Organometallic Sulfur Complexes. XII. Structure of a Hexameric Mercaptocobalt Carbonyl Sulfide Complex, $SCo_6(CO)_{11}(SC_2H_5)_4$[1,2]

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Abstract: The structural determination of $SCo_6(CO)_{11}(SC_2H_5)_4$ by a three-dimensional, single-crystal X-ray analysis has shown a tinker-toy construction of a hexameric molecular complex by the junction of a $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ building block through three of its bridging mercapto groups to the three cobalt atoms of a $SCo_3(CO)_6$ fragment. The former $Co_3X_6Y_3$ system is stereochemically analogous and electronically equivalent to the trimeric residue of same formula in $Co_5(CO)_{10}(SC_2H_5)_5$ and to the molecular complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$. The idealized configuration of the other tricobalt atom cluster, $SCo_3(CO)_6(S)_3$ (including the three mercapto sulfur atoms), of C_{3v} symmetry consists of an apical sulfur atom coordinated by three Co–S bonds to a basal $Co_3(CO)_6(S)_3$ fragment of three equilaterally arranged Co(CO)(S) groups joined in pairs to one another by both a bridging carbonyl and a Co–Co bond. A comparison of its structural features with those of related organometallic complexes is made, and its nature of bonding is discussed. A rationalization for $SCo_6(CO)_{11}(SC_2H_5)_4$ being the chemical precursor of the trimeric complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ is made on the basis of "steric compression" effects involving the stereochemical disposition of the mercapto methylene groups. Crystals of $SCo_6(CO)_{11}(SC_2H_5)_4$ are monoclinic with four molecules in a unit cell of symmetry $P2_1/n$ and lattice parameters $a = 12.25$, $b = 15.93$, $c = 16.24$ Å, $\beta = 92° 50'$. Refinement of the structure by isotropic least squares yielded an unweighted $R_1 = 8.8\%$ and weighted $R_2 = 7.0\%$ for 1403 observed reflections collected photographically with Mo Kα radiation.

This structural investigation was a consequence of a mutual interest of Drs. L. Markó and G. Bor of the Hungarian Oil and Gas Research Institut (Veszprém) and our laboratory in the reaction products of dicobalt octacarbonyl with ethyl mercaptan. From this reaction in hexane at room temperature Klumpp, Markó, and Bor[3] reported the synthesis of two complexes formulated as $Co_4(CO)_5(SC_2H_5)_7$ and $Co_4(CO)_7(SC_2H_5)_3$, whereas our efforts to prepare the presumed complex $[C_2H_5SCo(CO)_3]_2$[4] by reaction at 0° *without solvent* instead led to the isolation of a pentameric complex, $Co_5(CO)_{10}(SC_2H_5)_5$, which was unambiguously characterized by a single-crystal X-ray diffraction study.[1] A subsequent X-ray characterization of the presumed $Co_4(CO)_5(SC_2H_5)_7$ showed the atomic arrangement to conform to a new kind of trimeric $M_3X_6Y_3$ complex of formula $Co_3(CO)_4(SC_2H_5)_5$.[5] The present paper reports the structural analysis of the presumed $Co_4(CO)_7(SC_2H_5)_3$, which not only revealed the first known example of a hexanuclear cobalt carbonyl complex but also afforded considerable stereochemical insight concerning the reaction mechanisms and the existence of these complexes.

Experimental Section

A sample of the presumed $Co_4(CO)_7(SC_2H_5)_3$ was kindly made available to us by Drs. L. Markó and G. Bor of the Hungarian Oil and Gas Research Institute in Veszprém, Hungary. An infrared spectrum, carried out on the Perkin-Elmer Model 421 grating spectrometer, was found to be in close agreement with their spectrum,[3] which indicated the existence of both bridging and terminal carbonyl groups. Single crystals were obtained by slow recrystallization of the sample from petroleum ether (bp 60–68°). Two rhombic-shaped crystals of dimensions 0.09 × 0.23 × 0.36 mm and 0.15 × 0.26 × 0.38 mm were mounted inside thin-walled glass capillaries and used for collecting intensity data with Zr-filtered Mo Kα radiation. Absorption corrections were neglected because of the low absorption coefficients ($\mu R_{max} < 0.4$). Multiple-film equiinclination Weissenberg photographs were obtained about the *c* rotation axis for 16 reciprocal levels (*hk*0–*hk*15).

Timed-exposure precession photographs of the 0*kl*, 1*kl*, 2*kl*, and *h*0*l* layers were taken to supplement the Weissenberg data as well as to place all the data initially on one relative scale. All intensity measurements were made visually by comparison with sets of standard intensity strips. A total of 1403 independent reflections was recorded of which 145 were obtained only from precession photographs.

Magnetic measurements of small samples of $SCo_6(CO)_{11}(SC_2H_5)_4$ were made at room temperature by the Faraday method in solid state and by nuclear magnetic resonance[6] in solution. The molar susceptibilities of the sample were found to be extremely sensitive to small amounts of paramagnetic decomposition products; repeated recrystallizations and magnetic determinations were carried out under an argon atmosphere. Although the paramagnetic impurities were not sufficiently eliminated to establish unambiguously the diamagnetic character of the hexameric molecules by the Faraday method, as expected for a diamagnetic substance the nmr method applied to carefully filtered solutions showed no frequency shift of the proton lines of the cyclohexane molecules utilized as the inert reference. This latter technique was calibrated by magnetic measurement of various paramagnetic solutions of nickelocene and cobaltocene.

Results

Unit Cell and Space Group. The compound crystallizes in a monoclinic system with lattice parameters $a = 12.25 \pm 0.02$ Å, $b = 15.93 \pm 0.02$ Å, $c = 16.24 \pm 0.02$ Å, $\beta = 92° 50' \pm 10'$; volume of unit cell = 3165 Å^3; $\rho_{obsd} = 1.91$ g cm^{-3} (by the flotation method). The observed systematic absence of $\{h0l\}$ for $h + l \neq 2n$ and $\{0k0\}$ for $k \neq 2n$ are consistent with the space group $P2_1/n$ [nonstandard setting of $P2_1/c(C_{2h}{}^5$,

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(1) Previous paper in this series: C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3969 (1968).

(2) Presented in part at the National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 27–July 2, 1965.

(3) E. Klumpp, L. Markó, and G. Bor, *Chem. Ber.*, **97**, 926 (1964).

(4) W. Hieber and P. Spacu, *Z. Anorg. Allgem. Chem.*, **233**, 353 (1937).

(5) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **90**, 3960 (1968).

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

No. 14)[7]. Refinement of the derived structure indicated the correctness of the space group chosen.

Determination of the Composition and Structure

Although the percentage composition based on the presumed formula $Co_4(CO)_7(SC_2H_5)_3$ is in close agreement with the experimentally determined composition, the unit-cell volume and observed density then require approximately six of these formula species per unit cell which is incompatible with the space group symmetry of $P2_1/n$. With the assumption of one crystallographically independent formula species occupying the fourfold general positions of this centrosymmetric monoclinic space group, the resulting formula weight is 910.3. This value suggested a hexanuclear cobalt carbonyl mercaptan complex of possible formulas $Co_6(CO)_{10(11)}(SC_2H_5)_{6(5)}$ which were within the assumed limits of error of the elemental analyses.

