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Synthesis and Structural Systematics of Ethane-1,2-dithiolato Complexes

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Reaction systems with a constant 2:1 Na_2edt:M(II,III) mole ratio (edt = ethane-1,2-dithiolate) have been shown to yield the following complexes, isolated as quaternary ammonium salts: $[Ti(edt)_3]^{2-}$ (**1**), $[V_2(edt)_4]^{2-}$ (**2**), $[Cr(edt)_2]^{2-}$ (**3**), $[Mn(edt)_2]^{2-}$ (**4**), $[Mn_2(edt)_4]^{2-}$ (**5**), $[Fe_2(edt)_4]^{2-}$ (**6**), $[Co(edt)_2]^{2-}$ (**7**), $[Co(edt)_2]^-$ (**8**), $[Ni_2(edt)_3]^{2-}$ (**9**), $[Cu_3(edt)_3]^{3-}$ (**10**), $[Zn(edt)_2]^{2-}$ (**11**), and $[Cd(edt)_2]^{2-}$ (**12**). The following compounds have been structurally characterized by single-crystal X-ray diffraction (space group; crystal parameters; Z; unique data ($I > (2-3)[\sigma(I)]$); R/R_w). $(Et_4N)_2$(**1**): $Pna2_1$; $a = 21.151$ (4) Å, $b = 9.671$ (1) Å, $c = 15.046$ (3) Å; 4; 1865; 3.4/3.4. $(Et_4N)_2$(**3**): $C2/c$; $a = 13.023$ (2) Å, $b = 17.369$ (3) Å; $c = 12.825$ (2) Å, $\beta = 103.97$ (1)°; 4; 1631; 4.5/6.0. $(Me_4N)_3$(**7·8**): $Pbca$; $a = 26.366$ (6) Å, $b = 16.943$ (4) Å, $c = 15.722$ (3) Å; 8; 1695; 5.4/5.3. Na$(Me_3NCH_2Ph)_2$(**10**)·MeOH: $P2_1/n$; $a = 10.344$ (4) Å, $b = 9.839$ (4) Å, $c = 36.511$ (11) Å, $\beta = 96.72$ (3)°; 4; 4525; 5.4/6.4. $(Et_4N)_2$(**11**): $P2_1/a$; $a = 12.793$ (2) Å, $b = 16.321$ (4) Å, $c = 12.942$ (2) Å, $\beta = 94.52$ (2)°; 4; 3523; 3.6/4.1. $(Et_4N)_2$(**12**): $P2_1/a$; $a = 12.987$ (4) Å, $b = 16.465$ (6) Å, $c = 13.015$ (3) Å, $\beta = 95.28$ (2)°; 4; 3370; 3.6/4.0. Crystals of $(Me_4N)_3[Co_2(edt)_4]$ contain a 1:1 mixture of **7** and **8**. These results, together with previously published information, lead to the recognition of *seven* structural types of homoleptic edt complexes, which closely approach or achieve the indicated symmetry: octahedral (C_3)—**1**; planar (D_{2h})—**3**, **8**; tetrahedral (D_{2d})—**4**, **7**, **11**, **12**; nonoctahedral tetrabridged dimer (D_2)—**2**; lateral doubly bridged dimer (C_i)—**5**, **6**; doubly bridged folded planar (C_i)— **9**; cyclic trimer (C_3)—**10**. The complex unit in crystals containing **10** is $[Na(MeOH)[Cu_3(edt)_3]]^{2-}$, displaying a nonplanar $Cu_3(\mu\text{-}S)_3$ ring, trigonal Cu(I) coordination, and three Cu(edt) chelate rings projecting outward from the same face of the Cu_3S_3 ring. Na^+ is situated on the C_3 axis and is tetrahedrally coordinated by three S atoms and the O atom of methanol. Metal(II) complexes follow normal stereochemical preferences. Extended Hückel MO calculations suggest that D_2 dimers of M(III) d^n ions will be unstable when $n \geq 4$ and provide a rationale of the stability of C_i dimers with $n = 4, 5$. Complex **8** is an example of the rare planar spin-triplet Co(III) configuration; its existence emphasizes the strong in-plane antibonding character induced by edt. The most significant metric feature of this ligand is its large bite distance flexibility (~3.1–3.6 Å). Parametric correlations of bite distance and M–S bond distance with the ionic potential per ligand are offered. M(edt) chelate rings have conformations ranging from half-chair to envelope, with the majority of conformations intermediate of these but biased toward the half-chair. Complexes **1–12** constitute the most structurally diverse set of homoleptic complexes yet characterized.

Introduction

Evolvement of the metal complex chemistry of thiolates, a fundamental ligand type, has proceeded so rapidly, particularly over the last half-dozen years, that our knowledge of synthetic and structural aspects of discrete, soluble metal thiolates is approaching that of the venerable metal alkoxides. Among the recent significant developments in the field are these: (i) experimental realization of families of mono- and polynuclear species, including $c\text{-}[Ni_n(SR)_{2n}]^{2-}$[4] ($n = 4, 6, 8$), linear $[Ni_n(SR)_{2n+2}]^{2-}$[5,6] ($n = 2, 3$), $[M(SR)_n]^{(n-1)-}$[7,8] ($n = 2, 3$), $[M_n(SR)_{n+2}]^{2-}$ ($n = 4$–6),[8–11] and $[M_5(SR)_6]^-$[12] (M = Cu(I), Ag(I)); (ii) demonstration of the three species $[M(SR)_4]^{2-}$,[13] $[M_2(\mu\text{-}SR)_2(SR)_4]^{2-}$,[5,6,14] and adamantane-like $[M_4(\mu\text{-}SR)_6(SR)_4]^{2-}$[15] for all transition-element M(II) ions with a tetrahedral stereochemical preference; (iii) stabilization of Fe(III) in $[Fe(SR)_4]^-$ derived from *mono*functional thiolates;[16] (iv) preparation of homoleptic complexes of second-transition-series elements (Mo;[17] Ru, Os[18]); (v) use of M(II) thiolates in reactions with S(0) or sulfide as precursors to M–S–SR clusters (M = Fe(II,III);[13b,19] Co(II);[20] Zn(II), Cd(II)[21]). In these works and in other contemporary investigations of metal thiolates, the largest body of information accumulated is structural in nature. This is an expected situation in the development of any new family of compounds, and especially so with thiolate complexes, where polynuclear species are the rule, not the exception, and are not amenable to secure structural definition by any means other than X-ray analysis.

Despite the formidable body of structural and related data, there has been insufficient information to address this fundamental question: at a fixed thiolate:metal reactant mole ratio, what compounds are formed by all elements of the first transition series and what are their structures? Such a question is clearly highly

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pertinent to the development of any new family of metal complexes. It has been pursued here by using homoleptic complexes derived from ethane-1,2-dithiolate. The basis for this choice is our own observations of Fe(III)[22] and Mn(II,III)[15a] systems and the early aqueous solution studies by Leussing et al.,[23,24] all results making clear the strong affinity of this ligand for first-transition-series ions. We have briefly described our initial results[25] in relation to the above question. Here we report a more extensive set of results including full synthetic and structural details. Our findings, and those of others,[26-28] are integrated into a description of some 12 homoleptic ethane-1,2-dithiolate complexes. As already observed,[25] this is the most structurally diverse set of homoleptic complexes yet characterized.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere; solvents were degassed prior to use. Disodium ethane-1,2-dithiolate was prepared as follows. A mixture of 34.5 g (0.37 mol) of the dithiol and 15.3 g (0.67 mol) of finely divided sodium in 700 mL of THF (dried over CaH_2) was refluxed for 1 week. The product was collected by filtration, washed thoroughly with THF and then ether, dried in vacuo, and stored under anaerobic conditions. $Na_2(S_2C_2H_4)$ was obtained as a white powder and was used in the following preparations unless generated in situ.

$(Et_4N)_2[Ti(S_2C_2H_4)_3]$. (a) From $TiCl_4$. To 1.9 g (10 mmol) of $TiCl_4$ in sufficient acetonitrile to give a clear solution was added 3.4 g (20 mmol) of Et_4NCl, resulting in an orange-red solution. After the reaction mixture was stirred for 1 h, 4.6 g (33 mmol) of $Na_2(S_2C_2H_4)$ was added. After it was stirred for 2 days, the dark orange-red mixture was filtered, and the filtrate was reduced to one-fifth of its original volume. Ether (8 mL) was added to the filtrate at 0 °C to give orange-red crystals. These were collected and washed with 5% v/v acetonitrile/ether and then ether. Repetition of this procedure gave a total of 4.8 g (82%) of pure product. Anal. Calcd for $C_{22}H_{52}N_2S_6Ti$: C, 45.17; H, 8.96; N, 4.79; S, 32.90; Ti, 8.20. Found: C, 45.34; H, 8.74; N, 4.92; S, 32.74; Ti, 8.11. ^1H NMR (CD_3CN): δ 3.34 (CH_2, anion).

(b) From $TiCl_3$. This compound (0.77 g, 5.0 mmol) and 1.05 g (5.0 mmol) of Et_4NBr were stirred for 5 h in ~50 mL of acetonitrile. $Na_2(S_2C_2H_4)$ (1.38 g, 10 mmol) was added, and the reaction mixture was stirred for 2 days. Filtration gave a deep orange-brown filtrate, which was concentrated to ~20 mL. Addition of ether and cooling to -20 °C produced orange-red crystals whose absorption and NMR spectra are the same as those of the product of the preceding preparation.

$(Et_4N)_2[V_2(S_2C_2H_4)_4]$. The following procedure is far more explicit than those given earlier for the same[29] and different[27] salts of the anion. To a solution of 1.79 g (13 mmol) of $Na_2(S_2C_2H_4)$ in 200 mL of methanol was added dropwise 1.01 g (6.5 mmol) of VCl_3 in 50 mL of methanol, causing a red-brown color. The solution was stirred for ~12 h (no color change) and then was treated with a solution of 2.12 g (26 mmol) of Et_4NCl in 20 mL of methanol. After 30 min of stirring the solvent was removed, and the residue was extracted with ~75 mL of acetonitrile. The filtrate from the acetonitrile suspension was reduced in volume by half and maintained at 0 °C. Large red-brown, block-shaped crystals separated, which are suitable for X-ray analysis. Further volume reduction and cooling gave a second crop. The combined crops were dried in vacuo, affording 1.5 g (65%) of pure product; analytical data are given elsewhere.[29]

$(Et_4N)_2[Cr(S_2C_2H_4)_2]$. A mixture of 1.23 g (10 mmol) of anhydrous $CrCl_2$ and 3.31 g (20 mmol) of anhydrous Et_4NCl in 100 mL of dry acetonitrile was stirred for 4 h, during which time a green color developed. $Na_2(S_2C_2H_4)$ (3.16 g, 20 mmol) was added, and stirring was continued for ~2.5 days. The violet filtrate from the reaction mixture was concentrated to ~30 mL and kept at -20 °C overnight. Violet crystals were collected, washed with 5% v/v acetonitrile/ether and ether, and dried. Ether diffusion into the filtrates gave two more crops, which when combined with the first two gave 2.20 g (45%). Anal. Calcd for $C_{20}H_{48}CrN_2S_4$: C, 48.35; H, 9.74; Cr, 10.47; N, 5.64; S, 25.81. Found: C, 48.33; H, 9.75; Cr, 9.82; N, 5.49; S, 25.51. ^1H NMR: δ -46.1 (CH_2, anion).

$(Me_4N)_x[Cr_x(S_2C_2H_4)_{2x}]$. To a solution of 24 mmol of $Na_2(S_2C_2H_4)$ (from 2.2 g of the dithiol and 2.6 g of NaOMe) in 150 mL of methanol was added a solution of 3.16 g (12 mmol) of $CrCl_3{\cdot}6H_2O$ in 50 mL of methanol. The reaction mixture was initially blue-gray, but after 20 min of stirring it turned dark green-brown and remained this color upon further stirring for 18 h. A solution of 1.30 g (12 mmol) of Me_4NCl in 30 mL of methanol was added, and the solvent was removed in vacuo. The brown residue was extracted with ~150 mL of warm acetonitrile. Cooling of the extract filtrate afforded 2.85 g (75%) of product as a gold microcrystalline solid. Anal. Calcd for $C_8H_{20}CrNS_4$: C, 30.94; H, 6.51; Cr, 16.74; N, 4.51; S, 41.30. Found: C, 30.57; H, 6.39; Cr, 16.33; N, 4.54; S, 41.17.

