Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Trinuclear Metal(II)–Sulfide–Thiolate Complexes: Synthesis, Structures, and Properties of $[M_3S(1,2\text{-}(SCH_2)_2C_6H_4)_3]^{2-}$ (M = Fe(II), Co(II))

K. S. HAGEN, G. CHRISTOU,[1] and R. H. HOLM*

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The reaction systems MCl_2–$Na_2(S_2\text{-}o\text{-}xyl)$–$Li_2S$ in 3:3:1 ratio in acetonitrile–ethanol (M = Co(II)) or ethanol (M = Fe(II)) afford the trinuclear complexes $[M_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ (S_2-*o*-xyl = *o*-xylene-α,α'-dithiolate), which were isolated as their Et_4N^+ salts. The compounds $(Et_4N)_2[M_3S(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$ crystallize in triclinic space group $P\bar{1}$ ($Z = 2$): Fe(II), $a = 10.788$ (4) Å, $b = 15.401$ (4) Å, $c = 16.125$ (5) Å, $\alpha = 99.43$ (2)°, $\beta = 97.51$ (3)°, $\gamma = 72.72$ (2)°; Co(II), $a = 10.710$ Å, $b = 15.382$ (4) Å, $c = 16.050$ (4) Å, $\alpha = 99.13$ (2)°, $\beta = 97.76$ (3)°, $\gamma = 72.81$ (3)°. On the basis of 4301 unique data ($I > 3\sigma(I)$) for the Co(II) compound and 3388 unique data ($I > 2\sigma(I)$) for the Fe(II) compound the structures were refined to $R = 4.3\%$ and 6.4%, respectively. The $[M_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ complexes contain an apical μ_3-S atom bonded to three M atoms arranged in a nearly equilateral triangle. Each M atom is coordinated to one terminal and one bridging sulfur atom of a dithiolate ligand, affording distorted-tetrahedral $M^{II}S_4$ units in structures that closely approach overall C_3 symmetry. The isotropically shifted ^1H NMR spectra of these complexes demonstrate retention of the solid-state structure in acetonitrile solutions. Solution spectral and magnetic properties are indicative of unexceptional $M^{II}S_4$ chromophores similar to those present in the mononuclear tetrahedral complexes $[M(S_2\text{-}o\text{-}xyl)_2]^{2-}$ and of spin exchange interactions among the M(II) ions. These species and the recently reported $[Fe_3S(S_2\text{-}o\text{-}xyl\text{-}4,5\text{-}Me_2)_3]^{2-}$ provide the first examples of the occurrence of discrete pyramidal $M_3(\mu_3\text{-}S)$ fragments in weak-field complexes. The two Fe(II) complexes and $[Fe_3(\mu_2\text{-}S)_4(SR)_4]^{3-}$ are the only structurally characterized trinuclear Fe–S–SR species of abiological origin.

Introduction

Ongoing exploratory synthesis in this laboratory in the field of homonuclear metal–sulfide–thiolate chemistry is directed toward several goals: (i) extension of the scope of Fe–S–SR systems beyond the relatively well-exposed chemistry of the ferredoxin site analogues $[Fe_2(\mu\text{-}S)_2(SR)_4]^{2-,3-}$[2-4] and $[Fe_4(\mu_3\text{-}S)_4(SR)_4]^{2-,3-}$;[2,3,5,6] (ii) development of a comparably extensive chemistry of clusters containing metals other than iron. Relevant to (i) are our recent syntheses and structural characterizations of $[Fe_3S_4(SR)_4]^{3-}$[7] and $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$,[8] which contain the new core units $[Fe_3(\mu\text{-}S)_4]^+$ and $[Fe_6(\mu\text{-}S)_6(\mu_3\text{-}S)_2(\mu_4\text{-}S)]^{2-}$, respectively. The preparations of $[Co_8S_6(SPh)_8]^{4-,5-}$ and structural proof of the concentric cubic Co_8 and octahedral S_6 arrangement in the $[Co_8(\mu_4\text{-}S)_6]^{4+,3+}$ cores of these clusters constitute our initial results in the area of (ii).[9] The syntheses and structural determinations of $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$[10] and $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$,[11] as well as of $[Ni_9(\mu_3\text{-}S)_6(\mu_4\text{-}S)_3(PEt_3)_6]^{2+}$,[12] present additional indications of a developing chemistry of clusters based on polyhedral metal–sulfide core units. In terms of core site population the first two clusters, containing octahedral M_6 and cubic S_8 units, are the inverse of $[Co_8S_6(SPh)_8]^{4-,5-}$.

In the search for additional Co–S–SR structural types the bidentate ligand *o*-xylene-α,α'-dithiolate (S_2-*o*-xyl) has been employed in an attempt to direct cluster assembly toward a product other than $[Co_8S_6(SR)_8]^{4-}$, which is formed with unidentate arenethiolates. Reported here are the synthesis, structure, and selected properties of the trinuclear cluster $[Co_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$. While this work was in progress, Henkel et al.[13] described the structure of a related Fe(II) complex, $[Fe_3S(S_2\text{-}o\text{-}xylMe_2)_3]^{2-}$, formed in a reaction mixture containing no sulfide. Subsequently, we have obtained $[Fe_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ by a rational route. The synthesis, structure, and properties of this complex are also provided here.

