

Synthesis, Crystal Structure, and Properties of the Hexa(μ -benzenethiolato)tetra(benzenethiolatocobaltate(II)) Dianion, the Prototype Cobalt(II)-Thiolate Molecular Cluster

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Abstract: The complexes $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$, and $[\text{Co}(\text{SPh})_4]^{2-}$ have been synthesized with Me_4N^+ and other cations, and the crystal structure of $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$ has been determined. Crystal data follow: $a = 13.031(2) \text{ \AA}$, $b = 23.590(4) \text{ \AA}$, $c = 12.806(2) \text{ \AA}$, $\alpha = 92.28(1)^\circ$, $\beta = 115.04(1)^\circ$, $\gamma = 79.12(1)^\circ$, $P\bar{1}$, $Z = 2$, 5121 observed reflections (Mo $K\alpha$), $R = 0.034$. The $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ molecular cluster contains a tetrahedron of cobalt(II) atoms (Co-Co $3.87 \pm 0.02 \text{ \AA}$) within an approximate octahedron of benzenethiolate ligands which bridge the edges of the Co_4 tetrahedron. One terminal benzenethiolate ligand completes the pseudotetrahedral $(\mu\text{-SPh})_3(\text{SPh})$ coordination of each cobalt atom. Principal features of the structure and bonding follow: (a) the bridging thiolate groups maintain the cluster structure, but without angular rigidity such that the T_d symmetry possible for the Co_4S_{10} core is only approximate; (b) there is no evidence of direct Co-Co bonding, but indirect electronic coupling between cobalt atoms influences the magnetic susceptibility and the S \rightarrow Co charge-transfer absorption; (c) charge-transfer spectral regions indicative of bridging benzenethiolate are described; (d) Co-S_{terminal} = $2.258 \pm 0.004 \text{ \AA}$, Co-S_{bridging} = $2.322 \pm 0.011 \text{ \AA}$. Spectrophotometric data are presented on the equilibrium sequence of species: $[\text{Co}(\text{SPh})_2]_n$ (molecular structure) $\rightleftharpoons [(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-} \rightleftharpoons [(\mu\text{-SPh})_2(\text{Co}(\text{SPh})_2)_2]^{2-} \rightleftharpoons [\text{Co}(\text{SPh})_4]^{2-}$. The benzenethiolate bridges of the $\{(\mu\text{-SPh})_6\text{Co}_4\}$ cluster core are relatively stable (thermodynamically) to bridge-opening reactions, including hydrolysis.

Introduction

The monothiolate (mercaptide) group RS^- is a fundamental monodentate ligand type, but its coordination chemistry is poorly developed in comparison with that of other elementary ligand types. The object of our research program is exploration of the syntheses, geometrical structures, electronic properties, and reactivities of metal complexes containing only (or at least predominantly) the monothiolate ligand. Elucidation of properties intrinsic to thiolate coordination requires the utilization of the simple monodentate RS^- group and avoidance of chelating ligands incorporating thiolate functions.

Binary complexes of many metals with monothiolate ligands have been encountered in conventional protic media as very insoluble compounds,¹⁻⁴ generally reputed to be intractable, and presumed (but rarely demonstrated⁵) to be structurally nonmolecular with thiolate bridges. Thus Bradley and Marsh⁶ in a limited survey of the mercaptides of cobalt, nickel, copper, and zinc did not obtain recrystallizable compounds (except for $\text{Ni}(\text{SAm}-n)_2$ ⁷). Williams et al.,⁸ endeavoring to form low molecular weight cobalt (II) complexes of thioglycollate and cysteine in aqueous media, encountered polymerization.

There are several reasons for anticipating the occurrence of a broad range of metal-thiolate complexes with a variety of structures. Guided by consideration of the significant thermodynamic influences of solvation in synthetic procedures with anionic ligands, we have successfully crystallized anionic complexes, $[\text{M}_x(\text{SR})_y]^{z-}$, for the metals Co(II),⁹ Cu(I),¹⁰⁻¹² Ag(I),^{11,13} Zn(II),¹³ Sn(IV),¹⁴ and OMo(V).^{15,16} Reported here are details⁹ of the formation and properties of the structurally molecular complex $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ and the related complexes $[\text{Co}_4(\text{SPh})_8\text{Cl}_2]^{2-}$ and $[\text{Co}(\text{SPh})_4]^{2-}$. The spectroscopic and structural properties of $[\text{Co}(\text{SPh})_4]^{2-}$ have been described.^{17,18}

Experimental Section

The reagent grade thiols, amines, and solvents used in the solution spectral measurements were distilled from appropriate drying agents and stored over molecular sieves. For the purposes of the synthetic

reactions, drying and purification of normal laboratory reactants were found to be unnecessary, and they were used as received. The thiolate anions were generated by in situ deprotonation of the thiols. The charge of the deprotonating agent should be zero rather than negative, in order to decrease the coordinating ability of the deprotonating agent relative to that of the thiolate ligand in aprotic or partially aprotic solvent systems. Thus tertiary amine bases are more satisfactory than hydroxide or alkoxide ions, and have been used. Inhibition of metal-amine coordination is effected sterically, and is adequate in triethylamine and higher trialkylamines. A useful isolatable source of the benzenethiolate ion as ligand is the crystalline acid-base complex formed by dicyclohexylamine and benzenethiol. Benzenethiol (10 mL) in acetonitrile (40 mL) was added to dicyclohexylamine (18 mL) in acetonitrile (300 mL) flushed with dinitrogen. The resulting white, crystalline precipitate was filtered, washed with acetonitrile, and vacuum dried. This complex is very soluble in chloroform, dichloromethane, and alcohols.

The metal-thiolate complex formation equilibria depend strongly on solvent properties and solution temperature: metal-thiolate association is favored by aprotic solvents and reduced temperatures. Success in crystallization of salts of anionic metal-thiolate complexes with inert cations (not the trialkylammonium conjugate acid of the deprotonating reagent) often depends on a balance between two opposing factors. One is the desirability of aprotic solvents to promote the complex formation equilibria, and the other is the utility of alcohols in adjusting solubility for good crystal growth.

In view of the partial dissociation of benzenethiolate-cobalt(II) complexes, particularly in protic solvents, recrystallization of isolated products does not always achieve purification or permit crystal growth. Careful control of the preparative mixtures was frequently the preferred method for growth of well-formed, uncontaminated crystals. All operations were performed in an atmosphere of dinitrogen.

$(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_{10}$. Benzenethiol (3.3 g, 30 mmol) and triethylamine (3.0 g, 30 mmol) were dissolved in acetonitrile (70 mL). A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.9 g, 10 mmol) in absolute ethanol (80 mL) at ca. 40 °C was added during several minutes, followed by addition of a solution of Me_4NCl (4.0 g, 36 mmol) in boiling methanol (30 mL). The resulting dark brown solution was maintained undisturbed at 0 °C for 48 h, while the dark brown-black crystals developed. The crystals were filtered, washed with 2-propanol, and vacuum dried, mp (scaled tube) 204 °C dec. Anal. Calcd for $\text{Co}_4\text{S}_{10}\text{N}_2\text{C}_{68}\text{H}_{74}$: Co, 15.97; S, 21.73; N, 1.90; C, 55.35; H, 5.05. Found: Co, 15.94; S, 22.20; N, 1.82; C, 55.60; H, 5.17. $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_{10}$ is readily soluble in

acetone, acetonitrile, and DMF, producing intensely orange-brown solutions. It is slightly soluble in methanol and insoluble in higher alcohols and chloroform. In solution it is not hydrolyzed by water at room temperature, but it is subject to rapid oxidation by dioxygen producing a totally insoluble, dark maroon powder. It dissolves in neat or dilute pyridine to give an uncharacterized green solution, and forms $[\text{Co}(\text{SPh})_4]^{2-}$ on treatment with PhSH plus R_3N .

$(\text{C}_6\text{H}_{11})_2\text{NH}_2)_2\text{Co}_4(\text{SPh})_{10}$. Benzenethiol (3.3 g, 30 mmol) and dicyclohexylamine (5.4 g, 30 mmol) were dissolved together in ethanol (100 mL). Addition of a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3.7 g, 12.7 mmol) in ethanol (40 mL) generated an intensely brown solution and precipitated colorless crystals (presumably $(\text{C}_6\text{H}_{11})_2\text{NH}_2^+\text{NO}_3^-$). Slow addition of water caused these crystals to redissolve and initiated separation of the product as black crystals, which after filtration were washed with water and vacuum dried, yield 4.6 g (85%). Anal. Calcd for $\text{Co}_4\text{S}_{10}\text{N}_2\text{C}_{84}\text{H}_{98}$: C, 59.63; H, 5.84; N, 1.66; S, 18.95. Found: C, 58.75; H, 5.81; N, 1.74; S, 15.0.¹⁹

$(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$. Benzenethiol (3.5 g, 32 mmol), tri-*n*-butylamine (4.5 g, 24 mmol), and tetramethylammonium chloride (2.2 g, 20 mmol) were dissolved together in methanol (70 mL). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 g, 3.4 mmol) in methanol (10 mL) was added, followed by 1-propanol (50 mL), and the emerald green solution stored at 0 °C while crystallization occurred. The separated product was washed with 2-propanol and vacuum dried. Anal. Calcd for $\text{CoS}_4\text{N}_2\text{C}_{32}\text{H}_{44}$: C, 59.69; H, 6.89; S, 19.92. Found: C, 58.48; H, 6.77; S, 20.01. The emerald green crystals are soluble in polar aprotic solvents, without appreciable ligand dissociation. They are slightly soluble in the lower alcohols, giving brown solutions indicative of benzenethiolate dissociation to yield $[\text{Co}_4(\text{SPh})_{10}]^{2-}$.

