Organometallic Sulfur Complexes. X. Structural and Bonding Characterization of a Trimeric Mercaptocobalt Carbonyl Complex, $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$, Containing a New Basic Polyhedral Unit for a Triangular Metal Cluster[1]

Chin Hsuan Wei and Lawrence F. Dahl

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received July 24, 1967

Abstract: An X-ray structural determination of the diamagnetic molecular complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ has provided the first known example of a new kind of trimeric metal cluster system. The three cobalt atoms form a triangular arrangement with three coplanar terminal carbonyl groups each attached to a cobalt atom along an internuclear line directed at the centroid of the triangle. The remaining carbonyl and five mercapto ligands are located in pairs above and below the tricobalt plane but essentially equidistant from each pair of adjacent cobalt atoms to give doubly bridging groups. Each cobalt atom is thereby surrounded by one terminal apical ligand and four bridging basal ligands arranged at the corners of a distorted rectangular pyramid; the resulting molecular configuration formally can be considered to arise from the fusion of the three rectangular pyramids at opposite basal edges. A comparison of the structural and bonding features is made with those of the $[Re_3Cl_{12}]^{3-}$ triangular cluster. The geometry of the trigonal-prismatic part of the sulfur–carbon polyhedron is related to the trigonal-prismatic geometry of sulfur atoms in several monomeric molecular metal complexes. The importance of the methylene groups in determining the stoichiometry of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ is discussed. Crystals of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ are monoclinic with four molecules in a unit cell of symmetry $P2_1/c$ and of dimensions $a = 8.32$ Å, $b = 14.55$ Å, $c = 20.28$ Å, and $\beta = 107°\ 55'$. A full-matrix isotropic least-squares refinement of the structure yielded an unweighted reliability index of $R_1 = 9.7\%$ for the observed three-dimensional film data.

From an extensive systematic investigation of the effect of various organosulfur compounds on both hydrogenation and hydroformylation of olefins, Markó, Bor, and coworkers[2-8] have produced by the reaction of the hydroformylation catalyst dicobalt octacarbonyl with sulfur, mercaptans, organic disulfides, and other sulfur-containing reagents a large number of unusual polymeric cobalt carbonyl sulfur complexes. The reaction by Klumpp, Markó, and Bor[6] between $Co_2(CO)_8$ and ethyl mercaptan in hexane solution at room temperature resulted in two new complexes formulated by them as $Co_4(CO)_5(SC_2H_5)_7$ and $Co_4(CO)_7(SC_2H_5)_3$. In an attempt to prepare the presumed complex $[C_2H_5SCo(CO)_3]_2$,[9] our investigation[10] of the same reaction at 0° *without solvent* instead yielded the first known example of a pentanuclear cobalt complex, $Co_5(CO)_{10}(SC_2H_5)_5$, whose formula and structure were completely characterized from an X-ray diffraction study and later verified by elemental analysis. Since the stoichiometry of these polymeric complexes cannot be unambiguously characterized by the usual chemical and physical methods,[11-13] X-ray studies of the presumed $Co_4(CO)_5(SC_2H_5)_7$ and $Co_4(CO)_7(SC_2H_5)_3$ were initiated in order to ascertain their formulas as well as to obtain more definitive information about the structural interrelationships and bonding of these ethylthiocobalt carbonyl complexes. This paper reports the X-ray structural determination of the presumed $Co_4(CO)_5(SC_2H_5)_7$ which revealed a new type of molecular complex of actual formula $Co_3(CO)_4(SC_2H_5)_5$.

Experimental Section

A sample of the presumed $Co_4(CO)_5(SC_2H_5)_7$ compound was most generously furnished to us by Drs. L. Markó and G. Bor of the Hungarian Oil and Gas Research Institute (Veszprém). Slow recrystallization from petroleum ether (bp 60–68°) provided suitable single crystals for X-ray work. A rhombic-shaped crystal of dimensions 0.20 × 0.28 × 0.34 mm was selected and oriented inside a thin-walled glass capillary such that the Weissenberg rotation axis approximately corresponded to a face-diagonal direction. Since μR_{max} was estimated to be less than 0.5 (*i.e.*, the linear absorption coefficient for Mo Kα radiation is 26.5 cm^{-1}), no absorption corrections were made. Precession photographs calibrated with a NaCl crystal were used for determination of unit cell parameters. Weissenberg intensity data of nine reciprocal levels, $0kl$ through $8kl$, and precession intensity data of four reciprocal levels ($hk0$, $h0l$, $h1l$, and $h2l$) were collected by the usual techniques with Mo Kα radiation. Relative intensities were estimated visually by comparison with a time-calibrated set of intensities for a given reflection made from the same crystal. A total of 1144 independent, observed reflections were obtained of which 88 were recorded only with the precession camera. Comparison of common reflections enabled the Weissenberg and precession data to be placed initially on one relative scale. Final adjustment of the 13 separate scale factors for the different reciprocal levels was made

---

(1) (a) Previous paper in this series: D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.*, 89, 3727 (1967); (b) presented in part at the National Meeting of the American Crystallographic Association, Gatlinburg, Tenn., June 27–July 2, 1965.