Experimental Section

Preparation of Compounds. All manipulations were performed under a pure dinitrogen atmosphere. Solvents were distilled and degassed prior to use. *o*-Xylene-α,α'-dithiol was prepared as described elsewhere.[14]

$(Et_4N)_2[Co_3S(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$. A solution of 4.76 g (20 mmol) of $CoCl_2\cdot 6H_2O$ and 3.3 g (20 mmol) of Et_4NCl in 100 mL of acetonitrile was added to a solution of 30 mmol of $Na_2(S_2\text{-}o\text{-}xyl)$ (from 5.11 g of the dithiol and 1.38 g of sodium) in 150 mL of ethanol. After the dark green reaction mixture was stirred for ~5 min, NaCl was removed by filtration, and a solution of 0.92 g (20 mmol) of Li_2S in 50 mL of ethanol was added. Black microcrystals began to separate from the solution after ~15 min. The reaction mixture was maintained at –20 °C for 3 h, and the product was collected by filtration, washed well with ethanol and ether, and dried in vacuo. The filtrate was concentrated in vacuo, and a second crop of crystalline product was obtained as just described. The combined yield was 5.6 g (83%). Recrystallization from ~400 mL of warm (~50 °C) acetonitrile afforded the pure product as large well-formed black prisms in 50% yield. The compound was obtained as an acetonitrile monosolvate. Anal. Calcd for $C_{42}H_{67}Co_3N_3S_7$: C, 49.69; H, 6.65; Co, 17.41; N, 4.14; S, 22.11. Found: C, 49.71; H, 6.81; Co, 16.96; N, 4.05; S, 22.61.

$(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-}xyl)_3]\cdot MeCN$. A solution of 3.81 g (30 mmol) of anhydrous $FeCl_2$ in 50 mL of ethanol was added to a solution of 30 mmol of $Na_2(S_2\text{-}o\text{-}xyl)$, giving a thick slurry of a fine brown precipitate. Addition of a solution of 0.46 g (10 mmol) of Li_2S in 20 mL of ethanol caused the solid to dissolve with formation of a deep red-brown solution. After 1 h of stirring a solution of 5.0 g (30 mmol) of Et_4NCl in 20 mL of ethanol was added, causing separation of a fine microcrystalline brown precipitate. This material was collected by filtration, washed with ethanol, and dried in vacuo. The solid was dissolved in ~100 mL of warm (~40 °C) acetonitrile; this solution was filtered, and the filtrate was stored overnight at –20 °C. Black needles were collected by filtration. Maintenance of the filtrate at –20 °C for 4 days yielded a second crop of crystals; the combined

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$ (M = Co(II), Fe(II))

	data	
quantity	M = Co(II)	M = Fe(II)
formula (mol wt)	$C_{42}H_{67}N_3S_7Co_3$ (1015.27)	$C_{42}H_{67}N_3S_7Fe_3$ (1006.01)
a, Å	10.710 (5)	10.788 (4)
b, Å	15.382 (4)	15.401 (4)
c, Å	16.050 (4)	16.125 (5)
α, deg	99.13 (2)	99.43 (2)
β, deg	97.76 (3)	97.51 (3)
γ, deg	72.81 (3)	72.72 (2)
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
V, $Å^3$	2483 (1)	2514 (1)
Z	2	2
d_{calcd}, g cm^{-3}	1.36	1.33
d_{obsd},[a] g cm^{-3}	1.33	1.31
cryst dimens, mm	0.24 × 0.50 × 0.48	0.2 × 0.3 × 0.5
radiation	Mo $K\bar{\alpha}$ (λ = 0.710 69 Å)	
abs coeff, μ, cm^{-1}	12.99	11.64
scan speed, deg min^{-1}	2.93–29.3 ($\theta/2\theta$)	2.0–29.3 ($\theta/2\theta$)
scan range, deg	$2.4 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$	$2.4 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$
bkgd/scan time ratio	0.25	0.25
data collected	$3° \leqslant 2\theta \leqslant 45°$ $(+h,\pm k,\pm l)$	$3° \leqslant 2\theta \leqslant 43°$ $(+h,\pm k,\pm l)$
unique data	4301 ($I > 3\sigma(I)$)	3388 ($I > 2\sigma(I)$)
no. of variables	619	553
goodness of fit	1.343	1.515
% *R*	4.3	6.4
% R_w	4.6	6.2

[a] Determined by neutral bouyancy in CCl_4–hexane.

yield was 3.8 g (38%). The compound was obtained as an acetonitrile monosolvate. Anal. Calcd for $C_{42}H_{67}Fe_3N_3S_7$: C, 50.15; H, 6.71; Fe, 16.66; N, 4.18; S, 22.31. Found: C, 49.60; H, 6.38; Fe, 16.96; N, 3.81; S, 21.18.

X-ray Data Collection and Reduction. Black air-sensitive crystals, grown by slow cooling of acetonitrile solutions of $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]$ (M = Fe(II), Co(II)), were sealed in glass capillaries under argon. The unit-cell dimensions and orientation matrices were calculated from 21 reflections (25° < 2θ < 30°) and 25 reflections (15° < 2θ < 25°) for the Co(II) and Fe(II) compounds, respectively. Diffraction experiments were performed at ambient temperature on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a graphite monochromator. The crystal and machine parameters used in the data collection are summarized in Table I. Three check reflections were measured every 123 reflections; these exhibited no significant decay over the duration of data collection. The data were processed with the program XTAPE of the SHELXTL package; empirical absorption corrections were applied with the program XEMP. Both compounds crystallize in the triclinic system. Statistical analysis of intensity distribution of the Co(II) compound indicated the centrosymmetric space group $P\bar{1}$, which was confirmed by solution and refinement of the structure.

Structure Solution and Refinement. The direct-methods program MULTAN located the positions of the three cobalt atoms in the $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ anion. The remaining non-hydrogen atoms of the anion, cations, and solvate molecule were located by successive Fourier difference maps and least-squares refinements. The asymmetric unit contains one anion, one cation, one solvate molecule, and two cations whose nitrogen atoms lie on the inversion centers at (0, 0, $^1/_2$) and (0, $^1/_2$, $^1/_2$) with occupancies of 0.5. This necessarily disorders the methylene groups into two positions, and their carbon atoms were refined with fixed occupancies of 0.5. On the basis of 4301 unique data ($I > 3\sigma(I)$) convergence was reached at *R* = 11% for isotropic and *R* = 5.5% for anisotropic refinement of all non-hydrogen atoms. In the final stages of refinement hydrogen atoms were included in the anion, cations, and solvate molecule at 0.96 Å from, and with isotropic thermal parameters 1.2 times those of the bonded carbon atoms. The unit cell of $(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$ proved to be isomorphous with that of its Co(II) analogue. Initial non-hydrogen atom coordinates were taken from the refined Co(II) structure. With use of 3388 unique data ($I > 2\sigma(I)$) the structure of the Fe(II) compound was refined in a manner similar to that of the Co(II) compound, with the exception that hydrogen atoms were included in the anion only. Final *R* factors and other data are included in Table I.

