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Synthesis and Stereochemistry of Mono-, Bi-, and Tetranuclear Manganese Thiolates

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The first systematic investigation of Mn–thiolate complexes is described. Anaerobic reaction of $MnCl_2$ with 2.5 equiv of NaSPh in methanol affords $[Mn_4(SPh)_{10}]^{2-}$. The compound $(Me_4N)_2[Mn_4(SPh)_{10}]$ crystallizes in triclinic space group $P\bar{1}$ with $a = 13.184$ (3) Å, $b = 23.743$ (4) Å, $c = 12.930$ (3) Å, $\alpha = 91.63$ (2)°, $\beta = 113.76$ (1)°, $\gamma = 79.53$ (2)°, and $Z = 2$. The structure was refined to R (R_w) = 4.5% (4.8%) with use of 5787 unique data ($I > 3\sigma(I)$). The anion contains an adamantane-like $Mn_4(\mu\text{-}S)_6$ cage composed of a nearly regular Mn_4 tetrahedron and an irregularly distorted S_6 octahedron and exhibits terminal and bridging Mn–S mean distances of 2.376 (7) and 2.46 (2) Å, respectively. Selected structural features are compared with those of five other $M_4(\mu\text{-}S)_6$ cages. Anaerobic reaction of $MnCl_2$ with 2 equiv of $Na_2(1,2\text{-}S_2C_2H_4)$ in methanol forms extremely oxygen-sensitive $[Mn(S_2C_2H_4)_2]^{2-}$. The compound $(Me_4N)_2[Mn(S_2C_2H_4)_2]\cdot MeCN$ crystallizes in monoclinic space group $P2_1/n$ with $a = 9.833$ (5) Å, $b = 17.325$ (7) Å, $c = 13.819$ (6) Å, $\beta = 93.43$ (2)°, and $Z = 4$. The structure was refined to R (R_w) = 4.4% (4.5%) with use of 1893 unique data ($I > 3\sigma(I)$). The anion is tetrahedral with mean dimensions Mn–S = 2.432 (7) Å, chelate ring $\angle$S–Mn–S = 91.5°, and a 92.3° dihedral angle between MnS_2 planes. Exposure of a solution of $[Mn(S_2C_2H_4)_2]^{2-}$ to air results in the immediate formation of a dark green color and thereafter isolation of salts of $[Mn_2(S_2C_2H_4)_4]^{2-}$. $(Et_4N)_2[Mn_2(S_2C_2H_4)_4]$ crystallizes in monoclinic space group $P2_1/n$ with $a = 12.039$ (4) Å, $b = 10.699$ (2) Å, $c = 15.012$ (3) Å, $\beta = 110.89$ (2)°, and $Z = 2$. The structure was refined to R (R_w) = 4.4% (4.9%) with use of 2175 unique data ($I > 3\sigma(I)$). The centrosymmetric anion exhibits the lateral dimer structure in which bis chelate monomers are joined by two Mn–S bonds of length 2.632 (2) Å. The two Mn–S_5 coordination units approach a trigonal-bipyramidal arrangement and are separated by a Mn···Mn distance of 3.596 (3) Å. $[Mn_2(S_2C_2H_4)_4]^{2-}$ is the first characterized Mn(III) thiolate. A compilation of the limited set of all known Mn–S bond distances is provided. $[Mn(S_2C_2H_4)_2]^{2-}$ and $[Mn_4(SPh)_{10}]^{2-}$ contain tetrahedral Mn(II) sites; $[Mn(S_2C_2H_4)_2]^{2-}$ remains tetrahedral and high spin in acetonitrile and DMF solutions. Magnetic and spectral properties of solutions prepared from $[Mn_2(S_2C_2H_4)_4]^{2-}$ indicate that the dimer partially (acetonitrile) or completely (Me_2SO, DMF) dissociates in solution to form monomeric $[Mn(S_2C_2H_4)_2(solv)_2]^-$. Cyclic voltammetry of these species are in accord with an E_iC_i mechanism, in which the initial reduction product, $[Mn(S_2C_2H_4)_2(solv)_2]^{2-}$, rapidly and irreversibly converts to $[Mn(S_2C_2H_4)_2]^{2-}$. This species is irreversibly oxidized to $[Mn(S_2C_2H_4)_2(solv)_2]^-$ at less cathodic potentials. The large ΔE_p values (0.52 V (acetonitrile), 0.76 V (DMF)) are consistent with different electroactive orbitals of $[Mn(S_2C_2H_4)_2]^{2-}$ and $[Mn(S_2C_2H_4)_2(solv)_2]^-$ required by tetrahedral and six-coordinate structures, respectively. Spectral evidence is presented for Mn(III) species of the type $[Mn(S_2C_2H_4)_2(py)_2]^-$ as the green chromophores formed in an aerobic colorimetric test for vicinal dithiols developed some years earlier.

Introduction

Metal thiolates have been defined as those molecules that, if mononuclear, involve ligation by RS^- groups only and, if polynuclear, contain as skeletal ligands these groups only.[2] The emerging chemistry of this class of compounds has already revealed a rich structural diversity and certain reactivity features that have led to the synthesis of significant types of metal–sulfide–thiolate clusters. With restriction to the transition series M(II,III) complexes and exclusion of organometallics, some stereochemical regularities are apparent. (i) The divalent mono-, bi-, and trinuclear complexes $[M(SR)_4]^{2-}$[3-5] (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II)), $[M_2(\mu\text{-}SR)_2(SR)_4]^{2-}$[6,7] (M = Mn(II), Fe(II), Co(II), Zn(II), Cd(II)), and $[Fe_3(\mu\text{-}SR)_3Cl_6]^{3-}$,[6] respectively, contain (distorted) tetrahedral M(II) coordination sites. The entire mononuclear series with R = Ph has been structurally characterized.[3,4] (ii) The most frequent structure thus far encountered in polynuclear molecules is based on the adamantane-like $M_4(\mu\text{-}SR)_6$ cage, which with idealized T_d stereochemistry contains a tetrahedron of metal atoms and an octahedron of bridging sulfur atoms. This structural type has been demonstrated for $[M_4(SPh)_{10}]^{2-}$ (M = Fe(II),[2,8] Co(II),[9] Zn(II),[10] Cd(II)[11]), $[Fe_4(SPh)_6Cl_4]^{2-}$,[12] $[Zn_4(SPh)_8Cl_2]^{2-}$,[13] and $[Zn_4(SPh)_8(MeOH)]_n$.[14] (iii) The Fe(III) complexes $[Fe(S_2\text{-}o\text{-xyl})_2]^-$[5] and $[Fe(2,3,5,6\text{-}Me_4C_6HS)_4]^-$[15] are mononuclear and tetrahedral whereas $[Fe_2(edt)_4]^{2-}$ (edt = 1,2-ethanedithiolate) is binuclear and contains five-coordinate Fe(III).[16,17] These structural differences are presumably controlled by ligand constraints. No other molecular M(III)–thiolate complexes of the first transition series have been reported. The utility of metal thiolates as synthetic precursors is well illustrated by reactions of $[Fe(SR)_4]^{2-,-}$, $[Fe_2(SR)_6]^{2-}$, and $[Fe_4(SR)_{10}]^{2-}$ with elemental sulfur or sulfide to yield $[Fe_nS_n(SR)_4]^{2-}$ (n = 2, 4), $[Fe_3S_4(SR)_4]^{3-}$, and $[Fe_6S_9(SR)_2]^{4-}$.[6,18-20] Further, $[Co_4(SPh)_{10}]^{2-}$ and sulfide afford

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$[Co_8S_6(SPh)_8]^{4-}$.[21] Lastly, $[M_4(SPh)_{10}]^{2-}$ (M = Zn(II), Cd(II)) has been shown to react with sulfur, forming the remarkable decanuclear cages $[M_{10}S_4(SPh)_{16}]^{4-}$.[22]

In contrast with the cases of Fe(II), Co(II), and Zn(II) in particular, the chemistry of manganese thiolates is essentially undeveloped. Studies of the reactions of Mn(II) with 2,3-dimercapto-1-propanol (H_2dmp) in aqueous solution have been reported,[23,24] and rather ill-defined complexes with several thiols have been isolated.[25] The only well-characterized species is $[Mn(SPh)_4]^{2-}$.[3] Manganese–sulfur complexes are otherwise primarily confined to those derived from 1,1′-dithio chelate ligands[26] such as dithiocarbamates. The present investigation was initiated as a means of defining the scope of Mn–thiolate complexes and their stereochemical features in light of observations i–iii above and, ultimately, the suitability of such complexes as precursors of new manganese cage and cluster molecules. Reported here are the syntheses, structures, and several additional properties of Mn(II,III) complexes of mono-, bi-, and tetranuclear types.

Experimental Section

Preparation of Compounds. All operations were carried out under strictly anaerobic conditions with use of degassed solvents. Compounds of $[Mn(edt)_2]^{2-}$ are extremely sensitive to oxidation and must be handled accordingly.

