X-Ray Structure of the Hexa(μ_2-arenethiolato-)tetra(arenethiolato)tetracobaltate(II) Dianion, $[(CoSPh)_4(\mu_2\text{-}SPh)_6]^{2-}$, a New Tetrahedral Tetracobalt Thiolate Cluster

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Summary The unique molecular cluster complex $[(CoSPh)_4(\mu_2\text{-}SPh)_6]^{2-}$($Me_4N^+$ cation) contains an approximately T_d Co_4S_{10} core, the clustering of four tetrahedral $\{Co^{II}(\mu_2\text{-}SPh)_3(SPh)\}$ co-ordination units being a consequence of ligand bridging, not metal–metal bonding.

Although binary complexes of many metals with monothiolate ligands RS^- have been encountered in conventional protic media as very insoluble compounds,[1] with structures presumed to be extensively non-molecular,[2] accumulating biochemical knowledge of metal–thiolate prosthetic groups, particularly the iron–sulphur–cysteine enzymes,[3] has revealed the existence of metal–thiolate complexes in protein environments[4] and redirected chemical attention to the importance of steric and medium influences on the structural and dynamic molecularity of metal–thiolate compounds.[5]

With cobalt(II), the only[6] characterized molecular binary thiolate complexes are the emerald-green tetrahedral species $[Co(SR)_4]^{2-}$, R = C_6H_5 or C_6F_5.[7] We report that the equilibrium (**1**) exists in MeCN–EtOH solutions of

$$5[Co(SPh)_4]^{2-} + 3Co^{2+} \rightleftharpoons 2[Co_4(SPh)_{10}]^{2-} \qquad (1)$$

cobalt(II) nitrate and PhS^- ($PhSH + Bu^n{}_3N$). The intensely orange-brown species $[Co_4(SPh)_{10}]^{2-}$ predominates at $[Co^{2+}]/[PhS^-]$ ratios greater than *ca.* 0·35, and may be crystallized readily with the Me_4N^+ cation. The structure† of the dianionic cluster is shown in the Figure. Four cobalt atoms form a tetrahedron, with six edge-bridging and four terminal thiolate groups. The Co_4S_{10} framework, structurally analogous to adamantane, $Me_4Ge_4S_6$,[8] and P_4S_{10}, is effectively but not rigorously of T_d symmetry; the six Co–Co distances are in the range 3·85—3·89 Å; Co–S (bridging) = 2·32 ± 0·01 Å, Co–S (terminal) = 2·25 ± 0·01 Å. The small distortion from the idealized Co_4S_{10} geometry in which all angles are tetrahedral is in the sense of increased Co–Co distances;‡ bridging angles at S are 113 ± 1°.

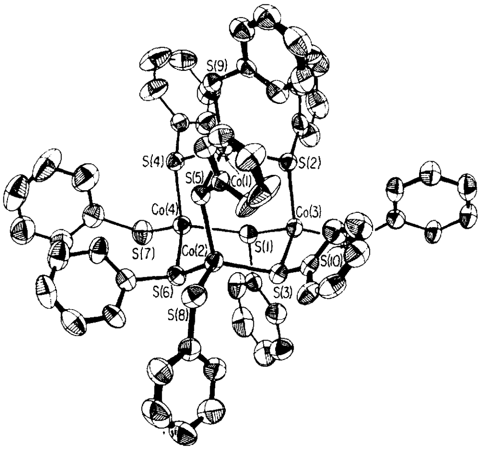

FIGURE. The $[(CoSPh)_4(\mu_2\text{-}SPh)_6]^{2-}$ cluster as it occurs in $(Me_4N)_2Co_4(SPh)_{10}$. Co–Co distances are in the range 3·85—3·89 Å; Co–S (bridging) = 2·32 ± 0·01 Å; Co–S (terminal) = 2·25 ± 0·01 Å; < Co–S–Co = 113 ± 1°.