$(Me_4N)_2[Co(S_2C_2H_4)_2]{\cdot}(Me_4N)[Co(S_2C_2H_4)_2]$. A solution of 4.34 g (34 mmol) of anhydrous $CoCl_2$ in 50 mL of methanol was added dropwise to a solution of 70 mmol of $Na_2(S_2C_2H_4)$ (from 3.23 g of sodium and 6.62 g of dithiol) in 100 mL of methanol. The resulting green solution was stirred for 12 h, after which time a solution of 7.70 g (71 mmol) of Me_4NCl in 50 mL of methanol was slowly added. The solution was stirred for 30 min, the solvent removed in vacuo, and the residue extracted with 100 mL of acetonitrile. The extract filtrate volume was condensed to ~25 mL. The green microcrystalline material that separated was collected and recrystallized from acetonitrile/ether; 6.50 g (58%) of green crystalline product was obtained. Anal. Calcd for $C_{20}H_{52}Co_2N_3S_4$: C, 33.87; H, 7.41; Co, 16.62; N, 5.92; S, 36.17. Found: C, 33.79; H, 7.48; Co, 16.64; N, 5.97; S, 35.97.

$(n\text{-}Bu_4N)_2[Ni_2(S_2C_2H_4)_3]$. To a solution of 119 mmol of $Na_2(S_2C_2H_4)$ (from 11.2 g of the dithiol and 4.76 g of NaOH) in 150 mL of water was added slowly a solution of 13.8 g (57 mmol) of $NiCl_2{\cdot}6H_2O$ in 100 mL of water. The dark green solution was stirred for several hours and filtered to remove a small quantity of insoluble brown material. The filtrate was treated with 36.7 g (114 mmol) of $(n\text{-}Bu_4N)Br$ in 75 mL of water, and the mixture was stirred for 3 h, during which time dark green-black microcrystals appeared. This material was collected, washed with 75 mL of cold water, and dried in vacuo; 20.3 g (50%) of pure product was obtained. Anal. Calcd for $C_{38}H_{84}N_2Ni_2S_6$: C, 51.92; H, 9.65; N, 3.19; Ni, 13.36; S, 21.88. Found: C, 51.62; H, 9.22; N, 3.14; Ni, 13.01; S, 21.41.

$(Me_3NCH_2Ph)_2Na[Cu_3(S_2C_2H_4)_3]{\cdot}MeOH$. A solution of 20 mmol of $Na_2(S_2C_2H_4)$ in 80 mL of methanol (from 0.92 g of sodium and 1.9 g of dithiol) was added to 1.35 g (10 mmol) of $CuCl_2$. The initially light brown mixture was stirred for ~1 day and filtered into a solution of 3.71 g (20 mmol) of $(Me_3NCH_2Ph)Cl$ in 30 mL of methanol. This solution was stirred for 2 h, during which time a fine yellow precipitate formed. After the solvent was removed in vacuo, the residue was dissolved with stirring in ~70 mL of acetonitrile and the solution was filtered. The filtrate was concentrated to ~35 mL, and the yellow-brown solution was cooled to -20 °C. The solid was collected, washed thoroughly with 10:1 v/v ether/acetonitrile and ether, and dried under a dinitrogen stream to give 1.10 g (40%) of pure product as a yellow crystalline solid. A second crop can be obtained by addition of ether to the filtrate and cooling. Anal. Calcd for $C_{27}H_{48}Cu_3NaOS_6$: C, 39.42; H, 5.88; Cu, 23.17; N, 3.41; Na, 2.79; S, 23.38. Found: C, 39.12; H, 5.62; Cu, 23.45; N, 3.35; Na, 2.68; S, 23.42.

$(Et_4N)_2[Zn(S_2C_2H_4)_2]$. A mixture of 1.36 g (10 mmol) of $ZnCl_2$ and 3.31 g (20 mmol) of Et_4NCl in 70 mL of acetonitrile was stirred for ~30 min, and then 2.76 g (20 mmol) of $Na_2(S_2C_2H_4)$ was added. The mixture was stirred for 2 days and filtered, and the filtrate was concentrated to ~20 mL. Ether (4 mL) was added, and the solution was maintained at -20 °C overnight. The crystals were collected by filtration, washed thoroughly with 10:1 v/v ether/acetonitrile and ether, and dried in vacuo. The product was obtained as 3.50 g (69%) of colorless crystals. Anal. Calcd for $C_{20}H_{48}N_2S_4Zn$: C, 47.08; H, 9.48; N, 5.49; S, 25.13; Zn, 12.81. Found: C, 46.89; H, 9.34; N, 5.55; S, 25.09; Zn, 12.69.

$(Et_4N)_2[Cd(S_2C_2H_4)_2]$. The preceding method was followed with $CdCl_2$ at half the scale. The product (1.42 g, 51%) was isolated as colorless crystals. Anal. Calcd for $C_{20}H_{48}CdN_2S_4$: C, 43.11; H, 8.68; Cd, 20.17; N, 5.03; S, 23.01. Found: C, 43.26; H, 8.44; Cd, 20.44; N, 5.09; S, 23.20.

Collection and Reduction of X-ray Data. Suitable crystals of compounds A, B, and D–F in Table I were obtained by crystallization from the solvents used in bulk purifications. Crystals of compound C were grown by slow cooling of an acetonitrile solution. All data were collected on a Nicolet R3m or P3F four-circle automated diffractometer at am-

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Table I. Crystal Data, Intensity Collections,[a] and Structure Refinement Parameters for $(Et_4N)_2[Ti(S_2C_2H_4)_3]$ (A), $(Et_4N)_2[Cr(S_2C_2H_4)_2]$ (B), $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$ (C), $Na(Me_3NCH_2Ph)_2[Cu_3(S_2C_2H_4)_3]\cdot MeOH$ (D), and $(Et_4N)_2[M(S_2C_2H_4)_2]$ (M = Zn(II) (E), Cd(II) (F))

	A	B	C	D	E	F
formula	$C_{22}H_{52}N_2S_6Ti$	$C_{20}H_{48}CrN_2S_4$	$C_{20}H_{52}N_3S_8Co_2$	$C_{27}H_{48}Cu_3N_2NaOS_6$	$C_{20}H_{48}N_2S_4Zn$	$C_{20}H_{48}CdN_2S_4$
mol wt	584.96	496.88	709.14	822.71	510.25	557.28
a, Å	21.151 (4)	13.023 (2)	26.366 (6)	10.344 (4)	12.793 (2)	12.987 (4)
b, Å	9.671 (1)	17.369 (3)	16.943 (4)	9.839 (4)	16.321 (4)	16.465 (6)
c, Å	15.046 (3)	12.825 (2)	15.722 (3)	36.511 (11)	12.942 (2)	13.015 (3)
β, deg		103.97 (1)		96.72 (3)	94.52 (2)	95.28 (2)
V, $Å^3$	3078 (1)	2815 (1)	7023 (3)	3690 (2)	2694 (1)	2771 (1)
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Z	4	4	8	4	4	4
d_{calcd} (d_{obsd}), g/cm^3	1.26 (1.25)	1.17 (1.18)	1.34 (1.35)	1.48 (1.46)	1.26 (1.26)	1.34 (1.35)
space group	$Pna2_1$	$C2c$	$Pbca$	$P2_1/n$	$P2_1/a$	$P2_1/a$
cryst dimens, mm	0.44 × 0.22 × 0.50	0.40 × 0.50 × 0.35	0.40 × 0.35 × 0.28	0.60 × 0.45 × 0.75	0.40 × 0.65 × 0.35	0.10 × 0.60 × 0.60
abs coeff, μ, cm^{-1}	6.89	6.90	14.2	20.8	10.9	10.8
transmission factors (max/min)	0.61/0.53	0.65/0.58	0.53/0.43	0.24/0.16	0.51/0.40	0.94/0.65
scan speed, deg/min	2.0–29.3	2.0–29.3	2.9–29.3	2.0–29.3	2.0–29.3	3.0–29.3
2θ limits, deg	$4.0 \leq 2\theta \leq 45.0$	$3.0 \leq 2\theta \leq 47.5$	$4.0 \leq 2\theta \leq 42.0$	$3.0 \leq 2\theta \leq 51.0$	$3.0 \leq 2\theta \leq 48.0$	$3.0 \leq 2\theta \leq 47.0$
scan range,[b] deg	1.6	1.4	1.6	1.4	1.4	1.8
data collected	2323 ($+h,+k,+l$)	4708 ($+h,+k,\pm l$)	4057 ($+h,+k,+l$)	7146 ($+h,+k,\pm l$)	4657 ($+h,+k,\pm l$)	4356 ($+h,+k,\pm l$)
unique data	1865[c]	1631[d]	1695[e]	4525[d]	3253[d]	3370[d]
no. of variables	280	145	298	361	244	244
goodness of fit (GOF)[g]	1.2	1.1	1.2	1.1	1.1	1.1
R (R_w), %[f]	3.4 (3.4)	4.5 (6.0)	5.4 (5.3)	5.4 (6.4)	3.6 (4.1)	3.6 (4.0)

[a] Mo K$\bar{\alpha}$ (λ = 0.71069 Å) used in all cases. [b] Value given is x in $x + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$; bkgd/scan time ratio 0.25. [c] $I > 2\sigma(I)$. [d] $I > 3\sigma(I)$. [e] $I > 2.5\sigma(I)$. [f] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$. [g] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v are the numbers of data and variables, respectively.

bient temperature (~23 °C) using graphite monochromatized Mo K$\bar{\alpha}$ radiation. The $\theta/2\theta$ scan mode was used for all compounds except A, whose data were collected by the ω-scan technique. No significant intensity changes were observed upon monitoring three check reflections after every 123 reflections. The crystal and machine parameters used in the data collections are summarized in Table I. The SHELXTL programs XTAPE and XEMP were used for data processing and empirical absorption corrections, respectively. Corrections were applied to all data sets with use of ϕ scan data collected every 10° for 10 of those reflections whose χ values were close to either 90 or 270°.

Structure Solution and Refinement. The SHELXTL program package (Nicolet XRD Corp., Madison, WI) was used throughout. All structures were solved by using the direct methods program SOLV, which revealed positions of the metal and some of the sulfur atoms. The remaining non-hydrogen atoms were located from difference Fourier maps computed after blocked-cascade least-squares refinement. Atom scattering factors were taken from a standard source.[30a] For all compounds except C, hydrogen atoms were located from difference Fourier maps computed upon convergence of anisotropic refinements. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were refined isotropically in the last stages of refinement. Hydrogen atoms of C were included at 0.96 Å from and with thermal parameters 1.2× that of the bonded carbon atom. Unique data used in the refinements and final *R* factors and related data are given in Table I. Individual structure refinements are briefly described.

(a) $(Et_4N)_2[Ti(S_2C_2H_4)_3]$. The systematic absences $0kl$ ($k + l = 2n + 1$) and $h0l$ ($h = 2n + 1$) together with *E* statistics suggested the noncentrosymmetric space group $Pna2_1$ (No. 33, with the following equivalent positions: x, y, z; $\bar{x}, \bar{y}, {}^1/_2 + z$; ${}^1/_2 + x, {}^1/_2 - y, z$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 + z$). Successful structure solution and refinement confirmed this choice. The asymmetric unit contains two cations and one anion, all of which were well-behaved during refinement. Isotropic refinement converged at $R = 8.4\%$.

(b) $(Et_4N)_2[Cr(S_2C_2H_4)_2]$. The systematic absences hkl ($h + k = 2n + 1$) and $h0l$ ($h, l = 2n + 1$) and *E* statistics indicated the centrosymmetric space group $C2/c$ (No. 15, with the following equivalent positions: $\pm(x, y, z; -x, y, {}^1/_2 - z)$). Successful structure solution and refinement confirmed this choice. The asymmetric unit contains one half-anion and two half-cations, with imposed centrosymmetry on the anion and twofold symmetry on the cations. Isotropic refinement converged at $R = 12\%$. This rather high value is due to disorder of one of the cations, which in subsequent refinements was modeled successfully in terms of two sites with 0.5 occupancies for each of the methylene carbon atoms.

