bulky methylene groups (*i.e.*, the van der Waals radius of a methylene group is 2.0 Å), the possible orientations of the S–CH_2 bonds relative to the $Co_3\{(S)_5(CO)\}(CO)_3$ fragment are such that (1) no two S–CH_2 bonds can both be equatorial when the sulfur atoms are located directly above and below the tricobalt plane, and (2) only one axial S–CH_2 bond can be accommodated on a given side of the tricobalt plane. These steric requirements are satisfied for five but not six S–CH_2 bonds. Hence, the replacement of the unique bridging carbonyl group with a sixth SC_2H_5 group would result in a destabilization of the trimeric molecular complex. These same steric factors also apply to the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ fragment contained in the pentameric and hexameric cobalt carbonyl complexes; the resulting effect on the chemical reactivity of these complexes will be discussed elsewhere.[29]

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Organometallic Sulfur Complexes. XI. Preparation and Structure of a Pentameric Mercaptocobalt Carbonyl Complex, $Co_5(CO)_{10}(SC_2H_5)_5$[1]

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Abstract: The reaction of $Co_2(CO)_8$ with ethyl mercaptan has resulted in the synthesis of a new pentanuclear metal complex, $Co_5(CO)_{10}(SC_2H_5)_5$. This complex has been characterized by physical means including a three-dimensional X-ray analysis which not only unambiguously provided the correct formula but also revealed the first known example of a thioalkoxide ligand bonded to three transition metal atoms through utilization of five valence electrons. The molecular structure consists of a basic $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue which is coordinated by two of its bridging thioalkyl ligands to the cobalt atoms of a $Co_2(CO)_5(SC_2H_5)$ fragment. The sulfur–(carbonyl carbon) polyhedron of the trimeric residue closely resembles that of the molecular complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$. The configuration of the $Co_2(CO)_5(S)_3$ fragment (*i.e.*, including the two triply bridging sulfur atoms but excluding the ethyl groups) in $Co_5(CO)_{10}(SC_2H_5)_5$ is stereochemically similar to that of the diamagnetic molecular complexes $Co_2(CO)_8$ and $[C_2H_5SFe(CO)_3]_2$. A detailed comparison of the molecular parameters of $Co_5(CO)_{10}(SC_2H_5)_5$ with those in two related thiomercaptocobalt carbonyl complexes, $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ and $SCo_6(CO)_{11}(SC_2H_5)_4$, is given. A qualitative description of the bonding in $Co_5(CO)_{10}(SC_2H_5)_5$ is presented. In direct contrast to most metal cluster halide and oxide systems (which contain no electrons in antibonding metal symmetry orbitals), the application of the Cotton–Haas metal atom cluster MO model shows that these and other metal cluster carbonyl systems contain electrons in antibonding metal symmetry orbitals. The stability of the mercaptocobalt carbonyl systems is apparently achieved by the use of empty π^* carbonyl and d_π sulfur orbitals to delocalize charge density from the metal atom cluster. Crystals of $Co_5(CO)_{10}(SC_2H_5)_5$ contain eight molecules in an orthorhombic cell of symmetry D_{2h}^{15}-Pbca and of dimensions $a = 18.34$, $b = 17.75$, $c = 20.43$ Å. The structure has been refined by full-matrix least-squares techniques to a final unweighted R_1 value of 10.5% for 1355 observed photographic data.

This work on the preparation and characterization of the pentanuclear cobalt complex, $Co_5(CO)_{10}(SC_2H_5)_5$, is an outgrowth of our attempt to prepare another complex for the purpose of demonstrating the importance of metal–metal bonds on molecular geometries of polynuclear metal carbonyl derivatives in which the metals are also linked by bridging ligands. X-Ray examinations of $[C_2H_5SFe(CO)_3]_2$,[2] $[SFe(CO)_3]_2$,[3] and $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$[4] showed for each of these diamagnetic molecular complexes containing a dinuclear iron carbonyl sulfur moiety a similarly shaped $S_2Fe_2(CO)_6$ conformation whose geometry possessing sharply acute Fe–S–Fe bridged angles of ~69° is in complete accord with a previous proposal[5] of a "bent" iron–iron bond. The presumed absence[6] of a metal–

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[1] Previous paper in this series: C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3960 (1968).

[2] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

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[4] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965).

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[6] In a dimeric molecular entity of formula $[RSCo(CO)_3]_2$ containing two cobalt-bridged mercapto ligands, a closed-shell electronic ground state corresponding to the so-called noble-gas configuration is achieved for each cobalt atom without the necessity of a cobalt–cobalt bond.

metal interaction in the reported isoelectronic cobalt analogs $[RSCo(CO)_3]_2$ (R = C_2H_5, C_6H_5)[7] led us to attempt a synthesis of the ethylmercapto derivative which instead resulted in the isolation of the first known example of a pentameric cobalt carbonyl complex (presented here). Later, our attempted preparation of the corresponding dimeric phenylthiocobalt carbonyl analog unexpectedly yielded a compound characterized by an X-ray structural determination[8] as $SCo_3(CO)_9$. This latter complex was first synthesized by Bor, Markó, and coworkers[9–11] who have prepared and systematically characterized a large number of unusual polymeric cobalt carbonyl sulfur complexes.[9–17]

Experimental Section

Preparation and Properties. The compound was prepared by the reaction of ethyl mercaptan and dicobalt octacarbonyl according to the procedure outlined by Hieber and Spacu.[7] Freshly prepared $Co_2(CO)_8$[18] (1.0 g) and ethyl mercaptan (3 ml) were allowed to react at 0° *without solvent* for 24 hr under a continuous slow stream of nitrogen gas in a small flask. After removal of the reaction contents through a glass-fiber-packed outlet at the bottom of the flask, the residue was washed three times with 2–4 ml of cold petroleum ether (bp 60–68°) to remove readily soluble, unreacted materials. The remaining product was dried at room temperature for at least 1 hr *in vacuo* to assure the complete removal of evaporating materials as well as unreacted materials. At this stage the yield was approximately 0.5 g. Although the compound can be recrystallized from a petroleum ether–benzene (4:1 ratio) mixture, the solution tends to decompose with the separation out of a brown amorphous material. Hence, the samples used for elemental analysis were those which were not recrystallized.

Anal. Calcd for $CoSC_4H_5O_2$: Co, 33.47; S, 18.21; C, 27.28; H, 2.86; O, 18.17. Found:[19] Co, 33.67; S, 18.13; C, 27.11; H, 2.89; O, 18.20. Upon being heated, the compound decomposes to yield a brown residue which is insoluble in organic solvents. The infrared spectrum in CCl_4 taken both with a Perkin-Elmer Model 112 single-beam, double-pass spectrometer with a calcium fluoride prism and with a Perkin-Elmer Model 421 grating spectrometer with NaCl plates shows five strong absorption bands in the terminal carbonyl stretching region at 2005, 2022, 2060, 2034, and 2083 cm^{-1} and three bands in the bridging carbonyl region at 1818 (s), 1839 (m), and 1793 (m) cm^{-1} (numbers are given in decreasing order of band intensities). Other spectral peaks recorded on the Perkin-Elmer Model 421 spectrometer include those at 2950 (w), 2920 (w), 2860 (vw), 2310 (vw), 1960 (vw), 1450 (w), 1425 (vw), 1373 (w), 1250 (w), 1041 (vw), 1023 (vs), and 962 (vw) cm^{-1}.