(a) $(Me_4N)_2[Mn(SPh)_4]$. A solution of 5.9 g (30 mmol) of $MnCl_2{\cdot}4H_2O$ in 40 mL of ethanol was added to a stirred solution of 75 mmol of sodium benzenethiolate in 100 mL of ethanol. After filtration to remove NaCl, the filtrate was treated with a solution of 5.0 g (32 mmol) of Me_4NBr in 20 mL of water. The white precipitate that appeared initially dissolved on stirring. When the solution was cooled to −20 °C, crystals separated. These were collected by filtration and recrystallized from 60 mL of warm methanol with slow cooling to −20 °C. This material was collected, washed with ethanol and ether, and dried in vacuo; 4.3 g (36% based on thiolate) of product as pink crystals was obtained. Anal. Calcd for $C_{32}H_{44}MnN_2S_4$: C, 60.06; H, 6.93; Mn, 8.59; N, 4.38; S, 20.04. Found: C, 60.09; H, 6.91; Mn, 8.63; N, 4.42; S, 20.07. Crystal data: monoclinic; $a = 9.829$ (3) Å, $b = 14.468$ (5) Å, $c = 12.095$ (3) Å, $\beta = 90.93$ (3)°. In a similar preparation involving 50 mmol of $MnCl_2{\cdot}4H_2O$ and 200 mmol of NaSPh in 180 mL of ethanol, $(Et_4N)_2[Mn(SPh)_4]$ was obtained in 62% yield (based on Mn) as large pink crystals after recrystallization of the precipitate from acetonitrile. This compound was not analyzed.

(b) $(Et_4N)_2[Mn_4(SPh)_{10}]$. A solution of 7.22 g (36.5 mmol) of $MnCl_2{\cdot}4H_2O$ in 50 mL of methanol was added dropwise to a stirred solution of 91.2 mmol of sodium benzenethiolate in 120 mL of methanol. The orange suspension was stirred for 30 min and then treated with a solution of 3.7 g (20 mmol) of $Et_4NCl{\cdot}H_2O$ in 15 mL of methanol. After the mixture was stirred for 10 min, it was cooled to −20 °C, and the liquid was decanted. The amorphous residue was extracted with 60 mL of hot acetonitrile, and the extract was filtered. Evaporation of the dark red filtrate gave a dark red gummy residue that slowly dissolved in methanol. Upon standing, this solution deposited large red-orange crystals, which were collected by filtration and washed with 1:3 v/v acetonitrile/ether and then with ether. After the solid was dried in vacuo, 5.5 g (38%) of brown-red crystalline product was obtained; mp 75 °C dec. Anal. Calcd for $C_{76}H_{90}Mn_4N_2S_2$: C, 58.07; H, 5.77; Mn, 13.98; N, 1.78; S, 20.40. Found: C, 58.42; H, 5.92; Mn, 13.78; N, 2.01; S, 20.68. Crystal data: monoclinic; $a = 15.43$ Å, $b = 13.21$ Å, $c = 41.52$ Å, $\beta = 96.29$°.

(c) $(Me_4N)_2[Mn_4(SPh)_{10}]$. The preparation is similar to (b) but with the precipitant being Me_4NCl. From the methanol solution to which Me_4NCl was added, salmon-colored microcrystalline $(Me_4N)_2[Mn(SPh)_4]$ and large dark red crystals formed. The latter were separated by fractional recrystallization from acetonitrile/ether, affording 2.17 g (10%) of the desired compound, mp 102 °C dec. Anal. Calcd for $C_{68}H_{74}Mn_4N_2S_{10}$: C, 55.95; H, 5.11; Mn, 15.05; N, 1.92; S, 21.95. Found: C, 55.50; H, 5.30; Mn, 14.87; N, 1.68; S, 21.53.

(d) $(Me_4N)_2[Mn(edt)_2]{\cdot}{}^1/_2CH_3CN$. To a solution of 35.7 mmol of disodium 1,2-ethanedithiolate (Na_2edt) in 60 mL of methanol was added dropwise 2.30 g (18.3 mmol) of anhydrous $MnCl_2$ dissolved in 20 mL of methanol. The resulting suspension is slightly yellowish and should not contain any greenish component if the proper degree of anaerobicity is maintained. After the reaction mixture was stirred for 2 h, a solution of 4.17 g (38.0 mmol) of Me_4NCl in 20 mL of methanol was added. The mixture was stirred for 12 h, and the solvent was removed in vacuo. Addition of 40 mL of acetonitrile gave a yellow suspension, which was filtered to remove undissolved salts. Volume reduction in vacuo by ~50%, addition of ether, and cooling to −20 °C gave large yellowish crystals. These were collected by filtration, washed with ether, and dried in vacuo. This procedure afforded 5.96 g (84%) of product as a yellow-brown solid. Analytical data are in reasonable agreement with an acetonitrile hemisolvate formulation. Anal. Calcd for $C_{13}H_{33.5}MnN_{2.5}S_4$: C, 38.25; H, 8.27; Mn, 13.46; N, 8.58; S, 31.42. Found: C, 38.00; H, 7.94; Mn, 13.86; N, 8.82; S, 31.37.

(e) $(Ph_4P)_2[Mn(edt)_2]$. A solution of 0.92 g (7.3 mmol) of anhydrous $MnCl_2$ in 10 mL of methanol was added dropwise to a stirred solution of 2.2 g (16 mmol) of Na_2edt in 50 mL of methanol. After 2 h, a solution of 6.0 g (16 mmol) of Ph_4PCl in 10 mL of methanol was added. The methanol was removed in vacuo and was replaced with 40 mL of acetonitrile. The mixture was filtered, and the yellow filtrate was reduced to ~20 mL in vacuo. Addition of ether and cooling of the solution to −20 °C caused separation of large orange-yellow crystals. These were collected by filtration, washed with ether, and dried in vacuo; 2.8 g (42%) of product was obtained. Anal. Calcd for $C_{52}H_{48}MnP_2S_4$: C, 68.05; H, 5.23; Mn, 5.97; P, 6.75; S, 13.98. Found: C, 67.62; H, 5.17; Mn, 6.04; P, 6.68; S, 14.23.

(f) $(Ph_4P)_2[Mn_2(edt)_4]$. The yellow filtrate in the preparation of $(Ph_4P)_2[Mn(edt)_2]$ was treated with ~300 mL of air, injected by syringe into a flask containing the filtrate. The solution immediately turned dark green, and small, flaky microcrystals separated. These were collected by filtration, washed with ether, and dried in vacuo. Recrystallization of this material from DMF/ether afforded 1.6 g (38%) of dark green microcrystals. Anal. Calcd for $C_{56}H_{56}Mn_2P_2S_8$: C, 58.12; H, 4.88; Mn, 9.49; P, 5.35; S, 22.16. Found: C, 57.93; H, 4.67; Mn, 9.63; P, 5.28; S, 22.22. The Et_4N^+ salt was prepared in an analogous fashion by oxidation of an acetonitrile solution of $(Et_4N)_2[Mn(edt)_2]$, obtained by use of Et_4NCl in preparation d. The compound was not analyzed, but it was identified by X-ray analysis.

Collection and Reduction of X-ray Data. Orange-yellow, extremely air-sensitive crystals of $(Me_4N)_2[Mn(edt)_2]{\cdot}MeCN$ (**1**) were grown by diffusion of diethyl ether into an acetonitrile solution at room temperature. A crystal of suitable size was cut from a large crystal. Red-orange, air-sensitive crystals of $(Me_4N)_2[Mn_4(SPh)_{10}]$ (**2**) and green air-sensitive crystals of $(Et_4N)_2[Mn_2(edt)_4]$ (**3**) were grown by similar procedures. Rectangular block-like crystals of **1**, **2**, and **3** were lodged in glass capillaries and sealed under argon. Data were collected at ambient temperature by using a Nicolet R3m four-circle automated diffractometer and graphite-monochromatized Mo K$\bar{\alpha}$ radiation. The orientation matrix and unit cell dimensions of each compound were calculated by least-squares treatment of 25 machine-centered reflections ($18° \leq 2\theta \leq 30°$). The data collection and crystal parameters are summarized in Table I. Three check reflections, measured every 120 (**1**), 123 (**2**), or 60 (**3**) reflections, exhibited no significant decay over the duration of data collection. The data were processed with the program XTAPE of the SHELXTL program package (Nicolet XRD Corporation, Fremont, CA). Empirical absorption corrections were applied by the program XEMP. Maximum and minimum transmission factors are 0.65 and 0.56 for **1**, 0.78 and 0.74 for **2**, and 0.73 and 0.68 for **3**. Extinction corrections were not made. The systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) uniquely define the nonstandard monoclinic space group $P2_1/n$ for **1** and **3**. The triclinic centrosymmetric space group $P\bar{1}$ for **2** was selected after analysis of intensities and axial photographs, which revealed no diffraction symmetry higher than C_i ($\bar{1}$). This compound is isomorphous with $(Me_4N)_2[Co_4(SPh)_{10}]$.[9] The space groups were confirmed by successful solution and refinement of the structures.