The electronic spectrum of $[(CoSPh)_4(\mu_2\text{-}SPh)_6]^{2-}$ (MeCN solution) is typical of tetrahedral Co^{II} and closely resembles that of $[Co(SPh)_4]^{2-}$ in the *d–d* transition regions. However, in the 19,000—28,000 cm^{-1} region the cluster possesses additional lower-energy intense charge-transfer absorptions. The magnetic susceptibility data for $[(Me_4N)_2Co_4(SPh)_{10}]$ also reveal electronic interactions between high-spin submolecules. A model with four spin-quartet sub-molecules, interacting under T_d symmetry with an interaction parameter[9]§ $J = -17$ cm^{-1} describes the magnetic susceptibility variation in the range 80—300 K with an average deviation of 2%. Although small, the discrepancies between the data and this model are systematic, and more detailed magnetic studies are in progress. Preliminary magnetic susceptibility data for the *p*-thiocresol homologue, crystallized as $[\{(C_6H_{11})_2NH_2\}_2Co_4(p\text{-}MeC_6H_4S)_{10}]$, indicate an increased magnitude for *J*, *ca.* −23 cm^{-1}.

The $[(CoSPh)_4(\mu_2\text{-}SPh)_6]^{2-}$ cluster structure is unprecedented for both Co^{II} and monothiolate ligands. The above geometric and electronic structural data indicate that the clustering is a consequence of ligand bridging, not metal–metal bonding.

More extensively bridged Co–SPh oligomers or polymers have not been detected in solutions where $[Co^{2+}]/[PhS^-] >$ 0·4. A compound $[Co(\mu_2\text{-}SPh)_{4/2}]_n$ with edge-shared tetrahedra might be expected; if it exists it has very high solubility in MeCN–EtOH. In solution $[Co_4(\mu_2\text{-}SPh)_6(SPh)_4]^{2-}$ is not subject to hydrolysis, but is oxidized rapidly by dioxygen (rate proportional to proticity of the medium) forming a dark maroon compound totally insoluble in all solvents.[10]

MeCN–EtOH solutions containing both PhS^- and Cl^- with Co^{2+}, at molar ratios $[Co^{2+}]:[PhS^-]:[Cl^-]$ *ca.* 1:2:1, contain another green-black cluster complex as the main component. This species, which is more sensitive to dioxygen than $[Co_4(\mu_2\text{-}SPh)_6(SPh)_4]^{2-}$, appears to be $[Co_4(\mu_2\text{-}SPh)_6\text{-}Cl_4]^{2-}$. It may be precipitated as its Me_4N^+ salt, which is also intramolecularly antiferromagnetic.

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† $[(Me_4N)_2Co_4(SPh)_{10}]$; brown black crystals: a = 13.031(2), b = 23·590(4), c = 12·806(2) Å, α = 92·28(1)°, β = 115·04(1)°, γ = 79·12(1)°: 5121 observed reflections (Mo-K_α radiation): with anisotropic refinement of all non-hydrogen atoms, R_F = 3·5%.

‡ The $\bar{d}_{Co-Co}/\bar{d}_{Co-S}$ index is 1·666, *vs.* the idealized value of 1·633.

§ Defined by the interaction Hamiltonian $H_{ex} = -\sum_{i>j} J\boldsymbol{S}_i\cdot\boldsymbol{S}_j$. The constraint g = 2·00 was imposed.

[1] (a) R. C. Mehrotra, V. D. Gupta, and D. Sukhani, *Inorg. Chem. Acta Rev.*, 1968, **2**, 111; (b) D. C. Bradley and K. J. Fisher, 'MTP International Review of Science, Inorg. Chem., Series One, 1972, **5**, 65.

[2] Exceptions are the cyclic hexametallic structures $M_6(SR)_{12}$, M = Ni or Pd, R = Et, Pr^n, or CH_2CH_2OH: P. Woodward, L. P. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, 1965, **87**, 5251; N. R. Kunchur, *Acta Cryst.*, 1168, 1623; R. O. Gould and M. M. Harding, *J. Chem. Soc.* (*A*), 1970, 875.

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[5] B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3523; L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4168.

[6] Some insoluble paramagnetic compounds $Co(SR)_n$, n = 2, 2·67, 2·75, 3, have been briefly reported, but with inadequate characterization data: D. C. Bradley and C. H. Marsh, *Chem. and Ind.*, 1967, 361.

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[8] R. H. Benno and C. J. Fritchie, Jr., *J.C.S. Dalton*, 1973, 543.

[9] I. G. Dance, *Inorg. Chim. Acta*, 1974, **9**, 77.

[10] This compound is probably analogous to the insoluble cobalt mercaptides reported by Bradley;[6] no structural information is available.