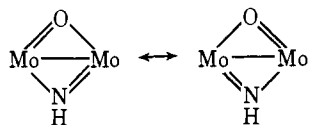


THF on standing at room temperature. Furthermore, the two independent Mo-terminal oxygen atom distances are identical.

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.

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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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- The orthorhombic space group is P_{bc} 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 $a = 11.636$ (8), $b = 18.290$ (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.
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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

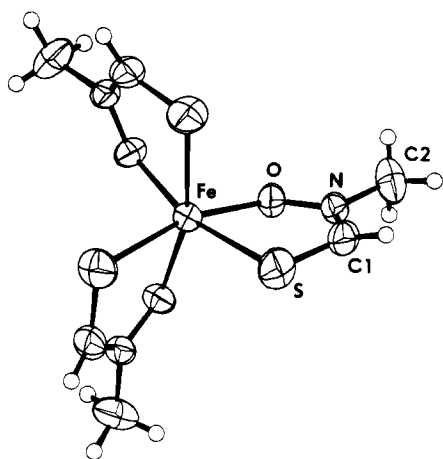


Figure 1. Tris(*N*-methylthioformohydroxamato)iron(III) viewed down the C_3 axis. Principal bond lengths (angstroms) follow: Fe-S, 2.444 (1); Fe-O, 2.010 (1); C(1)-S, 1.681 (2); C(1)-N, 1.295 (2); N-C(2), 1.458(2); N-O, 1.342 (2).

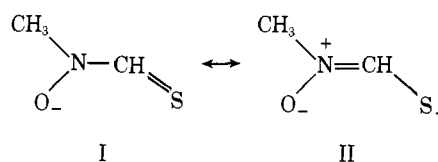
a Philips PW 1100 diffractometer using graphite crystal monochromated Mo $K\alpha$ radiation. The structure was solved by difference Fourier techniques and refined by full-matrix least squares on 1186 reflections (corrected for absorption, $\mu = 15.2 \text{ cm}^{-1}$) with $I \geq 3\sigma(I)$. On crystallization the complex is spontaneously resolved into its enantiomers, all molecules within a crystal being of the same configuration. The absolute configuration in the crystal studied here was established by the anomalous dispersion technique as Λ with final residuals R 0.0205, R_w 0.0191; the alternate Δ configuration had significantly higher residuals, R 0.0449, R_w 0.0480. Recently it has been shown that the Λ and Δ isomers of a related complex, tris(benzothiohydroxamato)iron(III), surprisingly can be resolved and stabilized in chloroform solutions.⁷

Unfortunately, it was not possible to obtain the circular dichroism spectrum of the present Λ isomer to compare with the spectra of $\text{Fe}(\text{PhC}(\text{S})\text{NHO})_3$, on account of the single crystal being too small to obtain a solution sufficiently strong to give a measurable rotation. It was also not possible to distinguish, by eye, crystals of the same chirality to obtain a more concentrated solution. Further, the low solubility of the chelate in organic solvents did not allow separation on an optically active column into the Λ and Δ enantiomers, although, if such a resolution were possible, a full structural determination would still be required on a crystal obtained from one of the solutions.

The molecular structure of the title complex, as shown in Figure 1, has exact C_3 symmetry with a Λ -cis arrangement of the ligands. Interestingly, only the cis geometric isomer has been found in all other tris chelates where the bidentate ligand has an O,S donor set. These include tris(*N,N*-dimethylthiocarbamate)iron(III),⁸ tris(benzohydroxamato)iron(III),⁹ tris(5,5-dimethyl-2-thio-4-phenyl-1-pyrrolidine 1-oxide)-iron(III),¹⁰ and iron(III) tris chelates of substituted thioacetylacetonate ligands.¹¹ It is interesting to note that the specific isomer, Λ -cis, has also been structurally characterized in ferrichrome A¹² and ferrichrysin¹³ in which the chelating groups are hydroxamates. A comparison of the absolute configuration of the naturally occurring fluopsin F with that of the present synthetic chelate would be particularly interesting.

Concerning the structural features, the Fe-S bond length, 2.444 (1) Å, is typical of those found in high-spin tris(dithiocarbamate)iron(III) complexes^{14,15} but is significantly longer than in tris(*N,N*-dimethyl thiocarbamate)iron(III),⁸ 2.413 Å, and tris(1,3-diphenyl-3-thioloprop-2-en-1-one)iron(III),¹¹ 2.368 Å, where the metal chelate rings are four- and six-membered respectively. The Fe-O bond length falls between

the values observed in the latter two complexes. The twist angle¹⁶ of the octahedron is 41.1° . The geometry of the thioformohydroxamate moiety is consistent with the canonical resonance forms I and II. In particular the C(1)-S and N-C(1)



bond lengths (Figure 1) are both indicative of substantial double bond character. In addition, the ligand is planar with the Fe atom 0.38 Å out of the plane.

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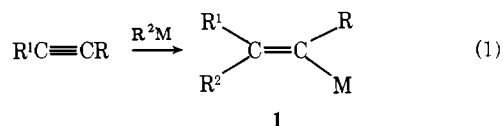
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Controlled Carbometalation. Reaction of Acetylenes with Organoalane-Zirconocene Dichloride Complexes as a Route to Stereo- and Regio-Defined Trisubstituted Olefins¹

Sir:

Over the past few decades, several hydrometalation reactions, such as those involving B,² Al,³ Si,⁴ Sn,⁵ and Zr,⁶ have provided convenient and selective routes to disubstituted olefins. On the other hand, their application to the synthesis of trisubstituted olefins via internal acetylenes is far from being general and satisfactory. An alternate and inherently more attractive approach would be to achieve controlled and selective carbometalation of acetylenes, such as the transformation represented by eq 1.



R = H or organic group; R¹ and R² = organic groups; M = a metal or metal containing group