The actual formula $SCo_6(CO)_{11}(SC_2H_5)_4$, subsequently determined by this crystallographic investigation, has a molecular weight of 938.3 and a calculated density of 1.97 g cm^{-3}. Its percentage composition compares reasonably well with the experimental elemental analyses given[3] for the presumed $Co_4(CO)_7(SC_2H_5)_3$. *Anal.* Calcd for $SCo_6(CO)_{11}(SC_2H_5)_4$: Co, 37.69; S, 17.09; C, 24.32; H, 2.15; O, 18.76., Found:[3] Co, 38.15, 37.95; S, 16.26, 16.42; C, 25.10, 25.18; H, 2.50, 2.45.

Both the computed regular and sharpened three-dimensional Patterson functions were closely examined on the basis of six independent cobalt atoms. After considerable difficulty, a trial structure for six cobalt atoms (consisting of an approximate antiprismatic arrangement of D_{3d}-$\bar{3}2/m$ symmetry) was arrived at which accounted for most of the large Patterson vector peaks. One cycle of isotropic least-squares refinement of this model with a block-diagonal program[8a] yielded an R_1 = 37.7%, which thereby indicated the over-all correctness of the model. An interpretation of the first three-dimensional Fourier synthesis phased on these six cobalt atoms provided initial atomic coordinates for five sulfur atoms and three carbonyl groups. After refinement of these parameters by least squares which reduced R_1 to 25.0%, another Fourier map allowed identification (from stereochemical considerations) of 30 additional atoms comprised of six terminal and five bridging carbonyl groups and eight ethyl carbon atoms. Two further least-squares cycles significantly lowered the unweighted discrepancy index to 13.0%. Correction of several minor errors incurred in the processing of the reflection data was made at this point. A final refinement of all atomic positional and thermal parameters along with 20 scale factors was made with the local version of the Busing–Martin–Levy full-matrix least-squares program.[8b]

After four cycles of refinement all individual parameter shifts became less than 30% of the corresponding standard deviations. Discrepancy factors of R_1 = 8.8% and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ = 7.0% were obtained on the last cycle. Calculation of a total difference Fourier synthesis indicated the correctness of the structure. No attempt was made to identify the hydrogen atoms. In this structural determination all 41 nonhydrogen atoms were found to occupy the general fourfold positions of $P2_1/n$: $\pm(x, y, z;\ ^1/_2 - x,\ ^1/_2 + y,\ ^1/_2 - z)$. The following weights were assigned to the observed structure amplitudes of individual reciprocal levels: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(\min)$; $\sqrt{w} = 1.25I_o^2/F_oI_o(\min)^2$ if $I_o < 4I_o(\min)$. Scattering factors used for cobalt were those of Thomas and Umeda,[9] for sulfur those of Dawson,[10] and for carbon and oxygen those of Berghuis, *et al.*[11] The atomic parameters and estimated standard deviations obtained from the last cycle of least-squares refinement are given in Table I.[12] Distances and angles with estimated

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	0.2835 (3)	0.3798 (2)	0.5546 (2)	2.6 (1)
Co_2	0.2446 (3)	0.2818 (3)	0.4338 (2)	3.0 (1)
Co_3	0.1067 (3)	0.3033 (3)	0.5387 (2)	3.1 (1)
Co_4	0.2743 (4)	0.0890 (3)	0.5877 (3)	3.6 (1)
Co_5	0.3046 (3)	0.1859 (3)	0.7044 (2)	3.3 (1)
Co_6	0.4456 (4)	0.1683 (3)	0.6021 (2)	3.2 (1)
S_1	0.1731 (7)	0.1737 (5)	0.4996 (4)	3.6 (2)
S_2	0.2177 (7)	0.2997 (5)	0.6568 (5)	4.1 (2)
S_3	0.4079 (6)	0.2753 (5)	0.5177 (4)	3.1 (2)
S_4	0.3015 (7)	0.4138 (6)	0.4247 (5)	4.0 (2)
S_5	0.3967 (7)	0.0719 (6)	0.6865 (5)	4.5 (2)
C_1 (B)	0.0904 (23)	0.3176 (18)	0.4298 (18)	3.8 (7)
O_1 (B)	0.0302 (16)	0.3336 (13)	0.3662 (11)	4.8 (5)
C_2 (B)	0.1397 (32)	0.4145 (25)	0.5472 (22)	8.0 (11)
O_2 (B)	0.0897 (17)	0.4822 (14)	0.5664 (13)	6.6 (6)
C_3 (B)	0.1788 (31)	0.1197 (20)	0.6800 (20)	6.1 (9)
O_3 (B)	0.0840 (19)	0.1110 (12)	0.6932 (12)	5.8 (6)
C_4 (B)	0.4401 (25)	0.2390 (22)	0.6896 (18)	5.4 (9)
O_4 (B)	0.4915 (15)	0.2994 (12)	0.7302 (11)	4.6 (5)
C_5 (B)	0.3911 (29)	0.0927 (22)	0.5146 (20)	6.9 (10)
O_5 (B)	0.4259 (16)	0.0666 (12)	0.4504 (12)	4.2 (5)
C_1 (T)	0.3460 (31)	0.4625 (26)	0.6183 (22)	7.6 (12)
O_1 (T)	0.3940 (21)	0.5131 (17)	0.6465 (16)	7.8 (8)
C_2 (T)	0.2666 (28)	0.2457 (25)	0.3317 (24)	7.0 (11)
O_2 (T)	0.2769 (22)	0.2248 (19)	0.2694 (17)	9.7 (9)
C_3 (T)	−0.0292 (33)	0.2983 (21)	0.5574 (21)	6.8 (10)
O_3 (T)	−0.1233 (21)	0.2911 (14)	0.5737 (13)	6.7 (6)
C_4 (T)	0.2186 (32)	−0.0189 (29)	0.5684 (24)	8.9 (13)
O_4 (T)	0.1944 (21)	−0.0800 (19)	0.5584 (14)	8.1 (8)
C_5 (T)	0.2903 (28)	0.1942 (20)	0.8046 (22)	6.3 (9)
O_5 (T)	0.2844 (18)	0.1995 (14)	0.8802 (14)	6.5 (6)
C_6 (T)	0.5751 (39)	0.1552 (22)	0.5929 (22)	8.4 (11)
O_6 (T)	0.6766 (22)	0.1442 (14)	0.5931 (13)	7.1 (6)
C_1 (E)	0.0652 (26)	0.1188 (20)	0.4340 (19)	5.3 (8)
C_2 (E)	0.1176 (27)	0.0537 (23)	0.3737 (19)	6.8 (10)
C_3 (E)	0.1748 (25)	0.3715 (19)	0.7455 (17)	5.4 (8)
C_4 (E)	0.0696 (31)	0.3282 (21)	0.7763 (21)	7.6 (10)
C_5 (E)	0.5324 (24)	0.3124 (17)	0.4710 (17)	4.5 (7)
C_6 (E)	0.6040 (21)	0.3690 (16)	0.5279 (14)	2.6 (6)
C_7 (E)	0.1970 (22)	0.4912 (17)	0.3840 (17)	3.5 (7)
C_8 (E)	0.1966 (28)	0.4727 (22)	0.2802 (22)	7.3 (10)

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(7) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 99.