The following results are tabulated: positional parameters (Table II), interatomic distances and angles (Table III), anisotropic thermal parameters for the Fe(II) (Table S-I) and Co(II) (Table S-II) anions, positional parameters for cations and solvate molecules of both compounds (Table S-III), anisotropic thermal parameters for cations and the solvate molecule of the Fe(II) (Table S-IV) and the Co(II) (Table S-V) compounds, and values of $10|F_o|$ and $10|F_c|$ for both structures (Table S-VI).[15]

Other Physical Measurements. All measurements were performed under anaerobic conditions. Absorption spectra were recorded on a Cary Model 17 or 219 spectrophotometer. Electrochemical measurements were made with standard Princeton Applied Research instrumentation using a glassy-carbon working electrode and solutions containing 0.1 M $(n\text{-}Bu_4N)(ClO_4)$ supporting electrolyte. Potentials were measured at ~25 °C vs. a saturated calomel electrode (SCE). ^1H NMR spectra (300 MHz) were measured with a Bruker WM-300 spectrometer; shifts downfield of the Me_4Si reference are designated as negative. Magnetic susceptibilities of complexes in solution were determined by the conventional NMR method using coaxial tubes and Me_4Si solution and reference shift differences. Diamagnetic corrections were applied.

Results and Discussion

Synthesis of Compounds. Previously it had been shown that substitution of bidentate $(S_2\text{-}o\text{-xyl})^{2-}$ for monofunctional thiolates, in reaction systems containing Fe(III) salts and sulfide or sulfur that otherwise assemble the tetranuclear clusters $[Fe_4S_4(SR)_4]^{2-}$,[6,16,17] resulted in formation of the binuclear complex $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$.[14,18] The latter presumably is formed because the chelate bite distance is insufficient to span the terminal ligand positions in the cubane-type cluster. This possibility is supported by the preparation of a cluster of composition $[Fe_4S_4(S_2\text{-}m\text{-xyl})_2]^{2-}$, whose properties are consistent with those of $[Fe_4S_4(SR)_4]^{2-}$ species.[19,20] While the structure of this complex has not been determined, models show that the $(S_2\text{-}m\text{-xyl})^{2-}$ bite distance is large enough to stabilize the indicated tetranuclear cluster.

Application of the "restricted-bite" idea to the synthesis of Co(II)–sulfide–thiolate clusters led to the development of reaction 1 (M = Co(II)). The new complex $[Co_3S(S_2\text{-}o\text{-xyl})_2]^{2-}$ was isolated from an acetonitrile–ethanol reaction mixture as its highly crystalline Et_4N^+ salt.

$$3MCl_2 + 3Na_2(S_2\text{-}o\text{-xyl}) + Li_2S \rightarrow Li_2[M_3S(S_2\text{-}o\text{-xyl})_3] + 6NaCl \quad (1)$$

The presence of a twofold excess of Li_2S was beneficial in increasing the yield, which was 50% after purification. A similar Fe(II) complex was unknown prior to the report of $(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-xylMe}_2)_3]$.[13] This compound is described as resulting from reaction of the dithiol, sodium methoxide, iron(III) chloride, and *p*-toluenethiol in anhydrous methanol and subsequent precipitation with Et_4NCl (amounts of reactants and yield unspecified). Sulfide was apparently not included as a component of the reaction system. We subsequently have obtained $(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-xyl})_3]$ from reaction 1, using stoichiometric

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(15) See paragraph at the end of this article concerning supplementary material.

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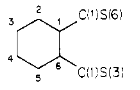
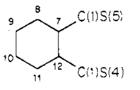
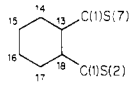
Table II. Positional Parameters for $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$

