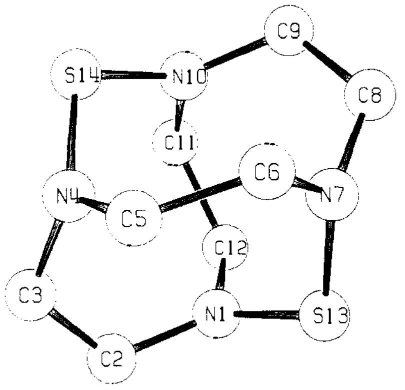

Figure 1. Structure of $C_8H_{16}N_4S_2$. Hydrogen atoms of the methylene groups are omitted for clarity.

methylamino) sulfide[6] for about 1 h until the color of the solution turns from yellow to red. Cooling the concentration in vacuum gives a total of 4.0–5.5 g (60–80% yield) of colorless crystalline air-stable $C_8H_{16}N_4S_2$. The analytical sample, mp 170 °C,[7] can be purified by vacuum sublimation at 110–120 °C (0.5 mm) or by recrystallization from methanol or chloroform. Similar reactions of 1,4,8,11-tetraazacyclotetradecane ("cyclam") and *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane[8] with bis(dimethylamino) sulfide give white $C_{10}H_{20}N_4S_2$, mp 175 °C, and white $Me_6C_{10}H_{14}N_4S_2$, mp, 195 °C, respectively.[7]

The compound $C_8H_{16}N_4S_2$ forms orthorhombic crystals by sublimation: space group *Pbcn*; $a = 11.367$ (2) Å, $b = 8.278$ (3) Å, $c = 11.266$ (2) Å; $Z = 4$; $d_{\mathrm{calcd}} = 1.45$ g/cm^3. The structure was solved by direct methods.[7] Least-squares refinement[7] using the 861 observed ($I > 3\sigma_I$) reflections after application of Lorentz–polarization corrections revealed the structure depicted in Figure 1 ($R = 0.080$ and $R_w = 0.085$).

The structure of $C_8H_{16}N_4S_2$ (Figure 1) exhibits a number of interesting features. Its topology is that of a tetrahedron in which the four vertices are occupied by nitrogen atoms, four of the six edges by $-CH_2CH_2-$ bridges, and the remaining two edges by sulfur atoms. This pattern of substitution reduces the symmetry of the tetrahedron from T_d to C_2 with the C_2 axis bisecting the C_5–C_6 and C_{11}–C_{12} bonds; this C_2 axis is also the C_2 axis of the space group *Pbcn*. The coordination at each nitrogen atom is nearly planar with the sums of the three bond angles at the nonequivalent nitrogen atoms N_1 and N_7 being 358.3° and 357.4°, respectively. The N–S–N bond angles are 117.2° and the S–N bond distances fall in the range 1.655–1.657 Å. These parameters compare with the N–S–N bond angles of 114.5°, 113.2°, and 110.7° and S–N bond distances of 1.688, 1.678, and 1.657 Å found by electron diffraction on bis(dimethylamino) sulfide[9] and by X-ray diffraction on dimorpholino sulfide[10] and bis(dicyclohexylamino) sulfide,[11] respectively, indicating relatively little effect of the cage structure on these important structural parameters.

The size of the approximate tetrahedral cavity in $C_8H_{16}N_4S_2$ formed by the nitrogen atoms is indicated by the three unique N–N distances: N_1–N_7 2.74, N_1–N_4 2.94, and N_1–N_{10} 2.98 Å. Each of these distances corresponds to two of the six edges of the distorted N_4 tetrahedron in $C_8H_{16}N_4S_2$. Assuming an average tetrahedral edge length of 2.89 Å and a covalent radius of 0.75 Å for nitrogen,[12] the largest sphere that can be contained in the cavity has a radius of 1.0 Å. Thus a potassium ion with an ionic radius of 1.33 Å is too large to occupy the cavity but lithium and sodium ions with radii of 0.60 and 0.95 Å, respectively, are candidates for incorporation into the cavity.

The proton and carbon-13 NMR spectra of $C_8H_{16}N_4S_2$ in $CDCl_3$ at ambient temperatures each exhibit single resonances at δ 3.46 and 56.7, respectively, indicating equivalence of all eight carbons and all 16 hydrogens on the NMR time and resolution scales. The mass spectrum of $C_8H_{16}N_4S_2$ exhibits not only the expected molecular ion but also the fragment ions $C_8H_{16}N_4^+$, $C_4H_8N_2S_2^+$, $C_4H_7N_3S^+$, $C_4H_9N_2^+$, $C_4H_8N_2^+$, $C_4H_7N_2^+$, $C_2H_4N_2^+$, and $C_2H_4N^+$.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant CHE-82-12166. We are also indebted to Dr. Jack Richman for helpful advice concerning the preparation of 1,4,7,10-tetraazacyclododecane.