$(\text{Et}_4\text{N})_2\text{Co}(\text{SPh})_4$. Benzenethiol (8.8 g, 80 mmol) and triethylamine (8.4 g, 83 mmol) were dissolved in acetonitrile (70 mL). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (4.0 g, 14 mmol) in ethanol (50 mL) was added, followed by tetraethylammonium bromide (10 g, 48 mmol) in ethanol (50 mL). After addition of 1-propanol (30 mL) the green solution was slowly pumped with stirring at room temperature to initiate crystallization of the emerald green crystals. The separated product was washed with 2-propanol and vacuum dried. Anal. Calcd for $\text{CoS}_4\text{N}_2\text{C}_{40}\text{H}_{60}$: C, 63.54; H, 8.00; S, 16.96. Found: C, 63.13; H, 7.94; S, 17.18.

$(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_8\text{Cl}_2$. A mixture of benzenethiol (3.5 g, 32 mmol) and triethylamine (3.1 g, 31 mmol) in acetone (60 mL) and tetramethylammonium chloride (3.2 g, 29 mmol) in methanol (60 mL) was prepared at room temperature. To this solution was added a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (6.0 g, 21 mmol) in methanol (60 mL), producing an intensely green solution. Crystallization of the product (which can be initiated by slight heating) was allowed to continue for 4 h. The black, microcrystalline product was filtered, washed with 1-propanol, and vacuum dried. Anal. Calcd for $\text{Co}_4\text{S}_8\text{Cl}_2\text{N}_2\text{C}_{56}\text{H}_{64}$: C, 50.64; H, 4.86; N, 2.11; S, 19.31. Found: C, 49.21; H, 4.83; N, 2.15; S, 15.0.¹⁹ This formulation of this compound is not evident from the available analytical data,¹⁹ but was confirmed by the fact that it is isostructural (see supplementary Table 1) with the zinc analogue, which has been fully characterized by crystal structure determination.¹³ $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_8\text{Cl}_2$ was previously⁹ formulated incorrectly as $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_6\text{Cl}_4$.

Reaction mixtures similar to the above, but with small variation in the amount of Me_4NCl or of aprotic solvent, have yielded products with polycrystalline diffraction patterns different from that of $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_8\text{Cl}_2$. In the absence of full structure determination these compounds are not formulated unambiguously; further investigations are in progress.

$(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_8\text{Cl}_2$ is soluble in acetonitrile and (to a lesser extent) in acetone. Attempted recrystallization from acetonitrile/propanol did not improve crystal quality. In solution it is rapidly oxidized by dioxygen to the maroon-black, insoluble product mentioned above.

Physical Measurements. Magnetic susceptibilities were measured on a Faraday balance with $\text{N}_2(\text{l})$ cryostat. Electronic spectra were recorded with Cary 14 and Cary 17 spectrophotometers. Solutions were prepared, and the cells filled, with rigorous deoxygenation using syringe/rubber septa transfer techniques. Reflectance spectra were obtained from powder samples smear-pressed into coarse filter paper and mounted over the port of the integrating sphere; dilution of the absorbing powder was easily achieved by further smearing. Polycrystalline diffraction data ($\text{Co K}\alpha$ radiation) for identification purposes are provided in supplementary Table 1.²⁰

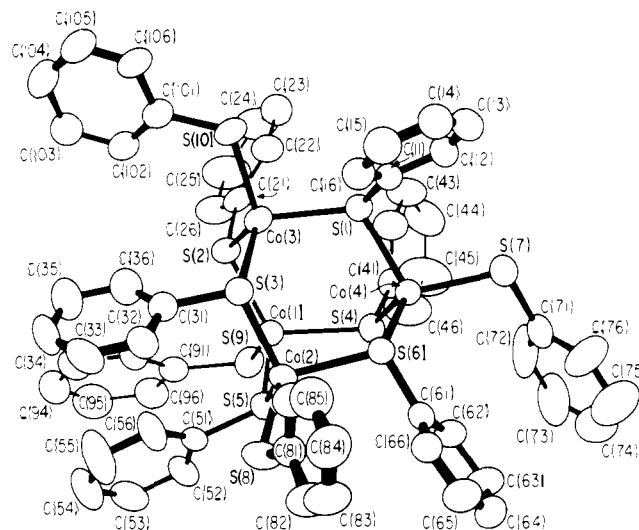


Figure 1. The $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ cluster, showing atom labeling.

Crystallography. $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_{10}$. The diffraction crystal was selected from the preparative reaction product and sealed in a Lindeman capillary. It was bounded by the forms $\{010\}$, $\{101\}$, and $\{001\}$, with the perpendicular distances between pinacoid faces equal to 0.24, 0.28, and 0.44 mm, respectively. The X-ray diffraction data were obtained with a Syntex P1 four-circle diffractometer equipped with a graphite monochromator, using $\text{Mo K}\alpha$ radiation. The unit cell parameters were determined and refined by least squares from 15 accurately centered diffraction maxima: $a = 13.031$ (2) Å, $b = 23.590$ (4) Å, $c = 12.806$ (2) Å, $\alpha = 92.28$ (1)°, $\beta = 115.04$ (1)°, $\gamma = 79.12$ (1)°.

Axial oscillation photographs did not reveal any lattice symmetry, and the assumed occurrence of space group $P\bar{1}$ containing $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_{10}$ per asymmetric unit was confirmed by the successful structure refinement: $d_{\text{calcd}} = 1.40$ g cm^{-3} , $d_{\text{obsd}} = 1.40$ g cm^{-3} .

Intensity data (293 K) were collected by the $\theta/2\theta$ scan technique, with variable scan rates (2–24°/min). Two standard reflections monitored every 50 measurements showed no significant change in diffraction intensity. A total of 6709 intensity observations were recorded, with $2\theta \leq 40^\circ$. Crystal absorption ($\mu = 12.95$ cm^{-1}) was assessed empirically from the intensity variation during stepped complete rotation of the crystal about the diffraction vector. The transmission factor for F varied by less than 4%, and absorption corrections were not made. After exclusion of 1197 unobserved reflections ($I < 2\sigma(I)$) the data set consisted of 5121 symmetry-independent observed reflections.

The Patterson function²¹ revealed the tetrahedron of four cobalt atoms. Successive Fourier syntheses, including one in space group $P1$ to improve the positions of the heavier atoms, permitted location of all nonhydrogen atoms. The least-squares refinement followed the normal sequence of introduction of atom parameters. Hydrogen atoms ($B_{\text{iso}} = 8.0$ Å²) were introduced at calculated positions ($\text{H}_3\text{C}-\text{NC}_3$ conformation staggered), and the structure was checked with a difference synthesis. The final least-squares refinement cycle was full matrix for all parameters other than those of hydrogen, which were not refined. In the calculation of estimated errors in interatomic distances and angles the complete variance-covariance matrix for all parameters was employed. In the final difference synthesis all electron density was less than 0.4 e Å⁻³. The scattering factors (neutral atom) were those of Hanson et al.^{22a} for nonhydrogen atoms and of Stewart et al.^{22b} for hydrogen. Anomalous dispersion corrections²³ were included for cobalt and sulfur: $R = 0.034$, $R_w = 0.043$, $(\sum w|\Delta F|^2)/(m-n)^{1/2} = 1.20$, $m = 5121$ data, $n = 757$ parameters. Atom labeling for the $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ cluster is shown in Figure 1. The phenyl ring atoms on S(*n*) are C(*nm*), $m = 1-6$ (C(*n*l) bonded to S(*n*)); the hydrogen atom on C(*nm*) is H(*nm*). The Me_4N^+ atoms are N(*p*), $p = 1, 2$; C(*qNp*), $q = 1-4$; H(*pqr*), $r = 1-3$.