Solution and Refinement of the Structures. The direct-methods program SOLV revealed the positions of the MnS_4 portions of **1** and **3**; these were confirmed by their locations in Patterson maps. Since

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for Mn Thiolates

quantity	$(Me_4N)_2[Mn(S_2C_2H_4)_2]\cdot MeCN$	$(Me_4N)_2[Mn_4(SPh)_{10}]$	$(Et_4N)_2[Mn_2(S_2C_2H_4)_4]$
formula (mol wt)	$C_{14}H_{35}MnN_3S_4$ (428.65)	$C_{68}H_{74}Mn_4N_2S_{10}$ (1459.74)	$C_{24}H_{56}Mn_2N_2S_8$ (739.17)
a, Å	9.833 (5)	13.184 (3)	12.039 (4)
b, Å	17.325 (7)	23.743 (4)	10.699 (2)
c, Å	13.819 (6)	12.930 (3)	15.012 (3)
α, deg		91.63 (2)	
β, deg	93.43 (2)	113.76 (1)	110.89 (2)
γ, deg		79.53 (2)	
cryst system	monoclinic	triclinic	monoclinic
V, Å^3	2349 (2)	3638 (2)	1807 (1)
Z	4	2	2
d_{calcd}, g/cm^3	1.21	1.33	1.36
d_{obsd}, g/cm^3	1.22	1.34	1.37[a]
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
cryst dimens, mm	0.3 × 0.2 × 0.2	0.42 × 0.35 × 0.28	0.25 × 0.30 × 0.25
radiation (λ = 0.710 69 Å)	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$	Mo $K\bar{\alpha}$
abs coeff, μ, cm^{-1}	8.83	9.65	11.3
scan speed, deg/min	2.0–29.3 ($\theta/2\theta$ scan)	2.0–29.3 ($\theta/2\theta$ scan)	3.0–29.3 ($\theta/2\theta$ scan)
scan range, deg	$2.0 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$	$2.0 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$	$2.2 + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$
bkgd/scan time ratio	0.50	0.50	0.25
data collected	$3° \leq 2\theta \leq 45°$; $+h,+k,\pm l$	$3° \leq 2\theta \leq 46°$; $+h,\pm k,\pm l$	$5° \leq 2\theta \leq 48°$; $+h,+k,\pm l$
total no. of reflcns	4206	10 996	3359
unique data ($I > 3\sigma(I)$)	1893	5787	2175
no. of variables	199	661	199
goodness of fit	1.14	1.31	1.65
R, %	4.4	4.5	4.4
R_w, %	4.5	4.8	4.9

[a] Determined by neutral buoyancy technique in CCl_4/n-hexane.

Z = 2 for **3**, the other half of the dimeric unit was generated by the imposed inversion center. The structure of **2** was solved by isomorphous replacement using as initial coordinates of the Mn_4S_{10} portion of the anion those of the Co(II) analogue.[9] For the three structures, all remaining non-hydrogen atoms were located and their positional parameters were refined by using difference Fourier techniques and blocked-cascade least-squares refinement. Atomic scattering factors were taken from the tabulation of Cromer and Waber;[27] scattering factors were corrected for $\Delta f'$ and $i\Delta f''$ terms. Isotropic refinement of all non-hydrogen atoms converged at 11.5% (**1**), 8.5% (**2**), and 8.4% (**3**). All non-hydrogen atoms of the cations and anions (and the solvate molecule of **1**) were refined with anisotropic thermal parameters. The methylene carbon atoms of the cations of **3** were found to exhibit modest disorder problems. The model used to simulate the disorder included two unique positions for each carbon atom, which refined to occupancy factors of 0.60 and 0.40. The ten phenyl rings of **2** were treated as rigid bodies with fixed C–C distances (1.395 Å). In the last stages of refinement of the three structures, hydrogen atoms with thermal parameters set at 1.2 times that of the bonded carbon atoms and the fixed C–H distance of 0.96 Å were included, except for the hydrogen atoms of the disordered carbon atoms of **3**. Unique data used in the refinement and final R values for all structures are given in Table I. Positional parameters of $[Mn_4(SPh)_{10}]^{2-}$, $[Mn(edt)_2]^{2-}$, and $[Mn_2(edt)_4]^{2-}$ are listed in Table II, and selected interatomic distances and angles are presented in Tables III–VI. Other structural data are available as supplementary material.[28]

Other Physical Measurements. All measurements were made under strictly anaerobic conditions. Absorption spectra were recorded on a Cary Model 219 spectrophotometer. Magnetic susceptibilities of solid and solution samples were determined by the Faraday method ($HgCo(NCS)_4$ calibrant) and the standard NMR method (Me_4Si reference and sample resonances; spectrometer frequency 300 MHz), respectively. Cyclic voltammograms were obtained by using conventional PAR instrumentation, a glassy-carbon working electrode, a saturated calomel reference electrode, and 0.1 M (n-Bu_4N)(ClO_4) supporting electrolyte.

Results and Discussion

Synthetic Reactions. The first example of a non-organometallic manganese–thiolate complex, $[Mn(SPh)_4]^{2-}$, was prepared in 1975 by the reaction of $[Mn(dts)(SPh)_2]^{2-}$ (dts = dithiosquarate dianion) with excess KSPh in acetonitrile.[29] The synthesis of the parent complex $[Mn(dts)_2]^{2-}$ was described in the same year,[30] and the tetrahedral structure of $[Mn(SPh)_4]^{2-}$, as its Ph_4P^+ salt, was reported subsequently.[3] Here it has been found that $[Mn(SPh)_4]^{2-}$ is more simply prepared by the stoichiometric reaction (1). When conducted

$$MnCl_2\cdot 4H_2O + 4NaSPh \xrightarrow{EtOH} Na_2[Mn(SPh)_4] + 2NaCl + 4H_2O \quad (1)$$

on a 50-mmol scale (in Mn) in 180 mL of ethanol, this reaction afforded the Et_4N^+ salt in 62% purified yield as large pink crystals. Reaction 2 gives the tetranuclear species $[Mn_4(SPh)_{10}]^{2-}$, obtained as the Me_4N^+ (10%) and Et_4N^+ (38%) salts in the indicated purified yields.

$$4MnCl_2\cdot 4H_2O \xrightarrow[MeOH]{10NaSPh} Na_2[Mn_4(SPh)_{10}] + Na_2[Mn(SPh)_4] \quad (2)$$

These rather low yields suggest the formation of at least two products. The compound $(Me_4N)_2[Mn(SPh)_4]$ was in fact isolated in 36% yield (based on thiolate) from a reaction system in ethanol having an initial mole ratio $PhS^-:Mn^{2+}$ = 2.5:1. The observations reflect our experience that in alcohol solvents the mole ratio $RS^-:M^{2+} \geq$ 4:1 affords $[M(SR)_4]^{2-}$ as the main or exclusive product. At lower ratios product mixtures may form, and successful isolation and purification of the desired complex are often dependent on the choice of solvent and countercation.

The affinity of Mn(II) for thiolate ligands was further examined by use of 1,2-ethanedithiolate in reaction 3. The

$$MnCl_2 + 2Na_2edt \xrightarrow[MeCN]{MeOH} Na_2[Mn(edt)_2] + 2NaCl \quad (3)$$

$$Na_2[Mn(edt)_2] \xrightarrow[MeCN]{O_2} Na_2[Mn_2(edt)_4] \quad (4)$$

extremely oxygen-sensitive bis chelate product complex was obtained as its Me_4N^+ (84%) and Ph_4P^+ (42%) salts. Aerial oxidation of $[Mn(edt)_2]^{2-}$ in solution afforded the dark green

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[28] See paragraph at end of paper regarding supplementary material.

