

have three very different structures, but all have five-coordinate copper ions and similar metal-nitroxyl binding configurations. It is likely that steric requirements of the ligand methyl groups are an important factor in determining the binding geometry and the coordination environment about copper. More surprising is the fact that the nitroxyl ligands, which are generally reluctant to form metal complexes, form such short, and apparently stable, Cu-O bonds. In the present case, as in the two previous complexes with short Cu-nitroxyl bonds, the sterically bulky nitroxyl ligands prefer the coordination sites associated with short Cu-O bond distances. Also interesting is the fact that in the presence of coordinated water the nitroxyl radical remains bound to copper and two carboxylate ligands become monodentate. Results like these suggest that, under appropriate conditions, the nitroxyl function may be a better ligand than has been appreciated.

The magnetic properties of this complex were of potential interest because of the formal presence of four $S = 1/2$ para-

magnetic centers per molecule. However, with the exception of a small (<1%) amount of paramagnetic impurity, the complex is diamagnetic from 6 to 300 K. This magnetic behavior is most reasonably explained by the presumption of strong coupling between copper and nitroxyl free spins. It is not clear whether this coupling is a consequence of use of the odd metal and ligand electrons to form the Cu-O bond or whether it is simply a result of antiferromagnetic coupling strong enough to give rise to diamagnetism at room temperature. Studies of other, simpler, systems now in progress may shed some light on this point.

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Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, distances and angles within the CCl_3 groups, least-squares planes, and magnetic susceptibility data (27 pages). Ordering information is given on any current masthead page.

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The Clusters $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$: Preparations, Properties, and Structural Relationship of Near-Cubic $\text{Co}_8(\mu_4\text{-S})_6$ Cores to the Clusters in Synthetic Pentlandite

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In a search for Co-S-SR clusters, $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ was found to react with NaSH in acetone to give the octanuclear cluster $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ (**1**), isolated as its $n\text{-Pr}_4\text{N}^+$ salt. Reduction of **1** in acetonitrile with sodium acenaphthylenide in THF afforded $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ (**2**), which was obtained as its Et_4N^+ salt. $(n\text{-Pr}_4\text{N})_4(\text{1})$ crystallizes in monoclinic space group $P2_1/c$ with $a = 23.912$ (4) Å, $b = 27.466$ (6) Å, $c = 17.173$ (6) Å, $\beta = 90.86$ (2)°, $Z = 4$, and two centrosymmetric, independent anions. $(\text{Et}_4\text{N})_5(\text{2})$ crystallizes in triclinic space group $P\bar{1}$ with $a = 14.126$ (6) Å, $b = 14.150$ (2) Å, $c = 14.470$ (2) Å, $\alpha = 113.37$ (1)°, $\beta = 97.73$ (3)°, $\gamma = 72.74$ (2)°, $Z = 1$, and a centrosymmetric anion. Both clusters contain near-cubic $\text{Co}_8(\mu_4\text{-S})_6$ cores, composed of a concentric Co_8 cube and S_6 octahedron, which are only slightly distorted. Each cobalt atom is in an approximately tetrahedral site with one terminal PhS^- ligand. Mean values of corresponding metric features of the two anions **1** and **2** are insignificantly different except for the tendency of Co-SPh distances in **2** to exceed those in **1** by ~ 0.04 Å. This result suggests that the odd electron in **2** has structurally detectable Co character. Electronic properties reveal spin-coupled clusters, $S = 0$ (**1**) and $1/2$ (**2**) ground states, contact-shifted ^1H NMR spectra, and in solution equivalent Co sites and complete delocalization of the odd electron in **2**. The core units have the same topology as the recognizable Co_9S_6 clusters in the synthetic pentlandite Co_9S_8 , in which the clusters are extensively bridged by sulfide. However, the $[\text{Co}_8\text{S}_6]^{4+}$ cores of **1** and **2** are not isoelectronic with the pentlandite clusters, which have the apparent $[\text{Co}_9\text{S}_6]^{2+}$ oxidation level, and volumes of the Co_8 and S_6 components are substantially smaller (81-84%) than those of the synthetic clusters. Despite differences in oxidation levels and detailed structural features, the formation of $[\text{Co}_9\text{S}_6(\text{SPh})_8]^{4-}$ is a favorable indicator of the ability to synthesize small solubilized fractions of nonmolecular inorganic solids, particularly those containing recognizable metal-sulfur clusters.

Introduction

Evidence, albeit not extensive, is accumulating that bears favorably on the prospect of the synthesis of portions of nonmolecular inorganic solids in the form of small solubilized fractions. This matter has been most extensively pursued in the course of examination of possible analogies between metal clusters, especially carbonyls, and metal surfaces under conditions of chemisorption and catalysis.^{2,3} An entirely different domain for investigation is provided by solids other than metals. In this respect, metal sulfide minerals and synthetic phases⁴⁻⁶ offer a dazzling variety of structures and properties not yet encountered in discrete molecules. In the broadest terms, these materials, which sometimes contain other elements, can be classified as (i) infinite polymers containing no recognizable M-S clusters or (ii) extended lattices

containing recognizable M-S clusters that are discrete except for the bridging interactions connecting them.

With regard to type i compounds, $(\text{C}_3\text{H}_5)_6\text{Ni}_6(\mu_4\text{-S})_3$ contains a fraction of the framework of one form of NiS ,⁷ $[\text{Fe}_3\text{S}_4(\text{SR})_4]^{3-8}$ has the same $\text{Fe}_3(\mu\text{-S})_4$ group that repeats in the linear polymers $\text{M}^{\text{I}}\text{FeS}_2$,^{6,9} and $(\text{MeCp})_2\text{V}_2\text{S}_4$ ¹⁰ may possess a $\text{V}_2(\eta^4\text{-}\mu\text{-S}_2)_2$ group similar to that in patronite¹¹ (VS_4), also a linear polymer. The $\text{Nb}_2(\mu\text{-S})(\eta^4\text{-}\mu\text{-S}_2)$ core of $\text{Nb}_2\text{S}_3\text{Br}_4(\text{tbt})_4$ ¹² resembles a portion of the NbS_3 structure.¹³ The cages $[\text{M}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ ($\text{M} = \text{Zn}(\text{II}), \text{Cd}(\text{II})$)¹⁴ have been proposed as congruent representations

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of a M₁₀S₂₀ portion of the sphalerite (β-ZnS) lattice. However, this description requires that sulfide and thiolate are interchangeable ligands in this structure. Observations relevant to type ii compounds are more incisive. The Mo₂(η⁴-μ-S₂)₂ portion of Mo₂(S₂)₂Cl₆¹⁵ is closely simulated in [Mo₂(S₂)₆]^{2-,16} as is the Mo₃(μ₃-S)(η⁴-μ-S₂)₃ cluster of Mo₃S(S₂)₃Cl₄¹⁵ in [Mo₃S(S₂)₆]^{2-,17} and [Mo₃S(S₂)₃(S₂PEt₃)₃]^{18,19}. Similarly, the cubane-type Mo₄(μ₃-S)₄ clusters in GaMo₄S₄²⁰ and MoSX²¹ (X = Cl, Br, I) are approached by the [Mo₄S₄] cores of [Mo₄S₄(CN)₁₂]^{8-,22} [(i-PrCp)₄Mo₄S₄]^{10+,2+,23} and [Mo₄S₄(EDTA)₂]^{3-,24}. The Mo₆S₈, Mo₉S₁₁, and Mo₁₂S₁₄ clusters (or their selenium congeners), which are the building blocks of the Chevrel phases,²⁵⁻²⁷ are especially attractive synthetic objectives. The only approach to these species is [Mo₆(μ₃-S)(μ₃-Cl)₇Cl₆]^{3-,28}. Several years ago we reported the octanuclear cluster [Co₈S₆(SPh)₈]⁴⁻²⁹ and observed that it and cobalt pentlandite³⁰ both contain Co₈S₆ clusters, which are formed from concentric Co₈ cubes and S₆ octahedra. Here we provide a fuller account of the synthesis, structure, and other properties of this species and its reduced form, [Co₈S₆(SPh)₈]⁵⁻. These join an enlarging group of high-nuclearity metal sulfide clusters of diverse structures that includes [Co₆S₈(PEt₃)₆]^{+,0,31,32}, Co₆S₈(C-O)₆,³³ [Fe₆S₆Cl₆]^{3-,34} [Fe₆S₆I₆]^{2-,35} [Fe₆S₈(PEt₃)₆]^{2+,36} [Fe₆S₉-