(8) (a) P. W. Sutton, "A Block-Diagonal Least-Squares Program for the CDC 1604 Computer," University of Wisconsin, 1962; (b) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

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(10) B. Dawson, *Acta Cryst.*, 13, 403 (1960).

(11) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, 8, 478 (1955).

(12) Calculated and observed structure factor tables for $SCo_6(CO)_{11}(SC_2H_5)_4$ are deposited as Document No. 9956 with ADI, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and remitting $2.50 for photoprints or $1.75 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table II. Intramolecular Distances (Å) with Standard Deviations[a]

	Distance		Distance		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_3, S_4, C_{3T}, and O_{3T})							
Co_1–Co_2	2.534 (6)	Co_1–S_2	2.272 (9)	Co_1–C_{2B}	1.84 (4)	C_{1B}–O_{1B}	1.27 (3)
		Co_2–S_1	2.229 (9)	Co_2–C_{1B}	1.97 (3)	C_{2B}–O_{2B}	1.29 (4)
Co_1–Co_3	2.488 (7)		2.251 (av)		1.97 (av)		1.28 (av)
Co_2–Co_3	2.481 (7)						
						S_1–C_{1E}	1.87 (3)
	2.485 (av)					S_2–C_{3E}	1.93 (3)
		Co_3–S_2	2.297 (10)	Co_3–C_{2B}	1.82 (4)	S_3–C_{5E}	1.84 (3)
		Co_3–S_1	2.319 (9)	Co_3–C_{1B}	1.78 (3)	S_4–C_{7E}	1.87 (3)
Co_1–S_4	2.200 (9)						
Co_2–S_4	2.223 (10)		2.308 (av)		1.80 (av)		
							1.88 (av)
	2.212 (av)					C_{1E}–C_{2E}	1.58
		Co_1–C_{1T}	1.82 (4)	C_{1T}–O_{1T}	1.09 (4)	C_{3E}–C_{4E}	1.57
Co_1–S_3	2.354 (9)	Co_2–C_{2T}	1.79 (4)	C_{2T}–O_{2T}	1.08 (4)	C_{5E}–C_{6E}	1.54
Co_2–S_3	2.366 (9)	Co_3–C_{3T}	1.71 (4)	C_{3T}–O_{3T}	1.20 (3)	C_{7E}–C_{8E}	1.71
	2.360 (av)		1.77 (av)		1.12 (av)		1.60 (av)
B. $SCo_3(CO)_6S_3$ Fragment (the *idealized* configuration posseses C_{3v}–3m symmetry)							
Co_4–Co_5	2.459 (7)	Co_4–S_1	2.286 (9)	Co_4–C_{3B}	2.01 (4)	C_{4T}–O_{4T}	1.03 (4)
Co_4–Co_6	2.450 (7)	Co_5–S_2	2.222 (10)	Co_5–C_{3B}	1.89 (4)	C_{5T}–O_{5T}	1.24 (3)
Co_5–Co_6	2.471 (8)	Co_6–S_3	2.221 (9)	Co_5–C_{4B}	1.89 (3)	C_{6T}–O_{6T}	1.26 (4)
				Co_6–C_{4B}	1.82 (3)		
	2.460 (av)		2.243 (av)	Co_6–C_{5B}	1.95 (3)		1.18 (av)
Co_4–S_5	2.159 (11)	Co_4–C_{4T}	1.87 (5)	Co_4–C_{5B}	1.91 (4)	C_{3B}–O_{3B}	1.20 (3)
Co_5–S_5	2.166 (10)	Co_5–C_{5T}	1.65 (4)		1.91 (av)	C_{4B}–O_{4B}	1.31 (3)
Co_6–S_5	2.163 (10)	Co_6–C_{6T}	1.61 (5)			C_{5B}–O_{5B}	1.22 (3)
	2.163 (av)		1.71 (av)				1.24 (av)
C. Nonbonding Carbon–Carbon and Sulfur–Carbon Distances (Å)							
$S_4\cdots C_{2B}$	2.88 (4)	$C_{1B}\cdots S_1$	2.73 (3)	$S_2\cdots C_{4B}$	2.92 (4)	$C_{5B}\cdots C_{4T}$	2.93 (6)
$S_4\cdots C_{1B}$	3.01 (3)	$S_3\cdots C_{1T}$	3.50 (4)	$S_2\cdots C_{3B}$	2.93 (3)	$C_{5B}\cdots C_{6T}$	2.72 (5)
$C_{2B}\cdots C_{1B}$	2.50 (5)	$S_3\cdots C_{2T}$	3.44 (4)	$S_1\cdots C_{3B}$	3.05 (3)	$C_{4B}\cdots C_{6T}$	2.69 (5)
$S_4\cdots C_{1T}$	2.36 (4)	$S_2\cdots C_{1T}$	3.11 (4)	$S_1\cdots C_{5B}$	2.97 (4)		
$S_4\cdots C_{2T}$	3.09 (4)	$S_1\cdots C_{2T}$	3.22 (4)	$S_3\cdots C_{5B}$	2.92 (4)	$C_{3B}\cdots S_5$	2.77 (4)
$C_{2B}\cdots C_{1T}$	2.83 (5)	$S_2\cdots C_{3T}$	3.36 (4)	$S_3\cdots C_{6T}$	3.02 (4)	$C_{4B}\cdots S_5$	2.72 (4)
$C_{1B}\cdots C_{2T}$	2.98 (5)	$S_1\cdots C_{3T}$	3.35 (4)	$S_2\cdots C_{5T}$	3.03 (3)	$C_{5B}\cdots S_5$	2.81 (3)
$C_{2B}\cdots C_{3T}$	2.79 (5)	$S_3\cdots S_2$	3.35 (1)	$S_1\cdots C_{4T}$	3.30 (4)		
$C_{1B}\cdots C_{3T}$	2.61 (5)	$S_3\cdots S_1$	3.30 (1)			$C_{4T}\cdots S_5$	3.18 (4)
$S_4\cdots S_3$	2.94 (1)	$S_2\cdots S_1$	3.27 (1)	$C_{4B}\cdots C_{5T}$	2.78 (5)	$C_{5T}\cdots S_5$	3.07 (4)
$C_{2B}\cdots S_2$	2.69 (4)			$C_{3B}\cdots C_{5T}$	2.66 (5)	$C_{6T}\cdots S_5$	3.03 (5)
		$S_3\cdots C_{4B}$	2.86 (3)	$C_{3B}\cdots C_{4T}$	2.91 (6)		

[a] Standard deviations of last significant figures are given in parentheses.

standard deviations, as obtained from the Busing–Martin–Levy function and error program,[13] are summarized in Tables II and III, respectively. Table IV gives the "best" molecular planes formed by sets of specified atoms and the perpendicular distances of these and other atoms from the planes.[14] All Patterson and Fourier syntheses were calculated with the Blount program.[15]