Magnetic susceptibility measurements[20] made by the Gouy method showed a bulk sample of $Co_5(CO)_{10}(SC_2H_5)_5$ to be paramagnetic. The susceptibility is not field dependent; after correction for diamagnetic effects, values of 1.72 ± 0.01 and 1.47 ± 0.04 BM were obtained at 296 and 82°K, respectively. The discrepancy between these low magnetic moments (normally equivalent at room temperature to one unpaired electron per molecular unit) and the value expected for two unpaired electrons per molecule (on the basis that the entire $Co_5(CO)_{10}(SC_2H_5)_5$ molecule contains two electrons in excess of the "krypton" closed-shell electronic configuration for each of the five cobalt atoms) was not understood at the time these magnetic studies were carried out. However, recent magnetic measurements[21] by the Faraday method in the solid state and by nuclear magnetic resonance in solution[22] have established the structurally and electronically related $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ and $SCo_6(CO)_{11}(SC_2H_5)_4$ molecules (*vide infra*) as being diamagnetic and in the process have provided a reasonable explanation that the observed magnetism of the sample of rather unstable $Co_5(CO)_{10}(SC_2H_5)_5$ is due to paramagnetic impurities. Considerable difficulty was encountered in the removal of trace amounts of the strongly paramagnetic cobalt oxide and other decomposition products from samples of the trinuclear and hexanuclear cobalt complexes; repeated recrystallizations and magnetic measurements under an "inert gas" atmosphere were necessary in order to ascertain the diamagnetic behavior of each of these two compounds. Since such extreme precautions were not taken for the pentanuclear cobalt complex, we believe that it is safe to assume that the $Co_5(CO)_{10}(SC_2H_5)_5$ molecule also contains no unpaired electrons.

Single-Crystal X-Ray Data. A tiny brownish-black crystal of dimensions 0.15 × 0.21 × 0.31 mm was selected for collecting both Weissenberg and precession data. This crystal was mounted inside a thin-walled glass capillary about the 0.31-mm direction (corresponding to the *b* rotation axis). The lattice parameters were determined from *hk*0 and 0*kl* precession photographs which were calibrated by the superimposed zero-level diffraction pattern of a NaCl crystal on the same film. Multiple-film equiinclination Weissenberg photographs were obtained for reciprocal levels *h*0*l* through *h*15*l* with Zr-filtered Mo Kα radiation; a total of 1323 independent diffraction maxima was recorded. Timed-exposure 0*kl* and *hk*0 precession data, acquired with Zr-filtered Mo Kα radiation, were used to place the Weissenberg reciprocal layers onto an initial single relative scale. An additional 32 reflections obtained from the precession data provided a total of 1355 independent *hkl* diffraction maxima. The intensities of all reflections were visually estimated with a calibrated set of intensities and then corrected for the usual Lorentz-polarization effects. Since the estimated absorption parameter, μR, was less than 0.3, absorption corrections were neglected.

Results

Unit Cell and Space Group. Crystals of $Co_5(CO)_{10}(SC_2H_5)_5$ (mol wt, 880.4) are orthorhombic with lattice parameters $a = 18.34 \pm 0.02$ Å, $b = 17.75 \pm 0.02$ Å, $c = 20.43 \pm 0.025$ Å; volume of unit cell = 6651 Å^3; $\rho_{obsd} = 1.67$ g cm^{-3} (by flotation) *vs.* $\rho_{calcd} = 1.76$ g cm^{-3} for eight pentameric formula species per unit cell. The total number of electrons per unit cell, *F*(000), is 3520. Systematic extinctions are $\{0kl\}$ for *k* odd, $\{h0l\}$ for *l* odd, and $\{hk0\}$ for *h* odd. The centrosymmetric space group Pbca (D_{2h}^{15}, no. 61),[23] uniquely defined by these absences, was confirmed by satisfactory refinement of the solved structure.

Determination of the Structure. At the beginning of this structural analysis, the molecular formula of the compound was not known. The crystallographic

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(17) It is noteworthy that besides our unsuccessful efforts to prepare $[RSCo(CO)_3]_2$, Bor, Markó, and coworkers[9–16] also failed to isolate this dimeric species among their many products. In fact, to our knowledge no dimeric complexes comprised of two five-coordinated metal atoms containing three monodentate terminal ligands per metal atom, two bridging ligands, but no metal–metal bond (*e.g.*, $[XCo(CO)_3]_2$ where X = halogen, R_2P, RS, or any other three-electron donor) have been conclusively shown to exist.

(18) *Cf.* W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall Inc., Englewood Cliffs, N. J., 1960, p 168.

(19) Alfred Bernhardt Mikroanalytisches Laboratorium in Max-Planck Institut für Kohlenforschung, 433 Mulheim (Rohr), Germany. Each value represents the average of three samples for each of which a double analysis was carried out.

(20) We wish to thank Mrs. Megan Thompson and Professor E. M. Larsen of the University of Wisconsin for carrying out this measurement for us on their Gouy balance.

(21) We are indebted to Mr. Alan Foust and Dr. Heinrich Vahrenkamp of the Structural Chemistry Group at the University of Wisconsin for performing these investigations.

(22) *Cf.* H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.* (Amsterdam), 1, 208 (1964), and references cited therein.

(23) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 150.

calculations based on the observed density and unit cell dimensions as well as the compound's infrared spectrum which contained bridging carbonyl bands showed that the initially assumed dimeric formula was incorrect. Even by the time a three-dimensional Patterson function[24] was computed from the corrected intensity data, the empirical formula of $Co(CO)_2(SC_2H_5)$ still was not available. Furthermore, the actual presence of 40 cobalt and 40 sulfur atoms in the unit cell (of which five cobalt and five sulfur atoms are crystallographically independent) greatly complicated the interpretation of the Patterson vector map based primarily on the relatively heavy cobalt and sulfur atoms. After several wrong trial models were selected, which from least-squares analysis and Fourier maps eventually led to uninterpretable results, a trial model involving a self-consistent set of coordinates for four cobalt atoms was found, of which three cobalt atoms formed a triangular array. A block-diagonal least-squares isotropic refinement[25] of these atomic parameters was then carried out in which an initial temperature factor of 2.0 Å^2 was arbitrarily assigned for each cobalt atom. After one cycle the conventional unweighted R_1 value stood at 41.0%. A three-dimensional Fourier synthesis[24] phased on these four cobalt atoms was then computed. This first approximation to the electron density function revealed six relatively large new peaks which were interpreted as one cobalt and five sulfur atoms. Two more cycles of block-diagonal least-squares refinement of atomic positional and isotropic thermal parameters for the cobalt and sulfur atoms (in which a thermal value of 3.0 Å^2 was assumed initially for each sulfur atom) markedly lowered the R_1 value to 23.2%. A second Fourier map phased on the refined parameters of the five cobalt and five sulfur atoms was computed next, and the assignment of 25 new peaks as two bridging carbonyl groups, seven terminal carbonyl groups, and seven ethyl carbon atoms was made. The introduction of these light carbon and oxygen atoms into the least-squares refinement decreased R_1 to 15.5%. A third Fourier map phased on the resolved 35 atoms unambiguously magnified five more peaks which were identified as one bridging carbonyl group and three ethyl carbon atoms. A block-diagonal isotropic least-squares refinement of all 40 atoms resulted in an R_1 value of 11.3%, after which a full-matrix least-squares program[26] was employed for the final refinement. The isotropic refinement with individual temperature factors and 18 reciprocal layer scale factors (whose final values ranged from 0.063 to 0.081 except for one value at 0.100) yielded after three cycles discrepancy factors of $R_1 = 10.5\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 8.4\%$; a value of 1.015 for the error of fit function, defined as $[\Sigma w||F_o| - |F_c||^2/(m - n)]^{1/2}$, was obtained. A three-dimensional difference Fourier map showed no anomalies; no attempt was made to identify the positive residual peaks as hydrogen atoms. All 40 independent nonhydrogen atoms were found to occupy the following general eightfold sets of positions (8c) of Pbca: $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, -z;\ -x, {}^1/_2 + y, {}^1/_2 - z;\ {}^1/_2 - x, -y, {}^1/_2 + z)$.

