Volume 24

Number 21

October 9, 1985

Inorganic Chemistry

Communications

A Square-Planar Cobalt(III) Tetrathiolate Complex[1]

Sir:

Complexes with metal–sulfur coordination centers are of significant interest as synthetic analogues for the active sites of metalloproteins and metal sulfide heterogeneous catalysts. We report the synthesis and structure of a cobalt(III) tetrathiolate complex that is the first example of a homoleptic Co(III) thiolate complex[2] and a rare example of a square-planar Co(III) complex.

The reaction of 5 equiv of lithium 2,4,6-triisopropylbenzenethiolate (LiS-2,4,6-i-$Pr_3C_6H_2$) with $CoCl_2$ in EtOH gives a brown solution, which reacts upon exposure to air to give an intensely red solution. A red crystalline complex, $[Ph_4P][Co(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H)_4]$ (**1**), can be isolated from this solution in 60% yield by the addition of $[PPh_4]Br$.[3] The NEt_4 salt of **1** was structurally characterized by X-ray diffraction.[4] The structure of the anion (Figure 1) has approximate S_4 symmetry. The $[CoS_4]$ unit is slightly distorted from square planar toward tetrahedral geometry with the sulfur atoms alternately displaced above and below the plane.[5] The extent of the ruffling of the CoS_4 square plane is defined by the trans S–Co–S angles of 160.4 (1) and 161.3 (1)°. The average Co–S bond length (2.207 (3) Å) is ca. 0.1 Å shorter than the distance in $(K)(NEt_4)[Co(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$[6] and other tetrahedral $[Co^{II}(SR)_4]$ complexes;[7,8] this distance is about 0.06 Å shorter than the Co–S distance in octahedral $Co^{III}S_6$ complexes.[9]

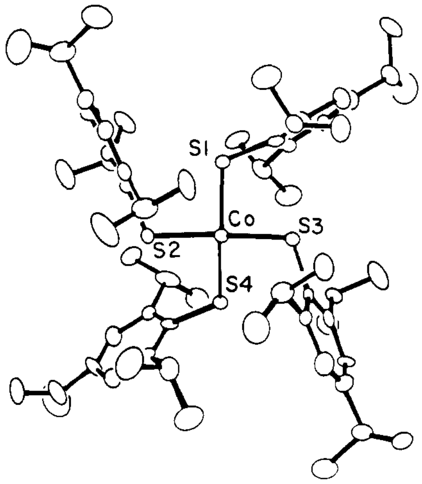

Figure 1. The $[Co(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^-$ anion of **1**. Selected distances (Å) and angles (deg): Co–S1 = 2.206 (3); Co–S2 = 2.211 (3); Co–S3 = 2.206 (3); Co–S4 = 2.204 (3); S1–Co–S2 = 91.8 (1); S1–Co–S3 = 91.3 (1); S1–Co–S4 = 160.4 (1); S2–Co–S3 = 161.3 (1); S2–Co–S4 = 91.8 (1); S3–Co–S4 = 91.4 (1); Co–S–C_{av} = 112 (2).

Although octahedral coordination is the predominate geometry for Co(III) complexes, there are several examples of five-coordinate[10] and a very limited number of four-coordinate compounds. Examples of tetrahedral Co(III) compounds are limited to the buried heteroatoms in heteropolyanions[11] and to a few coordination centers in solid-state compounds.[12] There are only two well-characterized examples of Co(III) square-planar compounds: bis(biuretato)cobalt(III) complexes[13] and bis(dithiolene)cobalt(III) complexes.[14] The magnetic moment of 3.5 μ_B (room temperature, solid state) for **1** indicates a triplet ground state, which is also the ground state for the other Co(III) square-planar complexes.[13,14] The electronic spectrum of **1** is dominated by intense transitions, which likely involve thiolate to Co(III) charge transfer.[3] The electronic spectra in solution and in the solid state are similar, which indicates that the solid-state structure is maintained in solution. The square-planar coordination in **1** is not enforced by

---

(1) Millar, M.; Koch, S. A., presented at the 188th National Meeting of the American Chemical Society, Philadelphia, Aug 1984, INOR 43.

