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Structural Diversity of Homoleptic Ethane-1,2-dithiolato Complexes of the First Transition Series

Sir:

The current rapid development of transition-metal thiolate chemistry has been stimulated primarily by the discovery of a diversity of structural types with variant nuclearity[1-4] and the utility of certain complexes as precursors to new clusters and cages.[5-7] Despite these advances, the types and structural patterns of homoleptic thiolate complexes of first transition series elements in their common oxidation states have not been fully derived. The present results, in conjunction with previous information,[2a,b,3,4] provide a close approach to this objective by utilizing as the common ligand ethane-1,2-dithiolate, whose strong binding leads to homoleptic species. Because previous complexes of this ligand have the 2:1 $(S_2C_2H_4)^{2-}$:$M^{II,III}$ ratio, this ratio was employed in the new reaction systems, which are considered in order of increasing atomic number of the metal component. All reactions and manipulations were performed at ambient temperature under a pure dinitrogen atmosphere. Structures of reaction products are shown in Figure 1.

The 2:1:1 $Na_2(S_2C_2H_4)$:$TiCl_3$:Et_4NBr[8] reaction system in 50 mL of acetonitrile—after 2 days of stirring and addition of ether to the cold concentrated filtrate—afforded orange diamagnetic $(Et_4N)_2[Ti(S_2C_2H_4)_3]$.[9a] With this stoichiometry established, the compound (45%) was prepared more rationally in the 3:1:2 $Na_2(S_2C_2H_4)$:$TiCl_4$:Et_4NBr system in acetonitrile after similar workup and recrystallization from acetonitrile/ether. Despite the reaction ratio and anaerobic conditions, the (isolable) product is a tris-chelate Ti(IV) complex. The oxidation state is an apparent consequence of the extreme oxidative instability of the Ti(III) species ($E_{p,c}$ = −2.0 V vs. SCE, acetonitrile). $(Et_4N)_2[Ti(S_2C_2H_4)_3]$ crystallizes in orthorhombic space group $Pna2_1$ with a = 21.151 (4) Å, b = 9.671 (1) Å, c = 15.046 (3) Å, and Z = 4.[10a] The anion structure approaches C_3 symmetry, as evident from these ranges of angles related under this symmetry, with one member of a set specified: S(1)–Ti–S(2), 3 at 82.8 (1)–82.9 (1)°; S(1)–Ti–S(3), 6 at 85.8 (1)–89.1 (1)°; S(1)–Ti–S(4), 3 at 105.1 (1)–108.3 (1)°; S(1)–Ti–S(6), 3 at 161.2 (1)–164.7 (1)°. Distances similarly divide into the sets Ti–S(1,3,5) and Ti–S(2,4,6) with mean values of 2.434 (4) and 2.419 (1) Å. The two S_3 planes are nearly parallel (dihedral angle 1.8°), and the projected twist angles ϕ = 35–42° indicate substantial distortion from octahedral (ϕ = 60°) toward trigonal-prismatic (ϕ = 0°) stereochemistry.