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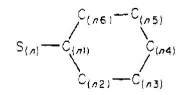
Table II. Positional Parameters of $[Mn(S_2C_2H_4)_2]^{2-}$, $[Mn_2(S_2C_2H_4)_4]^{2-}$, and $[Mn_4(SPh)_{10}]^{2-}$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			$[Mn(S_2C_2H_4)_2]^{2-}$				
Mn	−0.1279 (1)[a]	0.8019 (1)	0.0728 (1)	C(1)	−0.4296 (7)	0.8682 (6)	0.0534 (5)
S(1)	−0.3085 (2)	0.8642 (1)	0.1581 (1)	C(2)	−0.3745 (8)	0.8873 (5)	−0.0404 (5)
S(2)	−0.2501 (2)	0.8221 (1)	−0.0826 (1)	C(3)	0.1301 (6)	0.6951 (4)	0.1411 (5)
S(3)	−0.0510 (2)	0.6714 (1)	0.1123 (1)	C(4)	0.1862 (7)	0.7595 (4)	0.0865 (5)
S(4)	0.1024 (2)	0.8521 (1)	0.0989 (1)				
			$[Mn_2(S_2C_2H_4)_4]^{2-}$				
Mn	0.1061 (1)	0.5724 (1)	0.4571 (1)	C(1)	−0.1762 (4)	0.6160 (6)	0.3258 (4)
S(1)	−0.0835 (1)	0.6314 (1)	0.4527 (1)	C(2)	−0.1352 (4)	0.5125 (6)	0.2778 (3)
S(2)	0.0228 (1)	0.5254 (1)	0.2960 (1)	C(3)	0.3459 (4)	0.6916 (6)	0.6062 (4)
S(3)	0.1891 (1)	0.7339 (1)	0.5634 (1)	C(4)	0.3844 (4)	0.6541 (6)	0.5243 (4)
S(4)	0.2937 (1)	0.5247 (1)	0.4570 (1)				
			$[Mn_4(SPh)_{10}]^{2-}$				
Mn(1)	0.9525 (1)	0.7395 (1)	−0.1529 (1)	C(46)	1.0252 (4)	0.5784 (2)	−0.2965 (4)
Mn(2)	0.6166 (1)	0.8247 (1)	−0.2559 (1)	C(51)	0.8530 (4)	0.8831 (2)	−0.2294 (4)
Mn(3)	0.7711 (1)	0.7242 (1)	0.0405 (1)	C(52)	0.9376 (4)	0.8933 (2)	−0.2612 (4)
Mn(4)	0.6915 (1)	0.6466 (1)	−0.2702 (1)	C(53)	0.9807 (4)	0.9437 (2)	−0.2323 (4)
S(1)	0.7174 (1)	0.6410 (1)	−0.0713 (1)	C(54)	0.9391 (4)	0.9840 (2)	−0.1716 (4)
S(2)	0.9507 (1)	0.7348 (1)	0.0362 (1)	C(55)	0.8544 (4)	0.9738 (2)	−0.1397 (4)
S(3)	0.6331 (1)	0.8118 (1)	−0.0601 (1)	C(56)	0.8114 (4)	0.9234 (2)	−0.1687 (4)
S(4)	0.8683 (1)	0.6645 (1)	−0.2731 (1)	C(61)	0.4958 (3)	0.7478 (2)	−0.4852 (4)
S(5)	0.8002 (1)	0.8184 (1)	−0.2666 (1)	C(62)	0.5518 (3)	0.7179 (2)	−0.5471 (4)
S(6)	0.5499 (1)	0.7370 (1)	−0.3353 (1)	C(63)	0.5043 (3)	0.7244 (2)	−0.6649 (4)
S(7)	0.6305 (2)	0.5643 (1)	−0.3653 (2)	C(64)	0.4007 (3)	0.7607 (2)	−0.7208 (4)
S(8)	0.5087 (2)	0.9131 (1)	−0.3552 (2)	C(65)	0.3446 (3)	0.7907 (2)	−0.6589 (4)
S(9)	1.1298 (1)	0.7407 (1)	−0.1600 (2)	C(66)	0.3922 (3)	0.7842 (2)	−0.5411 (4)
S(10)	0.7725 (2)	0.7034 (1)	0.2195 (2)	C(71)	0.6372 (3)	0.5674 (2)	−0.5002 (4)
C(11)	0.5910 (4)	0.6262 (2)	−0.0664 (4)	C(72)	0.7336 (3)	0.5781 (2)	−0.5100 (4)
C(12)	0.5624 (4)	0.5727 (2)	−0.0981 (4)	C(73)	0.7368 (3)	0.5805 (2)	−0.6164 (4)
C(13)	0.4663 (4)	0.5591 (2)	−0.0920 (4)	C(74)	0.6435 (3)	0.5721 (2)	−0.7128 (4)
C(14)	0.3988 (4)	0.5991 (2)	−0.0542 (4)	C(75)	0.5472 (3)	0.5613 (2)	−0.7030 (4)
C(15)	0.4274 (4)	0.6526 (2)	−0.0226 (4)	C(76)	0.5440 (3)	0.5590 (2)	−0.5967 (4)
C(16)	0.5235 (4)	0.6662 (2)	−0.0287 (4)	C(81)	0.3632 (5)	0.9133 (2)	−0.3891 (4)
C(21)	1.0565 (3)	0.6745 (2)	0.1069 (4)	C(82)	0.2828 (5)	0.9391 (2)	−0.4921 (4)
C(22)	1.0327 (3)	0.6261 (2)	0.1448 (4)	C(83)	0.1683 (5)	0.9427 (2)	−0.5182 (4)
C(23)	1.1186 (3)	0.5789 (2)	0.1952 (4)	C(84)	0.1341 (5)	0.9204 (2)	−0.4414 (4)
C(24)	1.2282 (3)	0.5801 (2)	0.2075 (4)	C(85)	0.2146 (5)	0.8945 (2)	−0.3384 (4)
C(25)	1.2521 (3)	0.6285 (2)	0.1696 (4)	C(86)	0.3291 (5)	0.8910 (2)	−0.3123 (4)
C(26)	1.1662 (3)	0.6757 (2)	0.1192 (4)	C(91)	1.1908 (3)	0.7956 (2)	−0.0748 (4)
C(31)	0.6826 (3)	0.8744 (2)	0.0047 (4)	C(92)	1.1414 (3)	0.8290 (2)	−0.0108 (4)
C(32)	0.6091 (3)	0.9272 (2)	−0.0287 (4)	C(93)	1.1926 (3)	0.8724 (2)	0.0521 (4)
C(33)	0.6447 (3)	0.9770 (2)	0.0207 (4)	C(94)	1.2932 (3)	0.8825 (2)	0.0511 (4)
C(34)	0.7538 (3)	0.9741 (2)	0.1035 (4)	C(95)	1.3426 (3)	0.8491 (2)	−0.0129 (4)
C(35)	0.8272 (3)	0.9213 (2)	0.1369 (4)	C(96)	1.2914 (3)	0.8056 (2)	−0.0758 (4)
C(36)	0.7916 (3)	0.8715 (2)	0.0875 (4)	C(101)	0.8718 (4)	0.7349 (2)	0.3315 (3)
C(41)	0.9722 (4)	0.6003 (2)	−0.2260 (4)	C(102)	0.9457 (4)	0.7660 (2)	0.3169 (3)
C(42)	1.0006 (4)	0.5722 (2)	−0.1221 (4)	C(103)	1.0186 (4)	0.7913 (2)	0.4089 (3)
C(43)	1.0821 (4)	0.5221 (2)	−0.0887 (4)	C(104)	1.0176 (4)	0.7854 (2)	0.5155 (3)
C(44)	1.1351 (4)	0.5002 (2)	−0.1592 (4)	C(105)	0.9437 (4)	0.7544 (2)	0.5301 (3)
C(45)	1.1067 (4)	0.5283 (2)	−0.2631 (4)	C(106)	0.8708 (4)	0.7291 (2)	0.4381 (3)

[a] Estimated standard deviations in parentheses in this and succeeding tables. [b] Phenyl group numbering scheme (n = 1-10):



binuclear complex $[Mn_2(edt)_4]^{2-}$, which was isolated as its Et_4N^+ and Ph_4P^+ (38%) salts. The structures of the three new complexes were established by X-ray analysis.

Structures. The crystal structures of the following three compounds consist of well-separated cations and anions. Cation and solvate molecule structures are unexceptional and are not described.

(a) $(Me_4N)_2[Mn_4(SPh)_{10}]$. The structure of the Mn_4S_{10} portion of the anion is shown in Figure 1, and a stereoview of the entire anion is presented in Figure 2. The adamantane-like stereochemistry of the $Mn_4(\mu\text{-}S)_6$ cage, consisting of a nearly regular Mn_4 tetrahedron and a highly distorted S_6 octahedron, is immediately evident. Selected interatomic distances and angles are collected in Table III. The main structural features are briefly summarized. (i) The Mn_4 and S_6 fragments contain nonbonded component atoms, as indicated by the mean Mn···Mn and $S_b \cdots S_b$ distances of 4.17 (3) and 3.92 (15) Å, respectively. (ii) Departure of the cage from actual T_d symmetry is clearly reflected by variations in all distances and angles that would be equivalent under this symmetry. Prominent examples are the $S_b \cdots S_b$ distances (3.607 (3)–4.111 (4) Å) and S_b–Mn–S_b angles (94.3 (1)–112.9 (1)°), which span the indicated ranges. (iii) Each Mn(II) atom is terminally coordinated by one benzenethiolate group, resulting in distorted-tetrahedral stereochemistry at each site. Large deviations from C_{3v} local symmetry are evident from the ranges of S_b–Mn–S_t and S_b–Mn–S_b angles at each metal site. (iv) Mn–S_b distances are 0.08 Å longer than Mn–S_t distances. The

Table III. Selected Interatomic Distances (Å) and Angles (deg) of $[Mn_4(SPh)_{10}]^{2-}$