(c) $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$. The systematic absences $0kl$ ($k = 2n + 1$), $h0l$ ($l = 2n + 1$), and $hk0$ ($h = 2n + 1$) uniquely determine the space group to be $Pbca$ (No. 61, with the following equivalent positions: $\pm(x, y, z$; ${}^1/_2 - x, \bar{y}, {}^1/_2 + z$; $\bar{x}, {}^1/_2 + y, {}^1/_2 - z$; ${}^1/_2 + x, {}^1/_2 - y, \bar{z}$)). The metal atoms were located from a Patterson map, and other atoms were found as in other cases. The asymmetric unit contains three cations, one planar monoanion, and one tetrahedral dianion. Isotropic refinement converged at $R = 8.9\%$. The carbon atoms of the thiolate ligands, particularly those of the monoanion, have rather large thermal parameters, which are probably associated with conformational disorder of the chelate rings. Attempts to model this disorder in terms of fractional site occupancies of carbon atoms were unsuccessful.

(d) $(Me_3NCH_2Ph)_2Na[Cu_3(S_2C_2H_4)_3]\cdot MeOH$. The systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$) uniquely determine the space group as $P2_1/n$ (a nonstandard setting of $P2_1/c$, No. 14, with the following equivalent positions: $\pm(x, y, z$; ${}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$)). The asymmetric unit consists of two $(Me_3NCH_2Ph)^+$ cations and one complex anion, $[Na(MeOH)Cu_3(S_2C_2H_4)_3]^{2-}$, all of which were well behaved during refinement. Isotropic refinement converged at $R = 11\%$.

(e) $(Et_4N)_2[M(S_2C_2H_4)_2]$ (M = Zn(II), Cd(II)). These isomorphous compounds exhibited the systematic absences $h0l$ ($h = 2n + 1$) and $0k0$ ($k = 2n + 1$), which uniquely define the space group to be $P2_1/a$ (nonstandard setting of $P2_1/c$, No. 14, with the following equivalent positions: $\pm(x, y, z$; ${}^1/_2 - x, {}^1/_2 + y, -z$)). The asymmetric unit contains two cations and one anion, none of which exhibited disorder. Isotropic refinements converged at $R = 7.1\%$ for Zn(II) and 8.0% for Cd(II).

Atom coordinates for compounds A–F are compiled in Tables II–VII.[30b]

Results and Discussion

In seeking to define homoleptic ethane-1,2-dithiolate (edt) complexes of the first transition series, we have utilized reaction systems with a constant 2:1 Na_2edt:M(II,III) mole ratio. This choice was based on the observations that a number of solution species have this stoichiometry[23,24] as does $[Fe_2(edt)_4]^{2-}$, the first homoleptic edt complex isolated.[22,28] Described here are the structures of products from systems initially containing Ti(III,IV), Cr(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II). We and others have previously investigated edt complexes of V(III)[27,29] and

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(30) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) See paragraph at the end of this article concerning supplementary material available.

Table II. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[Ti(S_2C_2H_4)_3]$

atom	*x*	*y*	*z*
Ti	1713 (1)[a]	5073 (1)	−752 (1)
S(1)	876 (1)	3595 (2)	−176 (2)
S(2)	2388 (1)	3284 (2)	−146 (2)
S(3)	903 (1)	6834 (2)	−974 (2)
S(4)	2021 (1)	6567 (2)	463 (2)
S(5)	1438 (1)	4279 (2)	−2237 (1)
S(6)	2670 (1)	5834 (2)	−1486 (1)
C(1)	1251 (4)	1966 (7)	87 (6)
C(2)	1880 (3)	2207 (6)	529 (5)
C(3)	950 (3)	7974 (7)	−9 (5)
C(4)	1628 (4)	8174 (7)	261 (5)
C(5)	2075 (3)	4793 (9)	−2970 (5)
C(6)	2696 (3)	4834 (9)	−2493 (5)
N(1)	898 (3)	5133 (6)	3190 (4)
C(7)	807 (4)	4771 (8)	4165 (6)
C(8)	1409 (5)	4521 (12)	4658 (8)
C(9)	242 (3)	5414 (7)	2813 (5)
C(10)	244 (4)	5836 (9)	1869 (5)
C(11)	1219 (3)	3994 (8)	2677 (6)
C(12)	850 (4)	2647 (8)	2654 (7)
C(13)	1314 (3)	6408 (8)	3074 (7)
C(14)	1051 (4)	7724 (8)	3479 (7)
N(2)	1072 (2)	−246 (5)	6695 (4)
C(15)	4435 (4)	3645 (9)	1551 (7)
C(16)	4191 (7)	2354 (13)	1085 (10)
C(17)	1312 (4)	319 (9)	5820 (7)
C(18)	4184 (6)	5740 (13)	148 (7)
C(19)	749 (4)	880 (9)	7221 (7)
C(20)	496 (5)	515 (10)	8140 (7)
C(21)	1600 (4)	−935 (10)	7207 (7)
C(22)	2069 (4)	163 (11)	7602 (7)

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

Table III. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[V_2(S_2C_2H_4)_4]$

atom	*x*	*y*	*z*
V	0	8450 (1)	7500
S(1)	−647 (1)	9724 (1)	6741 (1)
S(2)	−843 (1)	7598 (1)	8483 (1)
C(1)	−141 (4)	10838 (4)	7016 (5)
C(2)	−405 (3)	7542 (6)	9602 (4)
N	2500	0	5713 (4)
C(1n)	2921 (3)	718 (4)	5129 (4)
C(2n)	1915 (4)	494 (5)	6275 (5)
C(3n)	2480 (5)	1266 (5)	4451 (6)
C(4n)	2243 (6)	1218 (7)	6960 (6)

Table IV. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[Cr(S_2C_2H_4)_2]$

atom	*x*	*y*	*z*
Cr(1)	7500	2500	0
S(1)	8364 (1)	1511 (1)	−763 (1)
S(2)	6434 (1)	1580 (1)	637 (1)
C(1)	9104 (4)	2080 (3)	−1513 (4)
C(2)	5536 (4)	2214 (3)	1107 (5)
N(1)	10000	657	2500
N(2)	5000	−294	2500
C(3)	9018 (3)	1135 (3)	2335 (3)
C(4)	4018 (4)	3264 (3)	−1812 (4)
C(5)	9915 (3)	152 (2)	1507 (3)
C(6)	8955 (4)	−364 (3)	1233 (3)
C(7)	4367 (6)	384 (4)	2190 (7)
C(7′)	4112 (6)	−196 (5)	1530 (6)
C(8)	6628 (4)	378 (4)	3578 (5)
C(9)	5562 (7)	−1034 (4)	2409 (7)
C(9′)	5529 (7)	−466 (5)	1460 (7)
C(10)	3779 (5)	1039 (4)	−1557 (6)

Table V. Atom Coordinates ($\times 10^4$) for $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$

atom	*x*	*y*	*z*
Co(1)	2532 (1)	6258 (1)	−181 (1)
Co(2)	−115 (1)	3613 (1)	2611 (1)
S(1)	3165 (1)	5666 (2)	−934 (2)
S(2)	3079 (2)	6614 (2)	880 (2)
S(3)	2049 (1)	7185 (2)	−865 (2)
S(4)	1832 (1)	5539 (2)	169 (3)
S(5)	−172 (2)	4382 (2)	1510 (2)
S(6)	233 (2)	2681 (2)	1866 (2)
S(7)	13 (2)	2911 (2)	3740 (2)
S(8)	−507 (2)	4507 (3)	3340 (3)
C(1)	3711 (5)	5979 (9)	−344 (8)
C(2)	3659 (6)	6152 (10)	535 (10)
C(3)	1423 (5)	6830 (8)	−610 (11)
C(4)	1353 (5)	6037 (7)	−429 (10)
C(5)	73 (7)	3785 (11)	639 (7)
C(6)	377 (7)	3154 (10)	881 (10)
C(7)	−271 (7)	3463 (9)	4573 (9)
C(8)	−471 (9)	4127 (11)	4406 (9)
N(1)	1517 (4)	1533 (5)	3472 (6)
C(11)	2032 (4)	1190 (7)	3418 (8)
C(21)	1377 (6)	1606 (8)	4385 (8)
C(31)	1166 (5)	1017 (7)	3017 (9)
C(41)	1508 (5)	2318 (7)	3059 (8)
N(2)	1065 (4)	5866 (6)	2521 (7)
C(12)	1109 (5)	5051 (9)	2226 (9)
C(22)	1594 (7)	6172 (9)	2609 (11)
C(32)	796 (9)	5856 (11)	3352 (11)
C(42)	792 (8)	6334 (10)	1878 (11)
N(3)	2216 (5)	8814 (6)	1479 (7)
C(13)	2066 (8)	9468 (9)	2016 (9)
C(23)	2099 (7)	8974 (8)	571 (7)
C(33)	2757 (6)	8677 (8)	1537 (10)
C(43)	1977 (7)	8075 (9)	1750 (9)

Mn(II,III).[15a,26] In order to present the complete set of edt complexes of the first transition series, the structures of these complexes are briefly reviewed. As will be seen, this set encompasses some three stoichiometric and seven stereochemical types I–VII, which are schematically represented in Figure 1. In the ensuing discussion ligands designated as "thiolates" or "dithiolates" are to be distinguished from dithiolenes.[31] While the latter often function as classical 1,2-dithiolates, they are not infrequently electronically ambiguous, especially in the more oxidized complexes.

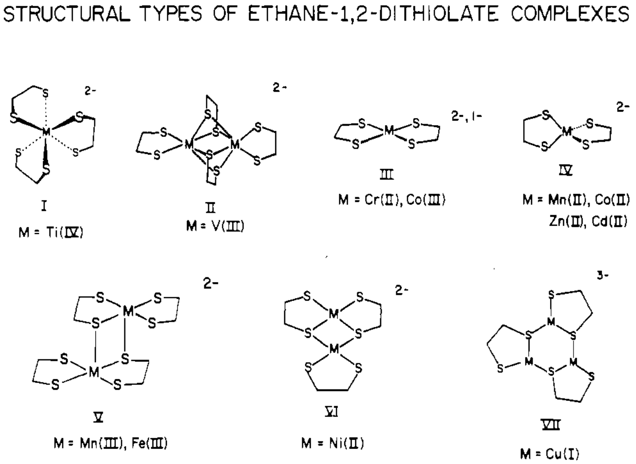

Figure 1. Schematic depictions of the seven stereochemical types I–VII of ethane-1,2-dithiolate complexes of the first transition series.

$[Ti(edt)_3]^{2-}$. Initial experiments revealed that the 2:1 Na_2edt:$TiCl_3$ system in acetonitrile afforded the tris complex as the only isolable product. Subsequently, the same orange-red crystalline product was obtained in 42% purified yield as its Et_4N^+ salt from the 3:1 Na_2edt:$TiCl_4$ reaction system. The structure of $[Ti(edt)_3]^{2-}$, shown in Figure 2, is that of a tris-chelate complex I with idealized C_3 symmetry. Distances and angles are organized under this symmetry in Table VIII. For example, the Ti–S bond distances divide into two sets, Ti–S(1,3,5) (2.434 (4) Å) and Ti–S(2,4,6) (2.419 (1) Å), with the indicated mean values. In addition to the data in Table VIII, the fairly narrow ranges of the angles S(*i*)–Ti–S(*j*) (*i*,*j* = 1,4; 2,5; 3,6) at 84.0 (1)–89.1 (1)°

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(31) Typical dithiolene ligands include benzene-1,2-dithiolate (bdt), toluene-3,4-dithiolate (tdt), ethene-1,2-dithiolate (ebt), maleonitriledithiolate (mnt), and bis(methoxycarbonyl)ethene-1,2-dithiolate (dma).