Table I. Crystallographic Data for (n-Pr₄N)₄[Co₈S₆(SPh)₈] (A) and (Et₄N)₅[Co₈S₆(SPh)₈] (B)

	A	B
formula	C ₉₆ H ₁₅₂ Co ₈ N ₄ S ₁₄	C ₈₈ H ₁₄₀ Co ₈ N ₅ S ₁₄
mol wt	2282.66	2188.48
a, Å	23.912 (4)	14.126 (6)
b, Å	27.466 (6)	14.150 (2)
c, Å	17.173 (6)	14.470 (2)
α, deg		113.37 (1)
β, deg	90.86 (2)	97.73 (3)
γ, deg		72.74 (2)
V, Å ³	11297 (5)	2535 (1)
cryst system	monoclinic	triclinic
space group	P2 ₁ /c	P1
d _{calcd} , g/cm ³	1.34	1.51
d _{obsd} , ^c g/cm ³	1.32 (2)	1.49 (2)
Z	4	1
radiation	Mo Kα (0.710 69 Å)	
abs coeff, μm, cm ⁻¹	14.4	15.9
cryst size, mm	0.24 × 0.26 × 0.56	0.14 × 0.24 × 0.46
scan speed, deg/min	2.9-29.3	2.9-29.3
scan range, deg ^a	1.7	2.0
bkdg/scan time ratio	0.50	0.25
data collected	+h, +k, ±l (3.5° ≤ 2θ ≤ 43°)	+h, ±k, ±l (3.5° ≤ 2θ ≤ 50°)
unique data (I > 3σ(I))	7830	5543
no. of variables	1011	583
goodness of fit ^b	1.58	1.06
R, %	6.0	3.9
R _w , %	6.3	4.2

^a Scan range = x + (2θKα₂ - 2θKα₁). ^b The goodness of fit is

defined as $(\sum w(|F_o| - |F_c|)^2 / (n_o - n_v))^{1/2}$, where n_o and n_v denote the number of data and variables, respectively. ^c Determined by flotation in cyclohexane/CCl₄.

(SR)₂]^{4-,37} and [Ni₉S₉(PEt₃)₆]^{2+,38}. Unlike [Co₈S₆(SPh)₈]⁴⁻⁵⁻, none of these clusters is, to our knowledge, a solubilized fraction of a metal sulfide structure.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere; solvents were degassed before use.

(n-Pr₄N)₄[Co₈S₆(SPh)₈]. A solution of 8.5 g (5.0 mmol) of (n-Pr₄N)₂[Co₄(SPh)₁₀]³⁹ in 200 mL of acetone was treated with 0.84 g (15 mmol) of NaSH. The mixture was stirred for ~15 min and allowed to stand overnight. A microcrystalline black solid was separated from the green mother liquor by filtration and was washed with 3 × 20 mL of ethanol and 2 × 50 mL of ether. A yield of 2.9 g (51%) was obtained. This material had a ¹H NMR spectrum (vide infra) identical with that of the previously described product of the reaction system containing the mole ratio 1/1/1.6 of CoCl₂/Li₂S/LiSPh in methanol.²⁹ That product, obtained in 10% yield, analyzed as the acetonitrile monosolvate after recrystallization from acetonitrile/ether.²⁹

(Et₄N)₅[Co₈S₆(SPh)₈]. A solution of 2.0 g (0.88 mmol) of (n-Pr₄N)₄[Co₈S₆(SPh)₈] in 60 mL of acetonitrile was treated with 2.4 mL of a 0.4 M solution of sodium acenaphthylenide (0.96 mmol, prepared from sodium metal and acenaphthylene in THF). The red-purple solution immediately turned orange. A solution of 1.0 g (6.0 mmol) of Et₄NCl in 20 mL of acetonitrile was slowly added, and the reaction mixture was allowed to stand for several days at ambient temperature. The large black crystals that deposited were collected by filtration, washed with THF/acetonitrile, and dried in vacuo; 0.90 g (45%) of product was obtained. Anal. Calcd for C₈₈H₁₄₀Co₈N₅S₁₄: C, 48.30; H, 6.45; Co, 21.54; N, 3.20; S, 20.51. Found: C, 47.71; H, 6.13; Co, 21.92; N, 3.34; S, 19.87.

Collection and Reduction of X-ray Data. Black air-sensitive crystals of (n-Pr₄N)₄[Co₈S₆(SPh)₈]⁴⁰ (A) and (Et₄N)₅[Co₈S₆(SPh)₈] (B) were

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grown by slow cooling of acetonitrile/ether and acetonitrile/THF solutions, respectively. The crystals were sealed in glass capillaries under argon. Data collection was carried out at ambient temperature on a Nicolet R3m diffractometer equipped with a Mo X-ray source and a graphite monochromator. Data collection parameters are provided in Table I. Intensities of 3 check reflections were monitored every 123 reflections; no significant decay was observed over the course of either data collection. Data sets were processed with the program XTAPE of the SHELXTL package (Nicolet XRD Corp., Madison, WI) and empirical absorption corrections were applied to both compounds with the program XEMP. Compound A crystallizes in space group $P2_1/c$, which is uniquely determined by the systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$). The reduced cell of compound B belongs to the triclinic crystal system, and its axial lengths a and b are equal within experimental uncertainty. This unit cell is approximately related to a C-centered monoclinic cell by the transformation matrix

$$\begin{pmatrix} 1 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

but the intensity-weighted reciprocal lattice of B does not possess true mirror symmetry. Data collection was therefore carried out with the triclinic cell, and the space group was determined to be $P\bar{1}$ by intensity statistics and subsequent refinement.

Structure Solution and Refinement. The Co atoms of compounds A and B were located by the direct-methods programs MULTAN and SOLV. The remaining non-hydrogen atoms were found in successive difference-Fourier maps (with intervening rounds of isotropic least-squares refinement). Atomic scattering factors were taken from a standard source.⁴¹ The asymmetric unit of compound A consists of two independent half-anions, each lying about inversion centers, and four cations. The phenyl rings were treated as rigid groups throughout the refinement. Isotropic refinement converged at a conventional R value of 10.6%. The α -C atoms and one β -C atom of one of the cations were found to be disordered, and site occupancies of the minor component refined to a value of 0.35. No hydrogen atoms were included in the model for compound A, and the final refinement was carried out with anisotropic temperature factors for all atoms except the carbon atoms of the disordered cation. The asymmetric unit of compound B contains half of the anion and three cations that lie on inversion centers, together with one cation in a general position. The methylene groups of cations on inversion centers are disordered and were given occupancy factors of 0.5. Isotropic refinement of all atoms converged at a conventional R value of 8.2%. All non-hydrogen atoms were allowed to refine anisotropically; hydrogen atoms were included at 0.96 Å from, and with isotropic thermal parameters 1.2× those of, bonded carbon atoms. Final R values are given for both compounds in Table I. Coordinates of the Co and S atoms of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ are listed in Table II.⁴²

Other Measurements. Absorption spectra were recorded on Cary Model 17 and 219 spectrophotometers. Electrochemical measurements were made with standard PAR instrumentation; details are given in the text. ¹H NMR spectra were determined with a Bruker AM-300 spectrometer; shifts downfield of Me_4Si reference are designated as negative. Magnetic susceptibility measurements of solid samples at 6–292 K were carried out with a SHE Model 905 SQUID-type susceptometer at 5 kG.

