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Steric Control of Metal-Thiolate Coordination: Synthesis and Structure of Monomeric Cobalt(II) and Copper(I) Thiolate Complexes

Sir:

The occurrence of polymeric materials and cluster compounds is a dominant theme of the coordination chemistry of metal thiolate complexes.[1-11] These compounds result from the strong affinity of thiolates to bridge between two or more metals. We wish to report that the ortho-disubstituted ligand 2,3,5,6-tetramethylbenzenethiolate ($C_{10}H_{13}S^-$) has a markedly reduced tendency to bridge metal centers.

One equivalent of $CoCl_2$, 3 equiv of $KSC_{10}H_{13}$, and 2 equiv of $[N(n\text{-}Pr)_4]Br$ were heated in acetonitrile under nitrogen for 30 min. After a hot filtration, dark brown crystals of $[Co(SC_{10}H_{13})_3(CH_3CN)][N(n\text{-}Pr)_4]$ (**1**) deposited from the filtrate in 70% yield. Acetonitrile solutions of **1** are green brown with λ_{max} (ϵ_M) 328 (sh) (7600), 388 (4050), 690 (453), and 728 (sh) nm (281). The structure of **1** was determined by an X-ray diffraction study (Figure 1).[12] The most notable features of the structure are as follows: it is a monomeric rather than a cluster compound, and it is a mixed-ligand complex containing three thiolate ligands and a coordinated acetonitrile. This result stands in strong contrast to the related chemistry with less sterically hindered thiolates. In the previously reported reaction of benzenethiolate with cobalt(II) salts, the adamantane-like cluster $[Co_4(SPh)_{10}]^{2-}$ is obtained with 3 equiv of PhS^- is used and the monomeric complex $[Co(SPh)_4]^{2-}$ is obtained when an excess of PhS^- is used.[2,13] Adamantane clusters and $[M(SPh)_4]^{2-}$ complexes are also the predominant complexes isolated in the benzenethiolate chemistry of Fe(II), Cd(II), and Zn(II).[3-8] The steric encumbrance of the durenethiolate ligand does not preclude a tetrathiolate complex; the reaction of 8 equiv of $C_{10}H_{13}S^-$ with $CoCl_2$ in CH_3CN gives emerald green crystals of the tetrathiolate

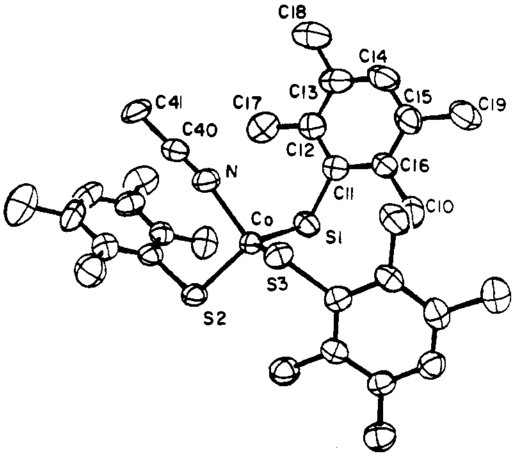

Figure 1. ORTEP diagram of the $[Co(SC_{10}H_{13})_3(CH_3CN)]^-$ anion of **1**. Selected bond distances (Å) and angles (deg) are as follows: Co–S1 = 2.270 (1), Co–S2 = 2.296 (1), Co–S3 = 2.267 (1), Co–N = 2.036 (4); S1–Co–S2 = 108.80 (6), S1–Co–S3 = 119.32 (5), S1–Co–N = 109.0 (1), S2–Co–S3 = 119.43 (5), S2–Co–N = 100.1 (1), S3–Co–N = 97.0 (1), Co–S1–C11 = 112.5 (1), Co–S2–C21 = 103.8 (1), Co–S3–C31 = 110.6 (1), Co–N–C40 = 165.6 (4).