(2) (a) Co(III) thiolates with the empirical formula $[Co(SR)_3]$ have been reported to be polymeric: McCormick, B. J.; Gorin, G. *Inorg. Chem.* **1963**, *2*, 928. Swan, C. J.; Trimm, D. L. *Chem. Ind.* (*London*) **1967**, 1363. (b) A complex containing a square-planar bis(ethane-1,2-dithiolato)cobalt(III) anion has been concurrently described: Dorfman, J. R.; Rao, C. P.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 453.

(3) The electronic spectrum of **1** in CH_3CN is as follows (nm): 733 (sh) (ϵ = 2090), 638 (sh) (3760), 513 (17 300), 397 (17 400), 306 (sh) (10 100), 273 (sh) (16 900), 268 (sh) (22 500), 250 (sh) (30 000).

(4) $[NEt_4][Co(SC_{15}H_{23})_4]\cdot CH_3CN$ crystallized from CH_3CN in the monoclinic space group Cc with a = 24.126 (5) Å, b = 14.895 (4) Å, c = 22.541 (4) Å, β = 117.84 (2)°, V = 7163 (5) Å^3, and Z = 4. Diffraction data were collected at room temperature with graphite-monochromated molybdenum radiation on an Enraf-Nonius CAD4 diffractometer. Intensity data were measured for 6018 reflections with use of θ–2θ scans in the range $0 < 2\theta < 48°$ with $+h,+k,\pm l$ such that $h + k = 2n$. The structure was solved with use of Patterson and difference Fourier methods. The calculated positions of the hydrogen atoms were used in the structure factor calculations but were not refined. Final least-squares refinement (for the correct enantiomorph) with all non-hydrogen atoms anisotropic gave R = 0.054, R_w = 0.059 for 2928 unique reflections with $I > 3\sigma(I)$.

(5) The displacement (Å) of the S atoms out of the least-squares CoS_4 plane are as follows: S1, –0.368; S2, 0.363; S3, 0.367; S4, –0.368.

(6) Koch, S. A.; Fikar, R.; Millar, M.; O'Sullivan, T. *Inorg. Chem.* **1984**, *23*, 121.

(7) Swenson, D.; Baenziger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1932.

(8) Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 418.

(9) Shannon, R. D. In "Structure and Bonding in Crystals"; O'Keeffe, M., Navrotsky, A., Eds.; Academic Press: New York, 1981; Vol. 2, Chapter 16.

(10) Bailey, N. A.; McKenzie, E. D.; Worthington, J. M. *J. Chem. Soc., Dalton Trans.* **1977**, 763.

(11) Baker, L. C. W.; Simmons, V. E. *J. Am. Chem. Soc.* **1959**, *81*, 4744.

(12) Wood, D. L.; Remeika, J. P. *J. Chem. Phys.* **1967**, *46*, 3595.

(13) Bour, J. J.; Beurskens, P. T.; Steggarda, J. J. *J. Chem. Soc., Chem. Commun.* **1972**, 221. Birker, P. J. M. W. L.; Bour, J. J.; Steggerda, J. J. *Inorg. Chem.* **1973**, *12*, 1254. König, E.; Schakig, R.; Kanellakoupulos, B. *J. Chem. Phys.* **1975**, *62*, 3907.

(14) van der Put, P. J.; Schilperoord, A. A. *Inorg. Chem.* **1974**, *13*, 2476 and references therein.

0020-1669/85/1324-3311$01.50/0 © 1985 American Chemical Society

any steric requirements of the ligands, since the corresponding Fe(III) complex has a distorted-tetrahedral coordination.[15b] Coordination of small axial ligands such as CH_3CN (the solvent of recrystallization) should not be precluded by the steric nature of the thiolate ligands. The reduced affinity of the metal for axial ligands likely reflects the high electron density on the cobalt atom, which results from the electron-donating capacity of the thiolate ligands. The fact that **1** has a square-planar structure rather than the tetrahedral structure found for the isoelectronic $[Fe^{II}(SR)_4]^{2-}$ complexes must reflect the higher ligand field splittings associated with a metal in the +3 oxidation state.

