M–X stretching constant force.

From the data available we are not able to assess the contribution of the impurities to the conduction mechanism.

To summarize, this is the first reported example of this type of linear-chain nickel compounds.[28]

The only example where mixed-valence Ni ions are present is in the class of compounds having the formula $Li_xNi_{1-x}O$.[29] The higher oxidation state, Ni^{III} or Ni^{IV}, occurs in few compounds, all of them having coordination numbers of 5 or 6, and are present, in the solid state, as discrete molecules.[30,31]

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Registry No. $Ni_2(CH_3CS_2)_4$, 95974-45-1; $Ni_2(CH_3CS_2)_4I$, 95974-44-0; Ni, 7440-02-0; I_2, 7553-56-2.

Supplementary Material Available: Listings of all atomic coordinates and thermal parameters and of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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

Systematic Stereochemistry of Metal(II) Thiolates: Synthesis and Structures of $[M_2(SC_2H_5)_6]^{2-}$ (M = Mn(II), Ni(II), Zn(II), Cd(II))

A. D. WATSON, CH. PULLA RAO, J. R. DORFMAN, and R. H. HOLM*

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Heterogeneous reaction of a 3:1:1 mole ratio mixture of $NaSEt/MCl_2/Et_4NCl$ in acetonitrile affords the isomorphous compounds $(Et_4N)_2[M_2(SEt)_6]$, with the following crystal data given in the order M = Mn(II), Zn(II), Cd(II): a = 10.993 (1), 10.986 (2), 10.983 (4) Å; b = 10.503 (1), 10.436 (2), 10.525 (4) Å; c = 18.306 (2), 18.116 (4), 18.445 (7) Å; β = 93.82 (1), 118.70 (1), 94.56 (3)°; space group $P2_1/n$ and $Z = 2$ in all cases. Structures were solved by standard methods and refined to a conventional R value of ≤5.0%. The three $[M_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$ anions are edge-shared tetrahedra with imposed centrosymmetry and an anti conformation of bridging ethyl groups. A similar reaction mixture but containing Me_4NCl yielded $(Me_4N)_2[Ni_2(SEt)_6]$, for which a = 10.775 (2) Å, b = 10.801 (2) Å, c = 16.891 (4) Å, α = 104.03 (2)°, β = 95.05 (2)°, and γ = 58.81 (1)°. The structure was refined to R = 3.7% in the triclinic space group $P\bar{1}$, revealing a centrosymmetric, nearly planar $[Ni_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$ anion formed by edge sharing of NiS_4 coordination units. From an analogous reaction system containing Et_4NCl, the trinuclear compound $(Et_4N)_2[Ni_3(SEt)_8]$ was isolated. The structure of $[Ni_3(\mu\text{-}SEt)_4(SEt)_4]^{2-}$ is briefly described. All known structures of metal(II) thiolates are summarized, and an empirical linear correlation between terminal and bridging ligand bond distances is presented. Coordination geometries tend to adhere closely to the normal stereochemical preference of M(II) ions. The dimensional flexibility of the $Ni_2(\mu\text{-}S)_2$ unit appears to be an important factor in its occurrence in four recognized structures, $[Ni_n(SR)_{2n+2}]^{2-}$ (n = 2, 3) and $Ni_n(SR)_{2n}$ (n = 4, 6).

Introduction

Our interest in the chemistry of discrete metal(II) thiolate complexes has arisen largely from their utility as precursors of metal–sulfide–thiolate clusters. In reactions with elemental sulfur the mononuclear tetrahedral complexes $[Fe(SR)_4]^{2-}$[1-4] yield one or more of the clusters $[Fe_2S_2(SR)_4]^{2-}$, $[Fe_3S_4(SR)_4]^{3-}$, $[Fe_4S_4(SR)_4]^{2-}$, and $[Fe_6S_9(SR)_2]^{4-}$, depending on the nature of the R group (Ph, alkyl) and experimental conditions.[1-3,5] The adamantane-like species $[Fe_4(SR)_{10}]^{2-}$,[1,6,7] with sulfur, affords $[Fe_4S_4(SR)_4]^{2-}$ in high yield.[1] The related cage complexes $[Fe_4(SPh)_6X_4]^{2-}$ (X = Cl, Br) can be formed from $[Fe(SPh)_4]^{2-}$ and $FeCl_2$ and, with dibenzyl trisulfide, produce $[Fe_4S_4(SPh)_2X_2]^{2-}$.[8] Further, $[Co_4(SPh)_{10}]^{2-}$[9] and hydrosulfide ion assemble the octanuclear cluster $[Co_8S_6(SPh)_8]^{4-}$,[10] and $[M_4(SPh)_{10}]^{2-}$[6,11,12] and sulfur yield the decanuclear cages $[M_{10}S_4(SPh)_{16}]^{4-}$ (M = Zn(II), Cd(II)).[13]

Stimulated by the earlier observations in this laboratory of the synthetic value of metal(II) thiolates,[1-3,10] we have undertaken a broader study of these compounds. The purpose of these investigations is to develop preparative routes to these compounds, thereby providing potential reactants leading to new clusters and cages, and to define structural types with the intention of evolving a systematic stereochemistry of metal(II) thiolate complexes. We have previously demonstrated that, with Fe(II), four types of species exist: $[Fe(SR)_4]^{2-}$, $[Fe_2(\mu\text{-}SR)_2(SR)_4]^{2-}$,[2,7] $[Fe_3(\mu\text{-}SR)_3Cl_6]^{3-}$,[2,14] and $[Fe_4(\mu\text{-}SR)_6(SR)_4]^{2-}$. In each, Fe(II) is tetrahedrally coordinated. Recent investigations of Mn(II),[15] Co(II),[7,9] and Cd(II)[12] systems, together with an earlier demonstration of a variety of $[M(SPh)_4]^{2-}$ complexes,[16] suggest that certain of these structural types may be of wide occurrence. The matter has been pursued here by the synthesis and structure determination of four complexes of the type $[M_2(SR)_6]^{2-}$, with M = Mn(II), Ni(II), Zn(II), and Cd(II). Also isolated in the course of this work was a trinuclear Ni(II) species of the type $[Ni_3(SR)_8]^{2-}$.