Final atom coordinates and their estimated standard deviations are set out in Table 1 for the nonhydrogen atoms. Complete listings of position parameters for the hydrogen atoms, and a summary of the atom thermal motion appear with the supplementary material.²⁰

Table 1. Nonhydrogen Atom Coordinates for $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$

atom	10^4x	10^4y	10^4z	atom	10^4x	10^4y	10^4z
Co(1)	9401.4 (6) ^a	7410.7 (3)	-1520.9 (6)	C(55)	8563 (7)	9724 (3)	-1398 (8)
Co(2)	6224.3 (6)	8202.9 (3)	-2514.0 (6)	C(56)	8107 (6)	9222 (3)	-1677 (6)
Co(3)	7730.6 (6)	7253.8 (3)	291.5 (6)	C(61)	5036 (4)	7482 (2)	-4853 (4)
Co(4)	6948.1 (6)	6538.1 (3)	-2672.6 (6)	C(62)	5645 (5)	7199 (2)	-5444 (5)
S(1)	7196 (1)	6452 (1)	-765 (1)	C(63)	5189 (6)	7260 (3)	-6631 (5)
S(2)	9477 (1)	7334 (1)	306 (1)	C(64)	4118 (6)	7596 (3)	-7245 (5)
S(3)	6378 (1)	8084 (1)	-652 (1)	C(65)	3505 (5)	7874 (3)	-6663 (5)
S(4)	8645 (1)	6683 (1)	-2696 (1)	C(66)	3961 (5)	7821 (2)	-5470 (5)
S(5)	7949 (1)	8161 (1)	-2647 (1)	C(71)	6513 (5)	5711 (2)	-4889 (5)
S(6)	5544 (1)	7374 (1)	-3334 (1)	C(72)	7497 (6)	5744 (3)	-4974 (7)
S(7)	6419 (1)	5722 (1)	-3541 (1)	C(73)	7531 (8)	5746 (3)	-6058 (8)
S(8)	5145 (1)	9031 (1)	-3537 (1)	C(74)	6573 (9)	5710 (3)	-7016 (7)
S(9)	11101 (1)	7394 (1)	-1604 (1)	C(75)	5584 (7)	5654 (4)	-6962 (6)
S(10)	7780 (1)	7010 (1)	2001 (1)	C(76)	5560 (5)	5658 (3)	-5896 (5)
C(11)	5930 (4)	6295 (2)	-722 (4)	C(81)	3665 (5)	9080 (2)	-3888 (5)
C(12)	5677 (5)	5746 (2)	-1005 (5)	C(82)	2839 (6)	9355 (3)	-4913 (6)
C(13)	4726 (6)	5604 (3)	-916 (5)	C(83)	1677 (6)	9423 (3)	-5185 (6)
C(14)	4048 (5)	5993 (3)	-532 (5)	C(84)	1321 (6)	9209 (3)	-4429 (6)
C(15)	4300 (5)	6526 (3)	-254 (5)	C(85)	2122 (6)	8929 (3)	-3428 (6)
C(16)	5238 (5)	6684 (2)	-340 (5)	C(86)	3288 (5)	8861 (3)	-3149 (5)
C(21)	10581 (4)	6725 (2)	1025 (4)	C(91)	11779 (4)	7940 (2)	-776 (4)
C(22)	10359 (5)	6251 (2)	1433 (5)	C(92)	11352 (5)	8286 (2)	-92 (5)
C(23)	11249 (6)	5781 (2)	1953 (5)	C(93)	11903 (5)	8731 (2)	509 (5)
C(24)	12354 (6)	5793 (3)	2067 (5)	C(94)	12891 (6)	8821 (3)	448 (6)
C(25)	12558 (5)	6270 (3)	1684 (6)	C(95)	13327 (6)	8474 (3)	-206 (6)
C(26)	11680 (5)	6736 (3)	1173 (5)	C(96)	12782 (5)	8042 (3)	-817 (5)
C(31)	6859 (5)	8717 (2)	39 (4)	C(101)	8716 (4)	7337 (2)	3192 (4)
C(32)	6098 (5)	9242 (2)	-300 (5)	C(102)	9530 (5)	7635 (2)	3172 (4)
C(33)	6466 (6)	9743 (2)	214 (6)	C(103)	10222 (5)	7888 (3)	4143 (5)
C(34)	7554 (6)	9723 (3)	1050 (6)	C(104)	10134 (6)	7832 (3)	5182 (5)
C(35)	8303 (6)	9201 (3)	1402 (6)	C(105)	9351 (5)	7523 (3)	5217 (5)
C(36)	7952 (5)	8702 (2)	868 (5)	C(106)	8651 (5)	7282 (2)	4249 (5)
C(41)	9734 (4)	6050 (2)	-2183 (4)	N(1)	6313 (5)	8951 (2)	3483 (4)
C(42)	9903 (5)	5708 (2)	-1268 (5)	C(1N1)	7436 (13)	9083 (6)	3985 (16)
C(43)	10771 (5)	5215 (3)	-903 (5)	C(2N1)	6204 (9)	8548 (5)	2540 (9)
C(44)	11435 (5)	5059 (3)	-1488 (6)	C(3N1)	5494 (13)	9427 (5)	3129 (14)
C(45)	11271 (6)	5402 (3)	-2397 (7)	C(4N1)	6296 (15)	8633 (7)	4316 (12)
C(46)	10421 (6)	5896 (3)	-2743 (6)	N(2)	12559 (4)	6305 (2)	-4572 (4)
C(51)	8481 (4)	8820 (2)	-2279 (4)	C(1N2)	12787 (7)	6580 (4)	-3476 (7)
C(52)	9316 (5)	8914 (2)	-2612 (5)	C(2N2)	13272 (7)	5718 (3)	-4367 (8)
C(53)	9755 (5)	9419 (3)	-2324 (6)	C(3N2)	11343 (6)	6268 (3)	-5169 (6)
C(54)	9386 (6)	9824 (3)	-1716 (6)	C(4N2)	12853 (8)	6640 (3)	-5314 (7)

^a Estimated standard deviations in parentheses refer to the least significant digit quoted.

$(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$. Oscillation and Weissenberg photography indicates space group $P4_12_12$, with $a = 10.34 \text{ \AA}$, $c = 32.75 \text{ \AA}$, $Z = 4$, $d_{\text{calcd}} = 1.22 \text{ g cm}^{-3}$, $d_{\text{obsd}} = 1.26 \text{ g cm}^{-3}$. Therefore the cobalt atoms must be separated by at least 8 \AA , and the molecular $[\text{Co}(\text{SPh})_4]^{2-}$ units possess C_2 point symmetry.

Results

Synthesis. Mixtures in nonaqueous solvents of cobalt(II) salts and benzenethiol, in the presence of hindered tertiary amine as deprotonating agent, readily yield a sequence of soluble cobalt(II)-benzenethiolate complexes. It is significant that throughout the full range of $\text{PhS}^-/\text{Co}^{2+}$ molar ratios (0- ∞) there is no evidence of any compound with very low solubility in the acetonitrile and/or alcohol solvent systems employed. Evidently all cobalt(II)-benzenethiolate complexes have molecular structures, at least in solution. This general solubility of cobalt(II)-benzenethiolate complexes contrasts with the absence of any detectable solubility for their common oxidation product.

The two complexes that can be formed in solution with high equilibrium concentration in solution are emerald-green $[\text{Co}(\text{SPh})_4]^{2-}$ and intense-brown $[\text{Co}_4(\text{SPh})_{10}]^{2-}$. In acetonitrile solution at room temperature $[\text{Co}(\text{SPh})_4]^{2-}$ is the principal species when the $\text{PhS}^-/\text{Co}^{2+}$ ratio is greater than ca. 4, while $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ predominates when this ratio is less

than ca. 3. Dark green solutions are formed when $\text{PhS}^-/\text{Co}^{2+} < \text{ca. 2}$ and $\text{Cl}^-/\text{Co}^{2+} \geq \text{ca. 2}$. A single experiment in which CoCl_2 is added to benzenethiol plus equimolar triethylamine, in acetonitrile forms, in sequence, $[\text{Co}(\text{SPh})_4]^{2-}$, then $[\text{Co}_4(\text{SPh})_{10}]^{2-}$, then the dark green solution. One component of the dark green solution is $[\text{Co}_4(\text{SPh})_8\text{Cl}_2]^{2-}$; other components, at least one of which can be isolated, are not fully characterized.

All three anionic complexes can be crystallized as Me_4N^+ salts from these preparative solutions. Other ammonium cations can be used. Crystallization of the dicyclohexylammonium salt of $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ can be achieved by addition of water to a preparative mixture containing $(\text{C}_6\text{H}_{11})_2\text{NH}$ as base, thereby demonstrating the hydrolytic stability of $[\text{Co}_4(\text{SPh})_{10}]^{2-}$.

Molecular Structure. Determination of the crystal structure of $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_{10}$ has revealed the molecular structure of the $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ cluster, shown from different viewpoints in Figures 1 and 2. The cluster is shielded over most of its periphery by the ten phenyl groups, and is bound in the crystal lattice only by weak interactions.