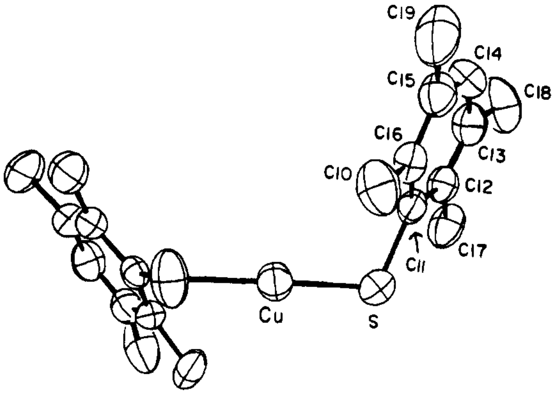

Figure 2. ORTEP diagram of the $[Cu(SC_{10}H_{13})_2]^-$ anion of **2**; Cu–S–C11 = 108.2 (2)°.

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(12) $[N(CH_2CH_2CH_3)_4][Co(SC_{10}H_{13})_3(CH_3CN)]$ crystallizes in the monoclinic space group $P2_1/n$ with a = 19.714 (4) Å, b = 11.863 (3) Å, c = 19.910 (4) Å, β = 95.59 (2)°, V = 4634 (3) Å^3, and Z = 4. X-ray diffraction data were collected with an Enraf-Nonius CAD4 diffractometer with molybdenum radiation. The structure was solved by normal Patterson and Fourier methods. Final least-squares refinement gave R = 0.054, R_w = 0.080 for 3524 unique reflections with $I > 3\sigma(I)$.

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compound $K[NEt_4][Co^{II}(SC_{10}H_{13})_4]$. The reaction of 2 equiv of $LiSC_{10}H_{13}$ with $CoCl_2$ in ethanol or CH_3CN gives a light green precipitate whose elemental analysis is consistent with a $Co(SC_{10}H_{13})_2$ formulation.[14] This compound is insoluble in alcohols, CH_3CN, hexane, and toluene but is soluble in DMF to give blue-green solutions.

The average Co–S bond length in **1** (2.28 (1) Å) is 0.03 Å shorter than the corresponding distance in $[PPh_4]_2[Co(SPh)_4]$.[13] The difference in the overall charge on the anions is principally responsible for the discrepancy in these parameters.[2,3] Also, the differences in the Co–S–Ph conformation may contribute to the change in the bond distances. In **1** the Co–S bonds are approximately orthogonal to plane of the durene ring, while in $Co(SPh)_4{}^{2-}$ the Co–S bonds lie in the plane determined by the phenyl rings.[13] The bond angles of the CoS_3N unit show large deviations from the normal tetrahedral angle of 109.5°; these deviations result from the mixed-ligand coordination and the steric interactions among the ligands.

White crystals of $[N(n\text{-}Pr)_4][Cu(SC_{10}H_{13})_2]$ (**2**) are obtained in 60% yield from the cooled filtrate of the room-temperature reaction of 1 equiv of $Cu(CH_3CN)_4BF_4$ and $[N(n\text{-}Pr)_4]Br$ with 3 equiv of $LiSC_{10}H_{13}$ in ethanol. The linear digonal coordination of the copper was revealed by an X-ray crystal structure determination (Figure 2).[15] The anion has crystallographic C_2 symmetry with the S–Cu–S′ angle equal to 178.6 (1)°. The Cu–S distance of 2.137 (2) Å is substantially shorter than the average Cu–S distance in the three-coordinate copper in $[Ph_4P]_2[Cu(SPh)_3]$[8] and slightly less than average Cu–S distance for the two-coordinate coppers in $[Cu_5(SPh)_7]^{2-}$ and $[Cu_5(S\text{-}t\text{-}Bu)_6]^-$.[9,10] The observed large change in the Cu–S distance as a function of coordination number should be a valuable consideration in the interpretation of EXAFS data of copper proteins.[16]

A benzenethiolate complex, $(PPh_4)[Cu(SPh)_2]$, which is analogous to **2**, was previously reported but was not structurally characterized.[8] $[Cu(SPh)_2]^-$ differs from **2** in that it readily undergoes oligomerization reactions to give the cluster compounds $[Cu_4(SPh)_6]^{2-}$ and $[Cu_5(SPh)_7]^{2-}$.[8,9,11] The reaction of Cu(I) salts with $C_{10}H_{13}S^-$ was studied for a variety of Cu/SR ratios (5/1 to 1.5/1) and under different reaction conditions; **2** was the only isolated product, and in no case was the yellow color, which is characteristic of many $Cu^I{}_x(SR)_y$ cluster complexes,[8-11] ever detected.