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Table I. Crystallographic Data for $(Et_4N)_2[Zn_2(SEt)_6]$ (A), $(Et_4N)_2[Cd_2(SEt)_6]$ (B), $(Et_4N)_2[Mn_2(SEt)_6]$ (C), and $(Me_4N)_2[Ni_2(SEt)_6]$ (D)

	A	B	C	D
formula	$C_{28}H_{70}Zn_2N_2S_6$	$C_{28}H_{70}Cd_2N_2S_6$	$C_{28}H_{70}Mn_2N_2S_6$	$C_{20}H_{54}Ni_2N_2S_6$
mol wt	758.00	852.06	737.11	632.42
a, Å	10.986 (2)	10.983 (4)	10.993 (1)	10.775 (2)
b, Å	10.436 (2)	10.525 (4)	10.503 (1)	10.801 (2)
c, Å	18.116 (4)	18.445 (7)	18.306 (2)	16.891 (4)
α, deg				104.03 (2)
β, deg	93.56 (2)	94.56 (3)	93.82 (1)	95.05 (2)
γ, deg				58.81 (1)
V, Å^3	2073 (5)	2125 (1)	2109 (1)	1630 (1)
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
d_{calcd}, g/cm^3	1.21	1.33	1.16	1.29
d_{obsd}, g/cm^3 [d]	1.23	1.35	1.17	1.30
Z	2	2	2	2
radiation[f]	Mo Kα	Mo Kα	Mo Kα	Mo Kα
abs coeff μ, cm^{-1}	14.9	12.9	8.8	15.4
transmission factors (min, max)	0.53, 0.72	0.55, 0.61	0.63, 0.67	0.54, 0.67
cryst size, mm	0.20 × 0.44 × 0.40	0.30 × 0.42 × 0.80	0.30 × 0.58 × 0.62	0.50 × 0.30 × 0.18
scan speed, deg/min[b]	2.0–29.3	2.9–29.3	2.9–29.3	2.0–29.3[e]
scan range, deg[c]	1.3	2.0	2.0	1.2
bkgd/scan time ratio	0.25	0.25	0.25	0.25
data collcd	$+h,+k,\pm l$	$\pm h,+k,+l$ ($3.0° \le 2\theta \le 50°$)	$\pm h,+k,+l$ ($3.0° \le 2\theta \le 50°$)	$+h,\pm k,\pm l$ ($3.0° \le 2\theta \le 49°$)
no. of unique data ($I > 3\sigma(I)$)	2655	2855	2756	3623
no. of variables	172	172	172	271
goodness of fit[a]	1.13	1.45	1.31	1.13
R, %	4.0	3.0	5.0	3.7
R_w, %	4.5	3.3	4.9	4.1

[a] Goodness-of-fit = $[\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v are the numbers of data and variables, respectively. [b] $\theta/2\theta$ scan. [c] Scan range = $x + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$. [d] Determined by flotation in CCl_4/cyclohexane. [e] ω scan. [f] λ = 0.71069 Å.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen or argon atmosphere. Sodium ethanethiolate was prepared from sodium and ethanethiol in THF. The white solid was collected, washed with ether, and dried in vacuo. Solvents were distilled from appropriate drying agents and were degassed immediately before use.

(a) $(Et_4N)_2[Zn_2(SEt)_6]$. To a solution of 2.72 g (20 mmol) of $ZnCl_2$ in 50 mL of acetonitrile and 5 mL of DMF was added 5.04 g (60 mmol) of solid NaSEt with stirring, forming a colorless solution and a precipitate of NaCl. After 50 min, 3.31 g (20 mmol) of Et_4NCl was added and the mixture was stirred for 24 h and filtered. The colorless filtrate was warmed to ~40 °C, allowed to cool slowly to −20 °C, and stored at this temperature for 24 h. The colorless crystals were collected, washed with 25 mL of 5:1 v/v ether/acetonitrile and 5 mL of ether, and dried in vacuo. A further crop was obtained by cooling the filtrate from this step at −20 °C, affording a total of 5.60 g (74%) of pure product as colorless crystals. Anal. Calcd for $C_{28}H_{70}N_2S_6Zn_2$: C, 44.37; H, 9.31; N, 3.70; S, 25.38; Zn, 17.25. Found: C, 43.78; H, 9.10; N, 3.69; S, 25.15; Zn, 17.65. ^1H NMR (CD_3CN, anion): δ 1.21 (t, CH_3), 2.48 (q, CH_2).

(b) $(Et_4N)_2[Cd_2(SEt)_6]$. To a solution of 3.67 g (19 mmol) of $CdCl_2$ in ~80 mL of acetonitrile was added 5.04 g (60 mmol) of solid NaSEt with stirring. The mixture was stirred for 4 h, and 3.31 g (20 mmol) of Et_4NCl was added. After the mixture was stirred for a further 4 h, NaCl was removed by filtration. The filtrate was condensed to ~20 mL and cooled slowly to ~0 °C. Large colorless rhomblike crystals were collected, washed with ether, and dried in vacuo. Cooling the filtrate from this step to −20 °C afforded a second crop of smaller crystals for a total of 7.20 g (89%) of pure product as colorless crystals. Anal. Calcd for $C_{28}H_{70}Cd_2N_2S_6$: C, 39.53; H, 8.29; Cd, 26.42; N, 3.29; S, 22.61. Found: C, 39.52; H, 8.14; Cd, 26.21; N, 3.32; S, 23.49. ^1H NMR (CD_3CN, anion): δ 1.19 (t, CH_3), 2.53 (q, CH_2).

(c) $(Et_4N)_2[Mn_2(SEt)_6]$. To a solution of 2.52 g (20 mmol) of $MnCl_2$ in 60 mL of acetonitrile and 20 mL of DMF was added 5.04 g (60 mmol) of solid NaSEt with stirring. The mixture was stirred for 4 h. The deep red-pink mixture was treated with 3.31 g (20 mmol) of Et_4NCl and was stirred for 2 h. Sodium chloride was removed by filtration and was washed with 2 × 20 mL of acetonitrile. The combined filtrate and washings were condensed to ~30 mL. Ether (10 mL) was slowly added, and the mixture was cooled slowly to ~0 °C and maintained at this temperature for 24 h. Deep red-orange, extremely air-sensitive, blocklike crystals were collected, washed with 20 mL of ether, and dried in vacuo; 5.90 g (80%) of pure product was obtained. Anal. Calcd for $C_{28}H_{70}Mn_2N_2S_6$: C, 45.63; H, 9.57; Mn, 14.91; N, 3.80; S, 26.10. Found: C, 45.26; H, 9.37; Mn, 15.15; N, 3.83; S, 26.03.

(d) $(Me_4N)_2[Ni_2(SEt)_6]$. To a stirred solution of 1.30 g (10 mmol) of $NiCl_2$ in 100 mL of acetonitrile was added 2.52 g (30 mmol) of solid NaSEt. The mixture was stirred for 16 h, during which time a dark green-brown color developed. The mixture was treated with 1.10 g (10 mmol) of Me_4NCl, and stirring was continued for 3 h. The brown filtrate of the reaction mixture was concentrated to ~50 mL and cooled to −20 °C. The black crystalline solid was collected; a second crop was obtained by slow diffusion of ether into the filtrate. The two crops gave 1.80 g (57%) of pure product. Anal. Calcd for $C_{20}H_{54}N_2Ni_2S_6$: C, 37.98; H, 8.60; N, 4.43; S, 30.41. Found: C, 37.58; H, 8.54; N, 4.39; S, 30.16. Absorption spectrum (acetonitrile): λ_{max} 305 nm (ϵ_M 26 000), 345 (sh, 13 500), 464 (sh, 2340), 620 (sh, 615). ^1H NMR (CD_3CN, anion): δ 1.05 (t, CH_3), 1.20 (t, CH_3), 1.79–1.87 (m, CH_2).