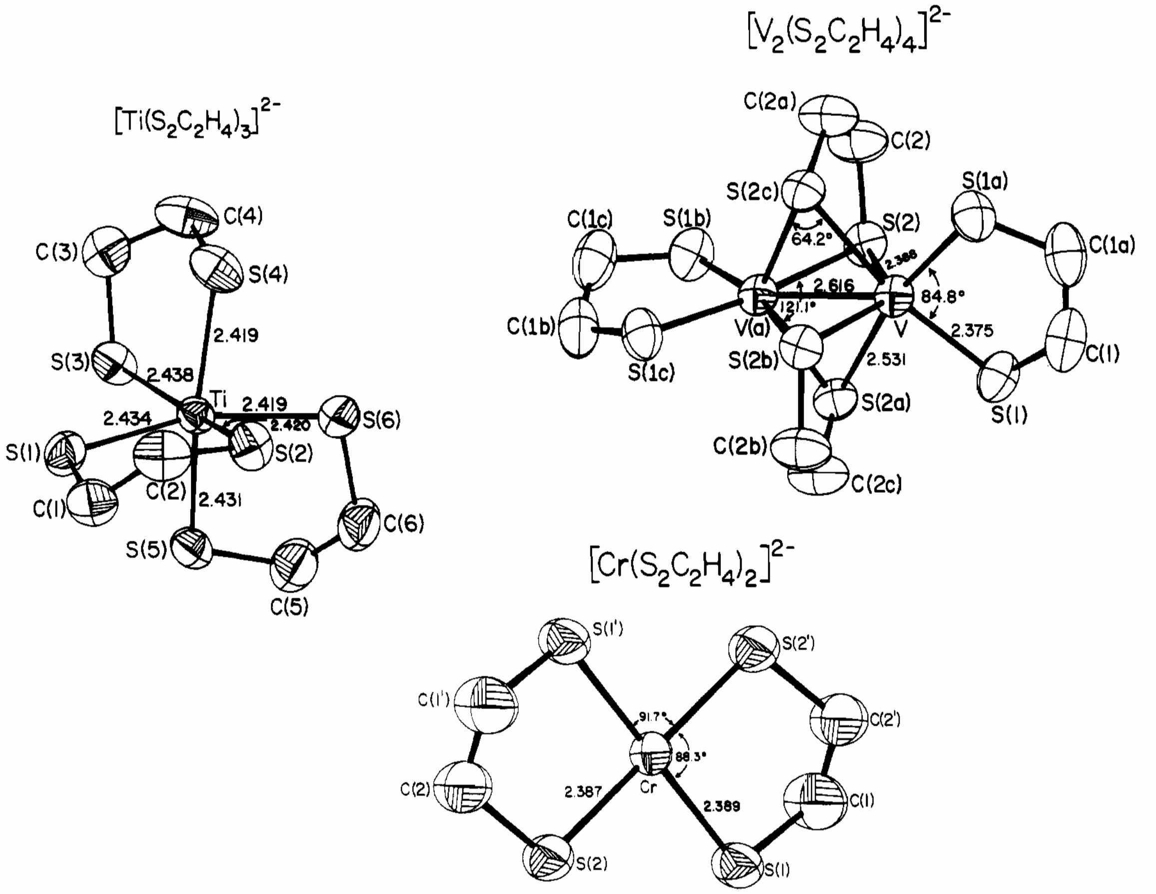

Figure 2. Structures of $[Ti(edt)_3]^{2-}$, $[V_2(edt)_4]^{2-}$,[29] and $[Cr(edt)_2]^{2-}$. In this and subsequent figures the atom-labeling schemes, 50% probability ellipsoids, and selected interatomic distances and angles or their mean values are given.

and S(m)–Ti–S(n) (m,n = 1,6; 2,3; 4,5) at 161.2 (1)–164.7 (1)° are consistent with C_3 near-symmetry. Planes S(1,3,5) and S(2,4,6) form a dihedral angle of 1.8°. Projected twist angles ϕ = 34.6, 38.4, and 41.0°, reflecting a geometry intermediate between an octahedron (ϕ = 60°) and a trigonal prism (ϕ = 0°). The average ligand bite distance (3.213 (1) Å) is nearly the same as that in $(Ph_3P)_2Pt(edt)$,[32] presumably because planar Pt(II) and octahedral Ti(IV) have identical Shannon radii.[33]

$[Ti(edt)_3]^{2-}$ is the first fully characterized homoleptic Ti thiolate,[34] and it is the only (edt)$_3$ complex that has been prepared in this work. The closest approaches to $[Ti(edt)_3]^{2-}$ are the tris(dithiolene) dianions,[35] which very likely are Ti(IV) complexes; none have been structurally characterized. Other Ti/SR species are principally of the type $Cp_2Ti(SR)_2$, whose Ti–S bond distances (2.40–2.41 Å[36]) are comparable with those found here.[37]

$[V_2(edt)_4]^{2-}$. This complex was reported nearly simultaneously by ourselves[29] and two other groups.[27] It is significant that, in anaerobic reaction systems conducted in methanol or ethanol with the mole ratio range (2–4):1 Na_2edt:VCl_3, the same product, $[V_2(edt)_4]^{2-}$, was obtained in each case. Its structure II, as the Et_4N^+ salt with imposed D_2 symmetry, is presented in Figure 2. In other salts[27] the same structure exists, with dimensions whose small differences are not chemically significant. Because this structure has been described on earlier occasions,[27,29] only its main features are briefly outlined. The anion contains two V(III) atoms bridged by four nearly coplanar sulfur atoms from two η^4-μ-edt groups and terminally coordinated by one edt ligand. The VS_6 coordination units have neither octahedral nor trigonal-prismatic geometry. Rather, each has the form of a twisted trigonal prism with one edge rotated 45° from the D_{3h} configuration. The V–V distance of 2.616 (2) Å is consistent with a single bond.[29] In addition to providing the first measure of V–SR bond lengths, $[V_2(edt)_4]^{2-}$ presents the initial proven example of a quadruple bridge in a first-transition-series compound and the only case, outside of certain M_2O_3 crystals,[38] of the specific type of nonoctahedral coordination stereochemistry displayed by the VS_6 groups.

$[Cr(edt)_2]^{2-}$. This complex as its Et_4N^+ salt was obtained as beautiful violet crystals; it is extremely susceptible to reaction with dioxygen in the solid state and in solution. In this salt the anion has imposed centrosymmetry and thus an exactly planar CrS_4 coordination unit, and closely approaches D_{2h} symmetry. The axial positions are unoccupied. This example of structure type III is displayed in Figure 2, and distances and angles are summarized in Table IX. No other discrete Cr thiolate complex has been prepared. The other structurally defined four-coordinate Cr(II) complexes, $Cr[H_2B(pz)_2]_2$,[39] $Cr(acac)_2$,[40] and $Cr[N(SiMe_3)_2]_2(THF)_2$,[41] are also planar.

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

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(37) In the Ti(IV) complex $Ti(diars)Cl_2(S\text{-}t\text{-}Bu)_2$ the Ti–S distance (2.332 (2) Å) is substantially shorter, for reasons unclear: Jones, R. A.; Schwab, S. T.; Whittlesey, B. R. *Polyhedron* **1984**, *3*, 505.

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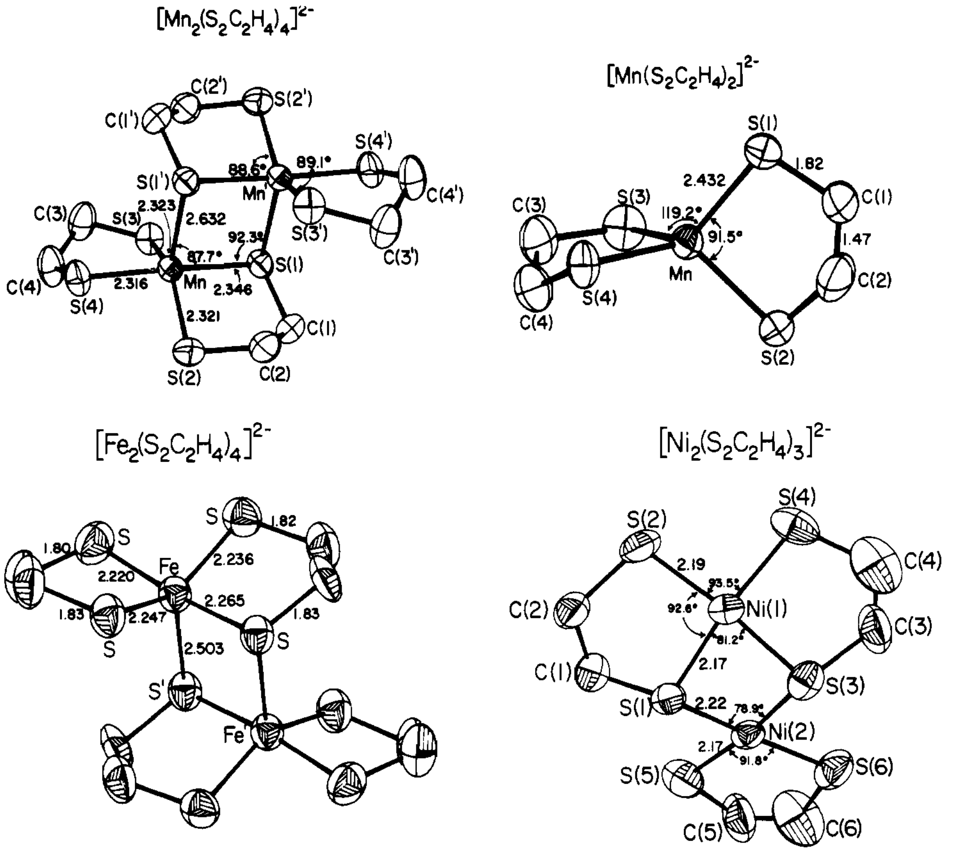

Figure 3. Structures of $[Mn_2(edt)_4]^{2-}$,[15a] $[Mn(edt)_2]^{2-}$,[15a] $[Fe_2(edt)_4]^{2-}$ (redrawn from published data[28]), and $[Ni_2(edt)_3]^{2-}$. Metric data for $[Mn(edt)_2]^{2-}$ (D_{2d}) and $[Ni_2(edt)_3]^{2-}$ (C_s) are mean values under the indicated symmetries; primed and unprimed atoms of $[Mn_2(edt)_4]^{2-}$ are related by a symmetry center.

Attempts to prepare a Cr(III)/edt species using the reaction system 2:1 Na_2edt:$CrCl_3{\cdot}6H_2O$ in methanol have thus far led only to a material of empirical composition $(Me_4N)_x[Cr_x(edt)_{2x}]$. Its physical properties suggest that $n \geq 2$,[25] but no diffraction-quality crystals have yet been obtained.

$[Mn(edt)_2]^{2-}$ and $[Mn_2(edt)_4]^{2-}$. In past work[15a] we have prepared $[Mn(edt)_2]^{2-}$ as its Et_4N^+ salt and shown that it is tetrahedral (IV) and convertible by aerial oxidation to $[Mn_2(edt)_4]^{2-}$. This reaction has also been reported by others.[26] Structures are displayed in Figure 3. $[Mn_2(edt)_4]^{2-}$ is configured completely differently from $[V_2(edt)_4]^{2-}$, adopting the centrosymmetric lateral dibridging dimeric structure V.[15a,26] The two Mn(III) atoms, separated by 3.596 (3) Å at ambient temperature,[15a] are antiferromagnetically coupled ($-J = 18$ cm^{-1} [42]). In coordinating solvents $[Mn_2(edt)_4]^{2-}$ exists in equilibrium with $[Mn(edt)_2(solv)_{1,2}]^-$.[15a] The mononuclear species has been trapped as the imidazole (HIm) adduct $[Mn(edt)_2(HIm)]^-$, which recently has been isolated and shown to have a slightly distorted square pyramidal structure.[43] In additional relevant experiments postdating our report of edt complexes,[15a] Mn(II,III)/tdt complexes have been prepared and structurally characterized.[44] $[Mn(tdt)_2]^{2-}$ is tetrahedral with bond angles and distances quite similar to those of $[Mn(edt)_2]^{2-}$. Oxidation of $(Ph_4P)_2[Mn(tdt)_2]^{2-}$ in methanol affords a crystalline solid containing both of the Mn(III) complexes $[Mn(tdt)_2]^-$ (planar) and $[Mn(tdt)_2(MeOH)]^-$ (square pyramidal). Thus in the set of homoleptic edt and tdt Mn complexes, there exist three structural types.