Results and Discussion

Synthesis. Initial attempts to prepare Co–S–SR clusters involved reactions of $[\text{Co}(\text{SPh})_4]^{2-}$ or $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ with elemental sulfur in acetonitrile. These systems, similar to those with the analogous Fe(II) complexes and sulfur that afford $[\text{Fe}_n\text{S}_n(\text{SPh})_4]^{2-}$ ($n = 2, 4$) in high yield,⁴³ gave intractable black precipitates and no evidence of the formation of new soluble products. Further experimentation, based on the preparation of $[\text{Fe}_6\text{S}_9(\text{S}-t\text{-Bu})_2]^{4-}$ from FeCl_3 , Li_2S , and $\text{Li}(\text{S}-t\text{-Bu})$ in the presence of excess LiOMe ,^{37a,b} led to the reaction system 1/1/1.6/2 $\text{CoCl}_2/\text{Li}_2\text{S}/$

anion 1

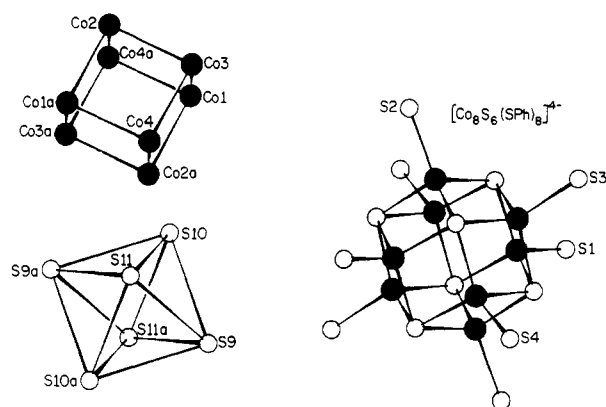


Figure 1. Structure and atom-labeling scheme of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$. The Co_8 and S_6 subunits have the same orientation as in the complete structure (phenyl groups omitted for clarity). Atoms $\text{Co}(n)$ $\text{Co}(na)$ ($n = 1-4$) and $\text{S}(n)$ $\text{S}(na)$ ($n = 9-11$) are related by an inversion center. These features apply to Figure 2, with label c in place of a.

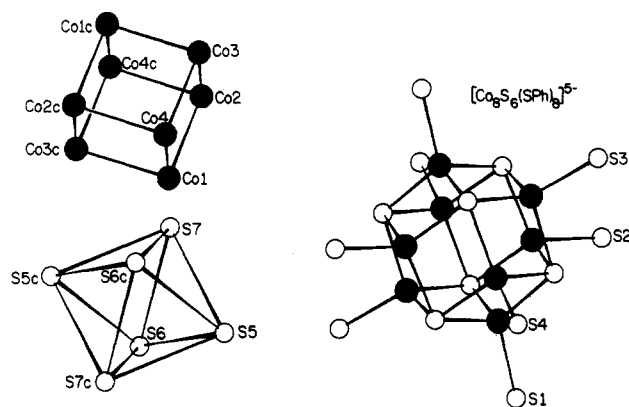
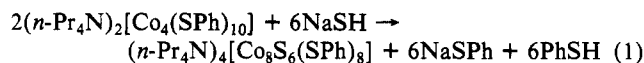
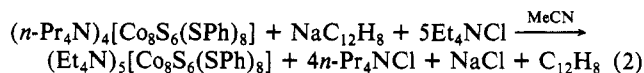


Figure 2. Structure and atom-labeling scheme of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$.

$\text{LiSPh}/\text{LiOMe}$ in methanol. This system also gave copious quantities of a black solid, but from the reaction mixture filtrate the $n\text{-Pr}_4\text{N}^+$ salt of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ was isolated. Recrystallization of this material from acetonitrile gave the pure compound as its acetonitrile monosolvate in reproducible but small (10%) yield.²⁹ With cluster stoichiometry established, reaction 1 in acetone was devised. The product cluster salt is sparingly soluble in acetone



and crystallizes as the reaction proceeds. This method affords the pure product in acceptable yield (50%). Identity of the products from the two reaction systems was established by their ¹H NMR spectra. The cluster was reduced in reaction 2 with



sodium acenaphthylenide as the reductant and Et_4N^+ as the counterion, a procedure that led to a highly crystalline product. Solutions of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ are extremely sensitive to oxidation.

Description of Structures. The structure of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ is depicted in Figure 1, and interatomic distances and angles are collected in Table III. Corresponding information for $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ is presented in Figure 2 and Table IV. The asymmetric unit of the $n\text{-Pr}_4\text{N}^+$ salt of the 4- cluster includes two independent half-anions, while the asymmetric unit of the Et_4N^+ salt of the 5- cluster includes a single half-anion. In each case the entire anion is generated by inversion through a crystallographic center of symmetry. A stereoview of anion 1 of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ is provided in Figure 3. Other than the orientations of the phenyl groups, the structures of anion 2 and $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ are nearly identical with that of anion 1. Because of the large number of

(40) Both unsolvated and acetonitrile monosolvate forms of this compound have been isolated in different recrystallizations from acetonitrile/ether. The analytical sample is the monosolvate, and the crystal on which the structural analysis was performed is the unsolvated form. As reported elsewhere,²⁹ an X-ray analysis of a relatively poor crystal of the monosolvate has been carried forward far enough to demonstrate the presence of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$.

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(42) See paragraph at the end of this article concerning supplementary material available.

(43) Hagen, K. S.; Reynolds, J. G.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4054.

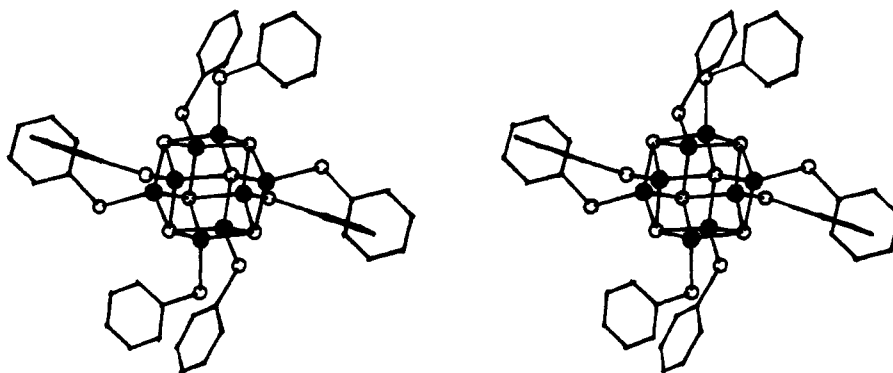


Figure 3. Stereoview of anion 1 of $(n\text{-Pr}_4\text{N})_4[\text{Co}_8\text{S}_6(\text{SPh})_8]$.