(e) $(Et_4N)_2[Ni_3(SEt)_8]$. To a solution of 1.30 g (10 mmol) of $NiCl_2$ in 100 mL of acetonitrile was added 2.26 g (27 mmol) of solid NaSEt with stirring. After the mixture was stirred for 14 h, 1.03 g (63 mmol) of Et_4NCl was added and stirring was continued for 1 h. The mixture was filtered, and the filtrate was condensed to ~50 mL. The solvent was removed in vacuo, and the brown residue was recrystallized from warm acetonitrile. After being dried in vacuo, the product (1.55 g, 50%) was obtained as a brown microcrystalline product. Anal. Calcd for $C_{32}H_{80}N_2Ni_3S_8$: C, 41.53; H, 8.71; N, 3.03; Ni, 19.03; S, 27.71. Found: C, 41.53; H, 8.76; N, 3.05; Ni, 18.91; S, 27.62. Absorption spectrum (acetonitrile): λ_{max} 316 nm (ϵ_M 33 000), 400 (sh, 12 300), 624 (sh, 1420). ^1H NMR (CD_3CN, anion): δ 1.04–1.08 (m, CH_3), 1.85–1.88 (m, CH_2).

Collection and Reduction of X-ray Data. Suitable crystals of compound A in Table I were obtained upon the addition of ether until turbidity to a concentrated acetontrile solution and maintaining the solution overnight at ~4 °C. Those of compounds B and C were produced by slow cooling of warm acetonitrile solutions to −25 °C over periods of 24–48 h. Compound D was crystallized by slow diffusion of ether into an acetonitrile solution. Crystals were mounted in glass capillaries and sealed under argon. Diffraction experiments were performed at ambient temperature on a Nicolet R3m or P3F four-circle diffractometer with a Mo X-ray source equipped with a graphite monochromator. The crystal and machine parameters used in the unit celll determinations and data collections are summarized in Table I. Intensity data were collected by the $\theta/2\theta$ technique, except in the case of D where the ω-scan technique was used. The intensities of three check reflections were measured every 123 reflections during data acquisition and revealed no significant changes in intensities. The SHELXTL programs XTAPE and XEMP were used for data processing and empirical absorption corrections, respectively. Corrections were applied to all data sets.

Structure Solution and Refinement. The SHELXTL program package (Nicolet XRD Corp., Madison, WI) was used throughout. Heavy-atom positions were revealed by the direct-methods program SOLV. All re-

Table II. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[Zn_2(SEt)_6]$[a]

atom	*x*	*y*	*z*
Zn	391 (1)	10768 (1)	5734 (1)
S(1)	673 (1)	8519 (1)	5384 (1)
S(2)	2241 (1)	11769 (1)	5957 (1)
S(3)	−818 (1)	10790 (1)	6729 (1)
C(1)	2262 (3)	8416 (3)	5144 (2)
C(2)	2743 (5)	7121 (6)	5202 (5)
C(3)	2615 (5)	12220 (5)	5031 (3)
C(4)	3528 (7)	13084 (10)	4959 (4)
C(5)	305 (3)	10135 (3)	7415 (2)
C(6)	−176 (5)	10021 (7)	8161 (2)
N	143 (2)	4835 (2)	2673 (1)
C(7)	607 (3)	5577 (3)	3356 (2)
C(8)	−31 (4)	5305 (4)	4041 (2)
C(9)	−1200 (2)	5130 (3)	2478 (2)
C(10)	−1477 (4)	6501 (4)	2293 (3)
C(11)	912 (3)	5233 (3)	2050 (2)
C(12)	581 (4)	4601 (6)	1326 (2)
C(13)	225 (3)	3408 (3)	2803 (2)
C(14)	1498 (4)	2901 (3)	2990 (2)

[a] Estimated standard deviations are given in parentheses in this and succeeding tables.

maining non-hydrogen atoms were located by using successive difference Fourier maps and blocked cascade least-squares refinement. Atomic scattering factors were taken from a standard source.[17] In the last stages of refinement of B and C, fixed contributions were included from hydrogen atoms with C–H distances of 0.96 Å and thermal parameters set at 1.2 times those of the bonded carbon atoms. In the case of A, all hydrogen atoms were recovered from difference Fourier maps and their temperature factors were refined isotropically during the last stage of refinement. With D all hydrogen atoms were also recovered from difference Fourier maps and were refined. Unique data used in the refinements and final *R* factors are given in Table I. Individual structural refinements are briefly described.

(a) $(Et_4N)_2[Zn_2(SEt)_6]$. The systematic absences $h0l$ ($h + l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely define the space group $P2_1/n$ (nonstandard setting of $P2_1/c$, No. 14; equivalent positions $\pm(x, y, z; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z)$). The asymmetric unit consists of half of the anion and one cation, the remainder being generated by an inversion center. Isotropic refinement converged at 8.7%. Final refinement was carried out with all non-hydrogen atoms anisotropically described. Before inclusion of hydrogen atoms the structure refined to $R = 4.8$ and 5.5% without and with the empirical absorption correction, respectively. Results of the former refinement are reported.

(b) $(Et_4N)_2[M_2(SEt)_6]$ (M = Cd(II), Mn(II)). These compounds are isomorphous with the Zn(II) compound, and their structures were solved similarly. Isotropic refinement coverged at 7.9% (Cd) and 6.9% (Mn). Hydrogen atoms were included on all carbon atoms, and all non-hydrogen atoms were refined anisotropically.

(c) $(Me_4N)_2[Ni_2(SEt)_6]$. The triclinic centrosymmetric space group $P\bar{1}$ (No. 2; equivalent positions $\pm(x, y, z)$) was selected after analysis of axial photographs and intensities. Attempts to locate higher symmetry unit cells were unsuccessful. The asymmetric unit contains half of each of two anions and two full cations. Remaining atoms are generated by an inversion center. Isotropic refinement of all non-hydrogen atoms converged at 12.0%. This rather high value arises from large anisotropic thermal motions, especially by methyl carbon atoms of terminal thiolate ligands. Attempts to model this motion in terms of two different positions with fractional site occupancies were unsuccessful. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms, located in difference Fourier maps, were treated isotropically with a σ-weighting scheme in the last phase of refinement. Refinement of the structure in the noncentrosymmetric space group $P1$ was less satisfactory and led to unusual C–S and C–C bond lengths. Atom coordinates for compounds A–D are compiled in Tables II–V.[18]

Table III. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[Cd_2(SEt)_6]$

atom	*x*	*y*	*z*
Cd	796 (1)	826 (1)	442 (1)
S(1)	402 (1)	−1552 (1)	744 (1)
S(2)	1850 (1)	828 (1)	−837 (1)
S(3)	1000 (1)	1925 (1)	2428 (1)
C(1)	155 (3)	−1603 (5)	2318 (4)
C(2)	81 (6)	−2848 (7)	2792 (6)
C(3)	2517 (2)	119 (4)	289 (4)
C(4)	3242 (3)	−22 (8)	−198 (7)
C(5)	67 (3)	2282 (7)	2742 (6)
C(6)	−67 (4)	3085 (10)	3522 (7)
N	2694 (1)	151 (3)	5117 (3)
C(7)	3378 (2)	−559 (3)	5562 (4)
C(8)	4032 (2)	−256 (5)	4892 (5)
C(9)	2465 (2)	−154 (4)	3795 (3)
C(10)	2280 (3)	−1533 (4)	3524 (4)
C(11)	2807 (2)	1568 (3)	5173 (4)
C(12)	3027 (3)	2084 (4)	6437 (4)
C(13)	2114 (2)	−268 (4)	5934 (4)
C(14)	1379 (3)	312 (7)	5647 (5)