$[Fe_2(edt)_4]^{2-}$. This complex was prepared in the reaction system 2:1 Na_2edt:$FeCl_3$ in methanol[22] and was the first synthetic Fe(III) thiolate species isolated. As its n-Bu_4N^+ salt $[Fe_2(edt)_4]^{2-}$ (Figure 3) provided the initial example of the thiolate lateral dimer structure V,[28] in which the two antiferromagnetically coupled Fe(III) atoms ($-J = 54$ cm^{-1} [22]) are separated by 3.410 (3) Å. The structures of $[Fe_2(mnt)_4]^{2-}$[45a] and $[Fe_2(dma)_4]^{2-}$[45b] are entirely similar. The two $[M_2(edt)_4]^{2-}$ species are the only cases of the occurrence of $M^{III}(\mu\text{-}SR)_2$ bridge units. We have not yet succeeded in crystallizing a salt of highly oxidatively sensitive $[Fe(edt)_2]^{2-}$.

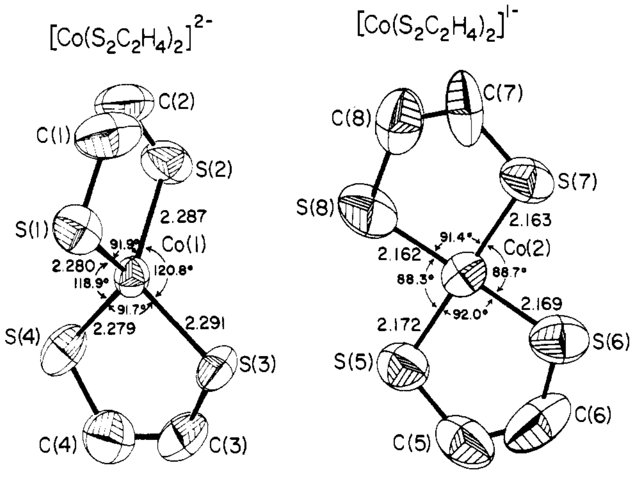

Figure 4. Structures of $[Co(edt)_2]^{2-}$ and $[Co(edt)_2]^-$.

$[Co(edt)_2]^{2-,-}$. The reaction system 2:1 Na_2edt:$CoCl_2$ in methanol affords brilliant green crystals, which as the Me_4N^+ salt have the composition $(Me_4N)_3[Co_2(edt)_4]$. The mixed-valence dimer or higher oligomer implied by this formulation is not found. Instead, the crystal consists of two discrete mononuclear complexes whose structures are set out in Figure 4: tetrahedral $[Co(edt)_2]^{2-}$

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Table VI. Atom Coordinates (×10^4) for $Na(Me_3NCH_2Ph)_2[Cu_3(S_2C_2H_4)_3]\cdot MeOH$

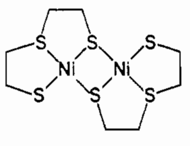
atom	*x*	*y*	*z*
Cu(1)	7543 (1)	243 (1)	1730 (1)
Cu(2)	8130 (1)	1432 (1)	1088 (1)
Cu(3)	5566 (1)	1420 (1)	1220 (1)
S(1)	8398 (2)	−1837 (2)	1676 (1)
S(2)	9390 (2)	1428 (2)	1622 (1)
S(3)	7874 (2)	185 (2)	561 (1)
S(4)	6511 (2)	2982 (2)	903 (1)
S(5)	4295 (2)	−422 (2)	1094 (1)
S(6)	5714 (2)	1220 (2)	1849 (1)
C(1)	9846 (7)	−1325 (7)	1475 (2)
C(2)	10463 (7)	−44 (10)	1630 (3)
C(3)	6400 (6)	995 (7)	345 (2)
C(4)	6345 (7)	2496 (8)	417 (2)
C(5)	4341 (7)	−1066 (7)	1562 (2)
C(6)	4404 (7)	−33 (7)	1860 (2)
N(1)	8801 (5)	191 (5)	2866 (1)
C(7)	8657 (8)	1637 (7)	2720 (2)
C(8)	9125 (7)	210 (7)	3272 (2)
C(9)	7495 (8)	−509 (9)	2763 (3)
C(10)	9801 (6)	−567 (6)	2674 (2)
C(11)	11184 (6)	−73 (6)	2777 (2)
C(12)	12006 (8)	−784 (9)	3032 (2)
C(13)	13265 (8)	−405 (10)	3123 (3)
C(14)	13722 (7)	760 (11)	2955 (3)
C(15)	12968 (9)	1415 (9)	2699 (3)
C(16)	11668 (8)	1036 (8)	2606 (2)
N(2)	1568 (5)	1759 (5)	446 (2)
C(17)	2873 (7)	2068 (8)	334 (3)
C(18)	545 (7)	2334 (8)	162 (2)
C(19)	1429 (6)	267 (6)	440 (2)
C(20)	1444 (7)	2279 (7)	830 (2)
C(21)	1491 (7)	3823 (7)	852 (2)
C(22)	2733 (8)	4479 (8)	920 (2)
C(23)	2721 (10)	5917 (10)	940 (3)
C(24)	1547 (13)	6638 (10)	886 (3)
C(25)	353 (12)	5990 (10)	843 (3)
C(26)	346 (8)	4584 (8)	818 (3)
Na	6728 (3)	8379 (3)	1026 (1)
SolO[a]	6285 (7)	6214 (5)	797 (2)
SolC[b]	5590 (12)	6265 (10)	442 (3)

[a] Solvate oxygen atom. [b] Solvate carbon atom.

(IV) and planar $[Co(edt)_2]^-$ (III). Distance and angle data are given in Tables IX and X. $[Co(edt)_2]^{2-}$ approaches D_{2d} symmetry; the dihedral angle between CoS_2 planes is 88.5°. The mean Co–S bond distance of 2.284 (6) Å is indistinguishable from that in the tetrahedral dimer $[Co_2(SEt)_6]^{2-}$[14a] (2.273 (14) Å). $[Co(edt)_2]^{2-}$ is a member of a small set, $[Co(SR)_4]^{2-}$,[15c,46] all members of which are tetrahedral. Of these, $[Co(SPh)_4]^{2-}$[46b] has also been characterized by X-ray diffraction; its longer mean Co–S distance (2.328 (11) Å) presumably has a steric origin.

The structure of $[Co(edt)_2]^-$ is nearly square-planar. Axial positions are vacant. Idealized D_{2h} symmetry is not achieved because, inter alia, the CoS_4 portion is not planar. The dihedral angle between the two CoS_2 planes is 6.8°, and the atom displacements from the unweighted CoS_4 least-squares plane (Table IX) are in the direction of a slight tetrahedral distortion. The innocent nature of the edt ligand requires that $[Co(edt)_2]^-$ contain Co(III). This oxidation state was unanticipated in a product of an anaerobic reaction system initially containing Co(II) and thiolate, and its formation is under investigation. The most closely related species occur in the series of bis(dithiolene)cobalt monoanions,[47] one member of which, $[Co(tdt)_2]^-$,[48] is square-planar with a mean Co–S distance (2.166 (11) Å) identical with that of $[Co(edt)_2]^-$.

$[Ni_2(edt)_3]^{2-}$. The aqueous reaction system 2:1 Na_2edt:$NiCl_2$ affords as a n-Bu_4N^+ salt a green-black diamagnetic solid whose analysis corresponds to $(n\text{-}Bu_4N)_2[Ni_2(edt)_3]$. Subsequently it was found that this system in methanol formed the same anion, whose Ph_4P^+ salt was suitable for X-ray study. The structure of $[Ni_2(edt)_3]^{2-}$ (VI) is shown in Figure 3; full details will be reported upon completion of a larger investigation of Ni thiolates.[49] The binuclear structure is formed by the bridged attachment of a Ni(edt) group to $[Ni(edt)_2]^{2-}$. The two NiS_4 coordination units are virtually planar but are not coplanar. The structure is folded along the S(1)–S(3) vector, with a dihedral angle between planes S(1–4) and S(1,3,5,6) of 62.1° and a Ni···Ni separation of 2.923 (3) Å. $(TcO)_2(edt)_3$ is configured in precisely the same way with a dihedral angle of 63.5°.[50] Among binuclear Ni(II) complexes, the most closely related species are $[Ni_2(SEt)_6]^{2-}$[5] and $Ni_2(S(CH_2CH_2S)_2)_2$[51] (VIII) with planar and nonplanar $Ni_2(\mu\text{-}S)_2$ bridge units, respectively. In VIII the dihedral angle is 82.3°, with the result that the Ni atoms are only 2.733 (5) Å apart. Terminal and bridging Ni–S distances in the two complexes are similar and unexceptional.



VIII

The isolation of $[Ni_2(edt)_3]^{2-}$, the sixth stereochemical type of edt complex, is foreshadowed by the demonstration of Leussing et al.[24] that in aqueous solution this species exists in equilibrium with $[Ni(edt)_2]^{2-}$ and edt. In the presence of excess edt we have isolated a salt of $[Ni(edt)_2]^{2-}$ and shown that this equilibrium persists in aprotic solvents such as DMF, where, as in water, the dimer is predominant in the absence of added edt.[49] It is not yet established why this equilibrium favors the binuclear form.

$[Cu_3(edt)_3]^{3-}$. The reaction system 2:1 Na_2edt:$CuCl_2$ in methanol, upon treatment with $(Me_3NCH_2Ph)Cl$, afforded a yellow crystalline material whose composition, $(Me_3NCH_2Ph)_2Na[Cu_3(edt)_3]\cdot MeOH$, was established by elemental analysis and X-ray crystallography. The anion has the cyclic structure VII; two views are provided in Figure 5, and dimensional data are collected in Table XI.

$[Cu_3(edt)_3]^{3-}$ consists of a triangle of nonbonded Cu(I) atoms that are bridged by atoms μ-S(2,4,6) located below the Cu_3 plane. Distorted-trigonal-planar coordination at the Cu atoms is completed by terminal ligands S(1,3,5) above this plane. The Cu_3 and two S_3 least-squares planes are virtually parallel (dihedral angles ≲2°); separations of these planes are 0.93 Å for Cu_3/S(2,4,6) and 1.90 Å for Cu_3/S(1,3,5). The Cu_3S_3 ring has a puckered-chair conformation, indicated by deviations of −1.02 and 1.45 Å by Cu(2) and S(6), respectively, from the Cu(1,3)S(2,4) mean plane. The three Cu(edt) chelate rings project outward from the same side of the Cu_3S_3 ring, forming "handles". Bonded to atoms S(1,3,5) at the molecular apex is Na^+, whose distorted-tetrahedral coordination is completed by an oxygen atom from methanol. Thus the complex unit in the crystal is $[Na(MeOH)[Cu_3(edt)_3]]^{2-}$, which has idealized C_3 symmetry with the threefold axis containing atoms O and Na and passing through the center of the Cu_3 triangle. Parameters in Table XI are organized under C_3 symmetry.