The cluster contains four cobalt atoms located at the vertices of an approximate tetrahedron, with six benzenethiolate ligands (S(1) to S(6)) bridging along the edges of the tetrahedron and four benzenethiolate ligands terminally bonded one

Table II. Selected Interatomic Distances and Angles^a in (Me₄N)₂[(μ-SPh)₆(CoSPh)₄]

Co-S _{terminal}		S _{terminal} -Co-S _{bridging}	
Co(1)-S(9)	2.254 (2)	S(9)-Co(1)-S(2)	116.00 (5)
Co(2)-S(8)	2.263 (2)	S(9)-Co(1)-S(4)	104.53 (6)
Co(3)-S(10)	2.256 (2)	S(9)-Co(1)-S(5)	113.34 (6)
Co(4)-S(7)	2.259 (2)	S(8)-Co(2)-S(3)	118.01 (6)
mean Co-S _{terminal}	2.258 ± 0.004 ^b	S(8)-Co(2)-S(5)	102.38 (6)
Co-S _{bridging}		S(8)-Co(2)-S(6)	114.02 (6)
Co(1)-S(2)	2.312 (1)	S(10)-Co(3)-S(1)	101.59 (6)
Co(1)-S(4)	2.316 (1)	S(10)-Co(3)-S(2)	116.06 (6)
Co(1)-S(5)	2.330 (1)	S(10)-Co(3)-S(3)	114.62 (6)
Co(2)-S(3)	2.331 (2)	S(7)-Co(4)-S(1)	107.64 (6)
Co(2)-S(5)	2.309 (2)	S(7)-Co(4)-S(4)	111.94 (6)
Co(2)-S(6)	2.328 (1)	S(7)-Co(4)-S(6)	115.61 (6)
Co(3)-S(1)	2.320 (1)	mean S _{terminal} -Co-S _{bridging}	111.3 ± 5.8 ^b
Co(3)-S(2)	2.312 (2)	S _{bridging} -Co-S _{bridging}	
Co(3)-S(3)	2.342 (1)	S(2)-Co(1)-S(4)	113.30 (6)
Co(4)-S(1)	2.336 (2)	S(4)-Co(1)-S(5)	95.54 (5)
Co(4)-S(4)	2.311 (2)	S(5)-Co(1)-S(2)	112.07 (5)
Co(4)-S(6)	2.326 (1)	S(3)-Co(2)-S(5)	115.29 (5)
mean Co-S _{bridging}	2.322 ± 0.011 ^b	S(5)-Co(2)-S(6)	106.41 (5)
mean S-C _α	1.776 ± 0.011 ^b	S(6)-Co(2)-S(3)	100.64 (5)
mean C-C (ring)	1.377 ± 0.014 ^b	S(1)-Co(3)-S(2)	106.10 (6)
mean N-C (cation)	1.43 ± 0.06 ^b	S(2)-Co(3)-S(3)	108.28 (6)
		S(3)-Co(3)-S(1)	109.53 (5)
		S(1)-Co(4)-S(4)	109.53 (5)
		S(4)-Co(4)-S(6)	110.24 (5)
		S(6)-Co(4)-S(1)	101.20 (5)
		mean S _{bridging} -Co-S _{bridging}	107.3 ± 5.8 ^b
		mean Co-S _{bridging} -Co	112.8 ± 1.1 ^b
Nonbonding Distances			
Co-Co		S _{bridging} -S _{bridging}	
Co(1)-Co(2)	3.881 (1)	S(1)-S(2)	3.702 (2)
Co(1)-Co(3)	3.862 (1)	S(1)-S(3)	3.807 (2)
Co(1)-Co(4)	3.858 (1)	S(1)-S(4)	3.796 (2)
Co(2)-Co(3)	3.845 (1)	S(1)-S(6)	3.602 (2)
Co(2)-Co(4)	3.880 (1)	S(2)-S(3)	3.772 (2)
Co(3)-Co(4)	3.894 (1)	S(2)-S(4)	3.866 (2)
mean Co-Co	3.870 ± 0.018 ^b	S(2)-S(5)	3.850 (2)
		S(3)-S(5)	3.919 (2)
		S(3)-S(6)	3.584 (2)
		S(4)-S(5)	3.440 (2)
		S(4)-S(6)	3.805 (2)
		S(5)-S(6)	3.713 (2)
		mean S _{bridging} -S _{bridging}	3.74 ± 0.14 ^b

^a Distances in ångströms, angles in degrees. Estimated standard deviations in parentheses refer to the least significant digit quoted. ^b Estimated standard deviation of the sample.

on each cobalt atom. The cluster is thus formulated as [(μ-SPh)₆(CoSPh)₄]²⁻. The Co(μ-SPh)₃(SPh) coordination is approximately tetrahedral at each cobalt atom.

The complete cluster possesses no crystallographic symmetry, nor any approximate symmetry. Details of the dimensions of the cluster may, however, be considered with reference to an obvious idealization of the structure. Disregarding the phenyl rings, the Co₄S₁₀ core can be idealized as possessing *T_d* point-group symmetry: the four cobalt atoms are arrayed as a tetrahedron, the six bridging sulfur atoms as an octahedron, and the four terminal sulfur atoms as an outer tetrahedron. The cluster can be idealized further, without increase in symmetry, by requiring all interatomic angles at the cobalt and bridging sulfur atoms to be 109.5°.

Selected dimensions of the Co₄S₁₀ core, relating to these idealizations, are presented in Table II. The following points can be made about the geometry of this core: (a) The Co₄ polyhedron is effectively the idealized tetrahedron. (b) The (S_{br})₆ polyhedron is strongly and irregularly distorted from the idealized octahedron. (c) This distortion is not due to variations in Co-S distances, nor to significant variations in

the Co-S_{br}-Co angles, but arises in variations in the S_t-Co-S_{br} and S_{br}-Co-S_{br} angles. (d) The angular distortions are most pronounced in the atom sequence S(8), Co(2), S(5), Co(1), S(4), S(9). The question then arises as to whether these distortions result from interion packing forces in the lattice. There are no unusually short interion contacts (see supplementary material²⁰), and no close approximately parallel phenyl rings, to which specific cluster distortions could be attributed. Therefore it is concluded that the [(μ-SPh)₆(CoSPh)₄]²⁻ cluster is angularly floppy. A similar conclusion was reached in connection with the more compact [(μ-SPh)₆Cu₄]²⁻ cluster and the hypothetical [(μ-SPh)₁₂Cu₈]⁴⁻ cluster.¹⁰

The cluster displays several regular geometrical characteristics. The cobalt atoms are displaced slightly outward along the pseudo-threefold axes. This displacement is manifest in the mean values of angles, S_t-Co-S_{br} (111.3°) > S_{br}-Co-S_{br} (107.3°), and of distances, Co-Co (3.87 Å) > S_{br}-S_{br} (3.74 Å); it can also be expressed in terms of the ratio of the mean Co-Co distance to the mean Co-S_{br} distance, which ratio is found to be 1.666 in contrast to the idealized value of 1.633 when all cluster angles are tetrahedral. In view of this elon-

Table III. Magnetic Susceptibility Data for $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$

T, K	$10^6 \chi_g$	$10^6 \chi_m(\text{cor})^a$	$10^6 \chi_m(\text{calcd})^b$	$10^6[\chi_m(\text{obsd}) - \chi_m(\text{calcd})]$	μ_{eff}^c
84.8	15.53	23 770	22 500	1270	2.01
94.5	14.84	22 750	22 100	650	2.07
104.2	14.29	21 940	21 680	260	2.14
113.9	13.79	21 200	21 250	-50	2.20
129.8	13.10	20 180	20 540	-360	2.29
145.2	12.56	19 380	19 870	-490	2.37
160.4	12.11	18 720	19 230	-510	2.45
176.0	11.66	18 060	18 600	-540	2.52
192.1	11.28	17 500	17 980	-480	2.59
208.2	10.93	16 980	17 390	-410	2.66
224.1	10.62	16 520	16 840	-320	2.72
240.3	10.33	16 100	16 310	-210	2.78
256.6	10.08	15 720	15 800	-80	2.84
273.2	9.83	15 360	15 310	50	2.90
295.0	9.32	14 600	14 710	-110	2.93
295.0	9.38	14 700	14 710	-10	2.94

^a The diamagnetic correction applied was that calculated for $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$, -850×10^{-6} cgs units. ^b Calculated for the model described in the text, with parameters $\text{TIS} = 0$, $J = -16.9 \text{ cm}^{-1}$, $g = 2.00$. ^c μ_B per cobalt atom.

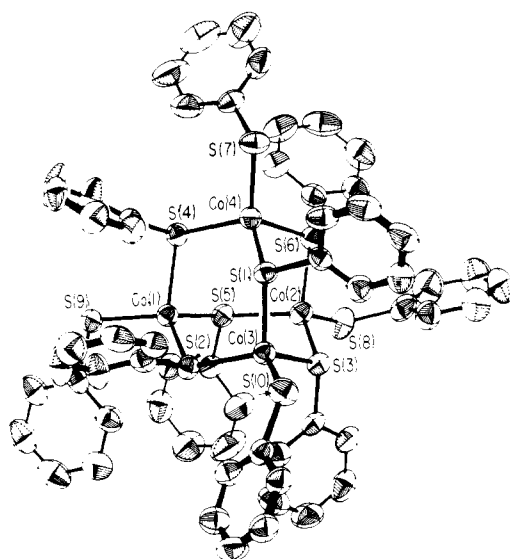


Figure 2. The $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ cluster, showing thermal ellipsoids of 50% probability.

gation of the Co-Co distances no thermodynamically significant direct Co-Co bonding can be proposed. It is clear that the existence of the cluster is a consequence of the thiolate bridging.