	$Mn-S_t$[a]		
Mn(1)-S(9)	2.382 (3)	Mn(4)-S(7)	2.368 (7)
Mn(2)-S(8)	2.382 (3)	mean	2.376 (7)[b]
Mn(3)-S(10)	2.372 (3)		
	$Mn-S_b$[a]		
Mn(1)-S(2)	2.460 (3)	Mn(3)-S(2)	2.449 (3)
Mn(1)-S(4)	2.448 (2)	Mn(3)-S(3)	2.489 (2)
Mn(1)-S(5)	2.472 (2)	Mn(4)-S(1)	2.458 (3)
Mn(2)-S(3)	2.475 (3)	Mn(4)-S(4)	2.459 (3)
Mn(2)-S(5)	2.458 (3)	Mn(4)-S(6)	2.486 (2)
Mn(2)-S(6)	2.444 (3)	mean	2.46 (2)
Mn(3)-S(1)	2.454 (3)		
	Mn· · ·Mn		
Mn(1)-Mn(2)	4.198 (3)	Mn(2)-Mn(4)	4.180 (3)
Mn(1)-Mn(3)	4.158 (3)	Mn(3)-Mn(4)	4.186 (3)
Mn(1)-Mn(4)	4.169 (3)	mean	4.17 (3)
Mn(2)-Mn(3)	4.122 (3)		
	$S_b\cdots S_b$		
S(1)-S(2)	3.903 (4)	S(3)-S(5)	4.111 (4)
S(1)-S(3)	4.021 (4)	S(3)-S(6)	3.771 (3)
S(1)-S(4)	3.968 (4)	S(4)-S(5)	3.607 (3)
S(1)-S(6)	3.777 (3)	S(4)-S(6)	3.996 (4)
S(2)-S(3)	3.946 (4)	S(5)-S(6)	3.908 (4)
S(2)-S(4)	4.091 (4)	mean	3.92 (15)
S(2)-S(5)	3.994 (4)		
	S_b-Mn-S_t		
S(9)-Mn(1)-S(2)	116.8 (1)	S(10)-Mn(3)-S(2)	117.1 (1)
S(9)-Mn(1)-S(4)	108.5 (1)	S(10)-Mn(3)-S(3)	113.5 (1)
S(9)-Mn(1)-S(5)	114.1 (1)	S(7)-Mn(4)-S(1)	111.5 (1)
S(8)-Mn(2)-S(3)	116.6 (1)	S(7)-Mn(4)-S(4)	114.2 (1)
S(8)-Mn(2)-S(5)	104.2 (1)	S(7)-Mn(4)-S(6)	114.9 (1)
S(8)-Mn(2)-S(6)	117.1 (1)	mean	112.8
S(10)-Mn(3)-S(1)	105.4 (1)		
	S_b-Mn-S_b		
S(4)-Mn(1)-S(2)	112.9 (1)	S(3)-Mn(3)-S(1)	108.9 (1)
S(5)-Mn(1)-S(2)	108.2 (1)	S(3)-Mn(3)-S(2)	106.1 (1)
S(5)-Mn(1)-S(4)	94.3 (1)	S(4)-Mn(4)-S(1)	107.6 (1)
S(5)-Mn(2)-S(3)	112.9 (1)	S(6)-Mn(4)-S(1)	99.6 (1)
S(6)-Mn(2)-S(3)	100.1 (1)	S(6)-Mn(4)-S(4)	107.8 (1)
S(6)-Mn(2)-S(5)	105.7 (1)	mean	105.8
S(2)-Mn(3)-S(1)	105.5 (1)		
	$Mn-S_b-Mn$		
Mn(3)-S(1)-Mn(4)	116.9 (1)	Mn(1)-S(5)-Mn(2)	116.8 (1)
Mn(1)-S(2)-Mn(3)	115.8 (1)	Mn(2)-S(6)-Mn(4)	115.9 (1)
Mn(2)-S(3)-Mn(3)	112.2 (1)	mean	115.7
Mn(1)-S(4)-Mn(4)	116.3 (1)		
	S-C		
range	1.772 (5)- 1.788 (6)	mean	1.781 (6)

[a] t = terminal, b = bridging ligand. [b] In this and succeeding tables, the standard deviation of the mean is estimated as $\sigma \approx s = [(\Sigma x_i^2 - n\bar{x}_i^2)/(n-1)]^{1/2}$.

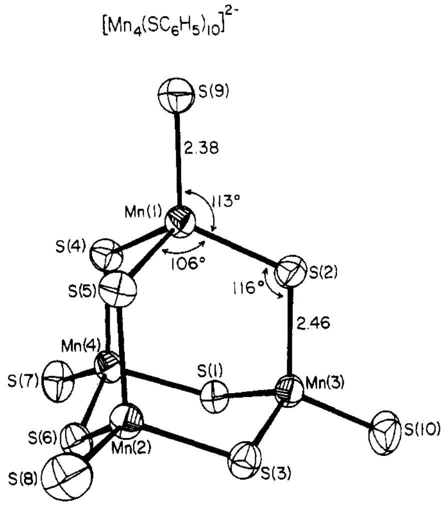


Figure 1. Structure of $[Mn_4(SPh)_{10}]^{2-}$ (phenyl groups omitted) showing 50% probability ellipsoids, the atom-numbering scheme, and mean values of independent bond distances and angles under idealized T_d symmetry.

mean of the latter values, 2.376 (7) Å, is apparently somewhat shorter than that (2.442 (15) Å) in $[Mn(SPh)_4]^{2-}$.[3] (v) The six axial phenyl groups in the four chair-type $Mn_3(\mu\text{-}S)_3$ rings of the cage are found in the 2-2-1-1 pattern, defined by the number of axial substituents in each ring.

Among transition-element thiolates, $[Mn_4(SPh)_{10}]^{2-}$ is the seventh species shown to possess adamantane-like cage stereochemistry.[2,8-14] All exhibit structural properties similar to (i)-(iv), but with different quantitative measures. Selected structural features of six discrete cages are set out in Table IV. Insufficient data have been reported for $[Zn_4(SPh)_{10}]^{2-}$[10] to allow its inclusion. Complexes are listed in order of increasing Shannon M(II) tetrahedral radii.[31] As observed earlier,[2] variable extents of cage distortion from T_d symmetry and different axial group patterns make precise metric comparisons somewhat unrewarding. However, mean bonded (not listed) and nonbonded distances follow trends expected from increases in M(II) radii. The same is true of M_4 and S_6 volumes, which have been calculated from atomic coordinates, with the exception of small inversions of S_6 volumes in the Zn(II) and Fe(II) cases. Experimental volume ratios (given in order of compound listing) scaled to $[Co_4(SPh)_{10}]^{2-}$ agree reasonably well with calculated values (also scaled to $[Co_4(SPh)_{10}]^{2-}$) on the assumptions of T_d symmetry and dimensional changes arising from differences in M(II) radii only.[2] Although $[Mn_4(SPh)_{10}]^{2-}$ is substantially larger than its Co(II) analogue, it does not represent a size limit. We have recently demonstrated the same cage structure for $[Cd_4(SPh)_{10}]^{2-}$,[11] whose M_4 and S_6 volumes are 36% and 29% larger, respectively, than those of $[Co_4(SPh)_{10}]^{2-}$, the smallest cage. In addition to the foregoing cases, adamantane-like stereochemistry is a frequent feature of oxo and sulfido compounds of the elements of groups 4A and 5A. With the structural determination of $[Ga_4S_{10}]^{8-}$, $[In_4S_{10}]^{8-}$, and $[In_4Se_{10}]^{8-}$,[32] this stereochemistry has been shown to extend to group 3A cages as well.

(b) $(Me_4N)_2[Mn(edt)_2]\cdot MeCN$. Bond distance and angle data are listed in Table V. The structure of $[Mn(edt)_2]^{2-}$ is provided in Figure 3. The complex is nonplanar and features two gauche chelate rings, a 92.3° dihedral angle between the two MnS_2 planes, and a $Mn(II)-S_4$ coordination unit that closely approaches D_{2d} symmetry. The four Mn-S bond lengths, which average to 2.432 (7) Å, are nearly identical, and S-Mn-S angles involving atoms of the same and different chelate ring(s) have mean values of 91.5 and 119.2°, respectively.

Relatively few bis chelate Mn(II) complexes have been characterized,[29,33-40] the majority of which are derived from

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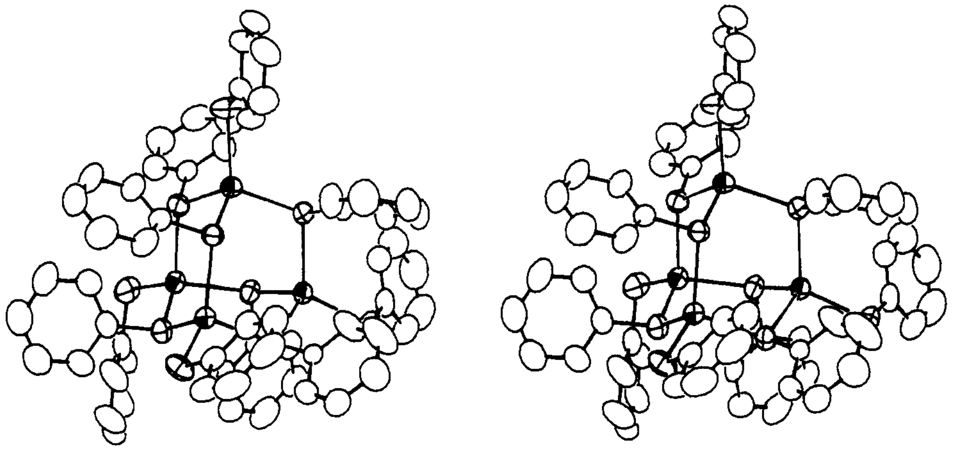

Figure 2. Stereoview of the structure of $[Mn_4(SPh)_{10}]^{2-}$ with 50% probability ellipsoids of Mn and S atoms depicted.

Table IV. Comparative Structural Features of Cage Complexes

	dist, Å		vol,[f] Å^3			
compd[a]	M···M	$S_b \cdots S_b$	M_4	S_6	axial group pattern	ref
$[Co_4(SPh)_{10}]^{2-}$ [c]	3.87 (2)	3.74 (14)	6.83	24.62	2-2-1-1	9
$[Zn_4(SPh)_8Cl_2]^{2-}$ [c]	3.90 (5)	3.81 (12)	7.00	26.13	2-2-1-1	13
$[Fe_4(SPh)_{10}]^{2-}$ [c]	3.94 (5)	3.81 (19)	7.18	26.09	3-2-1-0	2
$[Fe_4(SPh)_6Cl_4]^{2-}$ [d]	3.94 (4)	3.79 (18)	7.21	25.72	3-2-1-0	12
$[Mn_4(SPh)_{10}]^{2-}$ [c]	4.17 (3)	3.92 (15)	8.54	28.28	2-2-1-1	*b*
$[Cd_4(SPh)_{10}]^{2-}$ [e]	4.30 (10)	4.09 (22)	9.31	31.78	2-2-1-1	11

[a] Shannon tetrahedral radii:[30] Co(II), 0.72; Zn(II), 0.74; Fe(II), 0.77; Mn(II), 0.80; Cd(II), 0.92 Å. [b] This work. [c] Me_4N^+ salt. [d] Ph_4P^+ salt. [e] $(Et_4N^+)(Et_3NH^+)$ salt. [f] Ratios of observed volumes (ratios scaled to $[Co_4(SPh)_{10}]^{2-}$ are as follows. For M_4: 1:1.02:1.05:1.06:1.25:1.36 (1:1.03:1.08:1.08:1.13:1.34). For S_6: 1:1.06:1.06:1.04:1.15:1.29 (1:1.02:1.06:1.06:1.11:1.28).