Table IV. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[Mn_2(SEt)_6]$

atom	*x*	*y*	*z*
Mn	411 (1)	749 (1)	743 (1)
S(1)	717 (1)	−1524 (1)	389 (1)
S(2)	−822 (1)	800 (1)	1779 (1)
S(3)	2317 (1)	1818 (1)	980 (1)
C(1)	2296 (4)	−1629 (5)	143 (3)
C(2)	2776 (5)	−2901 (6)	174 (5)
C(3)	283 (4)	132 (5)	2466 (2)
C(4)	−194 (6)	16 (7)	3196 (3)
C(5)	2745 (6)	2216 (7)	70 (3)
C(6)	3499 (8)	3122 (10)	−44 (4)
N	135 (3)	4838 (3)	7687 (2)
C(7)	590 (4)	5566 (4)	8365 (2)
C(8)	−69 (6)	5280 (5)	9040 (3)
C(9)	−1196 (3)	5134 (4)	7484 (2)
C(10)	−1475 (4)	6496 (5)	7287 (3)
C(11)	211 (4)	3418 (3)	7815 (2)
C(12)	1473 (4)	2906 (4)	8015 (3)
C(13)	927 (4)	5249 (4)	7087 (2)
C(14)	615 (5)	4630 (6)	6356 (3)

Results and Discussion

Previously we have shown with Fe(II)[1–3,6,7] and several other divalent metals[2,7,15] that reaction of MCl_2 or $[MCl_4]^{2-}$ with a thiolate salt affords products with the same RS^-:M(II) ratio as present in the initial reaction mixture. This behavior has been further examined here in heterogeneous reaction systems in acetonitrile initially containing $NaSEt/MCl_2/R_4'NCl$ in a 3:1:1 mole ratio. For M = Mn(II), Ni(II), Zn(II), and Cd(II), salts (R′ = Me, Et) of the binuclear anions $[M_2(SEt)_6]^{2-}$ were isolated in >50% yield.

Structure types **1**–**8** of discrete metal(II) thiolates that have been crystallographically established are schematically illustrated in Figure 1. The set is restricted to species with nuclearities ≤6 derived from monofunctional thiolates.

Structures of $[M_2(SEt)_6]^{2-}$. Crystal structures of the four compounds in Table I consist of well-separated cations and anions. The structures of the cations are unexceptional and are not further considered. Certain carbon atoms of the ethanethiolate ligands in the structures exhibited substantial thermal motion, as seen from temperature factors[18] and thermal ellipsoids in Figures 2–5. For the purpose of clarity in presenting the structure of $[Ni_2(SEt)_6]^{2-}$, methyl carbon atoms of terminal thiolates are represented as spheres of arbitrary radius.

(a) M = Mn(II), Zn(II), and Cd(II). Anion structures are depicted in Figures 2–4. Selected interatomic distances are listed in Table VI. These species are formed from two edge-shared tetrahedra. The M(II) sites have distorted tetrahedral stereochemistry, and owing to imposed centrosymmetry, the complexes exist in the **2**-*anti* configuration of C_i symmetry (Figure 1). The bridge angles $M–S_b–M = 80.5–83.6°$ are substantially larger than the value of 70.5° for an edge-shared perfect tetrahedral dimer.[19] The $M_2(\mu\text{-}S)_2$ bridge units are rhomboids, owing to significant differences in the two independent $M–S_b$ distances. The cause of these differences is unclear. As expected from the large bridge

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(17) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

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

(19) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.

Table V. Atom Coordinates ($\times 10^4$) for $(Me_4N)_2[Ni_2(SEt)_6]$

atom	*x*	*y*	*z*
Ni(1)	127 (1)	3396 (1)	−510 (1)
S(1)	1549 (1)	4202 (1)	128 (1)
C(1)	2087 (7)	3505 (6)	1050 (3)
C(2)	852 (9)	3759 (8)	1527 (4)
S(2)	1827 (1)	1028 (1)	−843 (1)
C(3)	3643 (6)	714 (7)	−810 (6)
C(4)	4219 (12)	526 (19)	−1567 (7)
S(3)	−1634 (1)	3041 (1)	−1076 (1)
C(5)	−1096 (6)	1088 (6)	−1421 (5)
C(6)	−2177 (10)	778 (9)	−1539 (8)
Ni(2)	6317 (1)	4806 (1)	4431 (1)
S(4)	5766 (1)	3399 (1)	4914 (1)
C(7)	5251 (6)	2458 (6)	4014 (4)
C(8)	3995 (6)	3448 (7)	3600 (4)
S(5)	8369 (1)	2727 (1)	3947 (1)
C(9)	9625 (6)	2902 (7)	3402 (4)
C(10)	768 (9)	2911 (13)	−6139 (6)
S(6)	6772 (2)	6225 (2)	3915 (1)
C(11)	5196 (10)	8058 (10)	3960 (8)
C(12)	4864 (14)	8603 (16)	3427 (10)
N(1)	6420 (4)	3763 (4)	1305 (2)
C(13)	−5762 (6)	6637 (7)	−547 (3)
C(14)	8024 (7)	2666 (7)	1242 (5)
C(15)	5726 (9)	3751 (10)	2020 (4)
C(16)	6180 (8)	5265 (7)	1364 (4)
N(2)	10268 (4)	1934 (4)	6328 (2)
C(17)	9787 (8)	3488 (7)	6309 (4)
C(18)	11156 (6)	942 (6)	5564 (3)
C(19)	11143 (6)	1487 (7)	7052 (3)
C(20)	8984 (7)	1762 (7)	6369 (4)

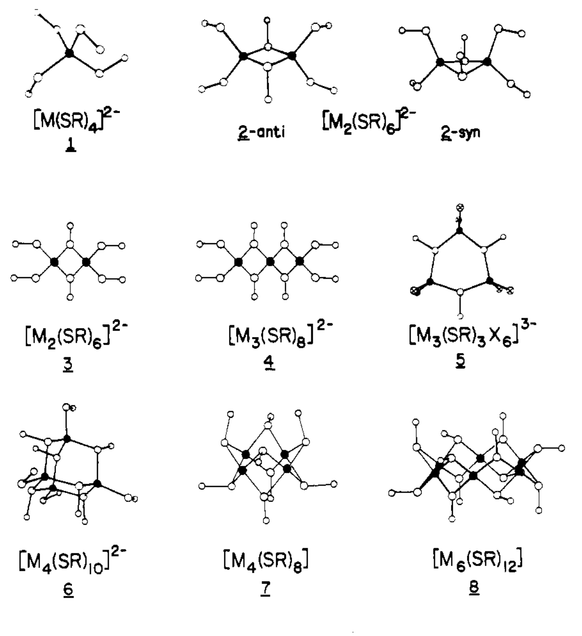

Figure 1. Structures **1**–**8** of metal(II) thiolates that have been crystallographically established. Only one of a number of possible conformations, arising from different relative positions of R groups, is shown for **3**–**8**.