Throughout the least-squares refinements, variable weights were assigned to the observed structure amplitudes of each layer as follows: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(\text{min})$, $\sqrt{w} = 1.25I_o^2/F_oI_o(\text{min})^2$ if $I_o < 4I_o(\text{min})$. Scattering factors used for cobalt were those of Thomas and Umeda,[27] for sulfur those of Dawson,[28] and for carbon and oxygen those of Berghuis, *et al.*[29] The atomic positional and thermal parameters from the last cycle of least-squares refinement are given in Table I.[30]

Table I. Atomic Parameters with Standard Deviations

Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
Co_1	0.0366 (3)	0.1903 (2)	0.0281 (2)	1.8 (1)
Co_2	0.1652 (3)	0.2010 (2)	0.0726 (2)	2.0 (1)
Co_3	0.1119 (3)	0.3044 (3)	0.0066 (2)	1.8 (1)
Co_4	0.0026 (3)	0.2321 (2)	0.2198 (3)	1.8 (2)
Co_5	−0.0495 (3)	0.3349 (2)	0.1566 (3)	1.7 (1)
S_1	0.0649 (5)	0.1648 (5)	0.1386 (5)	2.0 (2)
S_2	−0.0040 (5)	0.3075 (4)	0.0516 (4)	2.0 (2)
S_3	0.1223 (6)	0.1017 (5)	0.0160 (6)	3.0 (3)
S_4	0.1593 (6)	0.3189 (5)	0.1104 (5)	2.7 (3)
S_5	−0.0943 (6)	0.2199 (5)	0.1563 (5)	2.9 (2)
C_1	−0.0400 (22)	0.1462 (19)	−0.0040 (19)	3.2 (10)
O_1	−0.0899 (19)	0.1163 (18)	−0.0200 (16)	7.8 (9)
C_2	0.2418 (25)	0.1660 (18)	0.1067 (19)	3.6 (10)
O_2	0.3026 (20)	0.1571 (17)	0.1239 (15)	8.2 (10)
C_3	0.1286 (22)	0.3646 (22)	−0.0406 (21)	5.0 (11)
O_3	0.1315 (16)	0.4211 (15)	−0.0788 (14)	6.6 (8)
C_4	−0.0183 (18)	0.1682 (17)	0.2808 (18)	2.0 (8)
O_4	−0.0293 (14)	0.1246 (13)	0.3241 (13)	4.5 (7)
C_5	0.0847 (23)	0.2688 (18)	0.2496 (19)	3.8 (10)
O_5	0.1413 (17)	0.2840 (13)	0.2692 (13)	6.3 (8)
C_6	−0.1311 (24)	0.3841 (21)	0.1479 (21)	4.7 (10)
O_6	−0.1849 (18)	0.4223 (15)	0.1498 (15)	6.5 (8)
C_7	0.0047 (27)	0.4048 (23)	0.1651 (24)	6.5 (12)
O_7	0.0439 (16)	0.4568 (14)	0.1739 (13)	4.8 (7)
C_8	0.0622 (24)	0.2400 (25)	−0.0465 (25)	6.6 (13)
O_8	0.0532 (14)	0.2323 (13)	−0.1056 (14)	4.7 (7)
C_9	0.1977 (17)	0.2524 (18)	−0.0071 (18)	2.2 (8)
O_9	0.2501 (14)	0.2458 (12)	−0.0437 (12)	3.8 (5)
C_{10}	−0.0443 (17)	0.3171 (15)	0.2458 (16)	1.7 (7)
O_{10}	−0.0656 (13)	0.3506 (12)	0.2956 (13)	4.1 (7)
C_{11}	0.0619 (21)	0.0666 (17)	0.1590 (20)	3.5 (9)
C_{12}	0.1195 (24)	0.0447 (19)	0.2127 (21)	5.2 (10)
C_{13}	−0.0808 (19)	0.3355 (17)	−0.0065 (17)	2.5 (9)
C_{14}	−0.0800 (19)	0.4193 (18)	−0.0171 (17)	2.4 (8)
C_{15}	0.1620 (20)	0.0905 (16)	−0.0664 (18)	2.7 (8)
C_{16}	0.1088 (31)	0.0510 (26)	−0.1095 (24)	7.9 (14)
C_{17}	0.2545 (23)	0.3659 (19)	0.1048 (19)	4.3 (10)
C_{18}	0.2386 (32)	0.4498 (24)	0.1020 (23)	8.2 (14)
C_{19}	−0.1815 (19)	0.2207 (18)	0.2055 (18)	4.0 (9)
C_{20}	−0.2028 (26)	0.1386 (24)	0.2078 (27)	8.6 (14)

Atom C_1 through O_7: terminal carbonyls
Atom C_8 through O_{10}: bridging carbonyls
Atom C_{11} through C_{20}: ethyl carbons

Interatomic distances and angles together with estimated standard deviations calculated from the full

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Table II. Intramolecular Distances (Å) with Standard Deviations