Table II. Atom Coordinates ($\times 10^4$) of the Co and S Atoms of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-,5-}$

atom	x	y	z
[Co ₈ S ₆ (SPh) ₈] ⁴⁻			
Co(1) ^a	-378 (1) ^c	-531 (1)	4096 (1)
Co(2)	-474 (1)	733 (1)	4933 (1)
Co(3)	86 (1)	322 (1)	3762 (1)
Co(4)	923 (1)	128 (1)	4731 (1)
Co(5) ^b	4904 (1)	596 (1)	923 (1)
Co(6)	4603 (1)	-321 (1)	1100 (1)
Co(7)	4435 (1)	603 (1)	-499 (1)
Co(8)	4138 (1)	-318 (1)	-329 (1)
S(1) ^a	-830 (1)	-1114 (1)	3420 (2)
S(2)	-969 (1)	1424 (1)	4988 (2)
S(3)	76 (1)	637 (1)	2553 (1)
S(4)	1790 (1)	140 (1)	4281 (1)
S(5) ^b	4699 (1)	1159 (1)	1821 (2)
S(6)	4183 (1)	-771 (1)	2010 (1)
S(7)	3833 (1)	1111 (1)	-1100 (2)
S(8)	3317 (1)	-594 (1)	-788 (2)
S(9)	520 (1)	-393 (1)	3884 (1)
S(10)	-802 (1)	185 (1)	4082 (1)
S(11)	429 (1)	815 (1)	4686 (1)
S(12)	4559 (1)	6 (1)	-1360 (1)
S(13)	4089 (1)	268 (1)	567 (1)
S(14)	4718 (1)	-875 (1)	161 (1)
[Co ₈ S ₆ (SPh) ₈] ⁵⁻			
Co(1)	4220 (1)	6114 (1)	6493 (1)
Co(2)	5996 (1)	6060 (1)	6035 (1)
Co(3)	5273 (1)	6021 (1)	4202 (1)
Co(4)	3500 (1)	6088 (1)	4676 (1)
S(1)	3612 (1)	6997 (1)	8068 (1)
S(2)	6846 (1)	7275 (1)	6969 (1)
S(3)	5464 (1)	7195 (1)	3578 (1)
S(4)	1931 (1)	7141 (1)	4590 (1)
S(5)	4521 (1)	7034 (1)	5675 (1)
S(6)	5680 (1)	5035 (1)	6736 (1)
S(7)	6663 (1)	4948 (1)	4555 (1)

^a Anion 1: Co(1-4), S(1-4,9-11). ^b Anion 2: Co(5-8), S(5-8,12-14). ^c Estimated standard deviations in parentheses in this and succeeding tables.

independent structural parameters of the clusters, only ranges and mean values of certain sets of angles involving bridging (b) and terminal (t) sulfur atoms and three cobalt atoms are listed in Tables III and IV.⁴² The following are the principal structural features of the Co₈S₁₄ portion of [Co₈S₆(SPh)₈]^{4-,5-}. Unless otherwise noted, the ranges of data apply to both anions of the 4- cluster and the 5- cluster taken as a set.

(i) The [Co₈S₆]^{4+,3+} cores contain concentric, slightly imperfect Co₈ cubes and S₆ octahedra. The Co₈S₁₆ portions possess C₄ symmetry and deviate by small extents from perfect cubic (O_h) symmetry. Inequivalent atoms are evident from the listings in Tables II-IV. There and in Figures 1 and 2 symmetry-related atoms are designated numerically as *n* and *nx* (*x* = a, b, c).

(ii) Atom positional deviations from the three independent face planes⁴⁴ of the Co₈ units are ≤ 0.008 Å. Dihedral angles between

(nonparallel) face planes are 89.4-90.7°. The six diagonal planes are perfect and form dihedral angles of 59.1-60.9 and 89.8-90.8°. In exact cubic symmetry these angles are 60 and 90°. Dihedral angles between the three independent face planes of the S₆ units are 69.8-71.9°, compared to 70.5° for a perfect octahedron.⁴⁵ The three diagonal planes of the S₆ units are perfect.

(iii) Core polyhedra are built up of 12 fused Co₂S₂ nonplanar rhombs, six of which are independent. Atom deviations from these polyhedral face planes are 0.041-0.056 Å. The planes define two types of dihedral angles between adjacent rhombs. The 12 angles between planes with a common Co-S bond and the 2 angles between planes with a common sulfur atom fall in the ranges 118.9-121.4 and 88.6-90.6°. The values for perfect cubic symmetry are 120 and 90°.

(iv) Bridging sulfur atoms in the 4- and 5- clusters are situated 0.84-0.85 and 0.84-0.87 Å, respectively, above Co₄ faces and are quadruply bridging. Each Co₄S_b unit is a distorted square pyramid. Sulfur atom positions are not exactly centric with respect to these faces, as seen from the differences in Co-S_b distances to a common face. In the 4- cluster these differences range from 0.011 to 0.030 Å (both anions) and in the 5- cluster from 0.020 to 0.027 Å. There are also detectable differences in the acute and obtuse Co-S_b-Co angles.

(v) Cobalt atoms in the 4- and 5- clusters are located 1.19-1.21 and 1.17-1.21 Å, respectively, above S₃ faces and reside in distorted-tetrahedral sites. Coordination at each site is completed by a thiolate sulfur atom situated on an extension of the body diagonal of the Co₈ unit. Distortions are readily recognized from differences in Co-S_b distances to a common cobalt atom, which are 0.005-0.021 and 0.004-0.032 Å in the 4- (both anions) and 5- clusters, respectively. In addition, there are small differences in S_b-Co-S_b and substantially larger variations in S_b-Co-S_t angles at a given cobalt atom. Exterior angles of the latter type in cubane-type [Fe₄S₄(SR)₄]^{2-,3-} clusters⁴⁶ are also subject to larger variations than interior core angles. Here, as there, such differences must arise mainly as a consequence of crystalline packing forces. Inasmuch as six of the eight independent dihedral angles between Co-S-C and phenyl group planes of the 4- clusters and the four such planes of the 5- cluster are $\leq 20^\circ$, there appears to be some preference for a roughly coplanar orientation of these components. This orientation occurs in certain other benzethiolate complexes⁴⁷ and places an *o*-H between two sulfur atoms

- (44) All planes with four atoms referred to here and elsewhere are unweighted least-squares planes.
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Table III. Selected Interatomic Distances (Å) and Angles (deg) of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$