Double bridging by benzenethiolate extends the Co-S bond length by 0.064 Å. The bonding stereochemistry around the sulfur atoms, bridging and nonbridging, is effectively tetrahedral: for the bridging sulfur atoms the angles between the $\text{C}_\alpha\text{-S}$ vector and the normal to the Co-S-Co plane have a mean value of 36.3° , close to the tetrahedral value of 35.3° . The question of preferred disposition of the nonbonding electron pair on the sulfur atom of each bridging thiolate ligand, a disposition distinguishable^{24,25} and possibly significant^{16,24,25} in other systems, does not arise in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, since each $\text{S}_{\text{br}}\text{-C}_\alpha$ bond is axial to one and equatorial to another of the Co_3S_3 chairs which constitute the Co_4S_6 core.

The crystallographic data on $(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$ indicate that it contains the structurally molecular $[\text{Co}(\text{SPh})_4]^{2-}$ ion, which possesses crystallographic symmetry higher (C_2) than that of the same complex ion in $(\text{Ph}_4\text{P})_2\text{Co}(\text{SPh})_4$.¹⁸

Crystalline $(\text{Me}_4\text{N})_2\text{Co}_4(\text{SPh})_8\text{Cl}_2$, isostructural with its zinc analogue,¹³ contains the $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$

molecular cluster, in which two of the terminal benzenethiolate ligands of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ are replaced by chloride ligands.

Magnetic Properties. Magnetic susceptibility data for $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$ are presented in Table III. The electron spins at different cobalt atoms are clearly subject to weak antiparallel coupling. These data are examined here²⁶ in terms of a coupling model which involves three simplifying assumptions. The first is that the susceptibility due to each pseudotetrahedral cobalt site in the absence of coupling is only that of an orbitally nondegenerate $^4\text{A}_2$ ground state. The second arises in the use of the isotropic Heisenberg exchange Hamiltonian²⁷

$$H_{\text{ex}} = -2 \sum_i \sum_j J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1)$$

which assumes that interatomic exchange coupling of spins is much less than intraatomic exchange coupling.²⁸ Thirdly, on the basis of the structural data it is postulated that the six coupling constants J between the four cobalt atoms should be very similar, whatever be the orbital overlap responsible for the spin coupling, and the present model assumes that they are identical.

The manifold of cluster spin states is then $S_i = (i - 1)$, $i = 1-7$, with multiplicities $w_i = 4, 9, 11, 10, 6, 3, 1$, respectively, $i = 1-7$. The model contains two additional parameters: g (applied equally to all cluster spin states) and a single correction, TIS, for all unaccounted temperature-independent susceptibility (such as inadequacies in calculated closed-shell susceptibilities and second-order Zeeman contributions). The parameters J , g , and TIS were optimized by least-squares minimization of $\sum(\chi_{\text{cor}}(\text{obsd}) - \chi(\text{calcd}))^2$. Results for optimizations with different combinations of parameters variable are given in Table IV. When permitted to vary, g , which covaries strongly with TIS, drops to an unreasonable value of ca. 1.9. Since TIS is unlikely to be negative by more than 400×10^{-6} cgsu, and is expected to be positive, it is concluded from the results in Table IV that the best representation of the data in hand is $\text{TIS} = 0$, $J = -17 \text{ cm}^{-1}$, $g = 2.00$. The discrepancy between observed and calculated susceptibility, although generally less than experimental error, shows a systematic trend (Table III) which possibly reflects the neglect of the more complex susceptibility of the uncoupled cobalt centers.²⁹

The coupling parameter J is slightly larger than that ($-J = 13-16 \text{ cm}^{-1}$) obtained by Brookes and Martin³⁰ for the μ_4 -oxo-tetracobalt(II) complex $\text{OC}_4(\text{C}_7\text{H}_5\text{N}_2)_6$ (where $\text{C}_7\text{H}_5\text{N}_2^-$ is the conjugate base of 7-azaindole), which is,

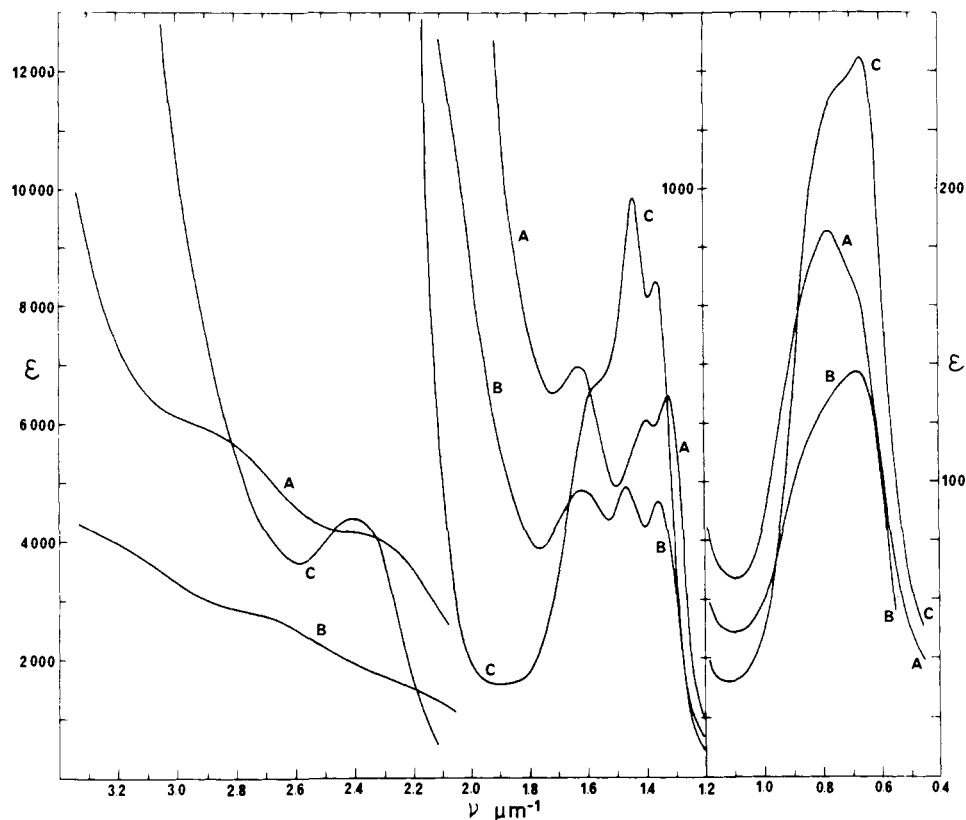


Figure 3. Absorption spectra, ϵ , (M_{Co}) $^{-1}$ cm^{-1} , in acetonitrile solution: A, $(Me_4N)_2[(\mu-SPh)_6(CoSPh)_4]$, 6.01×10^{-3} M Co; B, $(Me_4N)_2[(\mu-SPh)_6(CoSPh)_2(CoCl)_2]$, 4.13×10^{-3} M Co; C, $(Me_4N)_2[Co(SPh)_4]$, 3.36×10^{-3} M Co.

Table IV. Magnetic Parameters for $(Me_4N)_2[(\mu-SPh)_6(CoSPh)_4]$

variable parameters ^a	parameter values			$\sum \chi_{obsd} - \chi_{calcd} / \sum \chi_{obsd}$
	$-J$, cm^{-1}	g	$10^6 TIS$, cgsu	
J	16.9	2.00	0	0.020
J, g	14.9	1.92	0	0.017
J, TIS	15.9	2.00	-816	0.018
J, g, TIS	14.8	1.90	+268	0.017

^a See text for description of model.

however, quite different geometrically and electronically from $[(\mu-SPh)_6(CoSPh)_4]^{2-}$. It must be remembered that the parameter J is the mean of $4S^2 = 9$ orbital interactions between each pair of cobalt atoms,³¹ and therefore the dominant spin pairing interaction energy may be as large as 150 cm^{-1} in $[(\mu-SPh)_6(CoSPh)_4]^{2-}$. Nevertheless, this energy is negligible as a chemical-bonding influence.

Electronic Spectra. Comparison of crystal phase reflectance spectra for $(Me_4N)_2[(\mu-SPh)_6(CoSPh)_4]$, $(Me_4N)_2[(\mu-SPh)_6(CoSPh)_2(CoCl)_2]$, and $(Me_4N)_2[Co(SPh)_4]$ with absorption spectra of the same compounds dissolved in dry acetonitrile (see Figure 3 and Table V) leads to the conclusion that all three complexes undergo no appreciable structure modification with phase change. There are four distinct absorption regions in these spectra: region I, $0.55\text{--}1.0 \mu m^{-1}$, the ${}^4A_2 \rightarrow {}^4T_1(F)$ transition (ν_2) of tetrahedrally coordinated Co(II); region II, $1.3\text{--}1.7 \mu m^{-1}$, the ${}^4A_2 \rightarrow {}^4T_1(P)$ transition (ν_3) of tetrahedral Co(II); region III, $1.7\text{--}2.1 \mu m^{-1}$, a low-energy metal-ligand charge-transfer absorption region; region IV, $1.9\text{--}3.2 \mu m^{-1}$, a high-energy metal-ligand charge-transfer region. Higher frequency absorption contains contributions from the phenyl substituents.