	Distance		Distance
A. $Co_3(CO)_5(SC_2H_5)_4$ Fragment (the *idealized* cobalt–carbonyl–sulfur part has a mirror plane which passes through Co_3, S_1, S_3, C_3, and O_3)			
Co_1–Co_2	2.535 (7)	Co_1–C_8	1.82 (5)
		Co_2–C_9	1.96 (4)
Co_1–Co_3	2.491 (6)		
Co_2–Co_3	2.487 (7)		1.89 (av)
	2.485 (av)	Co_3–C_8	1.82 (5)
		Co_3–C_9	1.84 (3)
Co_1–S_3	2.237 (11)		
Co_2–S_3	2.251 (11)		1.83 (av)
	2.244 (av)	C_1–O_1	1.11 (4)
		C_2–O_2	1.18 (4)
		C_3–O_3	1.27 (4)
Co_1–S_1	2.360 (11)		
Co_2–S_1	2.369 (11)		1.19 (av)
	2.365 (av)	C_8–O_8	1.23 (4)
		C_9–O_9	1.22 (3)
Co_1–S_2	2.261 (9)		
Co_2–S_4	2.233 (9)		1.23 (av)
	2.247 (av)	S_1–C_{11}	1.79 (3)
		S_2–C_{13}	1.91 (3)
Co_3–S_2	2.317 (11)	S_3–C_{15}	1.85 (4)
Co_3–S_4	2.306 (11)	S_4–C_{17}	1.94 (4)
	2.312 (av)		1.87 (av)
		C_{11}–C_{12}	1.57 (5)
Co_1–C_1	1.74 (4)	C_{13}–C_{14}	1.50 (4)
Co_2–C_2	1.69 (5)	C_{15}–C_{16}	1.49 (5)
Co_3–C_3	1.47 (4)	C_{17}–C_{18}	1.52 (5)
	1.63 (av)		1.52 (av)
B. $Co_2(CO)_5(SC_2H_5)S_2$ Fragment (the *idealized* cobalt–carbonyl–sulfur part has a mirror plane which passes through S_5, C_{10}, and O_{10})			
Co_4–Co_5	2.430 (6)	Co_4–C_{10}	1.82 (3)
		Co_5–C_{10}	1.85 (3)
Co_4–S_5	2.211 (11)		
Co_5–S_5	2.201 (10)		1.84 (av)
	2.206 (av)		
		C_4–O_4	1.19 (3)
Co_4–S_1	2.341 (11)	C_5–O_5	1.14 (4)
Co_5–S_2	2.353 (11)	C_6–O_6	1.20 (4)
		C_7–O_7	1.19 (4)
	2.347 (av)		
			1.18 (av)
Co_4–C_4	1.73 (4)		
Co_5–C_6	1.74 (5)	C_{10}–O_{10}	1.24 (3)
Co_4–C_5	1.75 (4)		
Co_5–C_7	1.60 (5)	S_5–C_{19}	1.89 (4)
	1.71 (av)	C_{19}–C_{20}	1.51 (5)
C. Nonbonding C–C and S–C Distances Corresponding to Edges of Polyhedral Fragment in $Co_5(CO)_{10}(SC_2H_5)_5$			
$S_3\cdots C_8$	2.98 (5)	$S_1\cdots S_5$	3.101 (15)
$S_3\cdots C_9$	3.05 (3)	$S_2\cdots S_5$	3.121 (13)
$C_8\cdots C_9$	2.62 (6)	$S_4\cdots Co_5$	3.953 (12)
$S_3\cdots C_1$	3.11 (5)	$S_4\cdots Co_4$	3.952 (11)
$S_3\cdots C_2$	3.09 (5)	$S_1\cdots C_4$	3.28 (4)
$C_8\cdots C_1$	2.65 (6)	$S_2\cdots C_6$	3.34 (5)
$C_9\cdots C_2$	2.90 (5)	$S_1\cdots C_5$	2.95 (4)
$C_8\cdots C_3$	2.53 (6)	$S_2\cdots C_7$	2.90 (5)
$C_9\cdots C_3$	2.46 (5)	$S_5\cdots C_4$	3.04 (4)
$S_3\cdots S_1$	2.939 (15)	$S_5\cdots C_6$	3.96 (3)
$C_8\cdots S_2$	2.63 (5)	$S_4\cdots C_5$	3.28 (4)
$C_9\cdots S_4$	2.77 (4)	$S_4\cdots C_7$	3.41 (5)
$S_1\cdots C_1$	3.51 (5)	$C_4\cdots C_5$	2.68 (5)
$S_1\cdots C_2$	3.31 (5)	$C_6\cdots C_7$	2.54 (7)
$S_2\cdots C_1$	3.15 (5)	$C_4\cdots C_{10}$	2.78 (4)
$S_4\cdots C_2$	3.11 (4)	$C_6\cdots C_{10}$	2.82 (6)
$S_2\cdots C_3$	3.24 (5)	$C_5\cdots C_{10}$	2.52 (5)
$S_4\cdots C_3$	3.24 (5)	$C_7\cdots C_{10}$	2.44 (5)
$S_1\cdots S_2$	3.342 (12)	$S_5\cdots C_{10}$	2.68 (3)
$S_1\cdots S_4$	3.286 (13)	$S_4\cdots C_{10}$	4.65 (4)
$S_2\cdots S_4$	3.232 (15)		

inverse matrix[31] are given in Tables II and III, respectively. Table IV presents the "best" molecular planes formed by specified atoms and the distances of these and other atoms from these planes as calculated by a weighted least-squares method with the Smith program.[32]

Discussion

The crystalline structure is composed of discrete pentameric molecules (Figure 1) with normal intermolecular contacts. Each molecular unit of $Co_5(CO)_{10}(SC_2H_5)_5$ consists of a basic $Co_3X_6Y_3$ polyhedral residue (where X_6 represents four SC_2H_5 and two CO bridging groups and Y_3 designates three CO terminal groups) which is coordinated by two of its bridging mercapto sulfur atoms to the cobalt atoms of a $Co_2(CO)_5(SC_2H_5)$ fragment.

The sulfur–(carbonyl carbon) polyhedral framework of the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue in $Co_5(CO)_{10}(SC_2H_5)_5$ may be described as a tricapped trigonal prism of four sulfur and five carbonyl carbon ligands encompassing a triangular cobalt atom cluster system. This atomic ligand arrangement not only is essentially identical with that in the same residue found in $SCo_6(CO)_{11}(SC_2H_5)_4$[33] but also closely corresponds to the sulfur–(carbonyl carbon) geometry in the molecular complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$.[1] The substitution in this trimeric complex of a bridging carbonyl group in place of a bridging mercapto group to give the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ common building block found in the pentameric and hexameric cobalt complexes provides an explanation (details are given elsewhere[1]) for the observed isosceles triangle of cobalt atoms in this latter residue possessing two shorter Co–Co distances and one longer Co–Co distance compared to one shorter and two longer Co–Co distances for the isosceles triangle in the trinuclear cobalt complex. The approximate C_s-m symmetry possessed by the $Co_3\{(S)_4(CO)_2\}(CO)_3$ fragment (*i.e.*, without the ethyl groups) in $Co_5(CO)_{10}(SC_2H_5)_5$ is revealed both from the related molecular parameters (Tables II and III) and from the perpendicular distances of corresponding pairs of atoms from the plane through Co_3, S_1, and S_3 (Table IVg). Since the geometrical parameters of this tricobalt fragment in $Co_5(CO)_{10}(SC_2H_5)_5$ are compared with those of the trimeric complex in the previous paper,[1] the stereochemical implications of this new polyhedral metal cluster system are not reproduced here.

The equatorial attachment of two bridging mercapto sulfur atoms in the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue to the two chemically equivalent cobalt atoms (Co_4 and Co_5) of the $Co_2(CO)_5(SC_2H_5)$ fragment gives rise to an essentially identical square-pyramidal carbon–sulfur environment for each of these latter two cobalt atoms. The resulting geometry is not unlike that found about each metal atom in $Co_2(CO)_8$,[34] Co_2-

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(31) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(32) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

(33) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 90, 3977 (1968).

(34) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, 17, 732 (1964).

Table III. Bond Angles with Standard Deviations (in Degrees)

A. $Co_3(CO)_5(SC_2H_5)_4$ Fragment (the *idealized* Co–CO–S part has a mirror plane which passes through Co_3, S_1, S_3, C_3, and O_3)

M–M–M	
$Co_1–Co_2–Co_3$	59.6 (2)
$Co_2–Co_1–Co_3$	59.1 (2)
	59.4 (av)
$Co_1–Co_3–Co_2$	61.3 (2)
M–S–M	
$Co_1–S_3–Co_2$	68.8 (3)
$Co_1–S_1–Co_2$	64.8 (3)
$Co_1–S_2–Co_3$	65.9 (3)
$Co_2–S_4–Co_3$	66.2 (3)
	66.1 (av)
S–M–S	
$S_3–Co_1–S_1$	79.4 (4)
$S_3–Co_2–S_1$	79.0 (4)
	79.2 (av)
$S_1–Co_1–S_2$	92.6 (4)
$S_1–Co_2–S_4$	91.1 (4)
	91.9 (av)
$S_2–Co_3–S_4$	88.7 (4)
S–M–M	
$S_3–Co_1–Co_2$	55.9 (3)
$S_3–Co_2–Co_1$	55.3 (3)
	55.6 (av)
$S_1–Co_1–Co_2$	57.8 (3)
$S_1–Co_2–Co_1$	57.4 (3)
	57.6 (av)
$S_2–Co_1–Co_3$	58.1 (3)
$S_4–Co_2–Co_3$	58.3 (3)
	58.2 (av)
$S_2–Co_3–Co_1$	56.0 (2)
$S_4–Co_3–Co_2$	55.5 (3)
	55.8 (av)