anion 1		anion 2	
		Co...Co	
Co(1)-Co(2a) ^a	2.673 (2)	Co(5)-Co(6)	2.638 (2)
Co(1)-Co(3)	2.659 (2)	Co(5)-Co(7)	2.673 (2)
Co(1)-Co(4a)	2.658 (2)	Co(5)-Co(8b)	2.634 (2)
Co(2)-Co(3)	2.682 (2)	Co(6)-Co(7b)	2.651 (2)
Co(2)-Co(4a)	2.663 (2)	Co(6)-Co(8)	2.679 (2)
Co(3)-Co(4)	2.637 (2)	Co(7)-Co(8)	2.645 (2)
av	2.662 (15) ^c	av	2.653 (20)
		S _b ...S _b	
S(9)-S(10)	3.558	S(12)-S(13)	3.585
S(9)-S(11)	3.600	S(12)-S(14)	3.577
S(10)-S(11)	3.556	S(13)-S(14)	3.555
av	3.571 (25)	av	3.572 (16)
		Co-S _t ^b	
Co(1)-S(1)	2.244 (3)	Co(5)-S(5)	2.242 (3)
Co(2)-S(2)	2.239 (3)	Co(6)-S(6)	2.243 (3)
Co(3)-S(3)	2.250 (3)	Co(7)-S(7)	2.245 (3)
Co(4)-S(4)	2.224 (3)	Co(8)-S(8)	2.237 (3)
av	2.239 (11)	av	2.242 (3)
		Co-S _b ^b	
Co(1)-S(9)	2.216 (3)	Co(5)-S(12b)	2.216 (3)
Co(1)-S(10)	2.214 (3)	Co(5)-S(13)	2.227 (3)
Co(1)-S(11a)	2.237 (3)	Co(5)-S(14b)	2.218 (3)
Co(2)-S(9a)	2.240 (3)	Co(6)-S(12b)	2.220 (3)
Co(2)-S(10)	2.231 (3)	Co(6)-S(13)	2.220 (3)
Co(2)-S(11)	2.219 (3)	Co(6)-S(14)	2.237 (3)
Co(3)-S(9)	2.228 (3)	Co(7)-S(12)	2.230 (3)
Co(3)-S(10)	2.233 (3)	Co(7)-S(13)	2.221 (3)
Co(3)-S(11)	2.233 (3)	Co(7)-S(14b)	2.228 (3)
Co(4)-S(9)	2.246 (3)	Co(8)-S(12)	2.235 (3)
Co(4)-S(10a)	2.236 (3)	Co(8)-S(13)	2.231 (3)
Co(4)-S(11)	2.227 (3)	Co(8)-S(14)	2.223 (3)
av	2.230 (10)	av	2.226 (7)
		C-S	
range	1.748 (11)-1.773 (12)	range	1.759 (13)-1.774 (10)
av	1.758 (11)	av	1.770 (8)
		C-C	
range	1.34 (2)-1.42 (2)	range	1.31 (2)-1.41 (1)
av	1.38 (2)	av	1.38 (2)
		Co-S _b -Co	
Co(1)-S(9)-Co(3)	73.5 (1)	Co(7)-S(12)-Co(8)	72.6 (1)
Co(1)-S(9)-Co(4)	114.3 (1)	Co(7)-S(12)-Co(5b)	114.0 (1)
Co(3)-S(9)-Co(4)	72.2 (1)	Co(8)-S(12)-Co(5b)	72.6 (1)
Co(1)-S(9)-Co(2a)	73.7 (1)	Co(7)-S(12)-Co(6b)	73.1 (1)
Co(3)-S(9)-Co(2a)	115.1 (1)	Co(8)-S(12)-Co(6b)	114.3 (1)
Co(4)-S(9)-Co(2a)	72.8 (1)	Co(5b)-S(12)-Co(6b)	73.0 (1)
Co(1)-S(10)-Co(2)	115.8 (1)	Co(5)-S(13)-Co(6)	72.8 (1)
Co(1)-S(10)-Co(3)	73.4 (1)	Co(5)-S(13)-Co(7)	73.9 (1)
Co(2)-S(10)-Co(3)	73.8 (1)	Co(6)-S(13)-Co(7)	115.5 (1)
Co(1)-S(10)-Co(4a)	73.3 (1)	Co(5)-S(13)-Co(8)	115.2 (1)
Co(2)-S(10)-Co(4a)	73.2 (1)	Co(6)-S(13)-Co(8)	74.0 (1)
Co(3)-S(10)-Co(4a)	115.1 (1)	Co(7)-S(13)-Co(8)	72.9 (1)
Co(2)-S(11)-Co(3)	74.1 (1)	Co(6)-S(14)-Co(8)	73.8 (1)
Co(2)-S(11)-Co(4)	115.1 (1)	Co(6)-S(14)-Co(5b)	115.2 (1)
Co(3)-S(11)-Co(4)	72.5 (1)	Co(8)-S(14)-Co(5b)	72.8 (1)
Co(2)-S(11)-Co(1a)	73.7 (1)	Co(6)-S(14)-Co(7b)	72.8 (1)
Co(3)-S(11)-Co(1a)	115.4 (1)	Co(8)-S(14)-Co(7b)	115.3 (1)
Co(4)-S(11)-Co(1a)	73.1 (1)	Co(5b)-S(14)-Co(7b)	73.9 (1)
		S _b -Co-S _b	
range	105.5 (1)-107.6 (1)	range	105.8 (1)-107.5 (1)
av	106.5 (6)	av	106.5 (6)
		S _b -Co-S _t	
range	100.3 (1)-119.9 (1)	range	100.8 (1)-119.1 (1)
av	112 (7)	av	112 (6)
		Co-Co-Co	
range	89.2 (1)-91.1 (1)	range	89.7 (1)-90.5 (1)
av	90.0 (5)	av	90.0 (2)
		S _b -S _b -S _b	
range	59.6 (1)-60.8 (1)	range	59.5 (1)-60.3 (1)
av	60.0 (7)	av	60.0 (4)

Table III (Continued)

anion 1		anion 2	
range	113.1 (1)–115.0 (1)	Co–S–C	108.4 (1)–114.0 (1)
av	114.3 (9)	range	112 (2)
		av	

^a Symmetry operations: (a) $-x, -y, 1-z$; (b) $1-x, -y, -z$. ^b Key: t = terminal ligand; b = bridging ligand. ^c The standard deviations in this and the following table are estimated from $\sigma \approx x = [(\sum x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$

Table IV. Selected Interatomic Distances (Å) and Angles (deg) of [Co₈S₆(SPh)₈]⁵⁻

Co(1)–Co(2)	2.652 (1)	Co...Co	Co(2)–Co(4c)	2.690 (1)
Co(1)–Co(4)	2.678 (1)		Co(3)–Co(4)	2.651 (1)
Co(1)–Co(3c) ^a	2.674 (1)		av	2.674 (19)
Co(2)–Co(3)	2.697 (1)			
S(5)–S(6)	3.614	S _b ...S _b	S(6)–S(7)	3.560
S(5)–S(7)	3.566		av	3.580 (30)
Co(1)–S(1)	2.263 (2)	Co–S _t	Co(4)–S(4)	2.293 (2)
Co(2)–S(2)	2.273 (2)		av	2.276 (13)
Co(3)–S(3)	2.273 (2)			
Co(1)–S(5)	2.228 (2)	Co–S _b	Co(3)–S(7)	2.235 (1)
Co(1)–S(6)	2.252 (1)		Co(3)–S(6c)	2.232 (2)
Co(1)–S(7c)	2.215 (2)		Co(4)–S(5)	2.240 (2)
Co(2)–S(5)	2.255 (1)		Co(4)–S(6c)	2.238 (1)
Co(2)–S(6)	2.237 (2)		Co(4)–S(7c)	2.236 (2)
Co(2)–S(7)	2.223 (1)		av	2.236 (11)
Co(3)–S(5)	2.239 (1)			
range	1.748 (6)–1.768 (5)	C–S	av	1.755 (9)
range	1.34 (1)–1.41 (1)	C–C	av	1.38 (2)
Co(1)–S(5)–Co(2)	72.5 (1)	Co–S _b –Co	Co(1)–S(5)–Co(3)	114.4 (1)
Co(2)–S(5)–Co(3)	73.8 (1)		Co(1)–S(5)–Co(4)	73.7 (1)
Co(2)–S(5)–Co(4)	115.3 (1)		Co(3)–S(5)–Co(4)	72.6 (1)
Co(1)–S(6)–Co(2)	72.4 (1)		Co(1)–S(6)–Co(3c)	73.2 (1)
Co(2)–S(6)–Co(3c)	114.8 (1)		Co(1)–S(6)–Co(4c)	114.6 (1)
Co(2)–S(6)–Co(4c)	73.9 (1)		Co(3c)–S(6)–Co(4c)	72.7 (1)
Co(2)–S(7)–Co(3)	74.5 (1)		Co(2)–S(7)–Co(1c)	116.7 (1)
Co(3)–S(7)–Co(1c)	73.9 (1)		Co(2)–S(7)–Co(4c)	74.2 (1)
Co(3)–S(7)–Co(4c)	117.2 (1)		Co(1c)–S(7)–Co(4c)	74.0 (1)
S(5)–Co(1)–S(6)	107.5 (1)	S _b –Co–S _b	S(5)–Co(1)–S(7c)	106.4 (1)
S(6)–Co(1)–S(7c)	106.2 (1)		S(5)–Co(2)–S(6)	107.1 (1)
S(5)–Co(2)–S(7)	105.6 (1)		S(6)–Co(2)–S(7)	105.9 (1)
S(5)–Co(3)–S(7)	105.7 (1)		S(5)–Co(3)–S(6c)	107.2 (1)
S(7)–Co(3)–S(6c)	106.2 (1)		S(5)–Co(4)–S(6c)	107.0 (1)
S(5)–Co(4)–S(7c)	105.4 (1)		S(6c)–Co(4)–S(7c)	105.4 (1)
range	105.4 (1)–107.5 (1)	S _b –Co–S _b	av	106.3 (7)
range	102.6 (1)–120.2 (1)	S _b –Co–S _t	av	112 (6)
range	89.1 (1)–90.9 (1)	Co–Co–Co	av	90.0 (6)
range	59.4 (1)–60.9	S _b –S _b –S _b	av	60.0 (8)
range	114.0 (1)–116.8 (1)	Co–S–C	av	115 (1)

^a Symmetry operation c: $1-x, 1-y, 1-z$.

directly below the ring. Given the electronic differences between thiolate and sulfide ligands, the cobalt sites in the two clusters are best regarded as dominantly trigonally distorted. In the 5-cluster this distortion is accentuated by the relatively large difference of 0.040 Å between mean Co–S_t and Co–S_b distances.