The Cu_3S_3 ring exhibits alternating long (2.304 (11) Å) and short (2.215 (7) Å) Cu–S bridge bonds and terminal Cu–S bonds of intermediate length (2.257 (13) Å). These distances are

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Table VII. Atom Coordinates ($\times 10^4$) for $(Et_4N)_2[M(S_2C_2H_4)_2]$ (M = Zn(II), Cd(II))

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Zn	2573 (1)	570 (1)	2593 (1)	Cd	2412 (1)	5619 (1)	2600 (1)
S(1)	1733 (1)	−622 (1)	3159 (1)	S(1)	3299 (1)	4355 (1)	3231 (1)
S(2)	1998 (1)	1401 (1)	3892 (1)	S(2)	3039 (1)	6428 (1)	4044 (1)
S(3)	4372 (1)	429 (1)	2456 (1)	S(3)	530 (1)	5448 (1)	2366 (1)
S(4)	2230 (1)	919 (1)	834 (1)	S(4)	2746 (1)	5990 (1)	708 (1)
C(1)	1117 (3)	−130 (2)	4216 (3)	C(1)	3893 (4)	4870 (3)	4260 (4)
C(2)	1718 (4)	555 (3)	4728 (3)	C(2)	3295 (5)	5543 (3)	4803 (4)
C(3)	4154 (4)	100 (3)	1111 (3)	C(3)	894 (5)	5079 (4)	1051 (4)
C(4)	3498 (4)	674 (3)	410 (3)	C(4)	1494 (4)	5690 (3)	338 (4)
N(1)	164 (2)	6944 (2)	3895 (2)	N(1)	4837 (3)	1929 (2)	3839 (3)
C(5)	−1 (3)	7729 (2)	4473 (3)	C(5)	5689 (4)	1867 (3)	2955 (4)
C(6)	691 (4)	7822 (3)	5444 (4)	C(6)	5681 (4)	2544 (4)	2164 (4)
C(7)	−677 (3)	6883 (3)	2983 (3)	C(7)	3768 (3)	1976 (3)	3445 (3)
C(8)	−625 (5)	7534 (4)	2181 (4)	C(8)	3533 (5)	1303 (4)	2725 (5)
C(9)	1263 (3)	6960 (2)	3509 (3)	C(9)	4996 (4)	2710 (3)	4437 (4)
C(10)	1504 (5)	6286 (3)	2781 (5)	C(10)	4291 (4)	2799 (3)	5416 (4)
C(11)	77 (4)	6188 (2)	4577 (3)	C(11)	4903 (4)	1180 (2)	4522 (3)
C(12)	−925 (4)	6157 (3)	5128 (3)	C(12)	5857 (4)	1142 (3)	5092 (4)
N(2)	3737 (2)	3658 (2)	1246 (2)	N(2)	1246 (2)	8671 (2)	1261 (2)
C(13)	4043 (3)	2793 (2)	1586 (3)	C(13)	545 (4)	9270 (3)	1891 (4)
C(14)	5148 (4)	2551 (3)	1402 (5)	C(14)	893 (4)	10144 (3)	1835 (4)
C(15)	2595 (3)	3803 (3)	1450 (3)	C(15)	921 (3)	7811 (3)	1560 (3)
C(16)	2362 (4)	3770 (4)	2584 (4)	C(16)	−175 (5)	7595 (4)	1386 (8)
C(17)	4462 (3)	4261 (2)	1842 (4)	C(17)	2365 (3)	8789 (3)	1459 (3)
C(18)	4135 (4)	5153 (3)	1751 (4)	C(18)	2613 (4)	8701 (5)	2565 (4)
C(19)	3842 (4)	3772 (3)	97 (3)	C(19)	1143 (4)	8818 (3)	127 (4)
C(20)	3208 (1)	3185 (3)	−602 (3)	C(20)	1746 (5)	8247 (4)	−607 (4)

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) for $[Ti(S_2C_2H_4)_3]^{2-}$

Ti–S(1)	2.434 (2)	Ti–S(4)	2.419 (3)
Ti–S(3)	2.438 (2)	Ti–S(6)	2.419 (2)
Ti–S(5)	2.431 (3)	mean	2.428 (10)
Ti–S(2)	2.420 (2)		
S(1)···S(2)	3.212 (3)	S(5)···S(6)	3.213 (3)
S(3)···S(4)	3.214 (4)		
S(1)–Ti–S(2)	82.9 (1)	S(5)–Ti–S(6)	83.0 (1)
S(3)–Ti–S(4)	82.8 (1)		
S(1)–Ti–S(3)	87.0 (1)	S(3)–Ti–S(5)	85.8 (1)
S(1)–Ti–S(5)	88.1 (1)		
S(2)–Ti–S(4)	89.1 (1)	S(4)–Ti–S(6)	86.5 (1)
S(2)–Ti–S(6)	84.0 (1)		
C–S range		1.789 (7)–1.820 (7)	
mean		1.81 (1)	

Table IX. Selected Interatomic Distances (Å) and Angles (deg) for $[Cr(S_2C_2H_4)_2]^{2-}$ and $[Co(S_2C_2H_4)_2]^-$

	$[Cr(S_2C_2H_4)_2]^{2-}$		
Cr–S(1)	2.389 (1)	S(2)–C(2)	1.813 (6)
Cr–S(2)	2.387 (1)	C(1)–C(2′)	1.370 (7)
S(1)–C(1)	1.810 (6)		
S(1)···S(2′)	3.328 (2)	S(1)···S(2)	3.426 (2)
S(1)–Cr–S(2)	91.7 (1)	S(1)–Cr–S(2′)	88.3 (1)
	$[Co(S_2C_2H_4)_2]^-$		
Co–S(5)	2.172 (4)	Co–S(8)	2.162 (4)
Co–S(6)	2.169 (4)	mean	2.167 (5)
Co–S(7)	2.163 (4)		
S(5)···S(6)	3.124 (2)	S(5)···S(8)	3.017 (2)
S(7)···S(8)	3.096 (3)	S(6)···S(7)	3.028 (3)
S(5)–Co–S(6)	92.0 (2)	S(5)–Co–S(8)	88.3 (2)
S(7)–Co–S(8)	91.4 (2)	S(6)–Co–S(7)	88.7 (2)
C–S range		1.77 (2)–1.82 (2)	
mean		1.79 (2)	
CoS(5,6)/CoS(7,8)[a]		6.8	
Deviations (Å) from CoS(1–4) Least-Squares Plane			
Co(2)	−0.018		
S(5)	+0.093	S(6)	−0.084
S(7)	+0.094	S(8)	−0.085

[a] Dihedral angle between planes.

comparable with those for other Cu(I) thiolates.[7-12] The Na–O distance of 2.315 (6) Å is within the usual range of bond distances of this type.[52] We are unaware of any previous measure of tetrahedral Na–SR bond lengths. However, the present values are very close to the distances in a tetrahedral NaS_4 portion of $Na_6Sn_2S_7$.[53] The topology VII of the $[Cu_3(edt)_3]^{3-}$ part of the complex unit is not unique. Very recently it has been found in $[Cu_3(S_4)_3]^{3-}$.[54] This complex, with a puckered Cu_3S_3 central ring, three CuS_4 rings (in which two S atoms replace CH_2 groups in VII) disposed outward on one side of the central ring, and the same pattern of Cu–S bond lengths as in $[Cu_3(edt)_3]^{3-}$, approaches C_3 symmetry. The only other Cu(I) thiolate derived from a chelating ligand has a different structure. Trigonal $[Cu_4(S_2\text{-}o\text{-}xyl)_3]^{2-}$[9b] contains a Cu_4S_6 core with μ-S atoms spanning the edges of a Cu_4 tetrahedron. The chelate nature of this particularly flexible ligand would not appear to be a structure determinant inasmuch as $[Cu_4(SPh)_6]^{2-}$[8,9a] has the same core geometry. Edt ligands do not have a bite distance large enough to function in this way, given a requirement of trigonal-planar Cu(I), and are very likely regulators of structure VII.[55]

$[Zn(edt)_2]^{2-}$ and $[Cd(edt)_2]^{2-}$. These two complexes have been previously generated in solution[56] but not isolated. The reaction systems 2:1 $Na_2edt:MCl_2$ (M = Zn(II), Cd(II)) in acetonitrile yielded the isomorphous compounds $(Et_4N)_2[M(edt)_2]$ as colorless

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(55) Note, however, that five-membered chelate rings may be a sufficient but not necessary factor in forming the cyclic structure, given that $[Cu_3(S_6)_3]^{3-}$ adopts this structure: Müller, A.; Schimanski, U. *Inorg. Chim. Acta* **1983**, *77*, L187.

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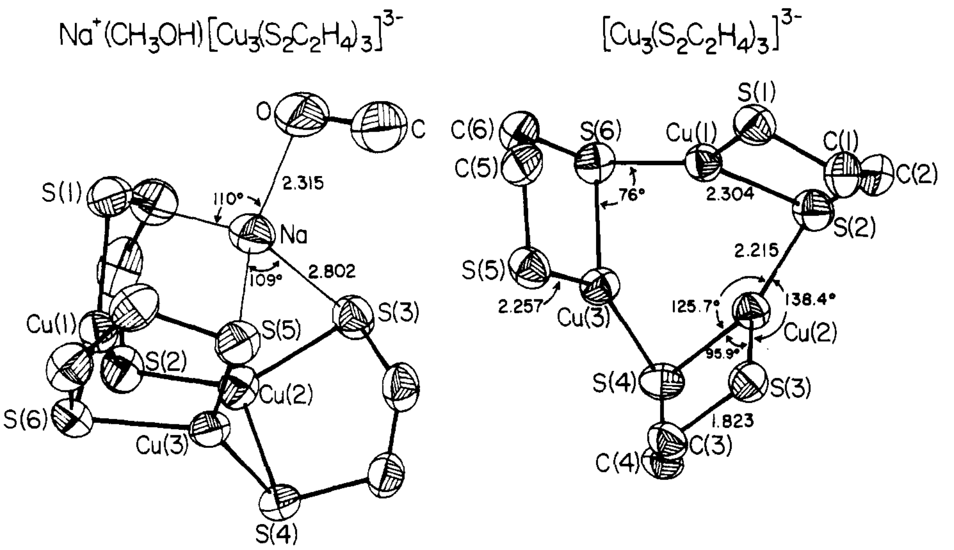


Figure 5. Structure of $[Na(MeOH)[Cu_3(edt)_3]]^{2-}$: (left) view showing Na^+ coordination; (right) view emphasizing idealized C_3 symmetry under which metric data are averaged.

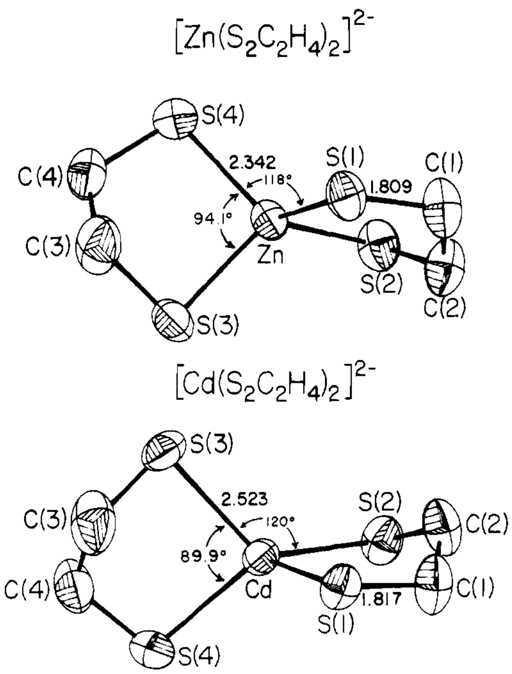


Figure 6. Structures of $[M(edt)_2]^{2-}$ (M = Zn(II), Cd(II)). Mean values under idealized D_{2d} symmetry are given.

Table X. Selected Interatomic Distances (Å) and Angles (deg) for $[M(S_2C_2H_4)_2]^{2-}$, M = Co(II), Zn(II), Cd(II)

	Co(II)	Zn(II)	Cd(II)
M–S(1)	2.280 (1)	2.366 (1)	2.547 (1)
M–S(2)	2.287 (4)	2.320 (1)	2.504 (1)
M–S(3)	2.291 (4)	2.329 (1)	2.508 (1)
M–S(4)	2.279 (4)	2.353 (1)	2.534 (1)
mean	2.284 (6)	2.342 (21)	2.523 (21)
S(1)···S(2)	3.281 (3)	3.443 (3)	3.581 (2)
S(3)···S(4)	3.278 (3)	3.411 (2)	3.550 (1)
C–S range	1.79 (2)–1.80 (2)	1.794 (5)–1.820 (5)	1.807 (5)–1.836 (6)
mean	1.80 (1)	1.81 (1)	1.82 (1)
S(1)–M–S(2)	91.9 (1)	94.6 (1)	90.3 (1)
S(3)–M–S(4)	91.7 (1)	93.5 (1)	89.5 (1)
S(1)–M–S(3)	117.7 (1)	114.6 (1)	114.8 (1)
S(1)–M–S(4)	118.9 (1)	116.4 (1)	117.8 (1)
S(2)–M–S(3)	120.8 (1)	118.8 (1)	122.7 (1)
S(2)–M–S(4)	118.4 (1)	120.8 (1)	124.3 (1)
S(1,2)M/S(3,4)M[a]	88.5	90.0	90.9

[a] Dihedral angle between planes.