$S_3–Co_1–Co_3$	99.4 (3)
$S_3–Co_2–Co_3$	99.4 (3)
	99.4 (av)
$S_1–Co_1–Co_3$	101.7 (3)
$S_1–Co_2–Co_3$	101.8 (3)
	101.8 (av)
$S_2–Co_1–Co_2$	99.3 (3)
$S_4–Co_2–Co_1$	98.6 (3)
	99.0 (av)
$S_2–Co_3–Co_2$	99.4 (3)
$S_4–Co_3–Co_1$	97.9 (3)
	98.7 (av)
S–M–CO	
$S_3–Co_1–C_1$	102.1 (11)
$S_3–Co_2–C_2$	102.4 (12)
	102.3 (av)
$S_1–Co_1–C_1$	116.9 (12)
$S_1–Co_2–C_2$	108.2 (13)
	112.6 (av)
$S_2–Co_1–C_1$	103.2 (11)
$S_4–Co_2–C_2$	104.1 (12)
	103.7 (av)
$S_2–Co_3–C_3$	115.7 (15)
$S_4–Co_3–C_3$	116.4 (15)
	116.1 (av)
$S_1–Co_1–C_8$	146.7 (15)
$S_1–Co_2–C_9$	146.6 (10)
	146.7 (av)
$S_3–Co_1–C_8$	93.8 (14)
$S_3–Co_2–C_9$	92.5 (10)
	93.2 (av)

$S_2–Co_1–C_8$	79.5 (14)
$S_4–Co_2–C_9$	82.3 (10)
	80.9 (av)
$S_2–Co_3–C_8$	78.0 (14)
$S_4–Co_3–C_9$	82.8 (11)
	80.4 (av)
$S_2–Co_3–C_9$	148.7 (11)
$S_4–Co_3–C_8$	143.8 (11)
	146.3 (av)
M–M–CO	
$Co_1–Co_2–C_2$	153.6 (12)
$Co_2–Co_1–C_1$	157.2 (11)
	155.4 (av)
$Co_2–Co_3–C_3$	145.2 (15)
$Co_2–Co_3–C_3$	144.4 (16)
	144.8 (av)
$Co_3–Co_1–C_1$	138.5 (11)
$Co_3–Co_2–C_2$	145.7 (12)
	142.1 (av)
$Co_1–Co_3–C_8$	46.9 (16)
$Co_2–Co_3–C_9$	51.4 (11)
	49.2 (av)
$Co_3–Co_1–C_8$	46.9 (15)
$Co_3–Co_2–C_9$	47.4 (10)
	47.2 (av)
M–CO–M	
$Co_1–C_8–Co_3$	86.2 (22)
$Co_2–C_9–Co_3$	81.2 (15)
	83.7 (av)
OC–M–CO	
$C_1–Co_1–C_8$	96.3 (19)
$C_2–Co_2–C_9$	105.1 (16)
	100.7 (av)

$C_3–Co_3–C_8$	99.7 (20)
$C_3–Co_3–C_9$	95.0 (19)
	97.4 (av)
$C_8–Co_3–C_9$	91.2 (17)
M–C–O	
$Co_1–C_1–O_1$	174.9 (39)
$Co_2–C_2–O_2$	163.6 (34)
$Co_3–C_3–O_3$	169.6 (36)
	169.4 (av)
$Co_2–C_8–O_8$	137.3 (38)
$Co_2–C_9–O_9$	134.6 (25)
$Co_3–C_8–O_8$	136.5 (39)
$Co_3–C_9–O_9$	144.1 (28)
	138.1 (av)
$M–S–CH_2$	
$Co_1–S_1–C_{11}$	113.6 (14)
$Co_2–S_1–C_{11}$	114.8 (13)
	114.2 (av)
$Co_1–S_3–C_{15}$	117.0 (11)
$Co_2–S_3–C_{15}$	114.5 (12)
	115.8 (av)
$Co_1–S_2–C_{13}$	110.5 (10)
$Co_2–S_4–C_{17}$	109.8 (12)
	110.2 (av)
$Co_3–S_2–C_{13}$	115.9 (11)
$Co_3–S_4–C_{17}$	109.4 (12)
	112.7 (av)
$S–CH_2–CH_3$	
$S_1–C_{11}–C_{12}$	112.4 (24)
$S_2–C_{13}–C_{14}$	109.8 (24)
$S_3–C_{15}–C_{16}$	109.3 (29)
$S_4–C_{17}–C_{18}$	104.5 (30)
	109.0 (av)

B. $Co_2(CO)_5(SC_2H_5)S_2$ Fragment (the *idealized* Co–CO–S part has a mirror plane which passes through S_5, C_{10}, and O_{10})

M–S–M	
$Co_4–S_5–Co_5$	66.8 (3)
S–M–S	
$S_1–Co_4–S_5$	85.9 (4)
$S_2–Co_5–S_5$	86.5 (4)
	86.2 (av)
S–M–M	
$S_5–Co_4–Co_5$	56.4 (3)
$S_5–Co_5–Co_4$	56.8 (3)
	56.6 (av)
$S_1–Co_4–Co_5$	101.5 (3)
$S_2–Co_5–Co_4$	100.9 (3)
	101.2 (av)
S–M–CO	
$S_1–Co_4–C_4$	106.6 (11)
$S_2–Co_5–C_6$	108.4 (15)
	107.5 (av)
$S_1–Co_4–C_5$	90.9 (12)
$S_2–Co_5–C_7$	92.2 (18)
	91.6 (av)

$S_5–Co_4–C_4$	100.4 (11)
$S_5–Co_5–C_6$	98.3 (12)
	99.4 (av)
$S_5–Co_4–C_5$	158.8 (12)
$S_5–Co_5–C_7$	162.3 (16)
	160.6 (av)
$S_1–Co_4–C_{10}$	149.6 (10)
$S_2–Co_5–C_{10}$	147.6 (10)
	148.6 (av)
$S_5–Co_4–C_{10}$	82.7 (10)
$S_5–Co_5–C_{10}$	82.2 (9)
	82.5 (av)
M–M–CO	
$Co_4–Co_5–C_6$	140.2 (14)
$Co_5–Co_4–C_4$	142.0 (11)
	141.1 (av)
M–M–CO	
$Co_4–Co_5–C_7$	106.4 (17)
$Co_5–Co_4–C_5$	104.1 (11)
	105.3 (av)

$Co_4–Co_5–C_{10}$	47.9 (9)
$Co_5–Co_4–C_{10}$	49.1 (10)
	48.5 (av)
M–CO–M	
$Co_4–C_{10}–Co_5$	83.0 (14)
OC–M–CO	
$C_4–Co_4–C_5$	100.6 (15)
$C_6–Co_5–C_7$	98.9 (20)
	99.8 (av)
$C_4–Co_4–C_{10}$	103.2 (13)
$C_6–Co_5–C_{10}$	103.3 (18)
	103.2 (av)
$C_5–Co_4–C_{10}$	89.7 (15)
$C_7–Co_5–C_{10}$	89.6 (20)
	89.7 (av)
M–C–O	
$Co_4–C_4–O_4$	176.8 (31)
$Co_4–C_5–O_5$	171.8 (31)
$Co_5–C_6–O_6$	171.2 (40)
$Co_5–C_7–O_7$	177.4 (46)
	174.3 (av)