Discussion

The crystal structure of $SCo_6(CO)_{11}(SC_2H_5)_4$ is comprised of discrete hexamers with a configuration depicted in Figure 1. Each molecule possesses a $Co_3X_6Y_3$ building block (where X_6 stands for both four SC_2H_5 and two CO bridging groups and Y_3 symbolizes three CO terminal groups) which is linked by three of

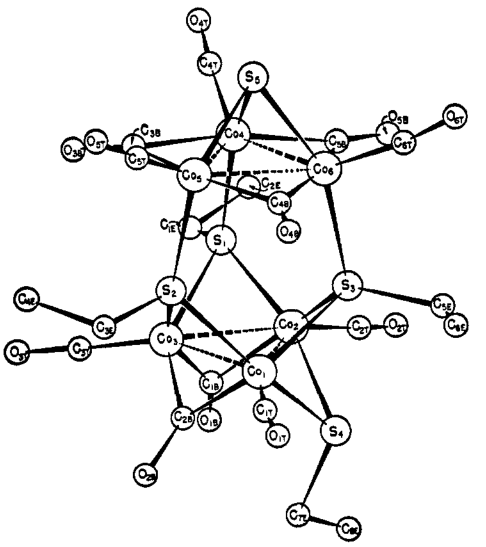

Figure 1. Molecular configuration of $SCo_6(CO)_{11}(SC_2H_5)_4$ which shows the $Co_3[(SC_2H_5)_4(CO)_2](CO)_3$ building block linked by three of its bridging mercapto groups to the cobalt atoms of a $SCo_3(CO)_6$ fragment. The resulting $SCo_3(CO)_6(S)_3$ residue ideally conforms to C_{3v} symmetry.

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(13) 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.

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

(15) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

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

A. $\mathrm{Co_3(CO)_6(SC_2H_5)_4}$ Fragment (the *idealized* cobalt–carbonyl–sulfur part has a mirror plane which passes through $\mathrm{Co_3}$, $\mathrm{S_3}$, $\mathrm{S_4}$, $\mathrm{C_{3T}}$, and $\mathrm{O_{3T}}$)

M–M–M	
$\mathrm{Co_1-Co_2-Co_3}$	59.5 (2)
$\mathrm{Co_2-Co_1-Co_3}$	59.2 (2)
	59.4 (av)
$\mathrm{Co_1-Co_3-Co_2}$	61.3 (2)
M–S–M	
$\mathrm{Co_1-S_4-Co_2}$	69.9 (3)
$\mathrm{Co_1-S_3-Co_2}$	65.0 (2)
$\mathrm{Co_1-S_2-Co_3}$	66.0 (3)
$\mathrm{Co_2-S_1-Co_3}$	66.1 (3)
	66.1 (av)
S–M–S	
$\mathrm{S_4-Co_1-S_3}$	80.4 (3)
$\mathrm{S_4-Co_2-S_3}$	79.7 (3)
	80.1 (av)
$\mathrm{S_3-Co_1-S_2}$	92.6 (3)
$\mathrm{S_3-Co_2-S_1}$	91.8 (3)
	92.2 (av)
$\mathrm{S_2-Co_3-S_1}$	90.3 (3)
S–M–M	
$\mathrm{S_4-Co_1-Co_2}$	55.5 (3)
$\mathrm{S_4-Co_2-Co_1}$	54.6 (2)
	55.1 (av)
$\mathrm{S_3-Co_1-Co_2}$	57.7 (2)
$\mathrm{S_3-Co_2-Co_1}$	57.3 (2)
	57.5 (av)
$\mathrm{S_2-Co_1-Co_3}$	57.5 (3)
$\mathrm{S_1-Co_2-Co_3}$	58.7 (3)
	58.1 (av)
$\mathrm{S_2-Co_3-Co_1}$	56.5 (3)
$\mathrm{S_1-Co_3-Co_2}$	55.2 (2)
	55.9 (av)
$\mathrm{S_4-Co_1-Co_3}$	98.5
$\mathrm{S_4-Co_2-Co_3}$	98.1
	98.3 (av)
$\mathrm{S_3-Co_1-Co_3}$	101.4
$\mathrm{S_3-Co_2-Co_3}$	101.3
	101.3 (av)
$\mathrm{S_2-Co_1-Co_2}$	99.1
$\mathrm{S_1-Co_2-Co_1}$	99.7
	99.4 (av)
$\mathrm{S_2-Co_3-Co_2}$	100.0
$\mathrm{S_1-Co_3-Co_1}$	98.6
	99.3 (av)
S–M–CO	
$\mathrm{S_4-Co_1-C_{1T}}$	107.9 (12)
$\mathrm{S_4-Co_2-C_{2T}}$	100.3 (12)
	104.1 (av)
$\mathrm{S_3-Co_1-C_{1T}}$	113.4 (12)
$\mathrm{S_3-Co_2-C_{2T}}$	111.0 (11)
	112.2 (av)
$\mathrm{S_2-Co_1-C_{1T}}$	98.4 (11)
$\mathrm{S_1-Co_2-C_{2T}}$	106.1 (12)
	102.3 (av)
$\mathrm{S_2-Co_3-C_{3T}}$	113.1 (12)
$\mathrm{S_1-Co_3-C_{3T}}$	111.4 (12)
	112.3 (av)
$\mathrm{S_3-Co_1-C_{2T}}$	145.4
$\mathrm{S_3-Co_2-C_{1T}}$	144.4
	144.9 (av)
$\mathrm{S_4-Co_1-C_{2B}}$	90.2 (11)
$\mathrm{S_4-Co_2-C_{1B}}$	91.5 (8)
	90.9 (av)
$\mathrm{S_2-Co_1-C_{2B}}$	81.0 (12)
$\mathrm{S_1-Co_2-C_{1B}}$	80.9 (9)
	80.9 (av)
$\mathrm{S_2-Co_3-C_{2B}}$	80.8 (12)
$\mathrm{S_1-Co_3-C_{1B}}$	82.4 (10)
	81.6 (av)
$\mathrm{S_2-Co_3-C_{1B}}$	149.7
$\mathrm{S_1-Co_3-C_{2B}}$	143.8
	146.8 (av)
M–M–CO	
$\mathrm{Co_1-Co_2-C_{2T}}$	152.2
$\mathrm{Co_2-Co_1-C_{1T}}$	160.7
	156.5 (av)
$\mathrm{Co_1-Co_3-C_{3T}}$	148.8
$\mathrm{Co_2-Co_3-C_{3T}}$	144.9
	146.9 (av)
$\mathrm{Co_3-Co_1-C_{1T}}$	138.9
$\mathrm{Co_3-Co_2-C_{2T}}$	145.1
	142.0 (av)
$\mathrm{Co_1-Co_3-C_{2B}}$	47.6 (12)
$\mathrm{Co_2-Co_3-C_{1B}}$	52.0 (9)
	49.8 (av)
$\mathrm{Co_3-Co_1-C_{2B}}$	46.8 (12)
$\mathrm{Co_3-Co_2-C_{1B}}$	45.5 (8)
	46.2 (av)
M–CO–M	
$\mathrm{Co_1-C_{2B}-Co_3}$	85.5 (18)
$\mathrm{Co_2-C_{1B}-Co_3}$	82.5 (12)
	84.0 (av)
OC–M–CO	
$\mathrm{C_{1T}-Co_1-C_{2B}}$	101.2 (16)
$\mathrm{C_{2T}-Co_2-C_{1B}}$	104.5 (14)
	102.9 (av)
$\mathrm{C_{3T}-Co_3-C_{2B}}$	104.3 (17)
$\mathrm{C_{3T}-Co_3-C_{1B}}$	96.9 (15)
	100.6 (av)
$\mathrm{C_{2B}-Co_3-C_{1B}}$	88.0
M–C–O	
$\mathrm{Co_1-C_{1T}-O_{1T}}$	168.8 (36)
$\mathrm{Co_2-C_{2T}-O_{2T}}$	177.9 (36)
$\mathrm{Co_3-C_{3T}-O_{3T}}$	176.2 (31)
	174.3 (av)
$\mathrm{Co_1-C_{2B}-O_{2B}}$	134.4 (29)
$\mathrm{Co_2-C_{1B}-O_{1B}}$	127.2 (21)
$\mathrm{Co_3-C_{2B}-O_{2B}}$	136.7 (30)
$\mathrm{Co_3-C_{1B}-O_{1B}}$	150.1 (23)
	137.1 (av)
M–S–CH₂	
$\mathrm{Co_1-S_3-C_{5E}}$	116.0 (10)
$\mathrm{Co_2-S_3-C_{5E}}$	116.4 (10)
	116.2 (av)
$\mathrm{Co_1-S_4-C_{7E}}$	113.6 (9)
$\mathrm{Co_2-S_4-C_{7E}}$	115.8 (9)
	114.7 (av)
$\mathrm{Co_1-S_2-C_{3E}}$	109.4 (10)
$\mathrm{Co_2-S_1-C_{1E}}$	111.8 (10)
	110.6 (av)
$\mathrm{Co_3-S_2-C_{3E}}$	115.9 (10)
$\mathrm{Co_3-S_1-C_{1E}}$	108.9 (10)
	112.4 (av)
S–CH₂–CH₃	
$\mathrm{S_1-C_{1E}-C_{2E}}$	111.2 (22)
$\mathrm{S_2-C_{3E}-C_{4E}}$	103.7 (21)
$\mathrm{S_3-C_{5E}-C_{6E}}$	113.7 (19)
$\mathrm{S_4-C_{7E}-C_{8E}}$	101.7 (18)
	107.6 (av)