angles, the angles S_b–M–S_b = 96.4–99.5° are smaller than the tetrahedral value. The three structures resemble those of previously characterized *anti*-$[M_2(SEt)_6]^{2-}$ with M = Fe(II) and Co(II),[7] except that in those cases the bridge units are rhombs; i.e., the two independent M–S_b bond lengths are indistinguishable. In the set of five *anti*-$[M_2(SEt)_6]^{2-}$ complexes the expected distance relationship M–S_b > M–S_t holds, and mean values of both types of distances decrease as M = Co(II) < Zn(II) < Fe(II) < Mn(II) < Cd(II), which is the order of the Shannon tetrahedral radii.[20] (An exception is found with the mean Zn–S_b value, which is ~0.05 Å longer than expected from the series of radii.) A similar behavior obtains in the series $[M(SPh)_4]^{2-}$ [4,16] and $[M_4(SPh)_{10}]^{2-}$ [6,7,9,11,12,15] and in $[Fe_4(SPh)_6Cl_4]^{2-}/[Zn_4(SPh)_8Cl_2]^{2-}$.[8,21]

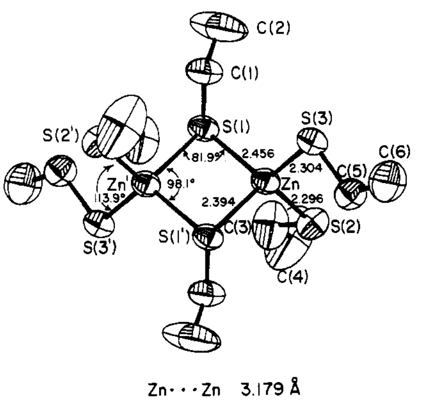

Figure 2. Structure of *anti*-$[Zn_2(SEt)_6]^{2-}$. In this and following figures atom-labeling schemes, selected interatomic distances (Å) and angles (deg), and 50% probability ellipsoids are shown. Primed and unprimed atoms are related by a center of symmetry.

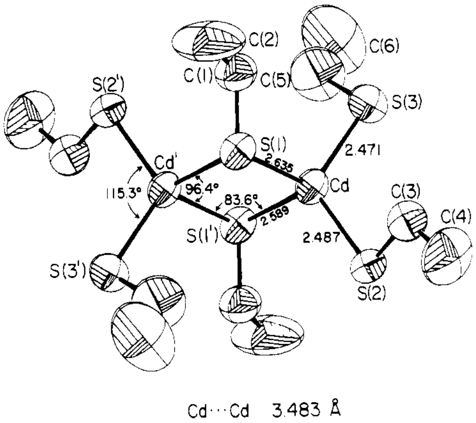

Figure 3. Structure of *anti*-$[Cd_2(SEt)_6]^{2-}$.

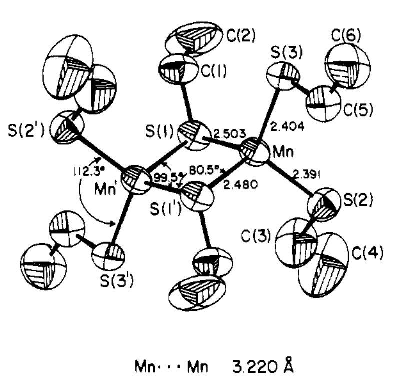

Figure 4. Structure of *anti*-$[Mn_2(SEt)_2]^{2-}$.

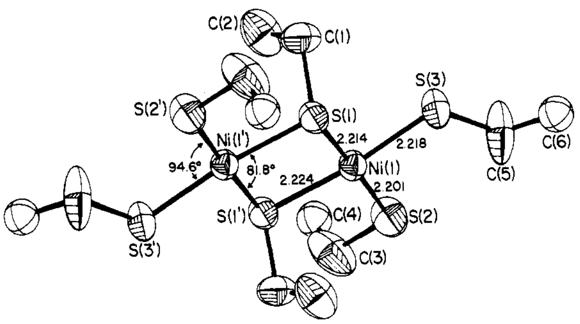

Figure 5. Structure of *anti*-$[Ni_2(SEt)_6]^{2-}$, anion 1.

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(20) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for *anti*-$[M_2(SEt)_6]^{2-}$ (M = Zn(II), Cd(II), Mn(II))

	$[Zn_2(SEt)_6]^{2-}$	$[Cd_2(SEt)_6]^{2-}$	$[Mn_2(SEt)_6]^{2-}$
	$M–S_b$[a]		
M–S(1)	2.456 (1)	2.635 (2)	2.503 (1)
M–S(1′)	2.394 (1)	2.589 (2)	2.480 (1)
	$M–S_t$[a]		
M–S(2)	2.296 (1)	2.487 (2)	2.404 (1)
M–S(3)	2.304 (1)	2.471 (2)	2.391 (1)
	M···M		
	3.179 (1)	3.483 (2)	3.220 (1)
	$S_b···S_b$		
S(1)···S(1′)	3.664 (1)	3.894 (1)	3.803 (2)
	$S_b–C$		
S(1)–C(1)	1.829 (3)	1.823 (5)	1.824 (4)
	$S_t–C$		
S(2)–C(3)	1.812 (5)	1.832 (5)	1.830 (4)
S(3)–C(5)	1.831 (3)	1.821 (7)	1.811 (6)
	$S_b–M–S_b$		
S(1)–M–S(1′)	98.1 (1)	96.4 (1)	99.5 (1)
	$S_t–M–S_t$		
S(2)–M–S(3)	113.9 (1)	115.3 (1)	112.3 (1)
	$M–S_b–M$		
M–S(1)–M	81.9 (1)	83.6 (1)	80.5 (1)
	$S_b–M–S_t$		
S(1)–M–S(2)	110.8 (1)	107.9 (1)	108.6 (1)
S(1)–M–S(3)	107.5 (1)	111.0 (1)	111.3 (1)

[a] b = bridging, t = terminal ligand in this and the following table.

The **2**-*anti* form in the $(Et_4N)_2[M_2(SEt)_6]$ set of compounds is presumably adopted to diminish steric interactions of bridge groups with themselves and terminal ligands on the same side of the M_2S_2 plane in the **2**-*syn* form. However, the syn isomer is found in the n-Bu_4N^+ salt of $[Co_2(SEt)_6]^{2-}$,[7] indicating an apparent dependence of the isomer isolated on crystal energy effects.