There have been two previous reports of the solution spectrum of $[Co(SPh)_4]^{2-}$. The data reported^{18b} for $(Ph_4P)_2Co(SPh)_4$ in acetonitrile are in general agreement in band frequencies but include intensities slightly less than those found

Table V. Electronic Absorption Spectra^a

compd	solution (CH_3CN)		reflectance ν , μm^{-1}
	ν , μm^{-1}	$(\epsilon, {}^b M^{-1} cm^{-1})$	
$(Me_4N)_2Co_4(SPh)_{10}$	0.67 sh ^c	(160)	0.65 sh
	0.78	(185)	0.76
	1.324	(645)	1.32
	1.398	(604)	1.40
	1.630	(695)	1.615
	2.27 sh	(4000)	2.16
$(Me_4N)_2Co_4(SPh)_8Cl_2$	2.85 sh	(5800)	2.75
	0.68	(138)	0.615
			0.745
	0.84 sh	(115)	0.86 sh
	1.357	(467)	1.350
	1.467	(491)	1.467
$(Me_4N)_2Co(SPh)_4$	1.620	(487)	1.615
	2.1 sh	(1300)	2.1 sh
	2.66 sh	(2700)	2.58
	0.670	(244)	0.650
	0.78 sh	(228)	0.80
	1.362	(840)	1.360
	1.442	(985)	1.440
	1.60 sh	(640)	1.56 sh
			1.85
	2.40	(4380)	2.40

^a See Figure 3. Minor unresolved absorption bands are shown only on the figure. ^b Molar extinction coefficient, per cobalt atom. ^c Shoulder.

here. However, the data reported^{17a} for $(Bu_4N)_2Co(SPh)_4$ in dichloromethane differ substantially in the frequencies of prominent peaks in region II, and intensities throughout are low. Possibly solvolytic dissociation of the type described below was caused by impurities in the dichloromethane. The previous

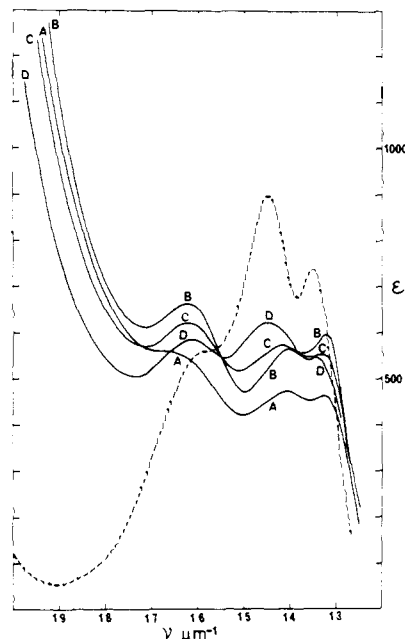


Figure 4. Absorption spectra, ϵ , $(M_{Co})^{-1} \text{ cm}^{-1}$, in acetonitrile solution. $\text{PhS}^-/\text{Co}^{2+}$ ratios: 2, A; 3, B; 4, C; 5, D. The dotted trace is the spectrum of $[\text{Co}(\text{SPh})_4]^{2-}$.

derivation³² of pseudotetrahedral ligand-field parameters for $[\text{Co}(\text{SPh})_4]^{2-}$ remains valid.

The ${}^4A_2 \rightarrow {}^4T_1(\text{F})$ and ${}^4A_2 \rightarrow {}^4T_1(\text{P})$ band envelopes for $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$ are not significantly different in frequency from those of $[\text{Co}(\text{SPh})_4]^{2-}$. The major difference is increased splitting of the ${}^4A_2 \rightarrow {}^4T_1(\text{P})$ envelope in the two cluster compounds, probably a consequence of the ligand inequivalence in the clusters. In the absence of detailed data on resolved transitions in regions I and II, further modeling of the electronic structure of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$ cannot be attempted. We conclude simply that the ligand field parameters Δ_t and B for the two ligand types $\text{PhS}^-_{\text{terminal}}$ and $\text{PhS}^-_{\text{bridging}}$ are not appreciably different. As previously noted,³² $\Delta_t(\text{PhS}^-) > \Delta_t(\text{Cl}^-)$. It is noteworthy that both $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$ have a well-resolved absorption at $1.62 \mu\text{m}^{-1}$, which is essentially absent in $[\text{Co}(\text{SPh})_4]^{2-}$. This absorption may therefore be characteristic of the bridging Co-SPh-Co function.

The charge-transfer regions III and IV are of greater interest for these compounds, owing to the limited published information^{32,33} on structure/spectra relationships for thiolate ligands in terminal and in bridging positions, and also for related halide and pseudohalide ligands with terminal or bridge bonding. The absorption in these regions is definitely due to ligand-metal charge-transfer transitions, since all $\text{Zn}(\text{II})$ -benzenethiolate compounds, including $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{ZnSPh})_4]$, which is isostructural with $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$, show no absorption less than $3.0 \mu\text{m}^{-1}$, with the lowest energy absorption maximum at $3.2 \mu\text{m}^{-1}$.

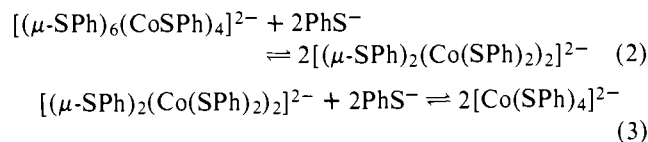
Referring to the solution spectra in Figure 3, two general points can be made. First, it can be seen that there are few well-resolved charge-transfer transitions, particularly in the two clusters, and it appears that these complexes contain a sequence of poorly separated thiolate levels. In terms of electronic structure, the angular distortions from possible high symmetry in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ would be expected to cause minor splitting of degenerate levels. The evidence of broad overlapping transitions suggests that spreading of energy levels is characteristic of the $\{(\mu\text{-SPh})_6\text{Co}_4\}$ core. Secondly, the question can be raised as to whether chromophore factoring

can be applied to the charge-transfer absorption, with chromophores $\{\text{Co-SPh}_{\text{terminal}}\}$ and $\{\text{Co-SPh}_{\text{bridging}}\text{-Co}\}$. It can be seen that in the $1.8\text{-}2.1\text{-}\mu\text{m}^{-1}$ region the absorption of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ is substantially greater than that of $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$ plus $[\text{Co}(\text{SPh})_4]^{2-}$, while in the $2.8\text{-}3.2\text{-}\mu\text{m}^{-1}$ region it is substantially less. A simplistic model with noninteracting $\{\text{Co-SPh}_{\text{terminal}}\}$ and $\{\text{Co-SPh}_{\text{bridging}}\text{-Co}\}$ chromophores is inadequate. Although the symmetrical idealized structures of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$, and $[\text{Co}(\text{SPh})_4]^{2-}$ might appear to favor them in development of the charge-transfer spectroscopy of $\text{Co}(\text{II})$ -thiolate coordination, progress in this area will depend on the availability of further complexes, including $[(\mu\text{-SR})_6(\text{CoX})_4]^{2-}$, with alkylthiolate ligands.

Nevertheless, the charge-transfer spectra contain some features with diagnostic value: (a) Rising absorption in the $1.8\text{-}2.0\text{-}\mu\text{m}^{-1}$ region is clearly correlated with the presence of bridging benzenethiolate. (b) A broad maximum in the $2.6\text{-}2.8\text{-}\mu\text{m}^{-1}$ region occurs in the compounds with bridging benzenethiolate. (c) Strongly rising absorption at energies higher than $2.8 \mu\text{m}^{-1}$ occurs in the complex with only terminal benzenethiolate: a reduced amount of $\text{Co-SPh}_{\text{terminal}}$ bonding decreases the absorption in this higher energy region.

Solution Equilibria. The equilibria existing in solutions containing $\text{Co}(\text{II})$ and benzenethiolate, involving $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, $[\text{Co}(\text{SPh})_4]^{2-}$, and possibly other species, have been investigated by means of the electronic spectra of two series of solutions. Figure 4 shows spectra of oxygen-free solutions prepared as mixtures of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in CH_3CN and PhSH plus Et_3N in CH_3CN , with $\text{PhS}^-/\text{Co}(\text{II})$ molar ratios of 2, 3, 4, and 5 in solutions 4A, 4B, 4C, and 4D, respectively. Figure 5 shows spectra of solutions prepared as mixtures of $(\text{Et}_4\text{N})_2\text{CoBr}_4$ in CH_3CN and PhSH plus Et_3N in CH_3CN , with $\text{PhS}^-/\text{Co}(\text{II})$ molar ratios of 0, 2, 3.5, and 10 in solutions 5A, 5B, 5C, and 5D, respectively. The spectra of solutions 4B, 4C, and 4D reveal isosbestic points at 1.39 and $1.55 \mu\text{m}^{-1}$ and spectrum 4B is that of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$.³⁵ Spectrum 5D is that of $[\text{Co}(\text{SPh})_4]^{2-}$, and is marked as a reference spectrum on Figure 4.