Table XI. Selected Interatomic Distances (Å) and Angles (deg) for $Na^+(MeOH)[Cu_3(S_2C_2H_4)_3]^{3-}$

Cu(1)–S(2)	2.313 (2)	Cu(3)–S(6)	2.292 (2)
Cu(2)–S(4)	2.306 (2)	mean	2.304 (11)
Cu(1)–S(6)	2.208 (2)	Cu(3)–S(4)	2.222 (2)
Cu(2)–S(2)	2.214 (2)	mean	2.215 (7)
Cu(1)–S(1)	2.245 (2)	Cu(3)–S(5)	2.256 (2)
Cu(2)–S(3)	2.270 (2)	mean	2.257 (13)
Cu(1)···Cu(2)	2.751 (1)	Cu(2)···Cu(3)	2.749 (1)
Cu(1)···Cu(3)	2.846 (1)		
S(1)···S(2)	3.387	S(5)···S(6)	3.378
S(3)···S(4)	3.391		
C(1)–S(1)	1.816 (8)	C(5)–S(5)	1.820 (8)
C(3)–S(3)	1.816 (6)	mean	1.817 (2)
C(2)–S(2)	1.822 (9)	C(6)–S(6)	1.838 (7)
C(4)–S(4)	1.826 (7)	mean	1.829 (8)
Na–S(1)	2.776 (3)	Na–S(5)	2.815 (3)
Na–S(3)	2.816 (3)		
Na–O	2.315 (6)		
S(2)–Cu(1)–S(6)	123.9 (1)	S(4)–Cu(3)–S(6)	126.9 (1)
S(2)–Cu(2)–S(4)	126.3 (1)		
S(1)–Cu(1)–S(6)	140.1 (1)	S(5)–Cu(3)–S(4)	137.1 (1)
S(3)–Cu(2)–S(2)	138.0 (1)		
Cu(1)–S(2)–Cu(2)	74.8 (1)	Cu(1)–S(6)–Cu(3)	78.4 (1)
Cu(2)–S(4)–Cu(3)	74.7 (1)		
S(1)–Cu(1)–S(2)	96.0 (1)	S(5)–Cu(3)–S(6)	95.9 (1)
S(3)–Cu(2)–S(4)	95.7 (1)		
Cu(2)–Cu(1)–Cu(3)	58.8 (1)	Cu(1)–Cu(3)–Cu(2)	58.9 (1)
Cu(1)–Cu(2)–Cu(3)	62.3 (1)		
S(1)–Na–S(3)	107.5 (1)	S(3)–Na–S(5)	103.4 (1)
S(1)–Na–S(5)	115.5 (1)		
S(1)–Na–O	108.4 (1)	S(5)–Na–O	105.9 (1)
S(3)–Na–O	116.3 (1)		
Cu(1–3)/S(1,3,5)	2.1	Cu(1–3)/S(2,4,6)	1.6
Cu(1–3)/Cu(1)S(2,6)	62.5	Cu(1–3)/Cu(3)S(4,6)	62.6
Cu(1–3)/Cu(2)S(2,4)	68.2		
Cu(1–3)/Cu(1)S(1,2)	61.7	Cu(1–3)/Cu(3)S(5,6)	63.9
Cu(1–3)/Cu(2)S(3,4)	67.5		

crystals. The anions are isostructural with the tetrahedral configuration IV. Detailed structures are provided in Figure 6 and dimensional data in Table X. Dihedral angles between MS_2 planes are 90.0° (Zn) and 90.9° (Cd). Both species approximate to D_{2d} symmetry, although the ranges in the four nonchelate S–M–S bond angles equivalent under this symmetry are substantial (6.2° for Zn and 9.5° for Cd) and each has a 0.021-Å esd of mean M–S distances. These bond distances are comparable with those of other tetrahedral $M(SR)_4$ units,[5,13a,15d,e,21,46b,57] of which the most pertinent are mononuclear $[Zn(SPh)_4]^{2-}$[46b] (2.353 (16) Å), $[Cd(SPh)_4]^{2-}$[46b] (2.535 (13) Å), and $[Cd(tdt)_2]^{2-}$[57a] (2.508 (18) Å).

Stereochemical Trends. Structures of homoleptic edt complexes of the first transition series are summarized in Figure 1. Seven structural types I–VII have been established in a set that includes at least one complex of each metal. Various structural aspects of this stereochemically exceptionally variegated set of complexes are next considered.

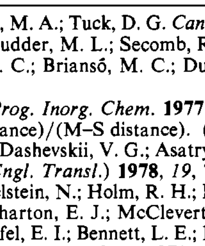
(a) Mononuclear Complexes. Structures of $[M(edt)_2]^{2-}$ follow the planar (P) and tetrahedral (T) distribution below, which holds for all bis(chelate)metal(II) complexes derived from weak-field ligands devoid of stereochemical constraints:

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

The structure of $[Ni(edt)_2]^{2-}$ has not been obtained from X-ray analysis, but its diamagnetism and absorption spectrum[49] ensure that the complex is planar. A comparably extensive series is formed by $[M_2(SEt)_6]^{2-}$. Unlike $[M(edt)_2]^{2-}$, this series includes Fe(II) but not Cr(II). All members are edge-shared tetrahedra except for $[Ni_2(SEt)_6]^{2-}$, which is planar.[10,14a]

$[Ti(edt)_3]^{2-}$ resembles tris(dithiolene) complexes such as $[Zr(bdt)_3]^{2-}$[35c] inasmuch as it does not fit the otherwise generally valid normalized bite distance/twist angle correlation of Kepert.[58] As with the dithiolenes, for reasons unclear, ϕ is smaller than predicted (~50°). As already noted, $[Ti(edt)_3]^{2-}$ is formed in the 2:1 $Na_2edt:TiCl_3$ system, but mole ratios as high as 4:1 $Na_2edt:VCl_3$ give $[V_2(edt)_4]^{2-}$ and not $[V(edt)_3]^{3-}$. This raises the question of the stability of $(edt)_3$ complexes of metals in oxidation states below IV. Indeed, with few exceptions such as the catecholates, tris complexes of *di*anionic ligands tend to be confined to metals with this oxidation state or higher. With edt, charges are localized on the sulfur atoms, enhancing ligand–ligand repulsion. Even among tris(dithiolenes), where some ligand charge delocalization is possible and electronegative substituents have been introduced,[31] few M(III) tris complexes have been isolated or are otherwise accessible except at rather negative potentials ($\lesssim$-1 V vs. SCE).[59] We have, therefore, been led to question the authenticity of a black insoluble material of claimed composition $Na_3[Co(edt)_3]\cdot 2H_2O$[60] and are reinvestigating it.

$[Co(edt)_2]^-$ is an example of a rare type: a planar spin-triplet[25] Co(III) complex. Other examples include biuretato complexes,[61] often of structure IX, $[Co(o\text{-}C_6H_4(NH)S)_2]^-$,[62] and bis(dithiolene) monoanions.[47,48] From these occurrences it is evident that this unusual structural–electronic configuration is promoted by, and possibly restricted to, ligands that furnish four negative, polarizable donor atoms. These are effective in stabilizing Co(III) by attenuating charge separation, which also has the effect of diminishing an affinity for additional ligands, and in raising the energy of the σ^* MO well above those of other d-type orbitals, thereby leading to a $S = 1$ ground state. The existence of $[Co(edt)_2]^-$ solidifies interpretation of $[Co(tdt)_2]^-$ and related species as dithiolate complexes of Co(III), albeit highly covalent in nature.[63] Similarly, $[Ti(edt)_3]^{2-}$, $[Mn_2(edt)_4]^{2-}$, and $[Fe_2(edt)_4]^{2-}$ strongly imply a classical oxidation-state description for species such as $[Ti(tdt)_3]^{2-}$,[35] $[Mn(tdt)_2]^-$,[44] and $[Fe_2(mnt)_4]^{2-}$,[45] respectively.



IX

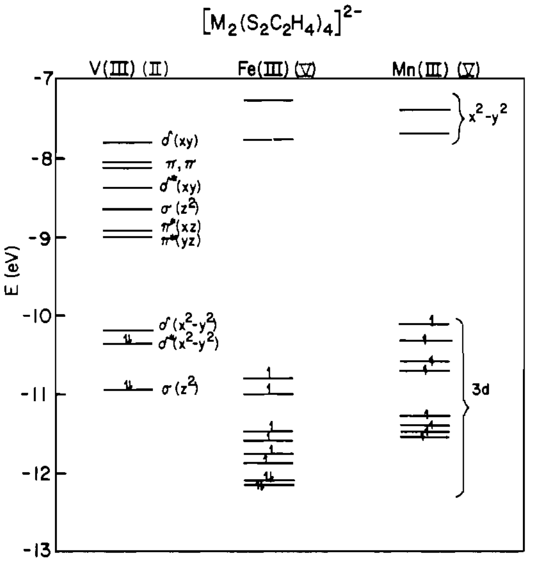


Figure 7. Partial MO energy diagrams of $[M_2(edt)_4]^{2-}$, M = V(III), Mn(III), and Fe(III), showing MO's of significant d character near the HOMO/LUMO gap. Dimer electron configurations are based on those for half-dimers, which for Fe(III) is taken as a $S = {}^3/_2$ state.

(b) Binuclear Complexes. A conspicuous feature of the set of edt complexes is the existence of two structural types (II, V) of $[M_2(edt)_4]^{2-}$. The stabilities of these types have been investigated theoretically at the extended Hückel level.[64] The fragment MO approach, whereby calculations were made for half-dimers and these were then combined to form dimers, was found instructive. The leading results, which bear some similarities to EHMO results for other dimers,[65,66] are briefly summarized. A partial energy level diagram appears in Figure 7. For $[V_2(edt)_4]^{2-}$ the z axes of V and V(a) are taken along the metal–metal vector. Because of extensive mixing of V and V(a) 3d with μ-S 3p orbitals, bonding and antibonding σ, π, and δ MO's do not follow the order usually resulting from direct metal–metal interaction. The latter is not expected to dominate at V–V(a) = 2.62 Å. Through-bond coupling such as found here is evident in similar treatments of other dimers.[65] The lowest d-type frontier orbital is $\sigma(z^2)$, which represents a V–V single bond and is ~0.6–0.7 eV below δ and δ^*. These approximate in-phase (δ) and out-of-phase (δ^*) combinations of $3d_{x^2-y^2}$ and are separated by 0.17 eV. Because $[V_2(edt)_4]^{2-}$ is essentially diamagnetic in the solid state, the scheme leads to the simplified ground-state configuration $\sigma^2\delta^{*2}$, neglecting δ/δ^* mixing and requiring the orbitals to be sufficiently split to ac-

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commodate spin pairing. (The small δ/δ^* separation raises the possibility of a low-lying triplet state.) The important point is that there is a relatively low-lying LUMO separated by a large gap (~1.2 eV) between it and the next block of d-type MO's.

Four closely spaced d-type MO's (spread <1 eV) and a σ^* MO at ≳3.5 eV higher energy, a typical planar array, are found for the half-dimers of V. These schemes support a $S = 2$ state for Mn(III) (observed for $[Mn(edt)_2(solv)_{1,2}]^-$ in Me_2SO solution[15a]) and $S = {}^3/_2$ for Fe(III). Combination of half-dimers into the observed structures leads to the energy level schemes in Figure 7. Metal–ligand orbital mixing is substantial, but the upper two orbitals in each case are fairly described as compounded of in-phase and out-of-phase $3d_{x^2-y^2}$ combinations. These are essentially σ^* in character, are separated from the lower set by ≳2.4 eV, and are unoccupied under the indicated electronic configurations. An earlier magnetic study of $[Fe_2(edt)_4]^{2-}$ led to the conclusion that the antiferromagnetically coupled Fe(III) atoms have $S = {}^5/_2$ and not $S = {}^3/_2$.[22] The distribution was made on the basis of a slightly better fit to the data above ~200 K with a spin-${}^5/_2$ model; below this temperature the fits are identical. Since that time it has been more clearly recognized that intermediate-spin Fe(III) has a much larger quadrupole splitting than high-spin Fe(III).[67] The value $\Delta E_Q = 3.09$ mm/s[22] is far more consistent with the former possibility.