The synthesis and stability of **1** serves as a further example of the ability of the sterically hindered thiolate ligand to stabilize monomeric complexes with metals in high oxidation states.[15] The observed chemistry with cobalt closely parallels that reported for iron.[15b] Red solutions of $[Co(SR)_4]^-$ generated with less sterically encumbered thiolate ligands such as 2,3,5,6-tetramethylbenzenethiolate are considerably less stable with respect to the autoredox reaction that produces Co(II) and disulfide. A analogous chemistry also exists for Mn(III).[16] The reaction of excess $LiS\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2$ with $(NEt_4)_2MnCl_5$ in CH_3CN/isopropyl alcohol at −20 °C gives purple solutions from which $[Mn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^-$ complexes can be isolated. A square-planar structure is highly likely for these complexes since the purple crystals of $[Ph_4P][Mn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$ are isomorphous with the PPh_4 salt of **1**. The thermal instability of this compound in the solid state and in solution has prevented a complete structural characterization.

Compound **1** shows a one-electron reduction at −1.60 V (SCE); the irreversible nature of this reduction may result from the necessary change in the geometry of the $[Co(SR)_4]$ unit from square-planar (Co(III)) to tetrahedral (Co(II)). Attempts to oxidize the tetrahedral $[Co^{II}(S\text{-}cys)_4]$ unit of Co(II)-substituted rubredoxin to a Co(III) state have not been successful;[17] this may reflect the inability of the $[Co^{III}(S\text{-}cys)_4]$ unit to assume a planar geometry. Interestingly, recent EXAFS and ESR studies have indicated that the recently discovered Ni(III) center in hydrogenase possesses a tetragonal ($S = {}^1/_2$) ligand field with three to four sulfur ligands.[18] The Ni(III) analogue of **1** might be a model for this center. Finally, the coordinatively unsaturated $Co^{III}S_4$ center in **1** is a possible structural model for cobalt in the CoMoS hydrodesulfurization catalyst.[19]

Acknowledgment. This work was supported by grants from the National Science Foundation (Grant CHE8310862) to S.K. and the National Institutes of Health (Grant GM 3252601) to M.M. We also thank Professor R. H. Holm for communication of the contents of ref 2b before its publication.

Registry No. **1**·Ph_4P, 97921-01-2; **1**·Et_4N, 97921-03-4; $[Ph_4P][Mn(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$, 97921-05-6.

Supplementary Material Available: Tables of fractional coordinates, thermal parameters, and bond distances and angles (12 pages). Ordering information is given on any current masthead page.

Department of Chemistry **Ronald Fikar**
State University of New York **Stephen A. Koch***
at Stony Brook
Stony Brook, New York 11794

Department of Chemistry **Michelle M. Millar***[20]
New York University
New York, New York 10003

Received June 13, 1985

---

(15) (a) Millar, M.; Lee, J. F.; Koch, S. A.; Fikar, R. *Inorg. Chem.* **1982**, *21*, 4105. (b) Millar, M.; Koch, S. A.; Fikar, R. *Inorg. Chim. Acta* **1984**, *88*, L15. (c) Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362. (d) O'Sullivan, T.; Millar, M. M. *J. Am. Chem. Soc.* **1985**, *107*, 4096.

(16) Mn(III) complexes of ethane-1,2-dithiolate have been reported: Costa, T.; Dorfman, J. R.; Hagen, K. S.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 4091. Christou, G.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1983**, 558. Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1985**, 58.

(17) May, S. W.; Kuo, J.-Y. *Biochemistry* **1978**, *17*, 3333.

(18) (a) Scott, R. A.; Wallin, S. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864. (b) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062 and references therein.

(19) (a) Topsøe, H.; Clausen, B. S. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 395. (b) Chianelli, R. R. *Catal. Rev.—Sci. Eng.* **1984**, *26*, 361.

(20) Address correspondence to this author at the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794.