(vi) Statistical differences at the 3σ level of significance do not exist between mean values of corresponding distances and angles of the 4- and 5- clusters listed in Tables III and IV. Those metric features that would be expected to respond most obviously to an increase in electron density upon passing from the 4- to the 5-

Table V. Comparison of Mean Structural Parameters of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ and Cobalt Pentlandite

	$[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$		$[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$	Co_9S_8^a
	anion 1	anion 2		
Co...Co, Å	2.662 (15)	2.653 (20)	2.674 (19)	2.505 (1)
$\text{S}_b\cdots\text{S}_b$, Å	3.571 (25)	3.572 (16)	3.580 (30)	3.336 (3)
Co- S_b , Å	2.230 (10)	2.226 (7)	2.236 (11)	2.227 (1) ^b
Co- S_t , Å	2.239 (11)	2.242 (3)	2.276 (13)	2.127 (1) ^c
Co-Co-Co, deg	90.0 (5)	90.0 (2)	90.0 (6)	90
Co- S_b -Co, deg	73.3 (6)	73.2 (6)	73.5 (7)	68.44 (6)
	115.1 (5)	114.9 (6)	115.5 (11)	120
S_b -Co- S_b , deg	106.5 (6)	106.5 (6)	106.3 (7)	111.44 (5)
S_b - S_b - S_b , deg	60.0 (7)	60.0 (4)	60.8 (8)	60
$V(\text{Co}_8)$, Å ³	18.86	18.68	19.10	15.72
$V(\text{S}_6)$, Å ³	21.51	21.42	21.59	17.50

^a Data from ref 30. ^b Co- μ_5 -S. ^c Co- μ_4 -S. ^d Calculated from atom coordinates.

cluster are the Co- $\text{S}_{b,t}$ bond distances. In terms of localized reduction at a tetrahedral cobalt site, the electronic change is $e^4t_2^3 \rightarrow e^4t_2^4$, leading to bond elongation. The inversion symmetry of the 5- cluster obviously precludes such a naive description, and delocalization would attenuate any bond length change. What can be said is that, at each of the four independent cobalt sites in the 5- cluster, individual Co- S_b distances are shorter than the Co- S_t distance by the 3σ criterion. Further, with two exceptions, the differences in the two types of distances are relatively large (0.034–0.055 Å). In the 4- cluster, differences in these distances at individual sites are usually not significant and do not exceed 0.030 Å. The Co- S_t distances are expected to be more sensitive to a redox change than are the Co- S_b distances of the presumably rigid core structures. Analogous behavior has been well documented for $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters.^{46,48} It is concluded that the electron added in forming the 5- cluster does have structurally detectable cobalt character. Values of Co- S_t distances otherwise fall in the 2.24–2.33-Å interval of terminal Co-SR bond lengths in complexes containing tetrahedral Co(II) sites.^{39,49}

Features i–vi serve to demonstrate the very close structural similarity of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4-}$ and deviations of their $[\text{Co}_8\text{S}_6]^{4+}$ cores from O_h symmetry that are sufficiently small to render this description meaningful. Key structural elements in these clusters are the μ_4 -S atoms, which, among discrete metal sulfide clusters, are preceded only in $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4-}$ ^{8,37} and $[\text{Ni}_9\text{S}_9(\text{PET}_3)_6]^{2+}$ ³⁸. This element is rather more common in metal-sulfur-carbonyl clusters,^{37b,50} including $\text{Co}_4\text{S}_2(\text{CO})_{10}$ ⁵¹ which contains rectangular pyramidal Co_4S units, and a number of osmium-sulfur-carbonyls.^{50,52} The cores of the present clusters might be described as having the *anti*- M_6X_8 arrangement in that the positions of metal and sulfur atoms are reversed compared to those of $[\text{Co}_6\text{S}_8(\text{PET}_3)_6]^{+0}$,^{31,32} $\text{Co}_6\text{S}_8(\text{CO})_6$,³³ and a variety of solid phases containing M_6S_8 clusters with $\text{M} = \text{Mo}^{25-27}$ and Re .^{6,53} Structures of this type contain concentric M_6 octahedra and S_8 cubes. The cluster topology found here was first encountered with $\text{Ni}_8(\text{PPh})_6(\text{CO})_8$, prepared and structurally characterized by Lower and Dahl.⁵⁴ The molecule possesses crystallographic inversion

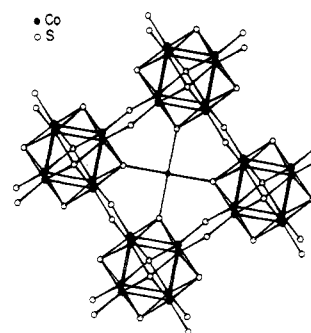
Pentlandite (Co_9S_8)

Figure 4. Portion of the refined crystal structure of Co_9S_8 drawn from published data,³⁰ showing the octahedral Co atom (center), Co- μ_5 -S bonds, and individual Co_8S_6 clusters linked by Co- μ_4 -S bonds. Omitted for the sake of clarity are the two additional clusters with Co- μ_5 -S bonds to the octahedral Co atom and the two additional clusters with Co- μ_4 -S bonds to each of the sulfur atoms bridging the clusters.

symmetry and contains a completely bonding Ni_8 cube with terminal carbonyl groups and faces capped by μ_4 -PPh ligands. Excluding the phenyl groups, the cluster closely approaches O_h symmetry. Very recently, $\text{Ni}_8(\text{PPh})_6\text{Cl}_4(\text{PPh}_3)_4$ and $\text{Ni}_8(\text{PPh})_6(\text{CO})_4(\text{PPh}_3)_4$ ⁵⁵ have been shown to be structurally analogous to $\text{Ni}_8(\text{PPh})_6(\text{CO})_8$.