its bridging thioalkyl groups to the cobalt atoms of a $\mathrm{SCo_3(CO)_6}$ fragment (Figure 1). The $\mathrm{Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3}$ residue is structurally equivalent with the trimeric residue of identical formula in $\mathrm{Co_5(CO)_{10}(SC_2H_5)_5}$. A detailed comparison of the molecular parameters (Tables II and III) and the "best" least-squares planes (Table IVa, b, d–f) of the $\mathrm{Co_3X_6Y_3}$ system in $\mathrm{SCo_6(CO)_{11}(SC_2H_5)_4}$ with those of the same system in $\mathrm{Co_5(CO)_{10}(SC_2H_5)_5}$ clearly shows that in each complex the distortions of the sulfur–(carbonyl carbon) polyhedron encompassing the triangle of cobalt atoms are alike. Since the structural features of this polyhedron have been discussed in the previous two papers,[1,5] they are not reproduced here.

The other tricobalt atom cluster, $\mathrm{SCo_3(CO)_6(S)_3}$ (*i.e.*, including the three axial cobalt-coordinated mercapto sulfur atoms), ideally possesses $\mathrm{C_{3v}}$ symmetry. The symmetrical orientation of the sulfur–(carbonyl carbon) polyhedron of the $\mathrm{Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3}$ residue relative to the attached $\mathrm{SCo_3(CO)_6}$ fragment is readily seen from an examination of the three least-squares planes (Table IVg–i), which to a close approximation are coincident with the three vertical mirror planes of the latter tricobalt fragment; the observed variations in the perpendicular distances of chemically equivalent atoms from these three least-squares planes in general are less than 0.2 Å.

The apical sulfur atom is symmetrically coordinated to the basal $\mathrm{Co_3(CO)_6(S)_3}$ residue containing three identical basal Co(CO)(S) groups positioned at the corners of an equilateral triangle and joined in pairs to one another by both a bridging carbonyl and a Co–Co bond. On replacement of the apical sulfur atom with an apical $\mathrm{Co(CO)_3}$ group and the three axial mercapto sulfur ligands with three carbonyl ligands, the derived structure is stereochemically analogous to that of $\mathrm{Co_4(CO)_{12}}$[16,17] and $\mathrm{Rh_4(CO)_{12}}$.[18] It is noteworthy that this basal $\mathrm{Co_3(CO)_6(S)_3}$ residue (containing bridging carbonyl groups) is dissimilar to the basal $\mathrm{M_3(CO)_9}$ frag-

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Table III (*Continued*)

B. $SCo_3(CO)_6S_3$ Fragment (the *idealized* configuration possesses C_3-3m symmetry)

M–M–M	
Co_4–Co_5–Co_6	59.6 (2)
Co_5–Co_6–Co_4	60.0 (2)
Co_6–Co_4–Co_5	60.4 (2)
	60.0 (av)

S–M–S	
S_1–Co_4–S_5	151.0 (4)
S_2–Co_5–S_5	151.8 (4)
S_3–Co_5–S_5	151.7 (4)
	151.5 (av)

M–S–M	
Co_4–S_5–Co_5	69.3 (3)
Co_5–S_5–Co_6	69.6 (3)
Co_6–S_5–Co_4	69.1 (3)
	69.3 (av)

S–M–M	
S_5–Co_4–Co_5	55.5 (3)
S_5–Co_5–Co_4	55.2 (3)
S_5–Co_5–Co_6	55.1 (3)
S_5–Co_6–Co_5	55.3 (3)
S_5–Co_6–Co_4	55.4 (3)
S_5–Co_4–Co_6	55.5 (3)
	55.3 (av)

S–M–M	
S_1–Co_4–Co_5	99.7 (3)
S_1–Co_4–Co_6	101.0 (3)
S_2–Co_5–Co_4	101.1 (3)
S_2–Co_5–Co_6	101.4 (3)
S_3–Co_6–Co_5	101.3 (3)
S_3–Co_6–Co_4	100.7 (3)
	100.9 (av)

S–M–CO	
S_5–Co_4–C_{4T}	104.0 (13)
S_5–Co_5–C_{5T}	106.3 (12)
S_5–Co_6–C_{6T}	105.7 (13)
	105.3 (av)
S_5–Co_4–C_{3B}	83.4 (10)
S_5–Co_4–C_{5B}	87.2 (10)
S_5–Co_5–C_{3B}	85.9 (11)
S_5–Co_5–C_{4B}	83.8 (11)
S_5–Co_6–C_{4B}	85.6 (11)
S_5–Co_6–C_{5B}	85.9 (10)
	85.3 (av)
S_1–Co_4–C_{4T}	104.8 (12)
S_2–Co_5–C_{5T}	101.9 (12)
S_3–Co_6–C_{6T}	102.5 (13)
	103.1 (av)