The results of EHMO calculations afford these main conclusions: (i) the tetrabridged dimer II is likely to be unstable for M(III) d^n ions with $n \geq 4$, owing to occupation of strongly antibonding orbitals; (ii) the lateral doubly bridged dimer V is a suitable structure for $n \geq 4$ inasmuch as strongly antibonding orbitals need not be occupied for at least $n = 4$ and 5. Conclusion i is subject to testing by structure determination of $[Cr_2(edt)_4]^{2-}$. Unfortunately, we have not been able to obtain single crystals of $(Me_4N)_x[Cr_x(edt)_{2x}]$ nor otherwise identify the desired Cr(III) dimer. Calculations for $[Co(edt)_2]^-$ give the typical pattern of four low-lying d-type MO's spread over 0.60 eV and a very high-energy σ^* orbital ~4.3 eV above these. This is the extreme example of the strong in-plane antibonding character induced by the edt ligand and readily accounts for the triplet ground state. The energy level scheme for $[Co(edt)_2]^-$ admits dimer stability based on half-dimer electron configurations. Thus far we have obtained this complex only in a mixed crystal with $[Co(edt)_2]^{2-}$, in which condition it is monomeric. In other cases, monomer and dimer forms may be finely balanced. Thus in the solid state $[Co(tdt)_2]^-$ is monomeric[48] whereas $[Co_2(S_2C_6Cl_4)_4]^{2-}$ has dimer configuration V,[68] presumably because the more electronegative ligand renders the metal more electrophilic.

(c) Correlations and Ring Conformations. Structurally characterized edt complexes, including the objects of this work and others previously mentioned and now cited,[69] provide an opportunity to search for correlations of structural parameters over wide ranges of stereochemistry and coordinated atom. As one example, the near-linear metal-dependent relationship between terminal and bridging M–S distances[5] extends to $[Ni_2(edt)_3]^{2-}$, $[Cu_3(edt)_3]^{3-}$, and $(TcO)_2(edt)_3$ (not shown). Edt complexes also show wide ranges of M–S bond distances (1.9–2.5 Å) and S···S bite distances (~3.1–3.6 Å). The former exhibit variations with metal oxidation state (Z), ionic radius[33] (r), and coordination number (n) when the effects of these variables are examined separately. Use of the unified parameter Z/rn, the ionic potential per ligand,[70] leads to a rather smooth correlation with M–S distances for terminal ligands shown in Figure 8. Bridging interactions obviously lengthen M–S bonds compared to their intrinsic values and for this reason are not included. Certainly the most significant geometric feature of the edt ligand is the pronounced flexibility in its bite distance. The extremes are 3.06 Å in $B_2(C_3H_3N_2)_2(edt)_2$[69a] and 3.57 Å in $[Cd(edt)_2]^{2-}$. Bite distances of terminal ligands also vary smoothly with Z/rn (Figure 8). The only cation in the set, $[P(edt)_2]^+$,[69a] does not fit either correlation. If extension of the plot from the Tc to the B points is accepted, the behavior is roughly exponential and at high Z/rn extrapolates to about 3.05 Å, suggesting that no combination of these factors is likely to stabilize a bite distance much below this value.

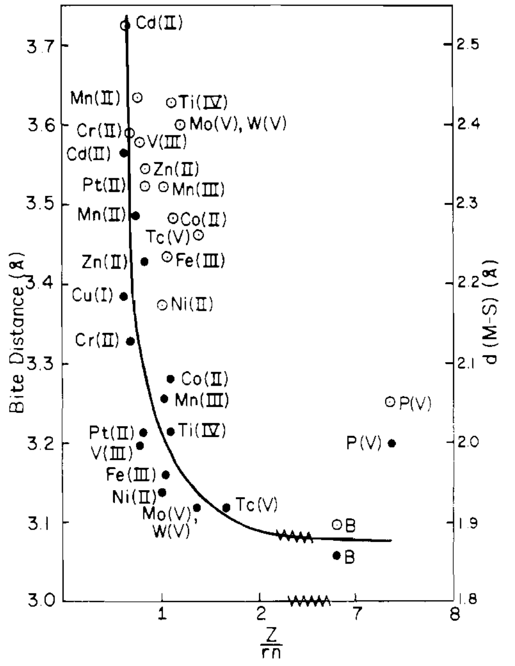

Figure 8. Correlations of terminal bite distance (●) and M–S bond distance (○) with the ionic potential per ligand, Z/rn: B = $B_2(C_3H_3N_2)_2(edt)_2$;[69a] Mo(V), W(V) = *anti*-$[M_2S_2(edt)_2]^{2-}$;[69b,c] Tc(V) = $(TcO)_2(edt)_3$;[50] Pt(II) = $(Ph_3P)_2Pt(edt)$;[32] P(V) = $[P(edt)_2]^+$.[69d] Other points refer to complexes in Figures 2–5. The solid line serves as a rough locus of points (●).

Also found is a roughly linear relationship between bite distances of terminal chelate rings and their torsional dihedral angles (SC–CS). The behavior (not shown) is such that as bite distance increases so does the dihedral angle, which approaches closely the value (65°) of the free dithiol.[71] However, this correlation is difficult to interpret inasmuch as M(edt) rings exhibit and approach the half-chair (C_2) and approach the envelope (C_s) conformations,[72] as well as display intermediate dispositions. The most frequent of these is one in which four of the five ring atoms are practically planar (within ±0.1 Å) and one carbon atom is much further out of the plane. This provides an approximate envelope conformation. Perfect half-chairs are found with $[V_2(edt)_4]^{2-}$ and $[P(edt)_2]^+$, and the perfect chair arrangement is nearly achieved in *syn*-$[Mo_2S_4(edt)_2]^{2-}$, among others. As found from a survey of some 20 complexes, conformations intermediate between the symmetric limits but biased toward the half-chair are by far the most common. In, e.g., $[Ti(edt)_3]^{2-}$ (Figure 2), two rings (0.342, −0.396; 0.449, −0.279 Å) approach the half-chair conformation, as shown by the carbon atom deviations from TiS_2 planes. The third ring, TiS(5,6)C(5,6), has carbon atom deviations of 0.586 and −0.077 Å and a 0.635-Å displacement of one carbon atom from the mean plane of the other four ring atoms. This ring has a near-envelope conformation. We have not discovered, from

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the sample at hand, any systematic factors influencing ring conformations.

With the scope of formation and stereochemical pattern of edt complexes largely defined, at least for first-transition-series elements, certain problems and possibilities remain for investigation. These include the means of formation of $[Co(edt)_2]^-$ in a reaction system initially containing no apparent oxidant, the synthesis of this complex free from $[Co(edt)_2]^{2-}$, attempted preparation of $[Cr_2(edt)_4]^{2-}$ in order to determine where the discontinuity between structures II and V occurs, examination of monomer–dimer equilibria in solution, and exploitation of the nucleophilic reactivity of thiolate sulfur atoms as a means of synthesizing new ligand types by template reactions. These matters are currently under investigation in this laboratory.

Acknowledgment. This research was supported by NIH Grant GM 28856. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank B. Snyder for experimental assistance and discussion.

Registry No. **1**·$2Et_4N$, 94750-78-4; **2**·$2Et_4N$, 87145-62-8; **2**, 87145-61-7; **3**·$2Et_4N$, 94750-80-8; **5**, 87526-32-7; **6**, 46847-88-5; **7**·**8**·$3Me_4N$, 94750-84-2; **9**·2*n*-Bu_4N, 99686-41-6; **10**·Na·$2Me_3NCH_2Ph$·MeOH, 99686-44-9; **11**·$2Et_4N$, 99686-45-0; **12**·$2Et_4N$, 99686-46-1; $TiCl_3$, 7705-07-9.

Supplementary Material Available: Listings of crystallographic data for the six compounds in Table I and $(Et_4N)_2[V_2(S_2C_2H_4)_4]$:[29] anisotropic thermal parameters; hydrogen atom coordinates and temperature factors; calculated and observed structure factors (114 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, Unité Associée au CNRS No. 420,
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Interactions in $Cu^{II}Cu^{II}Cu^{II}$, $Cu^{II}Zn^{II}Cu^{II}$, and $Cu^{II}Ni^{II}Cu^{II}$ Trinuclear Species. Crystal Structure of Bis(*N*,*N'*-bis(3-aminopropyl)oxamido)tricopper(II) Perchlorate

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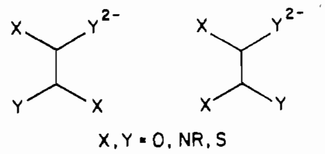
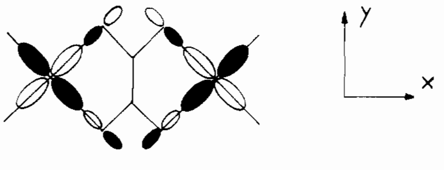
Four trinuclear complexes have been synthesized, namely $[Cu_3(oxpn)_2](ClO_4)_2$ (**1**), $[Cu_2Zn(oxpn)_2(H_2O)_2]X_2$ with X = ClO_4 (**2**) and BPh_4 (**3**), and $[Cu_2Ni(oxpn)(H_2O)_2](ClO_4)_2$ (**4**). The binuclear complex $[CuNi(oxpn)(bpy)_2](NO_3)_2 \cdot 2H_2O$ (**5**) has been joined to this study. oxpn is bis(*N*,*N'*-bis(3-aminopropyl)oxamido). The crystal structure of **1** has been determined. **1** crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12.257 (2) Å, b = 14.697 (5) Å, c = 15.872 (6) Å, and β = 104.62 (2)° at 293 K, Z = 4. The copper(II) ions are in square-pyramidal surroundings, the basal planes being slightly tilted with respect to one another. Two trinuclear units are related through an inversion center to form a bis trinuclear entity with a separation of 3.251 (2) Å between two central copper atoms. The structures of **2**–**5** have been deduced from the spectroscopic data. The relative energies of the low-lying states in **1**, **4**, and **5** have been derived from the magnetic properties studied in the 4.2–300 K temperature range. Weak interactions between two symmetry-related trinuclear units in **1** and between terminal copper(II) ions in **2** and **3** have been detected in addition to the strong interactions between adjacent magnetic centers. The EPR spectra of the compounds have also been investigated. The most interesting is that of **5**, which reveals a low-lying triplet state resulting probably from the interaction between two doublet pair states within a bis heterobinuclear entity.

Introduction

It has recently been demonstrated that the bis bidentate ligands like



may have a remarkable efficiency to propagate an antiferromagnetic interaction between two metal centers relatively far from each other.[2-4] Such a situation is realized, for instance, when a $C_2X_2Y_2^{2-}$ bis bidentate ligand bridges two copper(II) ions in elongated tetragonal surroundings with coplanar or almost coplanar basal planes.[3-4] In such surroundings, the magnetic orbitals centered on the copper(II) ions are as



They point from the metal toward the four nearest neighbors and overlap either side of the bridge, which favors a strong antiferromagnetic interaction. The same situation holds when a copper(II) ion is replaced by another magnetic ion with a d_{xy}-type magnetic orbital such as high-spin Fe(III) or Ni(II).[6,7]

So far, two kinds of strongly antiferromagnetically coupled compounds with $C_2X_2Y_2^{2-}$ bis bidentate bridging ligands have been investigated, namely binuclear complexes[2,4-6,8-14] and ribbon chains.[3,7,15,16] In contrast, to our knowledge, no molecular system with more than two magnetic ions bridged by a ligand of this type has been described. More generally, relatively few studies dealing with magnetic trinuclear systems have been reported in comparison

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