	M = Co(II)			M = Fe(II)		
atom	*x*	*y*	*z*	*x*	*y*	*z*
M(1)	0.2734 (1)[a]	0.5850 (1)	0.3022 (1)	0.2768 (1)	0.5829 (1)	0.3016 (1)
M(2)	0.1435 (1)	0.6766 (1)	0.1643 (1)	0.1466 (1)	0.6730 (1)	0.1617 (1)
M(3)	0.2791 (1)	0.7646 (1)	0.3000 (1)	0.2817 (1)	0.7616 (1)	0.2976 (1)
S(1)	0.3621 (1)	0.6382 (1)	0.2072 (1)	0.3687 (3)	0.6329 (2)	0.2029 (2)
S(2)	0.2418 (1)	0.7030 (1)	0.4138 (1)	0.2425 (3)	0.7027 (2)	0.4145 (2)
S(3)	0.0698 (1)	0.5819 (1)	0.2339 (1)	0.0696 (2)	0.5796 (2)	0.2341 (2)
S(4)	0.0716 (2)	0.8250 (1)	0.2318 (1)	0.0720 (3)	0.8236 (2)	0.2307 (2)
S(5)	0.0695 (2)	0.6686 (1)	0.0272 (1)	0.0652 (3)	0.6667 (2)	0.0228 (2)
S(6)	0.3859 (2)	0.4545 (1)	0.3524 (1)	0.3862 (3)	0.4495 (2)	0.3543 (2)
S(7)	0.3866 (2)	0.8717 (1)	0.3409 (1)	0.3896 (3)	0.8719 (2)	0.3423 (2)
C(1)S(2)	0.4041 (6)	0.6815 (4)	0.4752 (4)	0.4057 (10)	0.6806 (6)	0.4768 (6)
C(1)S(3)	0.1108 (6)	0.4708 (4)	0.1644 (3)	0.1088 (11)	0.4681 (8)	0.1664 (6)
C(1)S(4)	0.1038 (6)	0.8940 (4)	0.1570 (4)	0.1021 (10)	0.8941 (8)	0.1565 (7)
C(1)S(5)	0.0970 (7)	0.7710 (5)	−0.0064 (4)	0.0992 (11)	0.7684 (9)	−0.0050 (7)
C(1)S(6)	0.3658 (6)	0.3727 (4)	0.2591 (4)	0.3639 (10)	0.3701 (7)	0.2593 (6)
C(1)S(7)	0.5204 (6)	0.8149 (5)	0.4170 (4)	0.5203 (11)	0.8137 (8)	0.4160 (7)
C(1)[b]	0.2406 (6)	0.3453 (4)	0.2538 (3)	0.2400 (10)	0.3421 (7)	0.2536 (6)
C(2)	0.2451 (7)	0.2707 (4)	0.2942 (4)	0.2420 (12)	0.2670 (8)	0.2941 (7)
C(3)	0.1350 (7)	0.2408 (5)	0.2903 (4)	0.1362 (16)	0.2377 (10)	0.2919 (8)
C(4)	0.0189 (7)	0.2848 (5)	0.2501 (4)	0.0208 (15)	0.2810 (10)	0.2508 (8)
C(5)	0.0137 (7)	0.3596 (5)	0.2097 (4)	0.0130 (12)	0.3560 (10)	0.2113 (7)
C(6)	0.1236 (6)	0.3903 (4)	0.2106 (3)	0.1222 (11)	0.3864 (7)	0.2112 (6)
C(7)	−0.0097 (6)	0.8573 (4)	0.0116 (4)	−0.0063 (10)	0.8560 (9)	0.0113 (7)
C(8)	−0.1124 (7)	0.8832 (5)	−0.0499 (5)	−0.1077 (13)	0.8771 (11)	−0.0516 (9)
C(9)	−0.2095 (7)	0.9632 (6)	−0.0376 (6)	−0.2053 (19)	0.9595 (14)	−0.0387 (12)
C(10)	−0.2072 (7)	1.0200 (5)	0.0358 (6)	−0.2030 (14)	1.0162 (11)	0.0333 (12)
C(11)	−0.1065 (7)	0.9967 (5)	0.0991 (5)	−0.1039 (12)	0.9944 (9)	0.0983 (8)
C(12)	−0.0052 (6)	0.9148 (4)	0.0873 (4)	−0.0026 (11)	0.9123 (9)	0.0871 (7)
C(13)	0.4797 (6)	0.8253 (4)	0.5048 (4)	0.4791 (10)	0.8240 (7)	0.5036 (7)
C(14)	0.4981 (7)	0.8986 (4)	0.5624 (5)	0.5016 (12)	0.8986 (8)	0.5591 (7)
C(15)	0.4592 (8)	0.9156 (4)	0.6419 (5)	0.4639 (14)	0.9184 (8)	0.6410 (8)
C(16)	0.4004 (7)	0.8574 (4)	0.6679 (4)	0.4034 (13)	0.8619 (8)	0.6676 (7)
C(17)	0.3864 (6)	0.7829 (4)	0.6135 (4)	0.3849 (11)	0.7849 (7)	0.6136 (6)
C(18)	0.4231 (6)	0.7643 (4)	0.5314 (4)	0.4236 (10)	0.7647 (6)	0.5320 (6)

[a] Numbers in parentheses in this and succeeding tables are the estimated standard deviations in the last figure(s). [b] Numbering scheme of phenyl rings:







quantities of reagents, in 38% purified yield. (The presence of excess Li_2S gave large amounts of an intractable black solid, presumably FeS.) Both compounds were isolated as acetonitrile monosolvates, and both are sensitive to dioxygen in the solid and solution states.

Descriptions of the Structures. The compounds $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$ (M = Fe(II), Co(II)) crystallize in triclinic space group $P\bar{1}$ with nearly isometric unit cells (Table I). Their crystal structures consists of well-separated cations, solvate molecules, and anions. Metrical features of the first two components[15] and of the phenyl rings of the ligands are unexceptional and are not considered further.

The structure of the central (M_3S_7) portions of the anions and the atom-labeling scheme are shown in Figure 1. The metal–sulfide core portion consists of the apical μ_3-S(1) atom bonded to the three metal atoms in a plane 1.66 Å (Fe) or 1.60 Å (Co) below it. The metal atoms are bridged by the three atoms μ-S(2–4) and terminally coordinated by the atoms S(5–7). Thus each dithiolate ligand furnishes one bridging and one terminal atom to the M_3S_7 portion. The planes S(2–4) and S(5–7) are situated below and above the M_3 plane, respectively, and are virtually parallel with it (dihedral angles ≤1.2°). This arrangement affords idealized C_3 symmetry, with the C_3 axis normal to the M_3 and S_3 planes and containing atom S(1). The complexes are therefore chiral, and the unit cell contains an enantiomeric pair related by the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$). This arrangement is depicted in Figure 2 showing the entire anion structure.

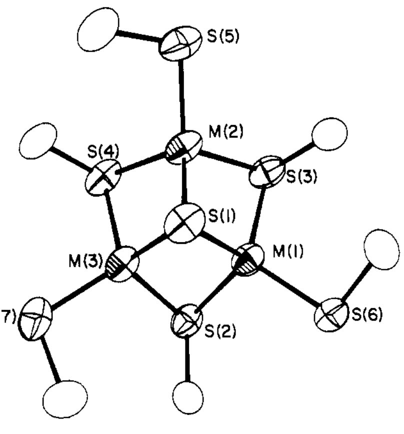


Figure 1. Structure of the central portion of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Fe(II), Co(II)), showing the atom-labeling scheme. M and S atoms are depicted as 50% probability ellipsoids with use of the thermal parameters of the Co(II) complex.