The only other examples of structure **2** (all ligands thiolate) are *anti*- and *syn*-$[Fe_2(S_2$-*o*-$xyl)_3]^{2-}$,[7,22] *anti*-$[Fe_2(S_2$-*o*-$xyl)_2(SPh)_2]^{2-}$,[22] and *syn*-$[Co_2(S_2$-*o*-$xyl)_3]^{2-}$[23] (S_2-*o*-xyl = *o*-xylene-α,α'-dithiolate). Other structurally characterized Mn(II),[24] Zn(II),[25] and Cd(II)[26] thiolates, not already referred to, are mononuclear, polynuclear in excess of two, or polymeric. The $Zn_2(\mu\text{-}SR)_2$ unit is present in the mixed-ligand complex $Zn_2(SC_5H_9NHMe)_2Cl_4$.[27]

(b) M = Ni(II). Structural data for the two independent $[Ni_2(SEt)_6]^{2-}$ anions are contained in Table VII. The structure of anion 1, provided in Figure 5, is of type **3**. It is formed by edge sharing of two planar units to generate a Ni_2S_2 planar rhomb. The anion is centrosymmetric with C_{2h} symmetry. Consequently, the Ni(1,1′)S(1,1′) core plane is perfect, opposite ethyl groups are above and below this plane, and the bridge unit has the anti conformation. The Ni_2S_6 portion is nearly planar, with a small nonzero dihedral angle (1.4°) between planes Ni(1)S(2,3) and Ni(1)S(1,1′). The deviation of the Ni(1) atom from the unweighted least-squares plane S(1′,1,2,3) is ≤0.017 Å. As with structure **2**, the expected distance order $Ni–S_b > Ni–S_t$ and angle order $S_t–Ni–S_t > S_b–Ni–S_b$ hold. Dimensions of the two anions are negligibly different. The dihedral angle between planes Ni(2)S(5,6) and Ni(2)S(4,4′) of anion 2 is 4.4°, indicating a slightly less close approach of its Ni_2S_6 portion to planarity.

Table VII. Selected Interatomic Distances (Å) and Angles (deg) for $[Ni_2(SEt)_6]^{2-}$

anion 1		anion 2	
	$Ni–S_b$		
Ni(1)–S(1)	2.214 (2)	Ni(2)–S(4′)	2.216 (1)
Ni(1)–S(1′)	2.224 (1)	Ni(2)–S(4)	2.225 (2)
	$Ni–S_t$		
Ni(1)–S(2)	2.201 (1)	Ni(2)–S(6)	2.202 (2)
Ni(1)–S(3)	2.218 (2)	Ni(2)–S(5)	2.210 (1)
	Ni···Ni		
Ni(1)···Ni(1′)	3.355 (2)	Ni(2)···Ni(2′)	3.356 (2)
	$S_b···S_b$		
S(1)···S(1′)	2.906 (4)	S(4)···S(4′)	2.907 (4)
	$S_b–C$		
S(1)–C(1)	1.813 (6)	S(4)–C(7)	1.828 (7)
	$S_t–C$		
S(2)–C(3)	1.803 (3)	S(5)–C(9)	1.812 (8)
S(3)–C(5)	1.822 (6)	S(6)–C(11)	1.810 (8)
	$S_b–Ni–S_b$		
S(1)–Ni(1)–S(1′)	81.8 (1)	S(4)–Ni(2)–S(4′)	81.8 (1)
	$S_t–Ni–S_t$		
S(2)–Ni(1)–S(3)	94.6 (1)	S(5)–Ni(2)–S(6)	95.1 (1)
	$Ni–S_b–Ni$		
Ni(1)—S(1)–Ni(1′)	98.2 (1)	Ni(2)–S(4)–Ni(2′)	98.2 (1)
	$S_b–Ni–S_t$		
S(1)–Ni(1)–S(2)	96.4 (1)	S(4′)–Ni(2)–S(6)	97.1 (1)
S(1)–Ni(1)–S(3)	169.0 (1)	S(4′)–Ni(2)–S(5)	167.4 (1)
S(1′)–Ni(1)–S(3)	87.2 (1)	S(4)–Ni(2)–S(5)	86.2 (1)
S(1′)–Ni(1)–S(2)	177.7 (1)	S(4)–Ni(2)–S(6)	177.2 (1)
	Dihedral Angles		
Ni(1)S(2,3)/ Ni(1)S(1,1′)	1.4	Ni(2)S(5,6)/ Ni(2)S(4,4′)	4.4

Comparative Structural Features. The species $[M_2(SEt)_6]^{2-}$ constitutes the largest set of homoleptic binuclear complexes of proven structure. Previous[2,7] and present results lead to the stereochemical series (1) in which planar (P) or tetrahedral (T)

$$\begin{array}{lcccccc} M = & \text{Mn(II)}, & \text{Fe(II)}, & \text{Co(II)}, & \text{Ni(II)}, & \text{Zn(II)}, & \text{Cd(II)} \\ & \text{T} & \text{T} & \text{T} & \text{P} & \text{T} & \text{T} \end{array} \qquad (1)$$

metal coordination is indicated. This is identical with that formulated some time ago for sterically unencumbered mononuclear complexes.[28,29] The series is well recognized to represent the intrinsic stereochemical preference of these M(II) ions with weak-field ligands devoid of structural constraints. Although $[Cr_2(SEt)_6]^{2-}$ has not been prepared, it is expected to be planar. The related chelate complex $[Cr(SCH_2CH_2S)_2]^{2-}$ is in fact planar,[30] and its Mn(II)[15] and Co(II)[30] analogues conform to series

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(21) Dance, I. G. *Inorg. Chem.* **1981**, *20*, 2155.

(22) Henkel, G.; Tremel, W.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 319.

(23) Tremel, W.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 634.

(24) $[Mn(SCH_2CH_2S)_2]^{2-}$: ref 15.

(25) (a) $Zn(phen)(S\text{-}p\text{-}C_6H_4Me)_2$: Cremers, T. L.; Bloomquist, D. R.; Willett, R. D.; Crosby, G. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 3097. (b) $[Zn_4(SPh)_8(MeOH)]_n$: Dance, I. G. *J. Am. Chem. Soc.* **1980**, *102*, 3445. (c) $[Zn_8Cl(SPh)_{16}]^-$: Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1980**, 818. (d) $Zn_8Me_8(S\text{-}i\text{-}Pr)_8$: Adamson, G. W.; Shearer, H. M. M. *Ibid.* **1969**, 897.

(26) (a) $[Cd(SCH_2CH_2OH)_2]_n$: Bürgi, H.-B. *Helv. Chim. Acta* **1974**, *57*, 513. (b) $[Cd_8I(SCH_2CH_2OH)_{12}]^{3+}$: Bürgi, H.-B.; Gehrer, H.; Strickler, P.; Winkler, F. K. *Ibid.* **1976**, *59*, 2558. (c) $[Cd_{10}(SCH_2CH_2OH)_{16}]^{4+}$: Strickler, P. *J. Chem. Soc., Chem. Commun.* **1969**, 655. Lacelle, S.; Stevens, W. C.; Kurtz, D. M., Jr.; Richardson, J. W., Jr.; Jacobson, R. A. *Inorg. Chem.* **1984**, *23*, 930. (d) $[Cd(SC_5H_9NHMe)_2]_n^{2+}$: Bayón, J. C.; Briansó, M. C.; Briansó, J. L.; Gonzalez Duarte, P. *Ibid.* **1979**, *18*, 3478. (e) $[Cd(SCH_2CO_2Et)_2]_n$: Dance, I. G.; Scudder, M. L., Secomb, R. *Inorg. Chem.* **1983**, *22*, 1794. (f) $[Cd(4\text{-}Me\text{-}C_6H_3\text{-}1,2\text{-}S_2)_2]^{2-}$: Bustos, L.; Khan, M. A.; Tuck, D. G. *Can. J. Chem.* **1983**, *61*, 1146. (g) $Cd(SCMe_2CH_2NH_2)_2CdCl_2$: Fawcett, T. G.; Ou, C.-C.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 2058.