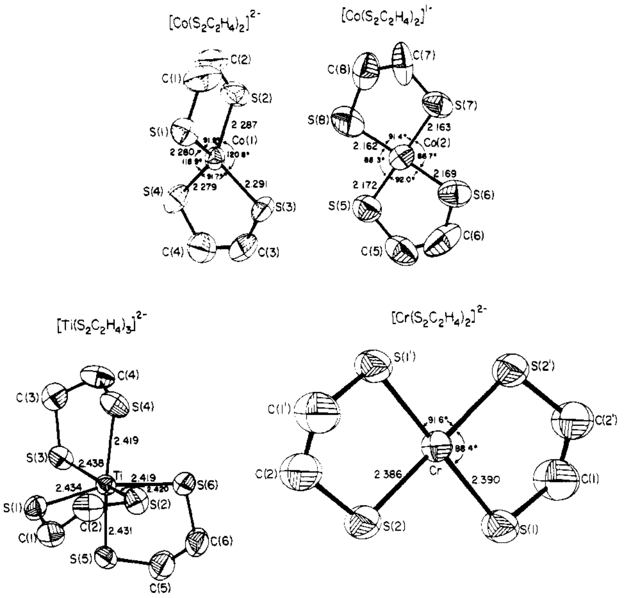

Figure 1. Structures of $[Ti(S_2C_2H_4)_3]^{2-}$, $[Co(S_2C_2H_4)_2]^{2-}$, $[Co(S_2C_2H_4)_2]^{-}$, and $[Cr(S_2C_2H_4)_2]^{2-}$, showing 50% probability ellipsoids, atom-labeling schemes, and selected bond angles and distances.

The 2:1:2 $Na_2(S_2C_2H_4)$:$CrCl_2$:Et_4NCl[8] reaction system in 100 mL of acetonitrile—after $2^1/_2$ days of stirring and workup similar to that of the Ti system—gave violet, highly air-sensitive $(Et_4N)_2[Cr(S_2C_2H_4)_2]$[9b] (45%) upon recrystallization from acetonitrile/ether. The compound occurs in monoclinic space group $C2/c$ with a = 13.023 (2) Å, b = 17.369 (3) Å, c = 12.825 (2) Å, β = 103.97 (1)°, and Z = 4.[10b] Mononuclear $[Cr(S_2C_2H_4)_2]^{2-}$

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(8) Molar ratios are given. The scale of each reaction is provided by the following quantities (mmol): $TiCl_3$, 5.0; $TiCl_4$, 5.0; $CrCl_2$, 10; $CrCl_3{\cdot}6H_2O$, 12; $CoCl_2$, 34; $NiCl_2{\cdot}6H_2O$, 57. All new compounds gave highly satisfactory total elemental analyses.

(9) Absorption spectra, λ_{max}, nm (ϵ_M): (a) $(Et_4N)_2[Ti(S_2C_2H_4)_3]$ (acetonitrile) 230 (38 900), 276 (sh, 8480), 355 (9810), 414 (10 400), 476 (sh, 4570); (b) $(Et_4N)_2[Cr(S_2C_2H_4)_2]$ (DMF) 556 (67), 620 (sh, 52); (c) $(Me_4N)_n[Cr_n(S_2C_2H_4)_{2n}]$ (Me_2SO) 296 (16 000), 500 (400), 560 (340), 660 (260) (calculated for n = 2); (d) $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$ (acetonitrile) 316 (15 200), 360 (8050), 417 (5070), ~500 (sh, 580), 676 (2920), 708 (sh, 1900), 970 (200), 1200 (180); (e) $(n\text{-}Bu_4N)_2[Ni_2(S_2C_2H_4)_3]$ (acetonitrile) 448 (900), 592 (400).

(10) Data were collected at ambient temperature on a Nicolet R3m or P3F diffractometer with graphite-monochromatized Mo K$\bar{\alpha}$ radiation. Empirical absorption corrections were applied. Structures were solved by a combination of direct methods and subsequent difference Fourier maps followed by full-matrix least-squares refinement. Calculations were performed with use of SHELXTL programs: (a) $(Et_4N)_2[Ti(S_2C_2H_4)_3]$, 1865 unique data ($F_o^2 > 2.0\sigma(F_o^2)$), $R(R_w)$ = 3.4 (3.4)%; (b) $(Et_4N)_2[Cr(S_2C_2H_4)_2]$, 1631 unique data ($F_o^2 > 3\sigma(F_o^2)$), R (R_w) = 4.5 (6.0)%; (c) $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$, 1695 unique data ($I > 2.5\sigma(I)$), R (R_w) = 5.4 (5.3)%.