$Co_4–C_{10}–O_{10}$	141.9 (24)
$Co_5–C_{10}–O_{10}$	135.2 (22)
	138.6 (av)
$M–S–CH_2$	
$Co_4–S_5–C_{19}$	111.6 (12)
$Co_5–S_5–C_{19}$	107.9 (11)
	109.8 (av)
$S–CH_2–CH_3$	
$C_5–C_{19}–C_{20}$	103.2 (28)

C. Bond Angles between Two Fragments

$Co_1–S_1–Co_4$	118.2 (4)
$Co_2–S_1–Co_4$	130.1 (4)
	124.2 (av)

$Co_1–S_2–Co_5$	120.0 (4)
$Co_3–S_2–Co_5$	133.8 (5)
	126.9 (av)

$Co_4–S_1–C_{11}$	108.4 (13)
$Co_5–S_2–C_{13}$	104.6 (11)
	106.5 (av)

Table IV. Equations of Best Weighted Least-Squares Planes and Distances of Atoms from These Planes[a]

(a) Plane through Co_1, Co_2, and Co_3

$0.355X - 0.423Y - 0.833Z + 1.670 = 0$

C_1	0.38	O_3	0.70	S_4	−1.57
O_1	0.55	S_3	1.43	S_2	−1.54
C_2	0.18	C_9	1.18	Co_4	−3.80
O_2	0.35	C_8	1.07	Co_5	−3.83
C_3	0.46	S_1	−1.51		

(b) Plane through S_2, S_4, C_8, and C_9

$0.110X + 0.896Y - 0.431Z - 4.419 = 0$

S_2	0.01	C_9	0.05	C_3	1.99
S_4	0.00	Co_3	0.59	O_3	3.23
C_8	−0.07				

(c) Plane through S_1, S_3, S_4, and C_9

$-0.784X + 0.383Y - 0.488Z + 1.212 = 0$

S_1	0.02	C_9	0.16	C_2	−2.20
S_3	−0.01	Co_2	−0.52	O_2	−3.31
S_4	−0.01				

(d) Plane through S_1, S_2, S_3, and C_8

$-0.849X - 0.511Y - 0.136Z + 2.880 = 0$

S_1	−0.01	C_8	−0.14	C_1	2.19
S_2	0.01	Co_1	0.51	O_1	3.28
S_3	0.01				

(e) Plane through S_1, S_2, and S_4

$0.364X - 0.407Y - 0.838Z + 3.130 = 0$

Co_1	1.52	S_3	2.94	Co_4	−2.29
Co_2	1.54	C_8	2.61	Co_5	−2.30
Co_3	1.57	C_9	2.75		

(f) Plane through Co_1, S_4, and S_5

$-0.392X + 0.764Y - 0.513Z - 2.023 = 0$

Co_2	−1.25	S_3	−1.69	O_9	−0.03
Co_3	1.23	S_8	1.27	C_{10}	0.02
Co_4	−1.19	C_{17}	0.01	O_{10}	0.11
Co_5	1.23	C_{19}	0.12	C_1	0.29
S_2	1.63	C_9	0.05	O_1	0.41
S_1	−1.71			Centroid (Co_1, Co_2, Co_3)	0.00

(g) Plane through Co_3, S_1, and S_3

$-0.930X - 0.068Y - 0.360Z + 2.327 = 0$

C_3	−0.01	S_2	1.64	O_1	3.87
O_3	0.15	S_4	−1.59	O_2	−3.94
C_{11}	0.02	C_8	1.32	C_6	3.01
C_{15}	−0.06	C_9	−1.30	C_7	0.54
Co_1	1.27	O_8	1.92	O_6	3.87
Co_2	−1.27	O_9	−1.92	O_7	−0.25
Co_4	0.39	C_1	2.86	C_{10}	0.89
Co_5	1.61	C_2	−2.79	O_{10}	0.85
S_5	2.52				

(h) Plane through S_5, C_{10}, and Midpoint of Co_4–Co_5

$-0.400X + 0.758Y - 0.515Z - 2.007 = 0$

Co_4	−1.21	O_5	−2.05	S_1	−1.72
Co_5	1.21	O_7	1.99	S_2	1.62
C_{19}	0.13	Co_1	−0.01	C_{11}	−3.24
O_{10}	0.08	Co_2	−1.28	C_{13}	3.17
C_4	−2.56	Co_3	1.20	C_2	−2.67
C_6	2.57	S_4	−0.05	C_3	2.38
O_4	−3.52	C_1	0.30	O_2	−3.42
O_8	3.46	O_1	0.43	O_3	3.52
C_5	−1.64	C_9	0.01	S_3	−1.71
C_7	1.67	O_9	−0.08	C_8	1.25

(i) Plane through S_2, C_7, S_5, and C_{10}

$-0.805X + 0.556Y - 0.210Z - 2.879 = 0$

Co_5	0.48	C_{19}	1.10	C_7	0.34
C_6	2.21	O_7	0.23	S_5	0.01
O_6	3.37	S_2	−0.01	C_{10}	−0.15
O_{10}	0.28				

(j) Plane through S_1, C_5, S_5, and C_{10}

$0.160X + 0.713Y - 0.683Z - 0.332 = 0$

Co_4	−0.46	C_{19}	−0.94	C_5	−0.17
C_4	−2.18	O_5	−0.08	S_5	−0.01
O_4	−3.37	S_1	0.01	C_{10}	0.12
O_{10}	−0.22				

(k) Plane through Co_4, Co_5, and C_{10}

$-0.874X - 0.484Y - 0.038Z + 2.207 = 0$

O_{10}	0.02	C_7	−1.47	S_2	−0.41
C_6	0.89	C_5	−1.66	S_1	−0.36
C_4	0.84	O_7	−2.56		
O_6	1.43	O_5	−2.71		
O_4	1.35	S_5	1.71		

(l) Plane through Co_4, Co_5, and S_5

$0.591X - 0.236Y - 0.771Z + 4.406 = 0$

C_6	−0.95	O_7	0.23	S_2	2.26
C_4	−0.92	C_5	0.51	S_4	3.06
O_6	−1.73	C_{10}	−1.27	Co_1	3.56
O_4	−1.54	O_{19}	−2.43	Co_2	4.21
C_7	0.16	S_1	2.24	Co_3	4.24
C_5	0.27				

(m) Plane through Co_5, S_5, and C_{10}

$0.922X - 0.371Y - 0.112Z + 3.402 = 0$

S_2	1.19	O_{10}	−0.70	C_{19}	−1.59
C_7	0.43	C_6	−1.68		
O_7	0.74	O_6	−2.85		

(n) Plane through Co_4, S_5, and C_{10}

$0.462X + 0.517Y - 0.720Z + 1.082 = 0$

S_1	1.11	O_{10}	−0.61	C_{19}	−1.46
C_5	0.59	C_4	−1.66		
O_5	0.92	O_4	−2.79		

[a] X, Y, and Z are orthogonal coordinates expressed in Å and are related to the monoclinic cell coordinates by the transformation $X_k = ax_k + cz_k \cos\beta$, $Y_k = by_k$, and $Z_k = cz_k \sin\beta$.