S–M–CO	
S_1–Co_4–C_{3B}	90.3 (10)
S_1–Co_4–C_{5B}	89.6 (10)
S_2–Co_5–C_{3B}	90.6 (10)
S_2–Co_5–C_{4B}	90.0 (10)
S_3–Co_6–C_{4B}	89.5 (10)
S_3–Co_6–C_{5B}	88.4 (10)
	89.7 (av)

M–M–CO	
Co_5–Co_4–C_{4T}	138.3
Co_6–Co_4–C_{4T}	142.5
Co_4–Co_5–C_{5T}	142.3
Co_6–Co_5–C_{5T}	141.6
Co_4–Co_6–C_{6T}	139.9
Co_5–Co_6–C_{6T}	143.1
	141.3 (av)
Co_4–Co_5–C_{3B}	53.0 (10)
Co_5–Co_4–C_{3B}	48.9 (10)
Co_5–Co_6–C_{4B}	49.4 (10)
Co_6–Co_5–C_{4B}	47.0 (10)
Co_4–Co_6–C_{5B}	49.7 (10)
Co_6–Co_4–C_{5B}	51.5 (11)
	49.9 (av)

M–CO–M	
Co_4–C_{3B}–Co_5	78.1 (14)
Co_5–C_{4B}–Co_6	83.6 (14)
Co_4–C_{5B}–Co_6	78.8 (13)
	80.2 (av)

OC–M–CO	
C_{4T}–Co_4–C_{3B}	97.4 (15)
C_{4T}–Co_4–C_{5B}	101.7 (15)
C_{5T}–Co_5–C_{3B}	97.3 (16)
C_{5T}–Co_5–C_{4B}	103.1 (16)
C_{6T}–Co_6–C_{4B}	103.1 (16)
C_{6T}–Co_6–C_{5B}	98.9 (17)
	100.3 (av)
C_{3B}–Co_4–C_{5B}	160.3 (17)
C_{3B}–Co_5–C_{4B}	159.1 (17)
C_{4B}–Co_6–C_{5B}	157.8 (17)
	159.1 (av)

M–C–O	
Co_4–C_{4T}–O_{4T}	175.4 (40)
Co_5–C_{5T}–O_{5T}	177.2 (31)
Co_6–C_{6T}–O_{6T}	174.4 (32)
	175.7 (av)
Co_4–C_{3B}–O_{3B}	135.2 (27)
Co_5–C_{3B}–O_{3B}	144.4 (28)
Co_5–C_{4B}–O_{4B}	131.9 (22)
Co_6–C_{4B}–O_{4B}	144.5 (23)
Co_4–C_{5B}–O_{5B}	145.9 (30)
Co_6–C_{5B}–O_{5B}	135.3 (29)
	139.5 (av)

C. Bond Angles between Two Fragments

Co_1–S_3–Co_6	120.2 (4)	Co_1–S_2–Co_5	122.1 (4)	Co_3–S_2–Co_5	124.4 (4)	Co_4–S_1–C_{1E}	115.2 (10)
Co_2–S_3–Co_6	122.2 (4)	Co_2–S_1–Co_4	122.8 (4)	Co_3–S_1–Co_4	122.8 (4)	Co_5–S_2–C_{3E}	111.5 (9)
	121.2 (av)		122.4 (av)		123.6 (av)	Co_6–S_3–C_{5E}	110.5 (10)
							112.4 (av)

[a] Standard deviations of last significant figures are given in parentheses.

ments in $SCo_3(CO)_9$,[19] $SFeCo_2(CO)_9$,[20] $Co_3(CO)_9CCH_3$,[21] and $Ir_4(CO)_{12}$[22,23] for which the $M(CO)_3$ groups are joined to one another by only metal–metal bonds (without bridging carbonyls).

This triply bridging metal-coordinated apical sulfur atom in the $SCo_3(CO)_6(S)_3$ residue is analogous to those found from X-ray studies in $SCo_3(CO)_9$,[19] $SFeCo_2(CO)_9$,[20] $[SCo_3(CO)_7]_2S_2$,[24] $[C_5H_5FeS]_4$,[25,26] the $S_2Fe_3(CO)_9$ species of $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$,[27] and $CsFe_4S_3(NO)_7 \cdot H_2O$;[28] in all of these molecular complexes a basic tetrahedral-like valency can be assumed for each triply bridging sulfur atom with an unshared electron pair in the fourth localized sulfur orbital. The average bond length of 2.16 Å for the three symmetry-related Co–S_{ap} distances in the $Co_3(CO)_6(S)_3$ residue of $SCo_6(CO)_{11}(SC_2H_5)_4$ is significantly shorter than the average values of 2.21 and 2.28 Å for the doubly and triply bridging Co–SR bonds, respectively; it compares favorably with the average Co–S_{ap} values of 2.14 Å in both $SCo_3(CO)_9$[19] and $[SCo_3(CO)_7]_2S_2$[24] and of 2.16 Å in $SFeCo_2(CO)_9$.[20]

The mean value of 2.46 Å for the distances in the equilateral cobalt triangle of the $Co_3(CO)_6(S)_3$ residue falls within the range of average Co–Co bond lengths in the diamagnetic complexes $[SCo_3(CO)_7]_2S_2$ (2.47 and 2.53 Å for the two isosceles triangles),[24] $Co_3(CO)_9CCH_3$ (2.46 Å),[21] $Co_4(CO)_{12}$ (2.49 Å),[16] and $SFeCo_2(CO)_9$ (2.55 Å)[20] but is considerably shorter than the average value of 2.64 Å found in the paramagnetic complex

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

(a) Plane through Co_1, Co_2, and Co_3

$-0.368X + 0.759Y - 0.537Z + 1.329 = 0$

C_{1T}	0.19	O_{3T}	0.59	S_2	−1.54
O_{1T}	0.35	S_4	1.43	S_3	−1.52
C_{2T}	0.32	C_{1B}	1.16	Co_4	−3.77
O_{2T}	0.55	C_{2B}	1.13	Co_5	−3.71
C_{3T}	0.39	S_1	−1.54	Co_6	−3.70

(b) Plane through S_1, S_2, and S_3

$-0.375X + 0.756Y - 0.536Z + 2.891 = 0$

Co_1	1.52	Co_4	−2.23	S_4	2.94
Co_2	1.53	Co_5	−2.17	C_{1B}	2.71
Co_3	1.54	Co_6	−2.18	C_{2B}	2.67

(c) Plane through Co_4, Co_5, and Co_6

$-0.389X + 0.740Y - 0.549Z + 5.299 = 0$

S_5	−1.63	C_{5T}	−0.69	O_{3B}	0.26
S_1	2.24	O_{5T}	−1.25	C_{4B}	0.11
S_2	2.17	C_{6T}	−0.69	O_{4B}	0.23
S_3	2.17	O_{6T}	−1.31	C_{5B}	0.12
C_{4T}	−0.85	C_{3B}	0.03	O_{5B}	0.19
O_{4T}	−1.37				