Consider first the behavior of solutions 4B, 4C, and 4D, in which $[\text{PhS}^-]$ is increasing above that required for $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$. The isosbestic point at $1.55 \mu\text{m}^{-1}$ is consistent with the equilibrium co-occurrence of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[\text{Co}(\text{SPh})_4]^{2-}$, but the spectra in the vicinity of the $1.39\text{-}\mu\text{m}^{-1}$ isosbestic point are not. Also, the high absorbance in the $1.8\text{-}1.9\text{-}\mu\text{m}^{-1}$ region is not consistent with formation of a substantial proportion of $[\text{Co}(\text{SPh})_4]^{2-}$ in solution 4D, but is indicative of bridging benzenethiolate. Therefore it is probable that the species in equilibrium with $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ in these solutions is not $[\text{Co}(\text{SPh})_4]^{2-}$ but another complex with tetrahedral coordination and a low proportion of bridging thiolate. An obvious suggestion is $[(\mu\text{-SPh})_2(\text{Co}(\text{SPh})_2)_2]^{2-}$, with edge-shared coordination tetrahedra. Acetonitrile solutions of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with larger excesses of PhS^- than 4D contain only $[\text{Co}(\text{SPh})_4]^{2-}$. Therefore it appears that the solution equilibria, in the absence of halide ligands, should be written



Spectrum A in Figure 4 also shows absorbance in the bridging benzenethiolate region ($1.8\text{-}1.9 \mu\text{m}^{-1}$) greater than can be accounted for by $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$. The $\text{PhS}^-/\text{Co}(\text{II})$ ratio in this solution is only 2, and it is possible that all benzenethiolate ligands are bridging, in a molecular aggregate of type $[(\mu\text{-SPh})_2\text{Co}]_n^0$. The high solubility of the components

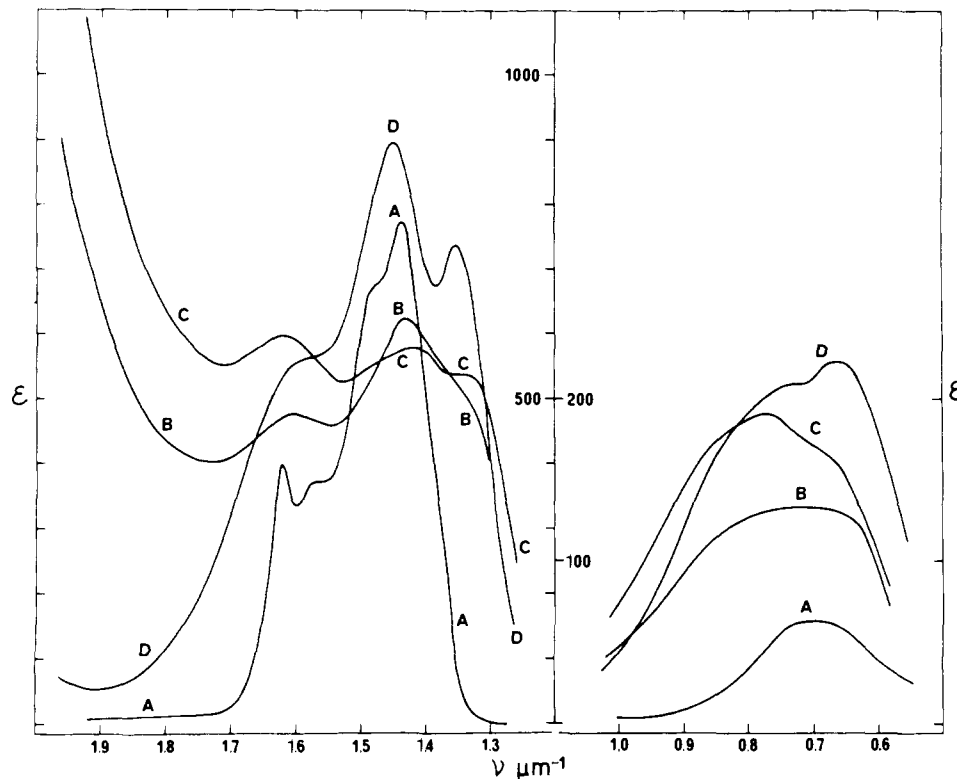


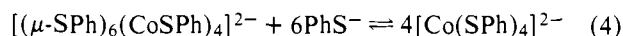
Figure 5. Absorption spectra, ϵ , $(M_{Co})^{-1} \text{ cm}^{-1}$, in acetonitrile solution. $\text{PhS}^-/\text{CoBr}_4^{2-}$ ratios: 0, A; 2, B; 3.5, C; 10, D.

of solutions with $\text{PhS}^-/\text{Co(II)}$ ratio ≤ 2 indicates that these components have molecular structures.

The spectra in Figure 5 provide information on complexes existing in the sequence between $[\text{CoBr}_4]^{2-}$ (spectrum A) and $[\text{Co}(\text{SPh})_4]^{2-}$ (spectrum D), as the PhS^- concentration increases.³⁷ Two general observations can be made: (1) absorbance in the 1.8–1.9- μm^{-1} region increases and then decreases as $[\text{PhS}^-]$ increases, indicating that the intermediate complexes contain bridging benzenethiolate; (2) the spectra (1.2–1.9 μm^{-1}) cross without isosbestic points, indicating the existence of sequences of intermediate complexes. Spectrum 5C ($\text{PhS}^-/\text{CoBr}_4^{2-} = 3.5$) is virtually that of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, and the spectra of solutions intermediate between 5C and 5D are essentially the same as those in Figure 4.³⁷ Thus Br^- does not interfere with the postulated equilibria (2) and (3). Spectrum 5B contains substantial absorbance in the 1.8–1.9- μm^{-1} region, indicative of bridging thiolate, and, with the characteristic maximum at 1.61 μm^{-1} , resembles the spectrum of $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$. Therefore the predominant complex in solution 5B ($\text{PhS}^-/\text{CoBr}_4^{2-} = 2$) is probably $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoBr})_2]^{2-}$, with $[(\mu\text{-SPh})_6(\text{CoBr})_4]^{2-}$ probably existing in solutions with $\text{PhS}^-/\text{CoBr}_4^{2-} < 2$.

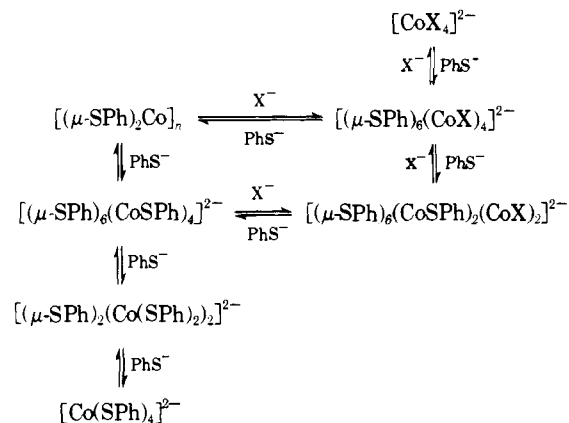
In summary, the complexes and equilibria existing in acetonitrile solutions containing Co(II) , PhS^- , and halide are postulated to be as shown in Scheme I.

The equilibria connecting $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[\text{Co}(\text{SPh})_4]^{2-}$, shown combined in the equation



are solvent dependent. Thus, an emerald-green solution of $(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$ in acetonitrile changes to the dark brown of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ when methanol is added in approximately equal volume, and $(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$ dissolved in methanol produces a brown solution. The addition of less than 10% water to $(\text{Me}_4\text{N})_2\text{Co}(\text{SPh})_4$ in acetonitrile causes pronounced change to dark brown, indicative of thiolate bridge formation. These observations are entirely consistent with

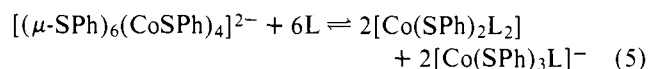
Scheme I^a



^aX = Cl, Br.

known solvent influences on anion activity. Of the species in eq 4, PhS^- has the largest negative charge density, and its activity relative to $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[\text{Co}(\text{SPh})_4]^{2-}$ is increased by aprotic solvents and decreased by protic solvents.

The thiolate bridges in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ are disrupted by coordinating solvents pyridine and Me_2SO (but not DMF), which produce green solutions containing pseudotetrahedral monometallic complexes. Equilibria represented by the overall equation



are probably involved, but the equilibrium constants are small. Dilution of a Me_2SO solution with an equal volume of inert solvent (CCl_4) causes more than 50% reversion from monometallic complexes to $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$.

Discussion

The advantages of the synthetic method used here follow: (1) it readily yields pure crystalline salts of $[\text{Co}(\text{SPh})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$; (2) it permits investigation of the full range of complexes in solution equilibria; (3) it is adaptable to the synthesis of related complexes. An unexpected aspect of the $\text{Co(II)}/\text{PhS}^-$ system is the complete absence of non-molecular structures insoluble in common aprotic and protic solvents.