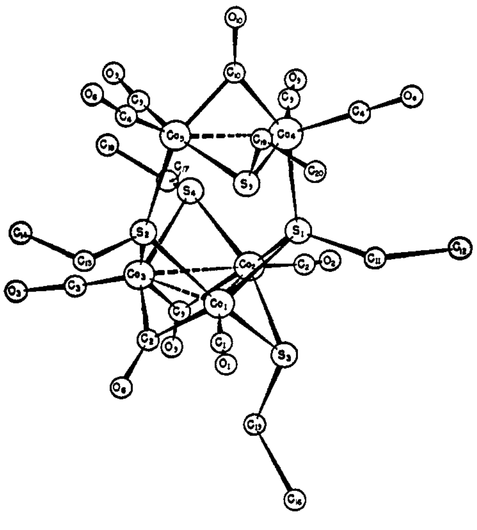

Figure 1. Molecular configuration of $Co_5(CO)_{10}(SC_2H_5)_5$ which clearly reveals the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue bonded by two bridging mercapto groups to the dimeric $Co_2(CO)_5(SC_2H_5)$ fragment.

$(CO)_8C_2H_2$,[35,36] $[C_2H_5SFe(CO)_3]_2$,[2] $[(C_6H_5)CSFe(CO)_3]_2$,[37] $[CH_3SFe_2(CO)_6]_2S$,[38] and $[(C_6H_5)_2PCo(C_5H_5)]_2$.[39] The considerable degree of distortion of the five carbon–sulfur ligands about each cobalt atom from ideality is shown from a calculation of the "best" basal plane (comprised of the two sulfur and two carbonyl carbon atoms) as given in Table IVi and j.[40] The cobalt atoms Co_4 and Co_5 are displaced by 0.46

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(35) A. A. Hock and O. S. Mills in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 640–648.

(36) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(37) H. P. Weber and R. F. Bryan, *J. Chem. Soc.*, *A*, 182 (1967).

(38) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967).

(39) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).

(40) The relative nonplanarity of each of the two sets of four basal atoms in the $Co_2(CO)_5(S)_3$ fragment of $Co_5(CO)_{10}(SC_2H_5)_5$ compared to that of each of the sets of basal atoms in $[C_2H_5SFe(CO)_3]_2$[2] and $[SFe(CO)_3]_2$[3] (for which the individual basal atoms are all within 0.05 Å of each "best" basal plane) presumably is largely a consequence of steric effects imposed on the triply bridging sulfur atoms through their additional coordination with two cobalt atoms in the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue.

and 0.48 Å from their respective basal planes in the direction of their apical carbonyl groups. A similar kind of square-pyramidal distortion of metal atoms from their basal (carbonyl carbon)–sulfur planes toward the apical carbonyl ligands has been observed in the stereochemically related molecular complexes $[C_2H_5SFe(CO)_3]_2$,[2] $[SFe(CO)_3]_2$,[3] $[(C_6H_5)CSFe(CO)_3]_2$,[37] and $[CH_3SFe_2(CO)_6]_2S$.[38] The resulting dimeric fragment $Co_2(CO)_5(S)_3$ (*i.e.*, including the two equatorial sulfur atoms but excluding the ethyl groups) in $Co_5(CO)_{10}(SC_2H_5)_5$ can be considered to be formed from the intersection of these two basal planes at the (bridging sulfur)–(bridging carbonyl carbon) line, S_5–C_{10}, with a sharp dihedral angle of 66°.[41] That this dimeric fragment ideally possesses C_s-m symmetry is shown by the corresponding perpendicular distances for the pairs of equivalent atoms located on opposite sides of the plane defined by S_5, C_{10}, and the midpoint of Co_4–Co_5 (Table IVh).

As postulated for the above iron and cobalt molecular complexes (which all require a metal–metal interaction to account for their observed diamagnetism), a bent Co_4–Co_5 bond involving the overlap of two cobalt σ-like orbitals at an angle of 102° is assumed to occupy the sixth octahedral-like coordination site in the $Co_2(CO)_5(S)_3$ fragment of $Co_5(CO)_{10}(SC_2H_5)_5$.[42] This angle of metal–metal overlap, obtained from the presumed intersection of the Co_4–C_4 and Co_5–C_6 vectors, is based on the assumption that the participating metal orbital for each cobalt atom is collinear with the cobalt apical carbonyl group.[43] The strong influence of the metal–metal interaction on the molecular geometry of the structurally related complex $[(C_6H_5)_2PCoC_5H_5]_2$ (containing two doubly bridging phosphorus atoms) was shown from X-ray studies of the cobalt dimer and its electronically equivalent nickel analog.[39]

The X-ray investigation of $Co_5(CO)_{10}(SC_2H_5)_5$ provides the first known example of a *thioalkoxide* group bonded to three metal atoms. It is noteworthy that X-ray investigations of two titanium alkoxides, $Ti(OC_2H_5)_4$[44] and $Ti(OCH_3)(OC_2H_5)_3$,[45] showed for the solid state a tetrameric molecular configuration formed by the stacking of four TiO_6 octahedra such that alkoxide groups are coordinated with one, two, and three titanium atoms. Although considerable variations were reported among Ti–O bonds of a given type, it was observed[44] for $Ti(OC_2H_5)_4$ that the average Ti–O bond length for a triply bridging OR group was 0.20 Å longer than that for a doubly bridging OR group and 0.46 Å longer than that for a terminal OR group.

Of interest is a similar comparison of cobalt-to-sulfur distances for the doubly bridging and triply bridging SR groups in $Co_5(CO)_{10}(SC_2H_5)_5$ with those in $SCo_6(CO)_{11}(SC_2H_5)_4$ and $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$. In all three of these cobalt thioalkoxide complexes large variations in the Co–S bond lengths of a given type also occur to the extent that in both the pentamer and hexamer individual cobalt-to-sulfur distances overlap for doubly and triply bridging SR groups. Nevertheless, corresponding to the observed trend in the two tetrameric titanium alkoxides of longer bonds for an OR group coordinated with a greater number of titanium atoms, the triply bridging SR groups in the cobalt pentameric and hexameric complexes similarly have larger average Co–S values for the triply bridging SR groups. In $Co_5(CO)_{10}(SC_2H_5)_5$ (for which the 12 Co–S distances range from 2.20 to 2.37 Å with individual esd, 0.01 Å), the average value of 2.33 Å for the six (triply bridging sulfur)-to-cobalt distances is 0.09 Å longer than the average value of 2.24 Å for the six (doubly bridging sulfur)-to-cobalt distances. In $SCo_6(CO)_{11}(SC_2H_5)_4$ the corresponding average Co–S bond lengths (which as in the pentamer have an identical spread of individual values) are 2.21 and 2.285 Å for the doubly and triply bridging SR groups, respectively. In $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ the ten (doubly bridging sulfur)-to-cobalt bond lengths of range 2.20–2.33 Å (individual esd, 0.01 Å) average to 2.25 Å.

Considerations of the closest nonbonding intramolecular distances for the molecular configurations of these three cobalt thioalkoxide complexes indicate that steric compression effects (rather than charge donor–acceptor capacities) play the dominant role in determining the individual Co–S distances in the tinker-toy buildup of the pentamer and hexamer from the basal polyhedral $Co_3X_6Y_3$ unit of the trimer.

As also observed for the trimer and hexamer, the one sulfur atom S_3 which forms an axial S–CH_2 bond in $Co_5(CO)_{10}(SC_2H_5)_5$ is 0.1 Å closer to the plane of the three cobalt atoms than the other three sulfur atoms (located on the opposite side of the tricobalt plane) which each form equatorial S–CH_2 bonds. Table IVa shows a perpendicular distance of 1.43 Å for S_5 *vs.* distances of 1.51, 1.54, and 1.57 Å for S_1, S_2, and S_4, respectively. This small but distinct difference can be rationalized in terms of a bending deformation of the Co_1–S_5–Co_2 part of the trimeric fragment away from the tricobalt plane in order to increase the nonbonding distances of the axial methylene group with other carbonyl ligands.