Selected interatomic distances and angles organized under C_3 symmetry are compiled in Table III. The following are the principal structural features of the anion (t = terminal ligand). (i) Both conform rather closely to C_3 symmetry but with particularly noticeable differences in M···M separations as seen from the large standard deviations of the mean values. (ii) Metal atoms occupy distorted-tetrahedral sites, which are appreciably "flattened" along the bisectors of $S(1)\text{–}M\text{–}S_t$ angles (Fe and Co, 121°). (iii) Mean values of bonded distances in the Fe(II) complex exceed those in the Co(II) com-

Table III. Selected Interatomic Distances (Å) and Angles (deg) in $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Fe(II), Co(II))

dist/angle	M = Fe(II)	M = Co(II)	dist/angle	M = Fe(II)	M = Co(II)
M(1)···M(2)	2.833 (3)	2.796 (1)	S(1)-M(1)-S(2)	105.4 (1)	103.5 (1)
M(1)···M(3)	2.780 (3)	2.785 (1)	S(1)-M(3)-S(4)	102.6 (1)	101.6 (1)
M(2)···M(3)	2.855 (3)	2.837 (1)	S(1)-M(2)-S(3)	102.7 (1)	102.0 (1)
mean	2.823 (39)[a]	2.806 (27)	mean	103.6	102.4
M(1)-S(1)	2.319 (4)	2.268 (2)	S(2)-M(1)-S(3)	107.2 (1)	108.1 (1)
M(2)-S(1)	2.325 (3)	2.277 (2)	S(3)-M(2)-S(4)	105.9 (1)	107.6 (1)
M(3)-S(1)	2.328 (3)	2.281 (2)	S(4)-M(3)-S(2)	104.6 (1)	105.3 (1)
mean	2.324 (5)	2.275 (7)	mean	105.9	107.0
M(1)-S(2)	2.350 (3)	2.321 (1)	S(1)-M(1)-S(6)	119.5 (1)	119.0 (1)
M(3)-S(4)	2.368 (3)	2.333 (2)	S(1)-M(2)-S(5)	122.7 (1)	121.6 (1)
M(2)-S(3)	2.374 (4)	2.330 (2)	S(1)-M(3)-S(7)	121.3 (1)	121.0 (1)
mean	2.364 (12)	2.328 (6)	mean	121.2	120.5
M(1)-S(3)	2.366 (3)	2.315 (2)	S(2)-M(1)-S(6)	108.4 (1)	109.0 (1)
M(2)-S(4)	2.355 (3)	2.319 (2)	S(3)-M(2)-S(5)	111.2 (1)	111.2 (1)
M(3)-S(2)	2.357 (4)	2.313 (2)	S(4)-M(3)-S(7)	111.9 (1)	111.9 (1)
mean	2.359 (6)	2.316 (3)	mean	110.5	110.7
mean of 6	2.362 (9)	2.322 (8)	S(3)-M(1)-S(6)	112.4 (1)	113.5 (1)
M(1)-S(6)	2.281 (3)	2.225 (2)	S(5)-M(2)-S(4)	109.8 (1)	110.0 (1)
M(2)-S(5)	2.293 (3)	2.233 (2)	S(7)-M(3)-S(2)	110.1 (1)	112.2 (1)
M(3)-S(7)	2.306 (4)	2.248 (2)	mean	110.8	111.9
mean	2.293 (12)	2.235 (12)	S(5)-C(1)S(5)	1.856 (16)	1.860 (9)
M(2)-M(1)-M(3)	61.2 (1)	61.1 (1)	S(6)-C(1)S(6)	1.835 (10)	1.832 (6)
M(1)-M(2)-M(3)	58.5 (1)	59.2 (1)	S(7)-C(1)S(7)	1.835 (11)	1.853 (7)
M(1)-M(3)-M(2)	60.4 (1)	59.6 (1)	mean	1.839 (6)	1.848 (15)
M(1)-S(1)-M(2)	75.2 (1)	75.9 (1)	S(2)-C(1)S(2)	1.876 (10)	1.844 (6)
M(1)-S(1)-M(3)	73.5 (1)	75.5 (1)	S(3)-C(1)S(3)	1.843 (11)	1.851 (6)
M(2)-S(1)-M(3)	75.7 (1)	77.0 (1)	S(4)-C(1)S(4)	1.857 (13)	1.851 (8)
mean	74.8	76.1	mean	1.859 (17)	1.849 (6)
S(1)-M(1)-S(3)	103.2 (1)	102.7 (1)	C(1)S(6)-C(1)	1.509 (16)	1.507 (10)
S(1)-M(2)-S(4)	103.1 (1)	102.1 (1)	C(1)S(3)-C(6)	1.512 (17)	1.505 (10)
S(1)-M(3)-S(2)	104.9 (1)	103.4 (1)	C(1)S(5)-C(7)	1.494 (16)	1.493 (9)
mean	103.7	102.7	C(1)S(4)-C(12)	1.479 (14)	1.495 (9)
M(1)-S(3)-M(2)	73.4 (1)	74.0 (1)	C(1)S(7)-C(13)	1.505 (17)	1.501 (10)
M(2)-S(4)-M(3)	74.4 (1)	75.2 (1)	C(1)S(2)-C(18)	1.494 (14)	1.483 (8)
M(3)-S(2)-M(1)	72.4 (1)	73.9 (1)	mean	1.499 (12)	1.497 (9)
mean	73.4	74.4	C-C(ring) range	1.34 (3)-1.41 (2)	1.35 (1)-1.40 (1)
			mean of 18	1.39 (2)	1.38 (2)

[a] The standard deviation of the mean was estimated from $\sigma \approx s = [(\Sigma x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$.