Structural Relationship to Cobalt Pentlandite. Natural pentlandite has the composition $(\text{Fe,Ni,Co})_9\text{S}_8$, with cobalt being the minority metal in most minerals.^{5,56} Synthetic pentlandite, Co_9S_8 , has been prepared by a vapor-transport method,³⁰ by direct combination of the elements at high temperature,^{57a} and, most recently, by heating the system $\text{CoSO}_4/\text{H}_2\text{S}/\text{H}_2$ at 525 °C.^{57b} The structure of Co_9S_8 was originally solved from X-ray powder data^{58a} and was subsequently refined.^{30,58b} The natural pentlandites $(\text{Fe,Ni})_9\text{S}_8$ have been shown to have the same structure.^{56,59} Co_9S_8 has a cubic unit cell containing 36 cobalt atoms and 32 sulfur atoms. A portion of the crystal structure, designed to depict cluster structural features, is shown in Figure 4. Immediately evident are the Co_8S_6 cluster units built up of concentric Co_8 cubes and S_6 octahedra, which are crystallographically perfect. Other views, some of which show the entire unit cell, are available elsewhere.^{56,58,60} The cell contains 32 cobalt atoms that comprise

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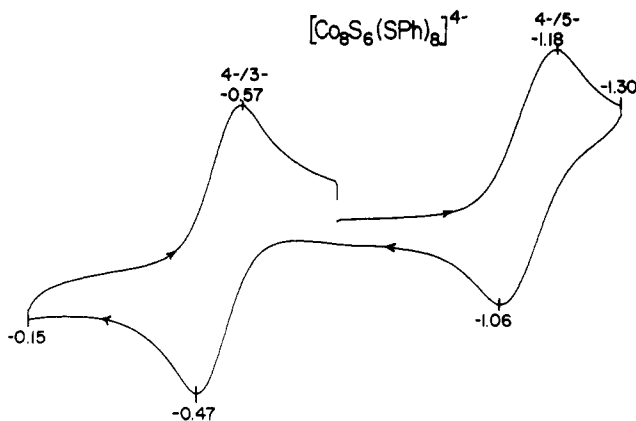


Figure 5. Cyclic voltammogram of [Co₈S₆(SPh)₈]⁴⁻ (100 mV/s, Pt electrode) in acetonitrile solution; peak potentials vs. SCE are given.

four Co₈ cubes; each atom resides in a distorted CoS₄ site. The two types of sulfur atoms at each site are roughly similar to the S_{b,n} atoms in [Co₈S₆(SPh)₈]⁴⁻⁵⁻. Those capping cube faces are μ₄-S with respect to the cube but in total are μ₅-S, because each is bonded to a noncluster cobalt atom. There are four such atoms in the unit cell, which, with μ₅-S atoms from separate clusters, form CoS₆ octahedra with a Co-S distance of 2.359 (2) Å.³⁰ The eight remaining sulfur atoms act as "terminal" ligands to cluster cobalt atoms but are actually μ₄-S, inasmuch as each atom bridges four cobalt atoms from different clusters in a tetrahedral arrangement. Because at each CoS₄ site there are three Co-μ₅-S bonds at 2.227 (1) Å and one Co-μ₄-S bond at 2.127 Å,³⁰ these sites are trigonally distorted. The depiction in Figure 4 contains four Co₈S₆ clusters and one octahedral cobalt atom. It has been simplified to the extent that, although μ₅-S atoms are evident, only four of six octahedral Co-μ₅-S bonds are shown. Also, only two of four Co-μ₄-S bonds at a given μ₄-S atom are shown. Sulfur atoms at the exterior of the figure are of the μ₄-S type.

Mean structural parameters of [Co₈S₆(SPh)₈]⁴⁻⁵⁻ and Co₉S₈ are compared in Table V. The most striking structural differences between the Co₈S₆ clusters of this metal-excess sulfide and [Co₈S₆(SPh)₈]⁴⁻⁵⁻ are found in the shorter Co...Co and S_b...S_b (S_b = μ₅-S) distances of the former. As one measure of this effect, the volumes of the Co₈ cube and S₆ octahedron of synthetic pentlandite are 81–84% of those in the 4- and 5- clusters. The cobalt mean oxidation state in Co₉S₈ is +1.778. In the 4- and 5- clusters these values are +2 and +1.875 (7 Co(II) + Co(I)), respectively. If, as suggested by the Co-μ₅-S distance, the octahedral cobalt atom is low-spin Co(II),³⁰ the corresponding formulation is Co²⁺[Co₈S₆S_{8/4}]²⁻. In this event, the cluster cobalt mean oxidation state is slightly lower (+1.75, 6 Co(II) + 2 Co(I)). This situation is equivalent to that the cluster [Co₈S₆(SR)₈]⁶⁻. We are not able to explain why the apparently more reduced pentlandite clusters are so much smaller than those of the synthetic clusters. The mixed-valence formulations are convenient for electron counting but are not manifested in any physical property. There is no convincing structural evidence for localized Co(I, II) sites in [Co₈S₆(SPh)₈]⁵⁻ and certainly none in Co₉S₈, whose Co₈S₆ clusters have imposed cubic symmetry. The decreased distances in these clusters strongly imply a larger extent of Co-Co bonding (or less Co-S antibonding) compared to that in the 4- and 5-species. All clusters in Table V have Co...Co separations that are comparable with, e.g., the nonbridged Co-Co electron-pair bonds in the Co₄ rectangles of Co₄(μ₄-S)₂(CO)₆⁵¹ (2.598 (10) Å) and Co₄(μ₄-X)₂(μ-CO)₂(CO)₈⁶¹ (X = PPh (2.697 (2) Å), S (2.60 (1) Å)).

Selected Properties. In acetonitrile solution [Co₈S₆(SPh)₈]⁴⁻ exhibits a chemically reversible (*i*_{p,c}/*i*_{p,a} ≈ 1) oxidation and reduction at *E*_{1/2} = -0.52 and -1.12 V vs. SCE, respectively. A

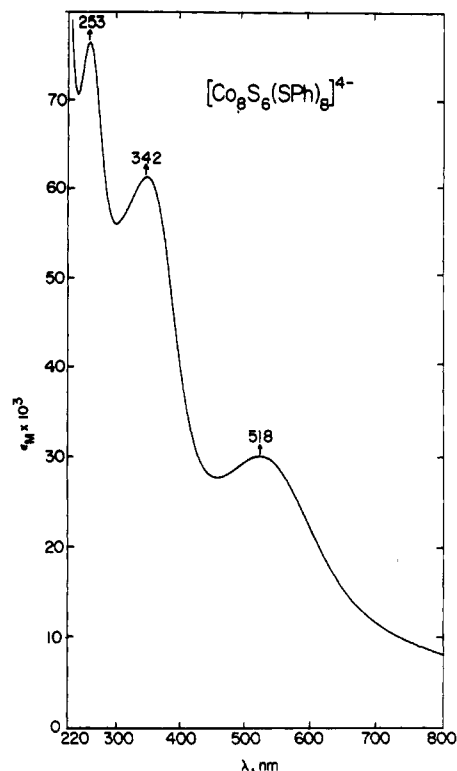
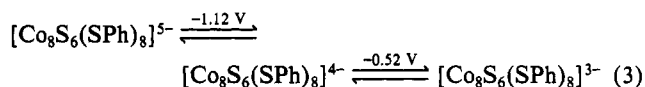


Figure 6. UV-visible absorption spectrum of (n-Pr₄N)₄[Co₈S₆(SPh)₈] in acetonitrile solution.

cyclic voltammogram showing the existence of the electron-transfer series (3) is given in Figure 5. No attempt has yet been made



to isolate the 3- cluster. The 5- cluster is readily obtained by reaction 2. A further, poorly resolved reduction was observed in cyclic voltammetry and conventional polarography (Hg electrodes) at ~-1.7 V, but this process was superimposed on ascending current from a subsequent, apparently multielectron, reduction. Consequently, we cannot confirm the existence of the 6- cluster, which presumably contains a core isoelectronic with the cluster in pentlandite. The absorption spectrum of [Co₈S₆(SPh)₈]⁴⁻ consists of three intense LMCT bands at λ_{max} (nm) (ε_M (M⁻¹ cm⁻¹)) = 253 (76 000), 342 (62 900), and 518 (30 800) and is provided in Figure 6. The 5- spectrum is similar, with bands at 260, 348 (sh), and 488 nm. The intense visible bands and their tailing in the near-IR region obscure the ν₂, ν₃ ligand field bands (if present as such) of tetrahedral Co(II)-S₄ units.⁶² The ¹H NMR spectra of the two clusters, presented in Figure 7, reveal equivalent phenyl groups. Signal assignments follow from spin multiplets and relative intensities. That the isotropic shifts are dominantly hyperfine contact in origin is indicated by alternating signs of *o*-, *m*-, and *p*-H shifts⁶³ and a reasonable correspondence between isotropic shift ratios in 4- and 5- clusters (*o*-H, 1.23; *m*-H, 1.44; *p*-H, 1.19) and the magnetic susceptibility ratio χ^M₄₋/χ^M₅₋ = 1.35 at 292 K. Magnetic moments per Co atom at this temperature are 1.56 μ_B (4-) and 1.35 μ_B (5-), indicating strong spin coupling. The χ^M(*T*) behavior of (n-Pr₄N)₄[Co₈S₆(SPh)₈] is qualitatively consistent with antiferromagnetic interactions. For (Et₄N)₅[Co₈S₆(SPh)₈] the moment per cluster at 6.0 K is 1.95 μ_B, consistent with the expected *S* = 1/2 ground state.