The reduced tendency of 2,3,5,6-tetramethylbenzenethiolate to bridge metal centers makes it an attractive ligand for the synthesis and study of monomeric metal thiolate complexes in cases where less sterically demanding ligands give clusters or polymeric compounds.[17,18]

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Supplementary Material Available: Tables of fractional coordinates and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(14) Anal. Calcd for $CoS_2C_{20}H_{26}$: C, 61.68; H, 6.73; S, 16.46. Found: C, 60.15; H, 6.74; S, 15.99.

(15) $[N(CH_2CH_2CH_3)_4][Cu(SC_{10}H_{13})_2]$ crystallizes in the monoclinic space group $C2/c$ with a = 10.763 (4) Å, b = 15.035 (7) Å, c = 21.176 (4) Å, β = 98.45 (2)°, V = 3390 (3) Å^3, and Z = 4. Final least-squares refinement gave R = 0.060 and R_w = 0.085 for 1140 unique reflections with $I > 3\sigma(I)$. The corresponding silver complex, $[NPr_4][Ag(SC_{10}H_{13})_2]$, is isomorphous with a = 10.803 (4) Å, b = 14.997 (9) Å, c = 21.212 (3) Å, β = 97.92 (2)°, and V = 3404 Å^3.

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Neutron Diffraction Analysis of $[H_3Pt_2(Ph_2PCH_2CH_2PPh_2)_2]^+[BPh_4]^-$: An Unusual Example of an Unsymmetrical $[P_2Pt(\mu\text{-}H)_2PtP_2H]$ Core

Sir:

Binuclear platinum hydride complexes of the type $[H_3Pt_2L_4]^+$ (L = tertiary phosphine) have been actively investigated in the last few years.[1-4] Interest arose in part from the easy displacement of dihydrogen by two-electron ligands[5] such as CO, CNR, or phosphine, a displacement which in some cases is reversible.[6] Specific examples of $[H_3Pt_2L_4]^+$ systems investigated to date include the bridging bis(phosphine) complexes of Puddephatt and co-workers[1] ($L_2 = Ph_2PCH_2PPh_2$ (dppm)), the monodentate phosphine complexes of Venanzi and his group[3] (L = PEt_3, PPh_3, PCy_3), and the chelating bis(phosphine) complexes of Otsuka et al.[4] ($L_2 = (t\text{-}Bu)_2PCH_2CH_2CH_2P(t\text{-}Bu)_2$ (dbpp)) and ourselves[2] ($L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe)). The first geometry observed for the $[H_3Pt_2L_4]^+$ unit was a symmetrical one (i.e., $[HL_2Pt(\mu\text{-}H)PtL_2H]^+$), as found in a crystal structure determination carried out by Ibers, Otsuka, and co-workers.[4] Subsequently, however, Venanzi et al. showed that the nonfluxional monodentate phosphine complexes $[H_3Pt_2(PR_3)_4]^+$ (R = ethyl, phenyl, cyclohexyl) had ^1H NMR spectra inconsistent with a symmetrical structure, and they proposed for the first time an unsymmetrical geometry (i.e., $[L_2Pt(\mu\text{-}H)_2PtL_2H]^+$) for the above compounds;[3a] this was later confirmed by an X-ray analysis.[3b] The unsymmetrical species was also mentioned as a possible intermediate in the interconversion of the fluxional molecule $[H_3Pt_2(dbpp)_2]^+$.[4] In an earlier publication,[2b] some of us reported (with H. D. Kaesz and C. B. Knobler) the synthesis and X-ray structure of $[H_3Pt_2(dppe)_2]^+$, which in-

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