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1. This series is also followed by all but one member of the $[M(SPh)_4]^{2-}$ set,[4,16] which have the tetrahedral structure 1. The single exception is $[Ni(SPh)_4]^{2-}$, for which a planar structure would have been expected (steric factors permitting). As its Ph_4P^+ salt, this complex is tetrahedral, and on the basis of its ligand field spectrum,[31] it at least partially retains this stereochemistry in solution. The cause of the nonplanar structure is unclear. Among other polynuclear thiolate complexes, the conventional stereochemical pattern is followed with $[M_3(\mu_3\text{-}S)(S_2\text{-}o\text{-xyl})_3]^{2-}$, M = Fe(II),[32,33] Co(II),[32,34] and Ni(II).[35]

The tetrahedral stereochemical preferences in series 1 are further manifested in the formation of the ring structure 5 (thus far obtained only with Fe(II)[2,14]) and the adamantane-like cages 6, which have been obtained with every M(II) ion except Ni(II).[6,7,9,11,12,15] In addition to 3, the planar stereochemical tendency of Ni(II) appears in the form of cyclic oligomers that are tetranuclear (7, R = $C_5H_9N^+HMe$[36]) or hexanuclear (8, R = Et,[37,38] $CHCH_2OH$,[39] and $(CH_2)_3NHMe$[40]).

Cyclic structures 7 and 8 are built up from edge-shared, approximately planar NiS_4 coordination units. Structure 8 is also found with $Pd_6(S\text{-}n\text{-}Pr)_{12}$.[41] The central Ni_2S_2 portion of $[Ni_2(SEt)_6]^{2-}$ is interpreted as an unconstrained version of Ni_2S_2 units in the cyclic oligomers. The Ni···Ni separations and Ni–S_b–Ni angles decrease drastically in passing from 3 (3.36 Å, 98.2°) to 8 (2.92 Å, 83°) and then to 7 (2.67 Å, 74.3°), where the Ni atoms are close enough for weak, direct bonding interactions. Other structural features remain nearly constant except for displacement of the Ni(II) atom from the S_4 plane, which appears to increase in the order 3 < 8 < 7.[36-40] The dimensional flexibility of the $Ni_2(\mu\text{-}SR)_2$ group suggests that it may be accommodated in structures other than 3, 7, and 8. Indeed, the cyclic octamer $Ni_8(SCH_2CO_2Et)_{16}$ exists,[42] and the acyclic trinuclear complex $[Ni_3(SEt)_8]^{2-}$ has been obtained as its Et_4N^+ salt in this work. Isolation of this species or $[Ni_2(SEt)_6]^{2-}$ from reaction mixtures in acetonitrile with a ~3:1 mole ratio mixture of $NaSEt/NiCl_2$ would appear to depend upon the relative solubilities of quaternary ammonium salts. $(Et_4N)_2[Ni_3(SEt)_8]$ crystallizes in the monoclinic system with a = 9.591 (2) Å, b = 28.263 (6) Å, c = 9.630 (2) Å, and β = 113.19 (1)°. Suitable single crystals were difficult to obtain, and a high-quality data set was not achieved. For this reason the crystal structure, which, however, was solved, is not reported in detail here. The centrosymmetric trinuclear structure 4 was established and has the following principal features: (i) The central NiS_4 portion is planar, but the entire Ni_3S_8 core is not planar, there being a dihedral angle of 53° between the $Ni(S_t)_2$ and $Ni(S_b)_2$ planes. (ii) The Ni–S distances and Ni–S_b–Ni and S_b–Ni–S_b angles internal to Ni_2S_2 units are 2.19–2.23 Å, 87°, and 80–81°, respectively. (iii) The Ni···Ni distance is 3.04 Å, ~0.3 Å shorter than in 3, and approaches the value in 8. In terms of feature iii the Ni_2S_2 units of 4 are intermediate between those of 3 and 8. The cause of the nonplanar structure, and therewith the dimensional differences between the Ni_2S_2 units of 3 and 4, is not clear. The only other complex of the $[Ni_3(SR)_8]^{2-}$ type is $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$.[22] This species has the overall (nonplanar) structure 4, with Ni···Ni distances (3.106 (1), 3.131 (1) Å) and other Ni_2S_2 metric properties similar to those of $[Ni_3(SEt)_8]^{2-}$. The detailed aspects of the NiS_4 coordination units in the two anions are somewhat different. A structurally related $Pd_3(\mu\text{-}SR)_4$ unit occurs in $[Pd_3(C_6H_{12}NS)_4]^{2+}$.[43]

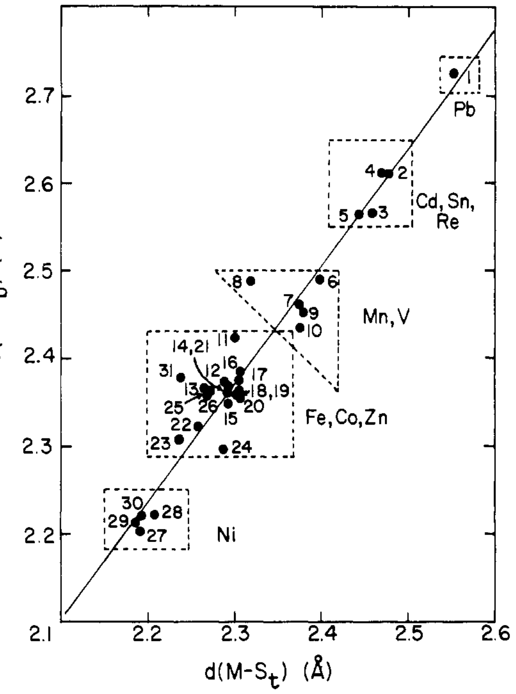

Figure 6. Correlation between bridging and terminal M–S(R) distances in metal thiolate complexes: 1, $Pb_3(SC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_6$;[44] 2, $[Cd_2(SEt)_6]^{2-}$; 3, $[Cd_{10}S_4(SPh)_{16}]^{4-}$;[13] 4, $Sn_3(SC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)_6$;[44] 5, $[Re_2(NO)_2(S\text{-}p\text{-}C_6H_4Me)_7]^-$;[45] 6, $[Mn_2(SEt)_6]^{2-}$; 7, $[Mn_4(SPh)_{10}]^{2-}$;[15] 8, $[Mn_2(S_2C_2H_4)_2]^{2-}$;[15,46] 9 and 10, $[V_2(S_2C_2H_4)_4]^{2-}$;[47-49] 11, $[Zn_2(SEt)_6]^{2-}$; 12, $[Zn_4(SPh)_{10}]^{2-}$;[11] 13, $[Zn_4(SPh)_8Cl_2]^{2-}$;[21] 14, $[Fe_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$;[32] 15, $[Fe_3S(S_2\text{-}o\text{-xylMe}_2)_3]^{2-}$;[33] 16, *anti*-$[Fe_2(S_2\text{-}o\text{-xyl})_3]^{2-}$;[22] 19, $[Fe_2(S_2\text{-}o\text{-xyl})_2(SPh)_2]^{2-}$;[22] 20, $[Fe_4(SEt)_{10}]^{2-}$;[7] 21, $[Fe_4(SPh)_{10}]^{2-}$;[6] 22, $[Co_4(SPh)_{10}]^{2-}$;[9] 23, $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$;[32,34] 24, $[Co_2(S_2\text{-}o\text{-xyl})_3]^{2-}$;[23] 25, *syn*-$[Co_2(SEt)_6]^{2-}$;[7] 26, anti-$[Co_2(SEt)_6]^{2-}$;[7] 27, $[Ni_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$;[35] 28, $[Ni_2(SEt)_6]^{2-}$; 29, $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$;[23] 30, $[Ni_3(SEt)_8]^{2-}$; 31, $[Fe_2(S_2C_2H_4)_4]^{2-}$.[50]