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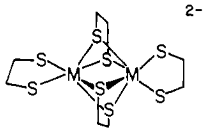
Table I. Types and Structures of Homoleptic Ethane-1,2-dithiolato Complexes of the First Transition Series



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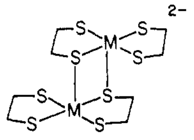

2

complex	structure[a]	ref
$[Ti(S_2C_2H_4)_3]^{2-}$	octahedral	*b*
$[V_2(S_2C_2H_4)_4]^{2-}$	nonoctahedral tetrabridging dimer 1	4
$[Cr(S_2C_2H_4)_2]^{2-}$	planar	*b*
$[Mn(S_2C_2H_4)_2]^{2-}$	tetrahedral	3a
$[Mn_2(S_2C_2H_4)_4]^{2-}$	lateral dibridging dimer **2**	3
$[Fe_2(S_2C_2H_4)_4]^{2-}$	lateral dibridging dimer **2**	2a
$[Co(S_2C_2H_4)_2]^{2-}$	tetrahedral	*b*
$[Co(S_2C_2H_4)_2]^{1-}$	planar	*b*
$[Ni_2(S_2C_2H_4)_3]^{2-}$	planar dibridging dimer	*b*

[a] Approximate description. [b] This work.

has an imposed twofold axis normal to the perfect CrS_4 plane; axial positions are vacant. The magnetic moment of 4.95 μ_B in acetonitrile[11] accords with a high-spin d^4 configuration. The 2:1:1 $Na_2(S_2C_2H_4)$:$CrCl_3·6H_2O$:Me_4NCl[8] system in 80 mL of methanol—in which the first two components reacted for 18 h, the third was added, and the residue after solvent removal was recrystallized from acetonitrile—afforded a gold microcrystalline Cr(III) compound of composition $(Me_4N)_n[Cr_n(S_2C_2H_4)_{2n}]$ (75%). Diffraction quality crystals have not been obtained. The reduced solid-state magnetic moment (2.50 μ_B) and appreciable solubility only in Me_2SO strongly imply $n \geq 2$. In this solvent the complex ([Cr] = 5.0 mM) has a moment of 3.85 μ_B and three LF visible bands[9c] of $^4A_{2g} \rightarrow {}^4T_{2g}$ parentage, consistent with mononuclear $[Cr(S_2C_2H_4)_2(Me_2SO)_2]^-$.

The 2:1:2 $Na_2(S_2C_2H_4)$:$CoCl_2$:Me_4NCl reaction system in 150 mL of methanol—treated as the Cr(III) system with 12 h of reaction and recrystallization from acetonitrile/ether—yielded a crystalline green material of composition consistent with the mixed-valence formulation $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$ (58%). The compound is found in orthorhombic space group *Pbca* with a = 26.366 (6) Å, b = 16.943 (4) Å, c = 15.722 (3) Å, and Z = 8.[10c] Mixed-valence behavior is expressed in a unique way: the crystal consists of a 1:1 mixture of $(Me_4N)_2[Co(S_2C_2H_4)_2]$ and $(Me_4N)[Co(S_2C_2H_4)_2]$. $[Co(S_2C_2H_4)_2]^{2-}$ is approximately tetrahedral, the CoS(1,2)/CoS(3,4) dihedral angle being 91.5°, but is distorted toward D_{2d} symmetry owing to ligand bite restrictions. The S–Co–S angles under this symmetry average to 91.8 and 119.0°; the mean Co–S distance of 2.284 (6) Å is somewhat shorter than that of tetrahedral $[Co(SPh)_4]^{2-}$ (2.33 (1) Å[12]). Mononuclear $[Co(S_2C_2H_4)_2]^-$ approaches D_{2h} symmetry, with a 6.8° dihedral angle between the two CoS_2 planes, near 90° bond angles, and a mean Co–S distance of 2.167 (5) Å. Axial positions are unoccupied. The solid-state moment of 3.92 μ_B, together with 4.6 μ_B for tetrahedral $[Co(SR)_4]^{2-}$,[1a] gives 3.1 μ_B for the monoanion. In solution the moment is 3.80 μ_B, the absorption spectrum[9d] contains LF and LMCT features typical of tetrahedral $Co^{II}S_4$ chromophores,[1a,13] and an additional band occurs at 960 nm similar to those (~900 nm) of [bis(biuretato)cobalt(III)](1–) complexes.[14] Thus, $[Co(S_2C_2H_4)_2]^-$ is a *planar spin triplet Co(III)* species.