(d) Plane through S_2, S_3, S_4, and C_{2B}

$-0.564X - 0.658Y - 0.500Z + 9.673 = 0$

S_2	−0.01	C_{1B}	0.16	C_{1T}	−2.31
S_3	0.00	Co_1	−0.52	C_{1T}	−3.39
S_4	−0.01				

(e) Plane through S_1, S_3, S_4, and C_{1B}

$0.308X - 0.403Y - 0.862Z + 7.589 = 0$

S_2	0.01	C_{1B}	−0.23	C_{2T}	2.29
S_3	−0.01	Co_2	0.52	O_{2T}	3.35
S_4	0.02				

(f) Plane through S_1, S_2, C_{1B}, and C_{2B}

$0.928X + 0.201Y - 0.314Z + 0.401 = 0$

S_1	0.00	C_{2B}	0.12	C_{3T}	−2.23
S_2	0.00	Co_3	−0.56	O_{3T}	−3.42
C_{1B}	−0.07				

(g) Plane through Co_1, S_1, Co_4, and S_5

$0.729X - 0.102Y - 0.677Z + 4.502 = 0$

Co_1	0.00	C_{1T}	−0.31	S_4	1.61
S_1	−0.01	O_{1T}	−0.29	C_{2B}	−1.25
Co_4	0.01	C_{1B}	−0.18	S_3	1.71
S_5	0.01	O_{1B}	−0.01	S_2	−1.64
Co_2	1.20	C_{1E}	−0.13	C_{5E}	3.30
Co_3	−1.27	C_{4B}	0.07	C_{3E}	−3.16
Co_6	1.24	O_{4B}	0.04	C_{5B}	−1.96
Co_5	−1.23	C_{4T}	−0.09	O_{5B}	2.99
Centroid (Co_1, Co_2, Co_3)	−0.02	O_{4T}	−0.09	O_{3B}	−2.94
		C_{2T}	2.65	C_{6T}	−2.53
Centroid (Co_4, Co_5, Co_6)	0.01	C_{3T}	−2.69	O_{6T}	3.44
		O_{2T}	3.49	O_{5T}	−3.46
		O_{3T}	−3.70		

(h) Plane through Co_2, S_3, Co_5, and S_5

$-0.852X - 0.517Y - 0.080Z + 5.145 = 0$

Co_2	0.00	C_{2T}	0.13	S_4	−1.68
S_2	0.00	O_{2T}	0.24	C_{1B}	1.31
Co_5	0.00	C_{2B}	−0.07	S_3	−1.70
S_5	0.00	O_{2B}	−0.12	S_1	1.60
Co_1	−1.29	C_{3E}	−0.21	C_{5E}	−3.28
Co_3	1.20	C_{5B}	−0.01	C_{1E}	3.22
Co_6	−1.26	O_{5B}	−0.12	C_{4B}	−1.84
Co_4	1.19	C_{5T}	0.02	C_{3B}	1.88
Centroid (Co_1, Co_2, Co_3)	−0.03	O_{5T}	−0.01	O_{4B}	−2.90
		C_{1T}	−2.66	O_{3B}	2.93
Centroid (Co_4, Co_5, Co_6)	−0.02	C_{3T}	2.64	C_{6T}	−2.49
		O_{1T}	−3.60	C_{4T}	2.67
		O_{3T}	3.67	O_{6T}	−3.46
				O_{4T}	3.44

(i) Plane through Co_3, S_3, S_4, Co_6, and S_5

$-0.138X - 0.625Y - 0.768Z + 9.866 = 0$

Co_3	0.00	C_{7E}	−0.12	O_{1B}	1.96
S_3	0.03	C_{5E}	0.03	O_{2B}	−2.10
S_4	−0.02	C_{3B}	−0.03	C_{1E}	3.21
Co_6	−0.01	O_{3B}	0.05	C_{3E}	−3.35
S_5	0.00	C_{6T}	0.02	S_1	1.67
Co_1	−1.26	O_{6T}	−0.04	S_2	−1.61
Co_2	1.28	C_{1T}	−2.98	C_{4B}	−1.78
Co_5	−1.21	C_{2T}	2.86	C_{5B}	1.92
Co_4	1.25	O_{1T}	−3.91	O_{4B}	−2.98
Centroid (Co_1, Co_2, Co_3)	0.00	O_{2T}	3.82	O_{5B}	2.92
		C_{1B}	1.23	C_{4T}	2.66
Centroid (Co_4, Co_5, Co_6)	0.01	C_{2B}	−1.27	C_{5T}	−2.50
				O_{4T}	3.44
C_{3T}	0.05			O_{5T}	−3.48
O_{3T}	0.08				

[a] The equations of the planes are given in an orthogonal ångstrom coordinate system (X, Y, Z) which is related to the monoclinic fractional unit cell coordinate system (x, y, z) by the transformation $X = ax + cz\cos\beta$, $Y = by$, and $Z = cz\sin\beta$.

$SCo_3(CO)_9$.[19,29] Hence, the determined Co–Co distances in the $Co_3(CO)_6(S)_3$ fragment of $SCo_6(CO)_{11}(SC_2H_5)_4$ are not incompatible with the reasonable assumption of a closed-shell electronic configuration for each of the three cobalt atoms. An electron count of the remaining valence electrons shows the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue of $SCo_6(CO)_{11}(SC_2H_5)_4$ to be an *electronic analog* of the $Co_3X_6Y_3$ system in the same trimeric residue of $Co_5(CO)_{10}(SC_2H_5)_5$ and in the $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ molecule. The nature of bonding and resulting implications of this triangular cobalt atom cluster system have been presented elsewhere.[1,5]

Each of the three symmetrically bridging carbonyl groups is slightly tipped upward from the plane of the three cobalt atoms toward the side of the apical sulfur atom to the extent that each oxygen is displaced by only 0.2 Å from the tricobalt plane (Table IVc). As expected, the mean length of 1.91 Å for the six bridging Co–CO bonds is approximately 0.2 Å longer than the mean value for the three terminal Co–CO bonds.

The ligand arrangement about each cobalt atom in the $SCo_3(CO)_6(S)_3$ residue provides considerable insight concerning the nature of bonding of this tricobalt atom cluster. Each cobalt atom is coordinated to seven groups: one terminal carbonyl, two bridging carbonyls, the apical sulfur atom, one mercapto sulfur atom, and the other two cobalt atoms. The localized sulfur–carbon environment (without the two cobalt atoms) is a distorted square pyramid with the terminal carbonyl group located at the apex. The upward disposition of each apical terminal carbonyl group from the tricobalt plane by approximately 26° is such to give four approximately equal OC(apical)–Co–(basal ligand) angles for this square-pyramidal configuration; the