A substantial body of structural data is now available for complexes, including a number not previously cited,[44-50] that contain both terminal and doubly bridging thiolate ligands. Demonstrated in Figure 6 is a sensibly linear correlation between M–S_t and M–S_b distances for some 30 molecules. This empirical relationship is expressed by eq 2, obtained by linear regression

$$d(\text{M–S}_b) = 1.34[d(\text{M–S}_t)] - 0.71 \qquad (2)$$

analysis of all data (correlation coefficient r = 0.97). Certain points, notably 8 and 31, fall off the line at least partly because they contain averages of two rather different M–S_b distances. Given the variation in metal, stereochemistry, and oxidation state, the linear relationship assumes some generality. While results for certain elements are obviously limited, metal ions occupy regions in the plot that tend to follow Shannon radii.[20] The plot shows that the difference $d(\text{M–S}_b) - d(\text{M–S}_t)$ increases upon

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passing to the heavier elements. Distinct regions for tetrahedral (Fe, Co, Zn) and planar (Ni) complexes are evident; the larger size of Mn(II) displaces $[Mn_2(SEt)_6]^{2-}$ from the tetrahedral region. This linear correlation should be useful in approximating $M-S_t$ and $M-S_b$ distances in hypothetical or structurally uncharacterized molecules.

In a biological context, the mononuclear tetrahedral sites **1** occur in several metallobiomolecules,[51] most notably in the Fe(II,III) proteins, rubredoxins.[52] None of the other coordination units in Figure 1 has as yet been established in any natural product. Synthetic polynuclear thiolate complexes containing tetrahedral Zn(II) and Cd(II) are, however, pertinent to metal binding in metallothioneins.[53,54] Spectroscopic evidence, which has been summarized,[53-55] strongly supports the presence of $Cd_3(Cys\text{-}S)_9$ and $Cd_4(Cys\text{-}S)_{11}$ aggregates in Cd_7(metallothionein), with tetrahedral $(Cys\text{-}S)_4$ coordination and $Cd_3(\mu\text{-}Cys\text{-}S)_3$ rings similar to the six-membered rings present in **6** (M = Cd(II)[12]). Stoichiometric replacement of Zn(II) and Cd(II) in native metallothioneins with Co(II) and Ni(II) puts the latter ions in tetrahedral sites,[56] but it is not known if the oligomeric units present in the Cd(II) protein are retained. For one Zn protein, EXAFS analysis has yielded a Zn–S distance of 2.29 (2) Å.[57] Since the protein contained 5–6 mol of Zn/mol, this value is an average over terminal and bridging interactions. Data for $[Zn_2(SEt)_6]^{2-}$ and other Zn(II) thiolates[11,16,21,25] reveal that, although the two types of distances span appreciable ranges, all $Zn-S_b$ and some $Zn-S_t$ distances are longer than 2.29 (2) Å. Consequently, the protein value may be too small, perhaps by about 0.05 Å. In Cd_7(metallothionein) the proposed structures of the two aggregates involve 60% of all Cd–S bonds as bridging. Lastly, the Ni–S distances in several reduced and oxidized hydrogenases,[58,59] although not yet accurately determined (ca. 2.20, 2.25 Å, by EXAFS), are close to the Ni–S distances of $[Ni_2(SEt)_6]^{2-}$. The $Ni-S_t$ distances (2.201 (1)–2.218 (2) Å) provide a good measure of those expected for unconstrained bonds in mononuclear enzyme sites containing Ni(II).

Summary. This investigation provides further evidence for the formation of metal thiolate complexes in stoichiometric reactions, in this case $[M_2(SEt)_6]^{2-}$ from 3 equiv of NaSEt and 1 equiv of MCl_2 in acetonitrile. Structures of the M = Mn(II), Zn(II), and Cd(II) complexes are centrosymmetric edge-shared tetrahedra, and that of the Ni(II) complex is also centrosymmetric but essentially planar. In the set of known metal(II) thiolate structures **1–8**, shown in Figure 1, coordination geometries tend to follow the usual stereochemical preferences of M(II) ions. Structures **2**, **5**, and **6** require (distorted) tetrahedral, and **3**, **4**, **7**, and **8** planar, coordination. A tetrahedral version of **4** may be possible with certain ions. However, the similarity of the RS^-:M(II) ratios in **4** and **6** and the coordination of the central M(II) ion, which when tetrahedral will be kinetically labile, by four relatively weak bridging interactions suggest that **6** will form at the expense of **4**. The pronounced dimensional flexibility of $Ni_2(\mu\text{-}SR)_2$ units, including accommodation of varying extents of nonplanarity, is an important factor in the stabilization of the arrays $[Ni_n(SR)_{2n+2}]^{2-}$ (n = 2, 3; **3**, **4**) and $Ni_n(SR)_{2n}$ (n = 4, 6; **7**, **8**). The extension of the latter type to the n = 8 case[42] (not shown in Figure 1) further underscores this point. Reaction of cyclic $Ni_n(SR)_{2n}$ with RS^- may provide a route to $[Ni_n(SR)_{2n+2}]^{2-}$ species with nuclearities in excess of that of **4**. It is not clear that all homoleptic metal(II) thiolate structures with nuclearities of ≤6 have been discovered. Certainly, exploration of the utility of known compounds as precursors to new cages and clusters is a next logical step in the development of metal(II)–thiolate chemistry. As noted at the outset, the syntheses of $[Co_8S_6(SPh)_8]^{4-}$[10] and $[M_{10}S_4(SPh)_{16}]^{4-}$[13] are favorable harbingers in this respect.

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Registry No. $(Et_4N)_2$[**2**-*anti*] (M = Zn, R = Et), 97316-41-1; $(Et_4N)_2$[**2**-*anti*] (M = Cd, R = Et), 97336-11-3; $(Et_4N)_2$[**2**-*anti*] (M = Mn, R = Et), 97316-43-3; $(Me_4N)_2$[**2**-*anti*] (M = Ni, R = Et), 97316-45-5; $(Et_4N)_2$[**3**] (M = Ni, R = Et), 97316-47-7; S, 7704-34-9.

Supplementary Material Available: Tables of crystallographic data for $(Et_4N)_2[M_2(SEt)_6]$ (M = Zn(II), Cd(II), Mn(II)) and $(Me_4N)_2[Ni_2(SEt)_6]$ including anisotropic thermal parameters, hydrogen atom coordinates and isotropic temperature factors, bond distances and angles of cations, and calculated and observed structure factors (63 pages). Ordering information is given on any current masthead page.

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