Lastly, the 2:1:2 $Na_2(S_2C_2H_4)$:$NiCl_2·6H_2O$:n-Bu_4NBr[8] system in 250 mL of water after 20 h gave $(n\text{-}Bu_4N)_2[Ni_2(S_2C_2H_4)_3]$ as green-black microcrystals whose diamagnetism and solution spectrum[9e] show the presence of planar Ni(II). The anion has been detected in aqueous solution.[15] Single crystals suitable for X-ray structural analysis have not been obtained.

Collective results demonstrate the formation, at constant 2:1 $(S_2C_2H_4)^{2-}$:$M^{II,III}$ reaction stoichiometries, of the *six* structural types of first transition series complexes in Table I. Conventional stereochemical preference is expressed by Ti(IV), Cr(II), Mn(II), Co(II), and Ni(II). Excluding the electronically ambiguous dithiolene complexes,[16] $[Ti(S_2C_2H_4)_3]^{2-}$ is the initial example of a homoleptic Ti thiolate.[17] $[Cr(S_2C_2H_4)_2]^{2-}$ is one of the few structurally defined four-coordinate Cr(II) complexes, all of which are planar.[18] The two possible isomers of $[Ni_2(S_2C_2H_4)_3]^{2-}$ are of the dibridging type, as established for $[Ni_2(\mu\text{-}SEt)_2(SEt)_4]^{2-}$.[1i] Structure **1** applies to $[V_2(S_2C_2H_4)_4]^{2-}$ in three different crystals and is formed at 2–4:1 reactant molar ratios.[4] A dimer structural transition to **2** occurs at M = Mn(III) and Fe(III). A remarkable result is the formation, under *anaerobic* conditions, of $[Co(S_2C_2H_4)_2]^-$ whose S = 1 planar structure is precedented only in several biuretato[14] and dithiolene[19] complexes. In the present case the oxidation state is unequivocally Co(III), showing that dimer formation ceases here and that innocent but polarizable dianionic ligands suffice to stabilize rarely encountered four-coordinate Co(III). The tabulated results reveal the most extensive structural diversity found in homoleptic complexes of the first transition series and additionally serve to dispel the notion that higher oxidation states are not sustainable in a thiolate environment. We are currently attempting both to determine whether the $\mathbf{1} \rightleftharpoons \mathbf{2}$ structural transition occurs at Cr(III) and to ascertain the means of formation of $[Co(S_2C_2H_4)_2]^-$. Full accounts of the solid and solution structures and other properties of ethane-1,2-dithiolate complexes will be reported subsequently.

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Registry No. $(Et_4N)_2[Ti(S_2C_2H_4)_3]$, 94750-78-4; $(Et_4N)_2[Cr(S_2C_2H_4)_2]$, 94750-80-8; $(Me_4N)_n[Cr_n(S_2C_2H_4)_{2n}]$, 94750-81-9; $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$, 94750-84-2; $(n\text{-}Bu_4N)_2[Ni_2(S_2C_2H_4)]_3$, 94750-86-4.

Supplementary Material Available: Listings of positional parameters for $(Et_4N)_2[Ti(S_2C_2H_4)_3]$, $(Et_4N)_2[Cr(S_2C_2H_4)_2]$, and $(Me_4N)_3[Co_2(S_2C_2H_4)_4]$ (3 pages). Ordering information is given on any current masthead page.

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(11) All magnetic moments in solution were determined by the usual NMR method (Me_4Si shift differences) and in the solid state by the Faraday method, both at ~297 K. Values per metal atom are given.

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