Although the eight Co–S bond lengths contained in the $Co\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue of $Co_5(CO)_{10}(SC_2H_5)_5$ compare closely with the corresponding Co–S lengths in the same residue of $SCo_6(CO)_{11}(SC_2H_5)_4$, the two Co–S bonds connecting the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue in $Co_5(CO)_{10}(SC_2H_5)_5$ to the $Co_2(CO)_5(SC_2H_5)$ fragment are 0.1 Å longer than the three Co–S bonds connecting the same trimeric residue in $SCo_6(CO)_{11}(SC_2H_5)_4$ to the $SCo_3(CO)_6$ fragment (*i.e.*, 2.35 Å (av) in the pentamer *vs.* 2.24 Å (av) in the hexamer).

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(41) The corresponding dihedral angles are 70° in $[C_2H_5SFe(CO)_3]_2$[2] and 60° in $[SFe(CO)_3]_2$.[3] These dihedral angles are defined as the angles directly between pairs of planes rather than as angles between the normals to these planes.

(42) This conceptually useful "bent" σ-bond description does not imply that the actual configuration of orbitals about the metal atoms need necessarily be octahedral. In fact, the observed angular distortions from 90° for the four equatorial ligands of the corresponding dimeric complexes suggest considerable variation in the metal equatorial orbitals from 90° angles in order to achieve maximum orbital overlap for the metal–ligand bonds. It must be emphasized that in general we invoke idealized valence-bond directed orbital models (in this case "octahedral-like") in order that the observed disposition of ligands about the metal may be advantageously described (with reference to the degree of deformation from idealized geometries) and correlated with those of related complexes. Our use of the term "octahedral-like" is simply to make clear that the degree of s, p, and d character in each hybrid orbital is not known; even if the ligand–metal–ligand angles were all 90°, the atomic orbital coefficients would not be the same for different bonds, thereby destroying the regular O_h octahedral symmetry of the metal orbitals.

(43) An angle of 122° results from the presumed intersection of the Co_4–O_4 and Co_5–O_6 vectors; with the assumption that the metal orbital for each cobalt atom is perpendicular to the basal plane of the cobalt-coordinated sulfur and carbon atoms, an angle of 114° is obtained.

(44) J. A. Ibers, *Nature*, **197**, 686 (1963).

(45) R. D. Witters and C. N. Caughlan, *ibid.*, **205**, 1312 (1965).

This significant bond-length change can be ascribed to the relatively close S···S contacts in the pentamer compared to the less stringently required van der Waals S···CO contacts in the hexamer. In $Co_5(CO)_{10}(SC_2H_5)_5$ the nonbonding S···S distances from the doubly bridging mercapto sulfur atom, S_5 (which is symmetrically bonded to Co_4 and Co_5 of the dimeric fragment), to the triply bridging mercapto sulfur atoms, S_1 and S_2, are both only 3.1 Å. In $SCo_6(CO)_{11}(SC_2H_5)_4$ the observed nonbonding S···CO distances from the three triply bridging mercapto sulfur atoms to the three bridging and three terminal carbonyl carbon atoms of the $SCo_3(CO)_6$ fragment average to 2.9 and 3.1 Å, respectively.

The bonding in $Co_5(CO)_{10}(SC_2H_5)_5$ can be shown to be closely interrelated with that described[1] for the $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ molecule. Each of the two cobalt atoms, Co_4 and Co_5, in the dimeric fragment of $Co_5(CO)_{10}(SC_2H_5)_5$ is presumed to possess a closed-shell electronic configuration analogous to the metal atoms in the structurally related dimeric complexes cited previously (*viz.*, $Co_2(CO)_8$, $[C_2H_5SFe(CO)_3]_2$, etc.) A bookkeeping immediately shows 20 valence electrons available to participate in the bonding of the tricobalt part of the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue of $Co_5(CO)_{10}(SC_2H_5)_5$. The trimeric residue in $Co_5(CO)_{10}(SC_2H_5)_5$ then is an *electronic analog* of the $Co_3X_6Y_3$ system in the $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ molecule and in the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue of $SCo_6(CO)_{11}(SC_2H_5)_4$.

The qualitative application of the simple metal atom cluster MO model developed by Cotton and Haas[46] in their semiquantitative treatment of several metal cluster halide systems is informative in throwing light on the nature of bonding of these three thioalkoxide cobalt carbonyl complexes. Their procedure of considering electronically the metal atom cluster system separate from the remaining part of the molecule is based on the "perfect pairing" approximation. The important structural feature common to these three cobalt complexes is that each cobalt atom in the triangular cobalt atom cluster has an essentially identical square-pyramidal CoX_4Y environment of five carbonyl carbon and sulfur ligands about it with the axial Co–Y bond in the tricobalt plane centripetally directed toward the centroid of the cobalt triangle. After utilization of five valence orbitals in σ bonding to these five carbon and sulfur ligands, each cobalt atom has four remaining d orbitals which under D_{3h} symmetry can be combined to form five-bonding and seven-antibonding metal symmetry orbitals.[1] The assumption of D_{3h} symmetry which gives rise to degenerate orbitals is made for convenience in order to simplify the energy level representations; the presumably small orbital splittings due to the lower chemically equivalent symmetry of C_s-m are not deemed to affect the general conclusions of this qualitative MO description. The accommodation of the 20 valence electrons to five-bonding and five-antibonding metal symmetry orbitals (*i.e.*, see ref 1 for the proposed entire ground-state electronic configuration of the tricobalt system) leads to a prediction[1] of a valence-bond cobalt–cobalt bond order of <1.0 rather than a metal–metal bond order of 1.0 found in most metal cluster carbonyl systems for which each metal conforms to a closed-shell electronic configuration. This lower valence-bond value of less than 1.0 results from the occupation of the two electrons in excess of the "krypton" configuration for each cobalt atom in the $Co_3X_6Y_3$ system in an antibonding metal symmetry orbital. Although the corresponding Co–Co distances in each of the three mercaptocobalt carbonyl complexes lie in the single-bond range, the presumed marked influence of the bridging carbonyl and mercapto groups on the cobalt–cobalt bond lengths does not make the observed distances incompatible with the valence-bond cobalt–cobalt order prediction based on the Cotton–Haas MO model.

Invariant to any assumptions concerning symmetry and relative stability of the metal symmetry orbitals in these three tricobalt carbonyl cluster systems, the most significant feature emerging from this particular MO approach is the basic general difference between metal cluster carbonyl systems and metal cluster halide and oxide systems. In contrast with these latter systems which usually contain no electrons in antibonding metal symmetry orbitals,[46] a metal cluster carbonyl system possesses electrons in antibonding metal symmetry orbitals. The stability of these thioalkoxide cobalt cluster carbonyl systems then is a consequence of empty π^* carbonyl and d_π sulfur orbitals which in combination with the appropriate metal symmetry orbitals will delocalize charge density from the metal fragment onto the ligands. Hence, the Cotton–Haas metal atom cluster MO model seems to offer a satisfactory qualitative explanation of the bonding in the three mercaptocobalt carbonyl complexes. The steric dictation of the methylene carbon atoms on the stoichiometry of the $Co_3X_6Y_3$ part of $Co_5(CO)_{10}(SC_2H_5)_5$ is given elsewhere.[1,33]

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[46] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, 3, 10 (1964).