Table V. Selected Interatomic Distances (Å) and Angles (deg) of $[Mn(S_2C_2H_4)_2]^{2-}$

Mn-S(1)	2.441 (2)	S(1)-Mn-S(2)	91.6 (1)
Mn-S(2)	2.423 (2)	S(3)-Mn-S(4)	91.4 (1)
Mn-S(3)	2.435 (2)	mean	91.5
Mn-S(4)	2.433 (2)	S(1)-Mn-S(3)	121.9 (1)
mean	2.432 (7)	S(1)-Mn-S(4)	117.9 (1)
S(1)-C(1)	1.819 (7)	S(2)-Mn-S(3)	117.6 (1)
S(2)-C(2)	1.791 (8)	S(2)-Mn-S(4)	119.2 (1)
S(3)-C(3)	1.845 (6)	mean	119.2
S(4)-C(4)	1.815 (6)	Mn-S(1)-C(1)	95.4 (3)
mean	1.82 (2)	Mn-S(2)-C(2)	96.6 (2)
C(1)-C(2)	1.472 (11)	Mn-S(3)-C(3)	97.1 (2)
C(3)-C(4)	1.474 (9)	Mn-S(4)-C(4)	95.4 (2)
S(1)-S(2)	3.484 (3)	mean	96.1
S(3)-S(4)	3.485 (3)	S(1)-Mn-S(2)/S(3)-Mn-S(4)	92.3
S(1)-S(3)	4.259 (3)	S(1)-C(1)-C(2)/C(1)-C(2)-S(2)	60.8
S(1)-S(4)	4.176 (3)	S(3)-C(3)-C(4)/C(3)-C(4)-S(4)	59.3
S(2)-S(3)	4.154 (3)		
S(2)-S(4)	4.186 (3)		
mean	4.19 (5)		

Table VI. Selected Interatomic Distances (Å) and Angles (deg) of $[Mn_2(S_2C_2H_4)_4]^{2-}$

Mn···Mn′	3.596 (3)	S(1)-Mn-S(1′)	87.7 (1)
Mn-S(1)	2.346 (2)	Mn-S(1)-Mn′	92.3 (1)
Mn-S(1′)	2.632 (2)	S(1)-Mn-S(2)	88.6 (1)
Mn-S(2)	2.321 (2)	S(3)-Mn-S(4)	89.1 (1)
Mn-S(3)	2.323 (2)	S(1)-Mn-S(3)	89.7 (1)
Mn-S(4)	2.316 (2)	S(2)-Mn-S(4)	90.6 (1)
mean	2.320 (4)	S(1′)-Mn-S(2)	105.7 (1)
S(1)-C(1)	1.840 (5)	S(1′)-Mn-S(3)	111.2 (1)
S(2)-C(2)	1.829 (6)	S(1′)-Mn-S(4)	95.6 (1)
S(3)-C(3)	1.821 (5)	S(1)-Mn-S(4)	176.7 (1)
S(4)-C(4)	1.828 (6)	S(2)-Mn-S(3)	143.0 (1)
mean	1.830 (8)	Mn-S(1)-C(1)	103.3 (2)
C(1)-C(2)	1.497 (9)	Mn-S(2)-C(2)	102.2 (2)
C(3)-C(4)	1.515 (10)	Mn-S(3)-C(3)	101.3 (2)
S(1)-S(1′)	3.455 (3)	Mn-S(4)-C(4)	102.9 (2)
S(1)-S(2)	3.953 (3)	S(1)-Mn-S(1′)/(S(1)-Mn-S(2)	74.2
S(3)-S(4)	3.254 (3)	S(1)-Mn-S(2)/S(3)-Mn-S(4)	142.9
		S(1)-C(1)-C(2)/C(1)-C(2)-S(2)	52.6
		S(3)-C(3)-C(4)/C(3)-C(4)-S(4)	57.2

1,1′-dithio ligands.[26,37-40] Subnormal magnetic moments of a number of Mn(II)–S_4 complexes in the solid state[38,40] have been taken as indicators of intermolecular association, as demonstrated for polymeric octahedral $Mn(S_2CNEt_2)_2$.[39,41] Other than $[Mn(edt)_2]^{2-}$, the only discrete Mn(II)–S_4 complex of crystallographically proven structure is $Mn(SPPh_2NPh_2PS)_2$.[36] This molecule is tetrahedral with a mean Mn–S bond distance of 2.44 (1) Å and S–Mn–S bond angles of 106.3–112.1°. The ligand bite (S···S) distance of ~4.0 Å in the six-membered rings accommodates angles near the tetrahedral value. In $[Mn(edt)_2]^{2-}$ the shorter bite distance (~3.5 Å) in five-membered rings affords chelate ring bond angles nearer 90°. Ligands with these dimensional features tend to stabilize planar structures in the absence of overriding ligand repulsion and ligand field stabilization effects. The

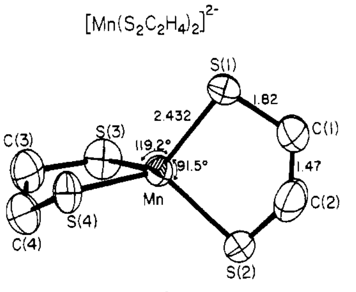

Figure 3. Structure of $[Mn(edt)_2]^{2-}$ showing 50% probability ellipsoids, the atom-numbering scheme, and mean values of selected bond distances and angles.

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(40) Eisman, G. A.; Reiff, W. M. *Inorg. Chem.* **1981**, *20*, 3481.

(41) Note that the claim that $Mn(S_2CNEt)_2$ has a quartet ground state and a planar structure (Lahiry, S.; Anand, V. K. *J. Chem. Soc. D* **1971**, 1111) has been disproven.[38,39]

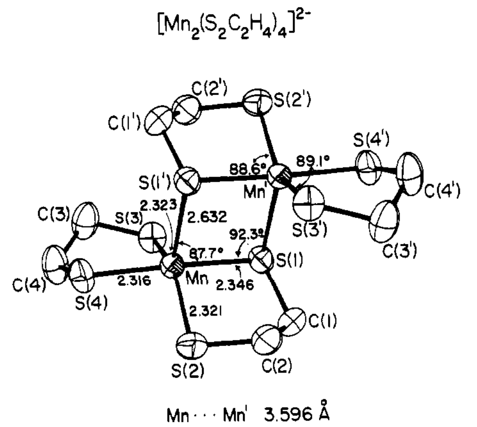

Figure 4. Structure of $[Mn_2(edt)_4]^{2-}$ showing 50% probability ellipsoids, the atom-numbering scheme, and selected bond distances and angles. Primed and unprimed atoms are related by an inversion center.

latter effect is absent in the high-spin Mn(II) complex but not in its Co(II) and Ni(II) analogues. In the brief $[M(edt)_2]^{2-}$ series, the stereochemical pattern M = Mn(II) (tetrahedral), Co(II) (tetrahedral[42]), and Ni(II) (planar[42]) conforms to that usually found in structurally unconstrained bis chelates.[35] Planar Mn(II) is known only in complexes where this structure is enforced (e.g., manganese(II) phthalocyanine[43]).

(c) $(Et_4N)_2[Mn_2(edt)_4]$. The structure of the anion, shown in Figure 4, is dimeric with the halves related by an imposed symmetry center.[44] Interatomic distances and angles are collected in Table VI. The mode of association is of the lateral type wherein two monomers dimerize by bridging through one sulfur atom of each, forming a nearly rectangular $Mn_2(\mu\text{-}S)_2$ unit that contains five-coordinate Mn(III). Monomers are joined by two Mn–S bonds of length 2.632 (2) Å. Within each monomer the Mn–S chelate ring bond involved in bridging is only slightly elongated (by ~0.03 Å) compared to terminal Mn–S bonds (~2.32 Å). The Mn···Mn separation of 3.596 (3) Å places the atoms beyond direct metal–metal bonding range. Chelate rings adopt the gauche configuration. The MnS_5 coordination unit does not conform to either the square-pyramidal (SP) or trigonal-bipyramidal (TBP) limiting configurations but does approach the latter somewhat more closely. In the SP description S(1′) is axial, and in the TBP arrangement this atom is equatorial with S(1,4) axial. The four nearly equal Mn–S(1–4) bond lengths conform to a SP configuration, but the basal atoms S(1–4) are decidedly nonplanar. Deviations from the least-squares plane are ±0.34 Å with trans atoms having the same sign of displacement from the plane. In terms of bond angles the limiting structures are distinguished only by S(1′)–Mn–S(2), S(1′)–Mn–S(3) (SP 90°, TBP 120° for both), and S(2)–Mn–S(3) (SP 180°, TBP 120°) if the Mn atom is in the SP basal plane. Observed values of the second (111.2 (1)°) and third (143.0 (1)°) angles are closer to the TBP limit. Further, the Mn atom is only 0.050 Å out of the TBP S(1′,2,3) equatorial plane. Deviations from the planes S(1,2,4) and S(1,3,4) are slightly larger, being 0.065 and 0.063 Å, respectively.