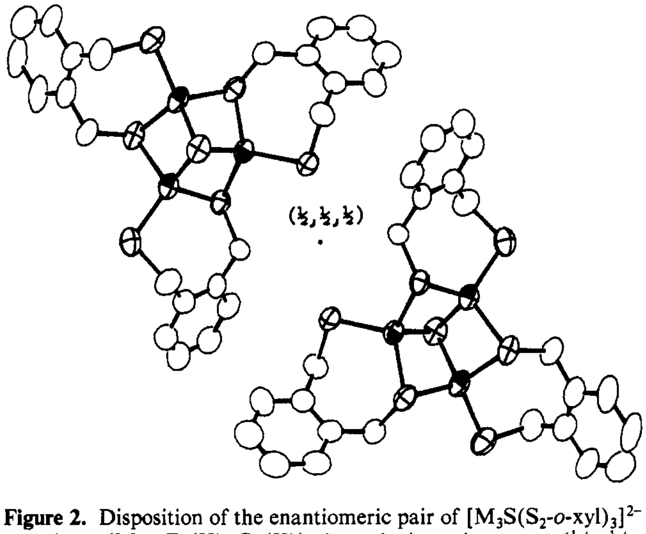


Figure 2. Disposition of the enantiomeric pair of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ complexes (M = Fe(II), Co(II)) about the inversion center (½, ½, ½). The entire structure of the anion is shown; M and S atoms are depicted as in Figure 1.

plex by 0.03–0.04 Å, consistent with the difference in tetrahedral radii of these ions (Fe(II), 0.77 Å; Co(II), 0.72 Å[21]). (iv) The $Fe_3(\mu_3\text{-}S)$ grouping structurally resembles the corresponding fragments of the cores of $[Fe_4S_4(SR)_4]^{2-,3-}$[3] and $[Fe_6S_9(S\text{-}t\text{-Bu})_2]^{4-}$[8] but with somewhat longer Fe–S (≳0.02 Å) and Fe···Fe (≳0.05 Å) differences due in part to the lower Fe oxidation state in $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$. Similarly, the $Fe_2(\mu\text{-}S)(\mu_3\text{-}S)$ units can be roughly likened to the Fe_2S_2 portions of the preceding clusters and $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$,[3,14] and the $Fe_3(\mu\text{-}S)_3(\mu_3\text{-}S)$ fragment can be compared to a Fe_4S_4 core unit with a Fe atom vacancy. A similar fragment is present in the core of $[Fe_6S_9(S\text{-}t\text{-Bu})_2]^{4-}$.[8] (v) The $Co_3(\mu_3\text{-}S)$ grouping resembles the corresponding fragment of $[Co_6S_8(PEt)_6]^{+}$[11] in which the mean Co···Co distance (2.794 (2) Å) is close to that in $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$. (vi) Mean values of corresponding Fe···Fe and Fe–S distances in $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ and $[Fe_3S(S_2\text{-}o\text{-xylMe}_2)_3]^{2-}$ (whose Et_4N^+ salt also crystallizes in space group $P\bar{1}$[13]) agree to within 0.02 Å. The approximate relationships noted in (iv) and (v) are of a topological rather than a chemical/electronic nature, owing to the lesser ability of bridging thiolate vs. sulfide ligands to mediate electronic interactions and to sustain stable $M_3(\mu_3\text{-}S)$ arrangements. The present complexes and $[Fe_3S(S_2\text{-}o\text{-xylMe}_2)_3]^{2-}$ present the first cases of the occurrence of discrete pyramidal $M_3(\mu_3\text{-}S)$ fragments, i.e., unsupported by additional metal–sulfide bonding, in complexes of weak-field ligands.[23] The function of $(S_2\text{-}o\text{-xyl})^{2-}$ as a terminal chelating ligand in $[Fe(S_2\text{-}o\text{-xyl})_2]^{-,2-}$

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(23) Such fragments are unexceptional structural components in many organometallic compounds, e.g., $Fe_3S_2(CO)_9$ (Wei, C.-H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 493) and $Co_3S(CO)_9$ (Wei, C.-H.; Dahl, L. F. *Ibid.* **1967**, *6*, 1229), $Fe_3S(SO)(CO)_9$ (Markó, L.; Markó-Monostory, B.; Madach, T.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 226), and $Fe_3S(SN\text{-}t\text{-Bu})(CO)_9$ (Maij, R.; van der Helm, J.; Stufkens, D. J.; Vrieze, K. *J. Chem. Soc., Chem. Commun.* **1978**, 506).

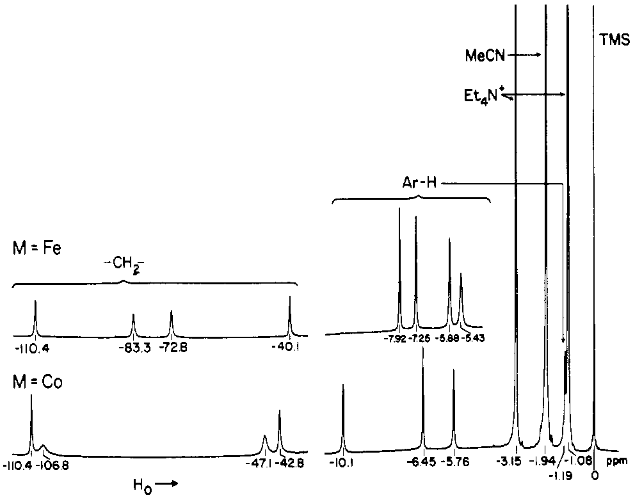

Figure 3. ^{1}H NMR spectra (300 MHz) of $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]$ (M = Fe(II), Co(II)) in CD_3CN solutions at ~297 K. Signal assignments are indicated.

and $[Co(S_2\text{-}o\text{-xyl})_2]^{2-}$[22] and as a terminal *and* bridging ligand in $[Fe_2(S_2\text{-}o\text{-xyl})_3]^{2-}$,[7,22] all of which contain tetrahedrally coordinated M(II) atoms, is well documented.

Properties in Solution. Certain properties of the $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ complexes have been examined in acetonitrile solution. Retention in solution of the structures established in the solid state is demonstrated by the ^{1}H NMR spectra in Figure 3. Under C_3 symmetry all ring and methylene protons of the symmetry-related $M(S_2\text{-}o\text{-xyl})$ fragments are inequivalent. Isotropic interactions afford well-resolved spectra of both the Fe(II) and the Co(II) complexes, which exhibit eight resonances of equal integrated intensity. The indicated assignment of the four resonances furthest downfield in each spectrum to methylene protons is made primarily on the basis of larger line widths, owing to the closer proximity of these protons to paramagnetic centers. Additionally, methylene protons are expected to experience larger contact (and, possibly, dipolar) contributions to their chemical shifts. The remaining narrower and less shifted set of four signals of each complex is assigned to ring protons.