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(63) (Δ*H*/*H*)_{iso} = (Δ*H*/*H*)_{obsd} - (Δ*H*/*H*)_{dia}(PhSH). [Co₈S₆(SPh)₈]⁴⁻: *o*-H, +2.81 ppm; *m*-H, -1.20 ppm; *p*-H, +4.46 ppm. [Co₈S₆(SPh)₈]⁵⁻: *o*-H, +2.28 ppm; *m*-H, -0.83 ppm; *p*-H, +3.74 ppm.

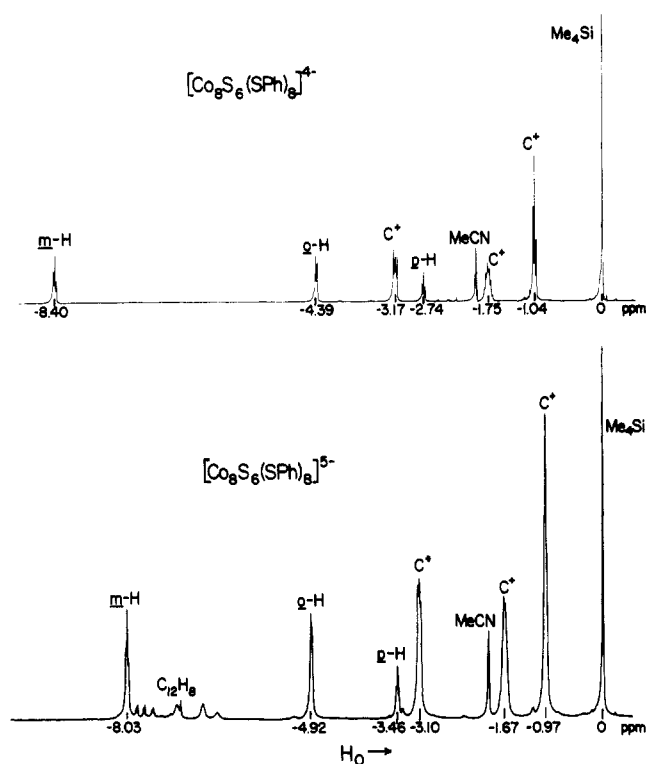


Figure 7. ^1H NMR spectra (300 MHz) of $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4+}$ (upper) and $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ (lower) in CD_3CN solutions at ~ 297 K. Signal assignments are indicated ($\text{C}^+ = n\text{-Pr}_4\text{N}^+$). The 5- cluster was generated in situ by the addition of a slight excess of a 0.4 M solution of $\text{NaC}_{12}\text{H}_8$ in $\text{THF-}d_8$ to a solution of the 4- cluster.

The cluster moment steadily increases with increasing temperature, to $3.82 \mu_B$ at 292 K, indicating thermal access to higher spin state(s) in this temperature interval. Magnetic properties will be reported in more detail subsequently.

Summary. The unique cluster $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{4+}$ is readily prepared by the assembly reaction (1). It can be oxidized and

reduced to generate the three-member electron-transfer series (3). The reduced cluster $[\text{Co}_8\text{S}_6(\text{SPh})_8]^{5-}$ is obtainable by means of reaction 2. The $[\text{Co}_8\text{S}_6]^{4+,3+}$ cluster cores closely approach cubic symmetry, being composed of concentric Co_8 cubes and S_6 octahedra. Spectroscopic and magnetic properties indicate antiferromagnetically coupled clusters, $S = 0$ (4-) and $1/2$ (5-) ground states, dominant hyperfine contact interactions in the ^1H NMR spectra, and, in solution, equivalent cobalt sites and thus complete delocalization of the odd spin of the 5- cluster (^1H NMR time scale). The cores have the same essential cubic topology as, but different oxidation states and much larger core volumes than, the Co_9S_6 clusters in the synthetic pentlandite Co_9S_8 . Other than the various pentlandites, cubic M_8S_6 clusters have been found only in $\text{K}_6\text{LiFe}_{24}\text{S}_{26}\text{Cl}$, a synthetic compound structurally analogous to djerfisherite,⁶⁴ and bartonite, a potassium iron sulfide mineral.⁶⁵

The clusters described here, as well as certain others cited at the outset, indicate that solubilized topological equivalents of metal sulfide clusters recognizable in extended lattices can be produced. It remains to be discovered to what extent structural and electronic features of discrete and bridged clusters are congruent. In this connection, a challenge in synthesis is the adjoining of discrete clusters into small aggregates, themselves discrete, by means of (largely) the same bridges that exist in the solid state.

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Supplementary Material Available: Complete listings for $(n\text{-Pr}_4\text{N})_4[\text{Co}_8\text{S}_6(\text{SPh})_8]$ and $(\text{Et}_4\text{N})_5[\text{Co}_8\text{S}_6(\text{SPh})_8]$ of atom coordinates, isotropic and anisotropic temperature factors, interatomic angles and distances, calculated hydrogen atom positions, and calculated and observed structure factors (102 pages). Ordering information is given on any current masthead page.

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A Further Example of a Dinuclear Copper(II) Complex Involving Monoatomic Acetate Bridges. Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties of Bis(μ -acetato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato(1-))dicopper(II)

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The synthesis, crystal structure, and spectroscopic and magnetic properties are reported for a dinuclear copper(II) complex, $[\text{Cu}(\text{AE})\text{CH}_3\text{COO}]_2$, where AE is the anion of 7-amino-4-methyl-5-aza-3-hepten-2-one. This complex provides a further example of a somewhat unusual bridging mode since the two copper atoms are connected by a single atom bridge through one of the oxygen atoms of an acetate ligand. The compound crystallizes in the triclinic space group $C_1^1\text{-}P\bar{1}$ with 1 formula unit in a cell having the dimensions $a = 8.1362$ (8) Å, $b = 9.9886$ (8) Å, $c = 7.3448$ (11) Å, $\alpha = 92.42$ (1)°, $\beta = 96.48$ (1)°, and $\gamma = 69.76$ (1)°. Magnetic susceptibility measurements show a weak antiferromagnetic interaction. $\Delta M_S = 2$ transitions are observed in ESR spectra related to solid samples and frozen solutions (noncoordinating solvents) but spectral parameter values suggest a modification of the dimer structure on going from the solid to solutions.

Introduction

Acetate bridging between transition-metal atoms is well-known in complexes such as copper(II) acetate hydrate^{1,2} and its analogues with other metal ions. This mode of bridging links adjacent

metal atoms via the two different oxygens of a carboxylate group to form a $\text{M}-\text{O}-\text{C}-\text{O}-\text{M}$ bridge. Although it is an obvious a priori possibility that acetate be involved in monoatomic bridging, the occurrence of $\text{M}-\text{O}-\text{M}$ bridges via one of the oxygen atoms of the acetate ligand has been firmly established in only four cases.³⁻⁷

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