The lateral centrosymmetric mode of association involving five-coordinate M(II, III) atoms is a frequent dimeric configuration. Among sulfur-containing chelates, it is found in, e.g., $M_2(S_2CNEt_2)_4$ (M = Fe(II),[45a] Cu(II),[45b] Zn(II)[45c]), $[Fe_2(mnt)_4]^{2-}$,[45d] and $[Fe_2(tfd)_4]^{2-}$.[45e] More pertinent to the present work is $[Fe_2(edt)_4]^{2-}$,[16] which is essentially isostructural with $[Mn_2(edt)_4]^{2-}$. Corresponding M–S bond distances are 0.07–0.13 Å shorter in the Fe(III) structure, the Fe–Fe separation is 3.410 (3) Å, angles agree to <1°, and the $Fe\text{-}S_5$ coordination unit is closer to a TBP than a SP geometry. Although the structure of $[Mn_2(edt)_4]^{2-}$ is not unprecedented, the complex itself is the first authenticated example of a Mn(III) thiolate. It is stable under anaerobic conditions and does not autoxidize, a process that, not unreasonably, was supposed to have hindered development of Mn–S chemistry.[46] However, as will be shown, a stable Mn(III)–thiolate species was in fact generated many years earlier.

Table VII. Manganese-Sulfur Bond Distances

bond[a]	coord no.	dist, Å	compd	ref
$Mn(II)\text{-}S_t$	4	2.37–2.46	$[Mn(SPh)_4]^{2-}$ $[Mn_4(SPh)_{10}]^{2-}$ $Mn(SPPhNPhPS)_2$ $[Mn(S_2C_2H_4)_2]^{2-}$	*b*, 3, 36
$Mn(II)\text{-}(\mu\text{-}S)$	4	2.44–2.49	$[Mn_4(SPh)_{10}]^{2-}$	*b*
$Mn(II)\text{-}S_t$	6	2.51–2.53	$[Mn(S_2CNEt_2)_2]_n$	39
		2.59	MnS, MnS_2	*c*, *d*
$Mn(II)\text{-}(\mu\text{-}S)$	6	2.56–2.79	$[Mn(S_2CNEt_2)_2]_n$	39
$Mn(III)\text{-}S_t$	5	2.32	$[Mn_2(S_2C_2H_4)_4]^{2-}$	*b*
$Mn(III)\text{-}S_t$	6	2.32–2.58	$Mn(S_2CNR_2)_3$ $Mn(PhC(S)N(O)Me)_3$	48 *e*
$Mn(III)\text{-}(\mu\text{-}S)$	5	2.35, 2.63	$[Mn_2(S_2C_2H_4)_4]^{2-}$	*b*
$Mn(IV)\text{-}S_t$	6	2.33	$[Mn(S_2CN(CH_2)_5)_3]^+$	*f*

[a] t = terminal ligand. [b] This work. [c] Offner, F. *Z. Kristallogr.* 1934, *89*, 182. [d] Hückel, W. "Structural Chemistry of Inorganic Compounds"; Elsevier; Amsterdam, 1951; Vol. II, p 589. [e] Freyberg, D. P.; Abu-Dari, K.; Raymond, K. N. *Inorg. Chem.* 1979, *18*, 3037. [f] Brown, K. L.; Golding, R. M.; Healy, P. C.; Jessup, K. J.; Tennant, W. C. *Aust. J. Chem.* 1974, *27*, 2075.

(d) Mn–S Bond Distances. In contrast to the extensive structural chemistry of, e.g., Fe–S complexes in general and Fe thiolates[2,4-8,16,47] in particular, structural data for Mn–S complexes of any type (excluding organometallics) are sparse. Other than those in sulfide lattices, the first Mn–S distances, in $Mn(S_2CNEt_2)_3$, were reported in 1972.[48a] In this investigation, the first examples of Mn(III)–SR and bridging Mn(II)–SR and the second example of terminal Mn(II)–SR distances in thiolate complexes have been determined. As a guide to structural work in this area, all Mn(II–IV)–S bond distances currently available are collected in Table VII. Tetrahedral $Mn(II)\text{-}S_t$ distances in four species fall into a relatively narrow range. Comparisons among other distances are not very informative because of differences in coordination number and ligand charge in the rather small set of data. This is especially true for $Mn(III)\text{-}S_t$ distances in six-coordinate complexes where large Jahn–Teller distortions intervene. Such distortions do not obtain for five-coordinate high-spin Mn(III) sites. The pattern of bond distances in $[Mn_2(edt)_4]^{2-}$ is intrinsic to the lateral dimer structure, a property emphasized by the near-congruency of the structures of this complex and $[Fe_2(edt)_4]^{2-}$.[16]

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(42) Dorfman, J. R.; Costa, T.; Holm, R. H., unpublished results.

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(46) Lawrence, G. D.; Sawyer, D. T. *Coord. Chem. Rev.* **1978**, *27*, 173.

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Table VIII. Properties of Mn-Thiolate Complexes[a]

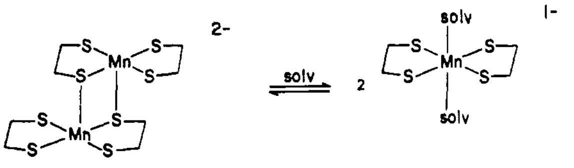
complex	λ_{max} (ϵ_{Mn}[b])	μ_{Mn},[b] μ_B solid	μ_{Mn},[b] μ_B soln	E, V[c]
$[Mn(edt)_2]^{2-}$	460 (17), ~400 (sh), ~360 (sh), ~298 (sh), 455 (14) (DMF)	6.02[d]	5.86	
$[Mn_4(SPh)_{10}]^{2-}$	490 (10), ~470 (sh), 430 (8), ~280 (sh), 258 (8460)	4.61[e]	4.43 (237 K), 4.49 (250 K), 4.57 (268 K), 4.63 (288 K), 4.70 (301 K)	−1.65[g] (irrev)
$[Mn_2(edt)_4]^{2-}$	638 (330), ~395 (sh), 356 (8630), ~295 (sh) (4.0 mM[f])	3.96[e]	4.62 (4.0 mM[f]), 4.84 (3.0 mM[f])	
$[Mn(edt)_2(DMF)_2]^-$	588 (200), 392 (4480), 349 (9850), 292 (3190) (3.6 mM, DMF)		5.08 (2.3 mM, Me_2SO)	−1.37[g] (1−/2−) −0.61[h] (2−/1−) (DMF)
$[Mn(edt)_2(Me_2SO)_2]^-$	596 (240), 394 (4900), 344 (9550), 290 (3230) (3.0 mM, Me_2SO)			
$[Mn(edt)_2(MeCN)_2]^-$	600 (190), ~390 (sh), 355 (10 100), ~295 (sh) (1.6 mM)		5.06 (1.6 mM)	−1.19[g] (1−/2−) −0.67[h] (2−/1−) (1.6 mM)
$[Mn(dmp)_2(H_2O)_2]^-$	555 (400), 390 (5300), 344 (7800) (~5 mM, 1:1 v/v i-PrOH/H_2O)			
$[Mn(dmp)_2(py)_2]^-$	584 (320), 392 (4200), 352 (7700) (~2 mM, 4:1:1 v/v py/i-PrOH/H_2O)			

[a] Data obtained at 298-301 K, solutions are in acetonitrile unless otherwise noted. [b] Per Mn atom. [c] Vs. SCE, 100 mV/s. [d] Ph_4P^+ salt. [e] Et_4N^+ salt. [f] Based on dimer molecular weight. [g] $E_{p,c}$. [h] $E_{p,a}$.

Other Properties. Magnetic, absorption spectral, and electrochemical properties of $[Mn(edt)_2]^{2-}$, $[Mn_4(SPh)_{10}]^{2-}$, and $[Mn_2(edt)_4]^{2-}$ are summarized in Table VIII.

(a) $[Mn(edt)_2]^{2-}$ and $[Mn_4(SPh)_{10}]^{2-}$. These two complexes contain tetrahedral Mn(II). In the solid and solution states $[Mn(edt)_2]^{2-}$ is high spin. Solution absorption spectra of this complex and $[Mn_4(SPh)_{10}]^{2-}$ are poorly resolved compared to those of tetrahedral $Mn(SPPhNPhPS)_2$[36] and $[MnX_4]^{2-}$,[49] whose ligand field bands have been analyzed. The ϵ_{Mn} value of 17 for the 460-nm feature of $[Mn(edt)_2]^{2-}$ and its light yellow-green color in acetonitrile indicate that the complex retains its tetrahedral structure in this solvent. $[Mn(edt)_2]^{2-}$ appears to be completely analogous to $[Mn(dmp)_2]^{2-}$, whose formation in aqueous solution was demonstrated in 1961 by Leussing and Tischer.[24] In acetonitrile solution at 237–301 K, the magnetic susceptbility of $[Mn_4(SPh)_{10}]^{2-}$ decreases with increasing temperature, a behavior indicative of antiferromagnetic interactions.