Other properties of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ complexes are summarized in Table IV; absorption spectra are presented in Figure 4. In terms of similarities in ligation, spectral and magnetic features are best compared with those of the mononuclear tetrahedral complexes $[M(S_2\text{-}o\text{-xyl})_2]^{2-}$ (M = Fe(II), Co(II)), which have been studied in some detail earlier.[22] The spectrum of $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ contains the LMCT (340 nm) and tetrahedral ligand field (1525 nm) bands found for $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$ (λ_{max}, in nm (ϵ_M), 323 (7710), 1800 (123), respectively). Similarly, the LMCT (355 (3450)) and $^4A_2 \rightarrow {}^4T_1(F)$ (1550 (242)) transitions of $[Co(S_2\text{-}o\text{-xyl})_2]^{2-}$ appear at 412 and 1500 nm, respectively, in the spectrum of $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$. Counterparts of the three bands (610, 684, 788 (460–645)) of $^4A_2 \rightarrow {}^4T_1(P)$ parentage in the $[Co(S_2\text{-}o\text{-xyl})_2]^{2-}$ spectrum are nearly obscured in the spectrum of $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ by intense charge-transfer absorption trailing into the visible region. Assignment of the shoulder at 830 nm to one component of the foregoing transition appears reasonable. Magnetic moments of $[M(S_2\text{-}o\text{-xyl})_2]^{2-}$ are 5.10 μ_B (Fe(II)) and 4.60 μ_B (Co(II)) at ambient temperature, values typical of tetrahedral $M^{II}S_4$ species of iron and cobalt. In contrast, moments per metal atom of both $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ complexes are markedly lower and show small increases with increasing temperature. The collective solution properties of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ complexes are consistent with the presence of

Table IV. Properties of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Fe(II), Co(II))

property[a]	Fe(II)	Co(II)
λ_{max} (ϵ_M[b]), nm		310 sh (15 000)
	340 (14 100) [S → Fe]	412 (9300) [S → Co]
		580 sh (1900)
		830 sh (530) [$^4A_2 \rightarrow {}^4T_1(P)$]
	1525 (250) [$^5E \rightarrow {}^5T_2$]	1500 (650) [$^4A_2 \rightarrow {}^4T_1(F)$]
$E_{1/2}$, V (vs. SCE)[f]	−0.59 (2−/1−)	
	−2.04 ($E_{p,c}$, irrev)	−1.86 (2−/3−)
μ,[c] μ_B (T, K)	2.05 (234)[e]	1.93 (234)[e]
	2.16 (260)	2.00 (295)
	2.22 (278)	2.05 (323)
	2.28 (301)[d,e]	2.09 (341)[e]

[a] Acetonitrile solution. [b] Molar extinction coefficient. [c] Magnetic moment per M atom; $\mu_M = \mu_{M_3}/3^{1/2}$. [d] Apparent decomposition at higher temperatures. [e] Data at other temperatures within the interval also monotonically increase with increasing temperature. [f] $E_{1/2} = (E_{p,c} + E_{p,a})/2$, measured at 100 mV/s by cyclic voltammetry.

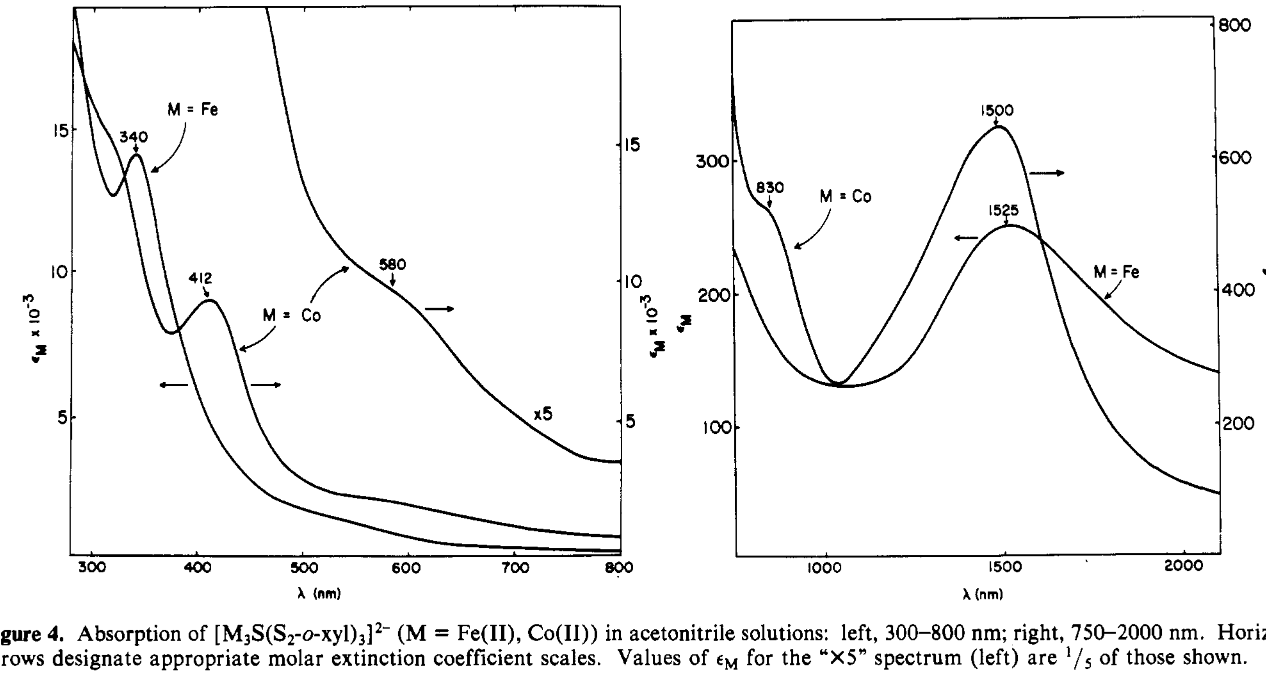

Figure 4. Absorption of $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Fe(II), Co(II)) in acetonitrile solutions: left, 300–800 nm; right, 750–2000 nm. Horizontal arrows designate appropriate molar extinction coefficient scales. Values of ϵ_M for the "X5" spectrum (left) are $^1/_5$ of those shown.