Supplementary Material Available: Tables of positional parameters and their estimated standard deviations, β's, and bond distances and angles and a drawing of the unit cell (4 pages). Ordering information is given on any current masthead page.

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Structure and Magnetic Properties of an Unsymmetrical (μ-Oxo)diiron(III) Complex

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(μ-Oxo)diiron(III) complexes have long been of considerable interest for their distinctive magnetic and spectroscopic properties[3] and relevance to diiron nonheme proteins such as hemerythrin,[4] ribonucleotide reductase,[5] and several purple acid phosphatases.[6] In contrast to other bridging ligands, where only weak antiferromagnetic coupling is observed, μ-oxo diiron(III) complexes show substantial coupling for which, with few exceptions, the values of J ($H = -2JS_1S_2$) lie in the remarkably narrow range of −90 to −110 cm^{-1} regardless of the geometry of the Fe–O–Fe moiety and of the number of ligands (4, 5, 6, or 7). With the exception of hemerythrin,[9] in all these complexes the stereochemistry about the two iron atoms is identical. See Table I.[4,7-17]

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Table I. Selected Metrical Details and Magnetic Properties of Selected (μ-Oxo)diiron(III) Species

complex	CN[a]	Fe–O, Å	Fe–O–Fe, deg	$Fe–N_{eq}$, Å	$Fe–N_{tr}$, Å	J, cm^{-1}	ref
singly bridged							
$[(PPIXDME)Fe]_2O$	5		see next entry			−131	8
$[(TPP)Fe]_2O$	5	1.763 (1)	174.5 (1)	2.087 (3)			14
$[Cl_3Fe]_2O^{2-}$	4	1.755 (3)	155.6 (7)			−92	10
$[(phen)_2(H_2O)Fe]_2O^{4+}$	6	1.785 (5)	155.1 (4)	2.148 (9)	2.258 (7)	−110	11
$[(pyDC)(H_2O)_2Fe]_2O^{b}$	6	1.773 (2)	180.0		2.105 (3)	−107	16
$[(HEDTA)Fe]_2O^{2+}$	6	1.79 (1)	165.0 (8)	2.23 (1)	2.27 (1)	−95[c]	15a,c
$[N_5FeOFeCl_3]^+$	4	1.751 (4)	149.8 (3)			−125(3)	this work
	6	1.782 (4)		2.094 (5)	2.358 (5)		
$[(phen)_2ClFe]_2O^{2+}$	6	1.787 (6)	161 (1)	2.12 (3)[d]	2.28 (2)		17
$[(B)(H_2O)Fe]_2O^{4+}$[e]	7	1.8	180	2.2		−100	13
triply bridged							
$[(BPz_3)(OAc)Fe]_2O$	6	1.784 (6)	123.6 (1)	2.153 (5)	2.19 (2)	−121(1)	7a
$[(TCN)(OAc)Fe]_2O^{2+}$[f]	6	1.79 (1)	118.3 (5)	2.17 (1)	2.21 (1)	1.84 μ_B at 283 K	7b
Met-Hr	5	1.68 (4)	127 (4)	2.17 (4)		−134	4e, 9a
	6	1.92 (3)		2.20 (5)	2.31 (2)		

[a] Coordination number. Standard deviations in parentheses are from least-squares refinements or from the scatter of values about their mean as appropriate. [b] PyDC is the 4-chloro-2,6-pyridinedicarboxylate dianion. Ignoring paramagnetic impurities and TIP leads to $J = -115$ cm^{-1}. [c] A value of −86 cm^{-1} has been reported.[15b] [d] That trans to the Cl is 2.20 (2) Å. [e] B is a pentadentate macrocyclic ligand. [f] TCN is the ligand triazacyclononane.

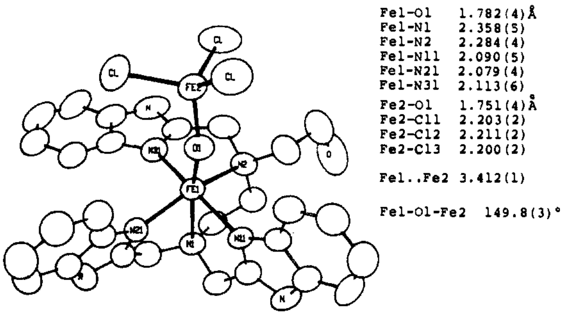
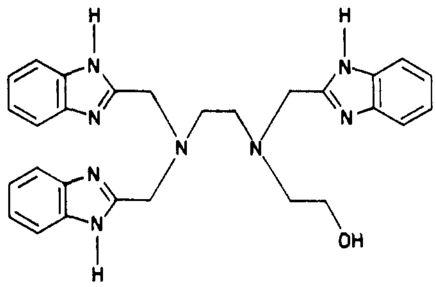


Figure 1. ORTEP diagram of the complex, with selected interatomic separations and angles.