(b) $[Mn_2(edt)_4]^{2-}$. The solid-state magnetic moment of 3.96 μ_B for this complex, being lower than 4.90 μ_B for spin-only d^4, signifies a spin-coupling interaction.[50] $[Fe_2(edt)_4]^{2-}$ is a molecular antiferromagnet with $J = -54$ cm^{-1}.[17] Magnetic and spectral features of $[Mn_2(edt)_4]^{2-}$ reveal that this complex does not retain its dimeric structure in solution. The complex does not obey Beer's law in acetonitrile but does so in DMF ([Mn] = 0.8–10 mM). Spectra in these solvents are presented in Figure 5. In Me_2SO, where the spectrum is essentially the same as in DMF, the magnetic moment $\mu_{Mn} = 5.08$ μ_B is consistent with mononuclear Mn(III). In acetonitrile μ_{Mn} values are concentration dependent, ranging from 5.06 to 4.62 μ_B for [Mn] = 1.6 and 8.0 mM, respectively. These observations conform to equilibrium 5, presumably initiated by



(5)

solvent-induced cleavage of the two long Mn–S bonds of the dimer (Figure 4). With 3.96 and 5.06 μ_B as limiting values for dimer and solvated monomer, respectively, a 8.0 mM solution in acetonitrile ($\mu_{Mn} = 4.62$ μ_B) is estimated to contain 60% monomer and 40% dimer. The solvated monomer formulation is based on the solvent dependence of the absorption spectra, especially of the weak visible bands at 588 nm (DMF) and 600 nm (acetonitrile). These solutions are dark green at the [Mn] ≥ 1 mM concentration level.

Under conditions where magnetic moments indicate that $[Mn(edt)_2(solv)_2]^-$ is the predominant or only solute species, redox potentials are markedly solvent dependent and charge transfer is irreversible. The extremely large peak separations $\Delta E_p = 0.76$ V (DMF) and 0.52 V (acetonitrile) reveal irreversible processes, but $i_{p,c}/i_{p,a} \cong 1$ indicates that current is

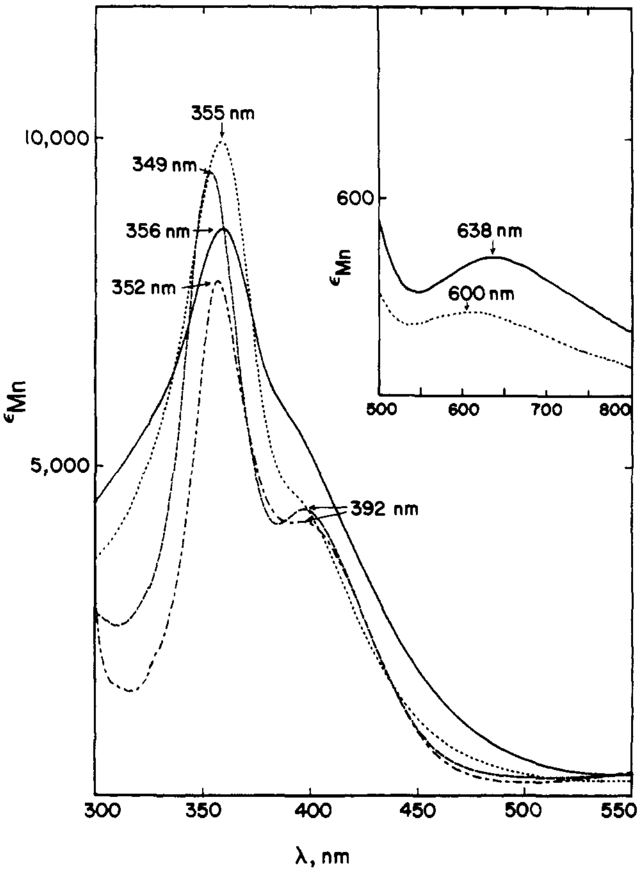


Figure 5. Absorption spectra of Mn(III) complexes: ···, $[Mn(edt)_2(MeCN)_2]^-$; ---, $[Mn(edt)_2(DMF)_2]^-$; -·-·, $[Mn(dmp)_2(py)_2]^-$; —, mixture of $[Mn_2(edt)_4]^{2-}$ + $[Mn(edt)_2(MeCN)_2]^-$.

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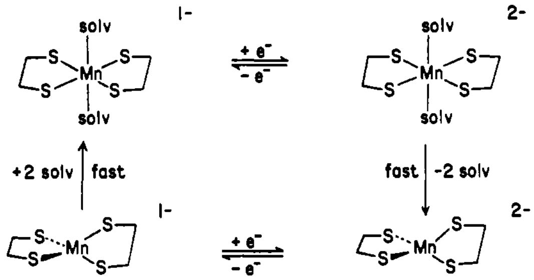
(49) Cotton, F. A.; Goodgame, D. M. L.; Goodgame, M. *J. Am. Chem. Soc.* **1962**, *84*, 167.

(50) The solid-state magnetic properties of this complex and $[Mn_4(SPh)_{10}]^{2-}$ are under investigation and will be reported subsequently.

conserved over the potential interval. The observations are suggestive of an irreversible chemical reaction following charge transfer[51] and are tentatively interpreted in terms of the reaction sequence (6). Reduction of $[Mn(edt)_2(solv)_2]^-$ results in addition of an electron to a σ^* orbital of e_g parentage whereas oxidation of $[Mn(edt)_2]^{2-}$ involves removal of an electron from an approximately nonbonding orbital of t_2 parentage. Differences in the electroactive orbitals are a consequence of the structural change in the fast reaction. This situation may be contrasted to the steps in the electron-transfer series (7).[52] The members are approximately octahedral in structure[48] (Table VI) and are high spin.[52] Each step approaches electrochemical reversibility, with $i_{p,c}/i_{p,a} \simeq 1$ and ΔE_p = 61–88 mV (first step) and 59–70 mV (second step) for a large number of examples. In both steps the electroactive orbitals are σ^* of e_g parentage. The electrochemical behavior of $[M_2(edt)_4]^{2-}$ complexes is under investigation.



(6)

$$[Mn(S_2CNR_2)_3]^- \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Mn(S_2CNR_2)_3]^0 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Mn(S_2CNR_2)_3]^+ \quad (7)$$

Rosenblatt and Jean[23] in 1955 devised a colorimetric test for vicinal dithiols based on the aerobic reaction with $Mn(OAc)_2$ in a pyridine/2-propanol/water solvent mixture. Systems with H_2edt and H_2dmp were reported to develop a green color. Leussing and Tischer[24] also reported that aerobic oxidation of aqueous alkaline $MnCl_2/H_2edt$ systems caused appearance of a green color. We have repeated the work with H_2dmp (using $MnCl_2$) and find a spectrum in reasonable agreement with that reported.[23] Comparison of this spectrum with those of $[Mn(edt)_2(solv)_2]^-$ (Figure 5, Table VIII) leaves little doubt that the green chromophore formed in the presence of pyridine is $[Mn(dmp)_2(py)_2]^-$. This is the initial example, mentioned earlier, of a Mn(III) thiolate, but it was not identified as such at the time.[23]

Lastly, in a biological context, there is at present no evidence for $Mn(II)-S_{Cys}$ bonds in native proteins. Recently, Sugiura et al.[53] have described a $Mn(III)-S_{Cys}$ interaction in a red-purple acid phosphatase from sweet potato, one spectral feature of which is an intense absorption band at 525 nm (ϵ 2460) assigned as LMCT (L = Tyr-O^- or Cys-S^-). Without intention to disprove claim of this interaction,[54] we observe that the visible bands of the Mn(III) thiolates in Table VIII (λ_{max} 560–638 nm, ϵ_{Mn} 190–330) are ~7–12 times less intense. These bands are probably d–d in character. The two far more intense features in the 340–400-nm range are most likely $RS^- \rightarrow Mn(III)$ charge-transfer absorptions.

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. T.C. acknowledges a research fellowship from NATO through DAAD, Bonn, Federal Republic of Germany. We thank J. M. Berg for volume calculations and Dr. J.-J. Girerd for assistance with magnetic measurements.

Registry No. **1**, 87860-08-0; **2**, 87802-58-2; **3**, 87526-33-8; $(Me_4N)_2[Mn(SPh)_4]$, 87802-55-9; $(Et_4N)_2[Mn_4(SPh)_{10}]$, 87802-57-1; $(Me_4N)_2[Mn(edt)_2]$, 87860-05-7; $(Ph_4P)_2[Mn(edt)_2]$, 87860-06-8; $(Ph_4P)_2[Mn_2(edt)_4]$, 87860-07-9; $[Mn(edt)_2(DMF)_2]^-$, 87802-59-3; $[Mn(edt)_2(Me_2SO)_2]^-$, 87802-60-6; $[Mn(edt)_2(MnCN)_2]^-$, 87802-61-7; $[Mn(dmp)_2(H_2O)_2]^-$, 87802-62-8; $[Mn(dmp)_2(py)_2]^-$, 87802-63-9.

Supplementary Material Available: Listings of cation and solvate positional and thermal parameters, calculated hydrogen atom coordinates, and $10|F_o|$ and $10|F_c|$ for $(Me_4N)_2[Mn(edt)_2]\cdot MeCN$, $(Me_4N)_2[Mn_4(SPh)_{10}]$, and $(Et_4N)_2[Mn_2(edt)_4]$ (65 pages). Ordering information is given on any current masthead page.

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