No. 3076, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

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).^{1,2} 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 fluopsin³ or thioformin⁴), 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.,⁴ 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.⁵ 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: λ_{max} 600 nm (ϵ 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.⁶

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, Λ and Δ . 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)°, $V = 329.6$ Å³, space group $R\bar{3}$, $D_{measd} = 1.64$ g cm⁻³, $D_{calcd} = 1.64$ g cm⁻³ for $Z = 1$. The crystallographic symmetry necessarily requires a *cis* arrangement of the ligands. Reflection data were collected on