We report here the first nonbiological nonsymmetrical (μ-oxo)diiron(III) complex, $[N_5Fe–O–FeCl_3]^+$, where N_5 = *N*,*N*,-*N*′-tris[(2-benzimidazolyl)methyl]-*N*′-(2-hydroxyethyl)-1,2-diaminoethane.[18-21] As drawn in Figure 1, one octahedrally coordinated iron is linked by a bridging oxo group to a tetrahedrally coordinated iron center. The Fe–Cl separations are identical with those observed (average 2.213 (7) Å) in the bis-tetrahedral complex $[Cl_3Fe–O–FeCl_3]^{2-}$.[10] The three $Fe–N_{Im}$ bonds are noticeably shorter than Fe–N bonds in FeOFe complexes with phenanthroline and pyridyl-derived ligands[11,16,17] and than those in a low-symmetry (μ_3-oxo)triiron(III) cluster formed from an *N*-methylimidazole-bearing ligand.[12] The bond lengths are, however, similar to those observed in several macrocyclic complexes.[13,14] The equatorial $Fe–N_{amine}$ bond is similar to those in an $[(HEDTA)Fe^{-}]_2O^{2+}$ complex.[15] The $Fe–N_{amine}$ bond trans to the oxo group is unusually long.



Despite the very different coordination around the two iron centers, the difference in the two Fe–O bond lengths, although significant, is small (0.031 (6) Å); both bond lengths lie within the range previously observed. The Fe–O–Fe bond angle and the Fe••Fe separation of 3.412 (1) Å are unremarkable. Thus the apparently unsymmetrical $Fe–O_{oxo}$ bonds in two met-hemerythrin derivatives[9] can now be attributed with high probability to a refinement artifact (a possibility noted by the authors), rather than to the differing coordination spheres around the two iron atoms.

The structural parameters and the UV–visible spectrum[20] are consistent with two oxo-linked Fe(III) centers, although the spectrum is sensitive to solvent. Both as KBr pellets and in acetonitrile solution, the complex exhibits two bands in the infrared region at ~835 and ~850 cm^{-1} not found in the free ligand. They are tentatively assigned to Fe–O modes, by comparison with other (μ-oxo)diiron(III) complexes.[10,11]

The magnetic susceptibility[20,21] of $[N_5Fe–O–FeCl_3]^+$ is significantly different from that observed for almost all other singly bridged μ-oxo complexes. The data in the range 80–300 K are well-fit,[3a,7a] assuming $g = 2$ and no TIP, yielding a value for J of −125 (3) cm^{-1}, after correction for a 2% paramagnetic Fe(III)

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(20) *Analytical data.* Satisfactory for $Fe_2C_{28}H_{30}N_8O_2Cl_4{\cdot}2C_2H_5OH$. *Crystal and refinement data.* Space group $P2_1/n$, $a = 15.712$ (2) Å, $b = 13.921$ (2) Å, $c = 19.094$ (3) Å, $\beta = 111.79$ (2)°, $Z = 4$; $d_{calcd} = 1.466$, $d_{obsd} = 1.46$ (1) g cm^{-3}; 3831 data with $I > 3\sigma(I)$, $(\sin\theta)/\lambda < 0.5958$ $Å^{-1}$, Mo Kα radiation ($\lambda = 0.7107$ Å). The structure was solved in $P2_1$ by using MULTAN82 and developed in $P2_1/n$ by using the SDP. Many H atoms were apparent and all nonsolvate ones were included at their calculated positions. At convergence the values for R and R_w were 0.055 and 0.073. *Magnetic susceptibility measurements.* A vibrating sample magnetometer was employed.[21] Sample magnetization was linear with field strength. Measured susceptibilities were corrected for sample diamagnetism, estimated from Pascal's constants, of −480 (20) × 10^{-6} emu mol^{-1}. *Cyclic voltammetry.* Quasi-reversible and an irreversible redox process (reduction waves at 0.02 and −0.55 V and oxidation waves at −0.2 (inflection) and at 0.23 V vs. Ag/AgCl (TBA ClO_4 as electrolyte)).

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$S = {}^5/_2$ impurity determined from data in the range 1.7–50 K. In CD_3CN solution at room temperature[22] an upper bound for the magnetic moment of 1.5 μ_B agrees well with that in the solid state of 1.59 μ_B. It is clear from Table I that the antiferromagnetic coupling is independent of the Fe–O separation and the Fe–O–Fe angle—the latter has been noted previously.[16] Stronger coupling is observed for multiply bridged species (e.g., the symmetrical $[(Bpz_3)Fe(CH_3COO)_2(O)Fe(Bpz_3)]$ complex[7a] and unsymmetrical methemerythrin[4e]), unsymmetrical species (this work and metHr[4e]), and, possibly, heme species with linear FeOFe groups.[8] The magnetic properties of the isosceles (μ_3-oxo)triiron(III) cluster are different from those of the more symmetrical clusters.[12] Weaker coupling is observed for oxyHr.[4e] Earlier theoretical work[23] offers few clues for consequences of asymmetry.