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(29) The significant influence of the extra unpaired electron in $SCo_3(CO)_9$ on the molecular geometry of the cobalt atom cluster system was shown from the fact that the average metal–metal bond length in the isomorphous, diamagnetic complex $SFeCo_2(CO)_9$ is 0.083 Å shorter than that in $SCo_3(CO)_9$; an explanation for this lengthening of the metal–metal bonds in $SCo_3(CO)_9$ relative to those in $SFeCo_2(CO)_9$ is that the unpaired electron in $SCo_3(CO)_9$ is accommodated in an MO which is antibonding with respect to the cobalt AO's.[20]

average values are 100° for the two OC(terminal)–Co–CO(bridging) angles, 105° for the OC(terminal)–Co–S(apical) angle, and 103° for the OC(terminal)–Co–S(axial) angle. These obtuse angles result from the displacement of the cobalt atoms from their respective basal planes in the direction of their apical terminal carbonyl groups. Similar displacements of the metal atoms in a square-pyramidal sulfur–carbon configuration occur in the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue of $SCo_6(CO)_{11}(SC_2H_5)_4$ (see Table IVd–f) as well as in $[C_2H_5SFe(CO)_3]_2$[30] and $[SFe(CO)_3]_2$.[31]

Since the square-pyramidal ligand surroundings of each cobalt atom in the $Co_3(CO)_6(S)_3$ residue resemble those about each metal atom in the $[Re_3Cl_{12}]^{3-}$ anion,[32] the results of the metal cluster MO model applied by Cotton and Haas[33] to the trirhenium part of $[Re_3Cl_{12}]^{3-}$ can also be utilized for the tricobalt part of $SCo_3(CO)_6(S)_3$. After allowance for cobalt–ligand σ bonding (which utilizes the s, p_x, p_y, p_z, and $d_{x^2-y^2}$ orbitals on each cobalt atom), the remaining four valence d orbitals per cobalt atom under C_{3v} symmetry yield *six* bonding and *six* antibonding metal symmetry orbitals for the tricobalt cluster system.[34] Based on the energy-level diagram calculated by Cotton and Haas[33] for the trirhenium fragment in the $[Re_3Cl_{12}]^{3-}$ anion being qualitatively applicable for the tricobalt system in $Co_3(CO)_6(S)_3$ fragment (*i.e.*, from overlap estimations this assumption of similar orbital ordering is not unreasonable), the 18 valence electrons available for direct cobalt–cobalt interactions are accommodated in the six bonding and three of the six antibonding cobalt symmetry orbitals, *viz.* $d_{z^2}(a_1)^2$, $d_{yz}(a_1)^2$, $d_{xz}(e)^4$, $d_{xy}(e)^4$, $d_{yz}(e^*)^4$, $d_{xy}(a_2^*)^2$. Since the corresponding occupied bonding and antibonding levels are assumed to practically cancel one another's bonding, the cobalt–cobalt bonding is effectively due to $d_{z^2}(a_1)^2$, $d_{xz}(e)^4$. This orbital configuration is analogous in valence-bond language to a localized electron-pair σ bond between each pair of cobalt atoms. A $(d_{z^2} \pm d_{xz})$ combination at each cobalt atom gives rise to two equivalent hybrid orbitals directed toward the other two cobalt atoms; the cobalt–cobalt single bond is then formed between each pair of cobalt atoms by direct overlap of two corresponding orbitals of this kind.[35] The net effect of π bonding of the ligands with the tricobalt system no doubt is to delocalize charge density from the cobalt atom cluster onto the ligands. From energetic considerations it appears reasonable that the greatest transfer of electron density to the appropriate ligand π orbitals will occur from the antibonding metal symmetry orbitals thereby resulting in an increased bond strength of the metal atom fragment. These bonding rationalizations appear to apply in general to all metal atom cluster carbonyl systems.[1,5]

Geometric considerations show the type and degree of polymerization of these polynuclear cobalt carbonyl sulfur complexes to be governed by the stereochemical arrangement of the mercapto methylene groups. For the three mercapto groups on one side of the tricobalt plane of the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ residue contained in both $SCo_6(CO)_{11}(SC_2H_5)_4$ and $Co_5(CO_{10}(SC_2H_5)_5$, the methylene carbon atoms are positioned equatorially relative to the tricobalt plane, whereas the fourth bridging mercapto group on the other side has its methylene carbon atom positioned axially relative to the tricobalt plane. As previously discussed in the paper[5] on the molecular $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ complex, the steric compression of the methylene groups is such that: (1) no two S–CH_2 bonds can both be equatorial for two sulfur atoms oriented 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. Consequently, two bridging carbonyl groups are required to occupy the other two X coordination sites in the $Co_3X_6Y_3$ system of both the $SCo_6(CO)_{11}(SC_2H_5)_4$ and $Co_5(CO)_{10}(SC_2H_5)_5$ complexes. The further reaction of ethyl mercaptan with either of these complexes presumably would take place at the bridging carbonyl position and hence would cause a breakdown to the known trimeric complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ for which five (but not six) S–CH_2 bonds satisfy the above steric requirements. These observations account for the experimental fact that the hexamer is the chemical precursor of the trimer.

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(34) A consideration of the transformation properties of the cobalt symmetry orbitals of this $SCo_3(CO)_6(S)_3$ fragment in terms of the observed chemically equivalent C_{3v} symmetry rather than D_{3h} symmetry invoked for the $[Re_3Cl_{12}]^{3-}$ anion has no practical effect concerning these qualitative bonding arguments. As in the $[Re_3Cl_{12}]^{3-}$ anion and $Co_3X_6Y_3$ system, local right-handed coordinate systems were chosen at each cobalt atom with the *z* axis directed inward along the apical Co–CO line toward the center of the cobalt triangle and the *x* axis located in the plane of the cobalt triangle and tangential to it. The angular positioning of the square-pyramidal array of ligands for each cobalt relative to the tricobalt plane is such that the three localized cobalt coordinate systems do not have their centripetally directed *z* axes intersect at the centroid of the tricobalt triangle but instead intersect below it; although this rotational distortion changes the weighting coefficients in the overlap integrals, it does not affect the C_{3v} classifications of the various metal symmetry orbitals.

(35) The MO bond order for a pair of metal atoms in the triangular cobalt array is $+^2/_3$ for a completely filled bonding representation and $-^2/_3$ for a completely filled antibonding one.[5] Hence, the *net* MO bond order for the four occupied bonding and two occupied antibonding representations in the $Co_3(CO)_6(S)_3$ fragment is $+^4/_3$ which has been shown for the triangular metal arrangement to correspond to a valence-bond metal–metal bond order of *one*.[5] This metal–metal electron pair σ bonding in the $Co_3(CO)_6(S)_3$ residue results in a closed-shell electronic configuration for each cobalt atom. For these triangular metal atom cluster systems which contain electrons in antibonding metal symmetry orbitals, it should be noted that the valence-bond metal–metal order number does *not* necessarily represent the difference between the number of electron pairs in the bonding and antibonding metal symmetry orbitals divided by the number of pairs of adjacent metal atoms. Although a correct valence-bond cobalt–cobalt order of *one* is obtained by application of this rule to the $Co_3(CO)_6(S)_3$ fragment (which has nine electron pairs distributed in *six* bonding and *three* antibonding metal symmetry orbitals), in the $Co_3X_6Y_3$ system (where 20 electrons are distributed in *five* bonding and *five* antibonding cobalt symmetry orbitals) this rule leads to an *incorrect* estimate of *zero* for the valence-bond cobalt–cobalt order.