species with overall trigonal symmetry, having unexceptional, approximately tetrahedral $M^{II}S_4$ chromophores that are magnetically coupled. Determination of the nature and magnitude of the exchange interactions requires extensive measurements over larger temperature intervals than those investigated here.

The complexes $[M_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ show one quasi-reversible oxidation and irreversible reduction (Fe(II)), and a reversible reduction (Co(II)) at a very negative potential (Table IV), properties that tend to restrict further investigations of isolated forms of these complexes to those with the overall 2– oxidation level. In a biological context trinuclear iron–sulfide species are of interest in relation to the cyclic $Fe_3(\mu\text{-}S)_3$ core unit of one Fe–S site in *Azotobacter vinelandii* Fd I.[24a] This unit exists in the $[Fe_3S_3]^{3+,2+}$ oxidation levels,[25] and in the oxidized form the Fe···Fe separations are ~4.1 Å. The complex $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ bears only a distant structural and no electronic relationship to that site (and to subsequently discovered 3-Fe sites in other proteins provided they have the same structure[24b]). Consequently, it should not be described[13] as a model for trinuclear iron–sulfur centers in proteins. However, it and $[Fe_3S_4(SR)_4]^{3-}$ are the only known trinuclear Fe–S–SR species[26] and may serve as precursors to complexes having Fe_3S_3 cores. This possibility is currently under investigation.

Acknowledgment. This research was supported by NIH Grant GM 28856. NMR and X-ray diffraction equipment used in this research were obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

Registry No. $(Et_4N)_2[Co_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$, 83546-51-4; $(Et_4N)_2[Fe_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$, 83546-54-7.

Supplementary Material Available: Crystal structure data for $(Et_4N)_2[M_3S(S_2\text{-}o\text{-xyl})_3]\cdot MeCN$ (M = Fe(II), Co(II)): anisotropic thermal parameters for the anions (Tables S-I, S-II), positional parameters for cations and solvate molecules (Table S-III), anisotropic thermal parameters for cations and solvate molecules (Tables S-IV, S-V), and calculated and observed structure factors (Table S-VI) (51 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405,
and the Institut für Chemie, Universität Regensburg, D-8400 Regensburg, West Germany

New Bridging Mode for Organodiazo Ligands. Molecular Structure of $(\eta^5\text{-}C_5H_5)(CO)_2W(N\overline{NCH_3)Cr}(CO)_5$[1]

GREGORY L. HILLHOUSE, BARRY L. HAYMORE,* SABINE A. BISTRAM, and WOLFGANG A. HERRMANN

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The interaction of $(\eta^5\text{-}C_5H_5)W(CO)_2(N_2CH_3)$ with $Cr(CO)_5(THF)$ (THF = tetrahydrofuran) gives a binuclear complex containing a bridging organodiazo ligand. Attachment of the $Cr(CO)_5$ group to the organodiazo ligand causes the W–N(1) distance to decrease (0.03 Å) and the N(1)–N(2) distance to increase (0.03 Å). Structural changes in the carbonyl and cyclopentadienyl ligands attached to tungsten are also observed. The geometry about chromium is typical of $Cr(CO)_5L$, where L is an ordinary sp^2 hybridized σ-donor ligand. This is the first example of an N,N′ bridging organodiazo ligand, and its relationship to isodiazene (hydrazido(2–)) ligands (W–N–NH–R) is discussed. Important structural parameters include W–N(1) = 1.830 (3) Å, N(1)–N(2) = 1.247 (4) Å, Cr–N(2) = 2.106 (3) Å, W–N(1)–N(2) = 174.4 (3)°, N(1)–N(2)–Cr = 122.3 (3)°, N(1)–N(2)–C(8) = 113.8 (3)°, and C(8)–N(2)–Cr = 123.9 (2)°. The X-ray crystal structure of the title complex was determined at –175 °C in space group $P2_1/c$ with $a = 15.257$ (6) Å, $b = 8.874$ (3) Å, $c = 13.279$ (5) Å, $\beta = 111.39$ (1)°, and $Z = 4$. On the basis of 3168 reflections with $F_o^2 > 3\sigma(F_o^2)$, the structure was refined by using full-matrix, least-squares methods to $R(F) = 0.021$ and $R_w(F) = 0.029$.

Introduction

We have maintained a continuing interest in organodiazo complexes because they are intermediates in the metal-assisted, synthetic reduction of dinitrogen to amines,[2] ammonia,[3] and diazenes.[4] The M–N–N linkage in organodiazo complexes has a partially delocalized π-bonding system that is strongly affected by the attached metal and coligands and by the nature of the group attached to the outer nitrogen atom. We undertook the present study to determine the effect on the W–N and N–N distances in $(C_5H_5)W(CO)_2(N_2CH_3)$ (I) when a metal-containing fragment such as $Cr(CO)_5$ was attached to the outer nitrogen atom of the methyldiazo ligand. Accurate structural parameters for the terminal methyldiazo ligand[5] in the parent complex are available for purposes of comparison.

Previous studies have shown that simple protonation (or alkylation) of organodiazo ligands can occur at the inner nitrogen atom, at the outer nitrogen atom, or at both nitrogen atoms. Doubly bent organodiazo ligands always protonate at

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* To whom correspondence should be addressed at the Corporate Research Laboratory, Monsanto Co., St. Louis, MO 63166.

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