The molecular cluster $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ is a complex unprecedented for cobalt(II) with any type of monodentate ligand.^{38,40} Hitherto the only cluster established for cobalt(II) and monodentate ligands was $[\text{Co}_2\text{Cl}_6]^{2-}$,^{41,42} with centrosymmetric structure $[(\mu\text{-Cl})_2(\text{CoCl}_2)_2]^{2-}$. It is postulated here that the benzenethiolate analogue, $[(\mu\text{-SPh})_2(\text{Co}(\text{SPh})_2)_2]^{2-}$, exists in solution. In the case of metals other than cobalt, with any monodentate ligands, the tetrametallic cluster structure reported here is known only for zinc(II) with benzenethiolate, in $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{ZnSPh})_4]$,¹³ $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{ZnSPh})_2(\text{ZnCl})_2]$,¹³ and $[\text{Zn}_4(\text{SPh})_8\text{CH}_3\text{OH}]$.¹³ The idealized T_d Co_4S_{10} framework of $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$, although previously unknown among binary transition metal complexes, is established for organic, organometallic, and inorganic compounds; examples are adamantane, $\text{C}_{10}\text{H}_{16}$,⁴³ $\text{S}_6(\text{CH})_4$,⁴⁴ $\text{S}_6(\text{SiCH}_3)_4$,⁴⁵ $\text{S}_6(\text{SnCH}_3)_4$,⁴⁶ $(\text{Me}_2\text{Ge})_6\text{P}_4$,⁴⁷ P_4S_{10} ,⁴⁸ and $[\text{Ge}_4\text{S}_{10}]^{4-}$.⁴⁹

There are several significant features of the structure and bonding in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$. (a) The cluster is maintained by the bridging thiolate ligands, not by direct cobalt-cobalt bonding. (b) There is electronic coupling between the cobalt atoms, manifest in the magnetic properties and charge-transfer spectra. (c) The cluster structure is not rigid, but angularly flexible. This property, observed also for other related clusters,^{10,11} together with the absence of direct cobalt-cobalt bonding, provokes the hypothesis that cobalt(II)-thiolate molecular clusters based on convex polyhedra larger than $\text{S}_6(\text{CoS})_4$ are unlikely to have comparable structural stability. (d) There is no evidence of directed bonding influencing the phenyl ring orientations. (e) Co-S_{br} is 0.064 Å longer than Co-S_{t} , whereas the analogous elongation in $[(\mu\text{-Cl})_2(\text{CoCl}_2)_2]^{2-}$ is 0.103 Å.⁴² (f) The mean Co-S_{t} bond length in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ is 0.070 Å shorter than the mean length of this bond in $[\text{Co}(\text{SPh})_4]^{2-}$.^{18b} In fact, the Co-S_{br} bond in the cluster is virtually the same length as Co-S_{t} in $[\text{Co}(\text{SPh})_4]^{2-}$. Our interpretation is that the reduced ability of bridging PhS^- in the cluster to neutralize the Lewis acidity of the cobalt center, compared with the ability of nonbridging PhS^- in $[\text{Co}(\text{SPh})_4]^{2-}$, causes greater charge neutralization and bond shortening in each Co-S_{t} bond of the cluster. An alternative statement of this interpretation is that in a cluster formulated $[\text{Co}_4(\text{SPh})_{10}]^{2-}$ the negative charge density per thiolate ligand must be less than in $[\text{Co}(\text{SPh})_4]^{2-}$; this results in closer approach between metal and ligand in the cluster to achieve the same degree of neutralization of metal positive charge.

In addition to these conclusions about structure, we can make several observations on the reactivity of this prototype cluster.

1. Oxidation⁵⁰ by dioxygen in nonaqueous solution occurs more rapidly for the cluster complexes than for $[\text{Co}(\text{SPh})_4]^{2-}$.

2. Four observations reflect the thermodynamic stability (with respect to substitution) of the benzenethiolate bridge in $[(\mu\text{-SPh})_6(\text{CoSPh})_4]^{2-}$ and $[(\mu\text{-SPh})_6(\text{CoSPh})_2(\text{CoCl})_2]^{2-}$: (a) small proportions of PhS^- added to $[\text{CoBr}_4]^{2-}$ form PhS^- -bridged species rather than monometallic complexes such as $[\text{PhSCoBr}_3]^{2-}$; (b) halide ion (Cl^- , Br^-) displaces terminal but not bridging PhS^- in the cluster; (c) considerable excesses of PhS^- ($\text{PhS}^-/\text{Co(II)} > 6$) are required to convert the

bridged complexes to $[\text{Co}(\text{SPh})_4]^{2-}$; (d) very large excesses of the donor solvents pyridine and Me_2SO are required to disrupt benzenethiolate bridges. This general thermodynamic stability of the $\{(\mu\text{-SPh})_6\text{Co}_4\}$ core resembles the substitutional integrity of the $\{\text{Fe}_4\text{S}_4\}$ and $\{\text{Fe}_2\text{S}_2\}$ cores described by Holm et al.⁵¹

3. Co(II) -benzenethiolate coordination is not hydrolytically unstable, but protic solvents, including water, strongly influence the coordination equilibria.

Acknowledgments. The assistance of Dr. J. C. Calabrese with the X-ray data collection and computing, and of Dr. J. Kleppinger with the magnetic measurements, is gratefully acknowledged. This research was supported by the National Science Foundation and the Australian Research Grants Committee.

Supplementary Material Available: Powder diffraction data, Table IS; F_{obsd} and F_{calcd} for $(\text{Me}_4\text{N})_2[(\mu\text{-SPh})_6(\text{CoSPh})_4]$, Table IIS; refined atom parameters, Table IIIS; hydrogen atom coordinates, Table IVS; summary of thermal motion, Table VS; interion distances, Table VIS (26 pages). Ordering information is given on any current masthead page.

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- (36) Other possible complexes are $[\text{Co}_n(\text{SPh})_{3n}]^{n-}$.
- (37) This experiment included solutions with $\text{PhS}^-/\text{CoBr}_4^{2-}$ ratios at close intervals; representative key spectra only are drawn in Figure 5.
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A Calorimetric Titration Study of the Reaction of Several Organic Ammonium Cations with 18-Crown-6 in Methanol^{1a}

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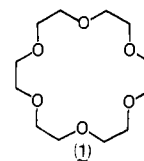
Abstract: Log K , ΔH , and $T\Delta S$ were determined by titration calorimetry for reaction of over 30 organic ammonium cations (guests) with 18-crown-6 (host) in methanol at 25 °C. The number of hydrogen atoms on the ammonium group available for bonding to the crown ether was the most important factor in determining complex stability. Steric hindrance of the approach of the guest to the host was also influential. Electronic factors showed no significant effect. Separation of charges on diammonium cations of varying chain length also had little effect on complex stabilities.

Introduction

Host-guest interaction has been termed² "a complementary stereoelectronic arrangement of binding sites in host and guest". In the chemical sense the host is usually an organic molecule containing specific receptor sites while the guest is normally a metal or organic cation. Host-guest interactions have recognized importance in many biological processes, including enzyme catalysis and inhibition, antibody-antigen interactions, and membrane transport. A particularly fruitful field of organic synthesis during the past several years has been the design and preparation of macrocyclic molecules of the cyclic polyether type with the intent to mimic certain biological host-guest interactions.²⁻¹¹ Cram and his co-workers⁴ as well as others^{6,7} have incorporated chiral barriers in host compounds which make possible "chiral recognition" between guest and host. By this means, the total optical resolution of host by guest and of guest by host has been accomplished.⁴ Several workers have reported the attachment of organic ammonium¹³ or sulfonium⁹ groups to hosts which are analogues of 18-crown-6 with the subsequent enhancement of a reaction between host and guest components away from the site of primary binding. Because of their ability to differentiate among inorganic cations and organic stereoisomers, these "functionalized crown ethers" have been suggested as model compounds for the investigation of mechanisms of enzyme action. Indeed Chao and Cram¹³ have reported a system which mimics transacylation.

We have attempted to define and investigate the parameters which determine the magnitude of log K for the formation of host-guest complexes from their constituents. Our earlier

studies have involved primarily metal cation guests. However, we have now embarked on a systematic thermodynamic study of these host-guest parameters as they apply to organic cations.¹⁴ Host parameters of importance in binding both metals and organic ammonium cations include cavity size, donor atom number and type, ring number and type, ring substituents, and ring conformation. Guest parameters for organic ammonium cations differ from those of metal cations because of the different binding mechanisms involved for the two types of guest. Metal cations are sequestered within the macrocyclic ring, whereas ammonium cations hydrogen bond to the ring donor atoms. Thus, guest parameters significant to organic ammonium cation binding include (1) number of hydrogen atoms available for hydrogen bonding, (2) steric hindrance of host-guest approach by the guest organic moiety, (3) electronic effects, and (4) separation of charges on diammonium cations of the type $^+\text{H}_3\text{N}(\text{CH}_2)_n\text{NH}_3^+$. In this paper we illustrate the effect of these four guest parameters on log K , ΔH , and $T\Delta S$ data for the reaction in methanol of over 30 organic ammonium cation guests with 18-crown-6 host (1).



The importance to host-guest interaction of the guest and host parameters listed has been alluded to previously by other workers. Log K values for the interaction of several derivatives