We intend examining in detail the proton NMR of this complex, which is the first (μ-oxo)diiron(III) complex with an imidazole-derived ligand, for comparison and amplification of the corresponding data for hemerythrin.[24] We are attempting to isolate the one-electron reduced, mixed-valence compound that we observe formed in a quasi-reversible manner under cyclic voltammetry[20] and to substitute other ligands at the tetrahedral site.

Acknowledgment. The partial support of the Research Corporation and of the NIH-BRSG is gratefully acknowledged.

Registry No. $[N_5Fe\text{-}O\text{-}FeCl_3]Cl\cdot 2C_2H_5OH$, 99688-36-5.

Supplementary Material Available: Tables of positional and thermal parameters and a table of structure factor amplitudes $10|F_c|$ vs. $10|F_o|$ (27 pages). Ordering information is given on any current masthead page.

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Haptotropic Rearrangements in Naphthalene–Chromium Tricarbonyl Complexes

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One type of haptotropic rearrangement under recent study involves the migration of a coordinated metal between the different rings in a polycyclic hydrocarbon. The most extensive experimental studies in this area have been on chromium[1] and manganese[2] complexes of fluorenyl and indenyl anions, in which metal migration occurs between five- and six-membered rings (i.e., $\eta^6 \rightleftarrows \eta^5$). Similar processes have also been reported for chromium complexes of related ligands including substituted fluorenyl, 2- and 4-azafluorenyl, and fluoradenyl anions.[3] The $\eta^6 \rightleftarrows \eta^5$ migration processes also accompany certain protonations.[4] There is considerable evidence that a haptotropic migration between the two six-membered ring complexes in naphthalene or substituted naphthalenes occurs,[5] but as yet no quantitative experimental studies on such systems have been reported. Such studies would be attractive since naphthalene will probably be regarded as the simplest and most common example of a polycyclic hydrocarbon amenable to ligation.

Table I. Rate Constants vs. Temperature for the Haptotropic Migration of the $Cr(CO)_3$ Group in I and II[a]

temp, K	$k \times 10^5$, s^{-1} Ia $\rightleftarrows$ Ib	$k \times 10^5$, s^{-1} II $\rightleftarrows$ IIb
305	0.28 ± 0.03	
314	1.0 ± 0.2	0.072 ± 0.042
323	3.3 ± 0.3	0.31 ± 0.06
335	15 ± 3	1.1 ± 0.4
343		4.4 ± 0.3
$\Delta G^‡$	26.8 ± 1.4 kcal/mol	28.4 ± 2.2 kcal/mol
$\Delta H^‡$	27.2 ± 1.4 kcal/mol	28.9 ± 2.2 kcal/mol
$\Delta S^‡$	1.3 ± 0.1 cal/(mol deg)	1.4 ± 0.1 cal/(mol deg)

[a] Each value represents the average of results from three different experiments. Rate constants were calculated from the following mechanistic scheme by standard methods: $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$

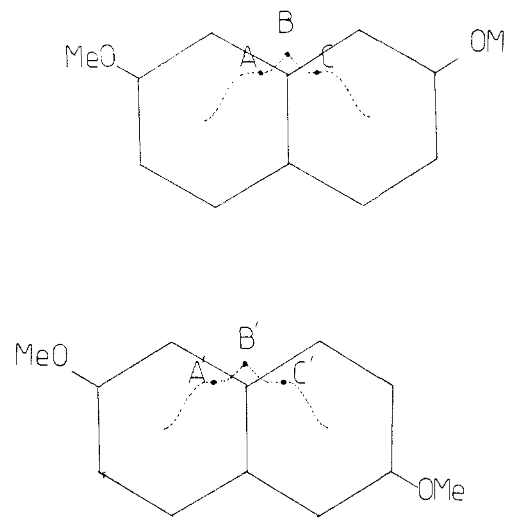

Figure 1. Pathways for haptotropic migration of the chromium carbonyl tricarbonyl group in I and II (proposed by theory, see ref 6).

A recent theoretical study on haptotropic processes has served to focus interest in this area.[6]

We have obtained kinetic data and calculated the activation energies for two complexes, (3-deuterio-2,7-dimethoxynaphthalene)chromium tricarbonyl, Ia, and (3-deuterio-2,6-dimethoxynaphthalene)chromium tricarbonyl, IIa. The undeuterated precursors to these species, I and II, are prepared by reaction of $Cr(CO)_6$ and the arene using standard techniques.[7,8]

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