(2) L. Markó, G. Bor, and G. Almásy, *Chem. Ber.*, 94, 847 (1961).

(3) L. Markó, G. Bor, and E. Klumpp, *Chem. Ind.* (London), 1491 (1961).

(4) L. Markó, G. Bor, E. Klumpp, B. Marko, and G. Almasy, *Chem. Ber.*, 96, 955 (1963).

(5) L. Markó, G. Bor, and E. Klumpp, *Angew. Chem.*, 75, 248 (1963).

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

(7) S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometal. Chem.* (Amsterdam), 1, 373 (1964).

(8) (a) L. Markó and G. Bor, *ibid.*, 3, 161 (1965); (b) E. Klumpp, G. Bor, and L. Markó, *Chem. Ber.*, 100, 1451 (1967).

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

(10) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, 90, 3969 (1968).

(11) Examples of other transition metal carbonyl sulfur complexes whose formulas were characterized by X-ray investigations include $[C_5H_5FeS]_4$[12] and $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$.[13]

(12) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, 5, 900 (1966).

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

by least-squares refinement. Variable weights were assigned to the derived structure factors according to the following scheme: $\sqrt{w} = 20/F_o$ if $I_o \geq 4I_o(\text{min})$; $\sqrt{w} = 1.25\ I_o^2/F_oI_o(\text{min})^2$ if $I_o < 4I_o(\text{min})$.

An infrared spectrum of the recrystallized sample was recorded on the Perkin-Elmer Model 421 grating spectrometer; all absorption bands including those in terminal and bridging carbonyl stretching regions were in accord with those reported by Klumpp, Markó, and Bor.[6]

Magnetic measurements at room temperature by the Faraday method in solid state and by nuclear resonance[14] in solution of small samples, carefully recrystallized several times under an argon atmosphere to remove trace amounts of paramagnetic decomposition products, showed $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ to be diamagnetic. The magnetic suceptibility measured by the Faraday method showed little field dependence from 5.0 to 8.15 kG thereby indicating the absence of ferromagnetic impurities. A mean diamagnetically corrected value of $\chi_{\text{mole}} = -81 \times 10^{-6}$ was found at 27°. The nmr solution method confirmed the diamagnetic character of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ in that no frequency shifts in the proton resonance lines of the inert reference, cylohexane, were observed. This latter method was calibrated by use of various paramagnetic solutions of cobaltocene and nickelocene.

Results

Unit Cell and Space Group. The lattice parameters of the monoclinic unit cell are $a = 8.32 \pm 0.01$ Å, $b = 14.55 \pm 0.02$ Å, $c = 20.28 \pm 0.03$ Å, and $\beta = 107° 55' \pm 10'$; volume of unit cell = 2336 Å^3. The observed systematic absences of $\{h0l\}$ for $l = 2n + 1$ and $\{0k0\}$ for $k = 2n + 1$ uniquely indicate the space group to be P2$_1$/c (C_{2h}^5, No. 14),[15] which subsequently was confirmed by the successful refinement of the resulting structure. An experimental density of 1.64 g cm^{-3} was obtained by the flotation method.

Determination of the Composition and Structure. An indication that the presumed formula $Co_4(CO)_5(SC_2H_5)_7$ was incorrect resulted from the calculation of only 2.9 formula species per unit cell on the basis of the unit cell dimensions and observed density. With the assumption of four formula species per unit cell (as suggested by the fourfold general positions of P2$_1$/c), a formula weight of 576.9 was calculated from the crystallographic data. From considerations of the reported elemental analyses, a formula $Co_3(CO)_4(SC_2H_5)_5$ with formula weight = 594.5 and $\rho_{\text{calcd}} = 1.69$ g cm^{-3} was deduced, which subsequently was shown by the structural analysis to be correct. The composition based on this formula is in excellent agreement with the elemental analyses for the compound given by Klumpp, Markó, and Bor.[6] *Anal.* Calcd for $Co_3(CO)_4(SC_2H_5)_5$: Co, 29.74; S, 26.97; C, 28.28; H, 4.24; O, 10.77. Found: Co, 29.53, 30.15; S, 27.79, 27.84, 28.27, 28.36; C, 28.11, 28.21; H, 4.29, 4.43.

Examination of the peaks of a computed three-dimensional Patterson function[16] showed a self-consistent set of three vectors of length ~2.5 Å which indicated a triangular array of cobalt atoms. The initial x and z coordinates of these three presumed cobalt atoms were fixed from an analysis of the Harker section (u, $^1/_2$, w). Although additional intramolecular Patterson vectors of length ~2.3 Å were detected (no doubt corresponding to Co–S vectors), attempts were not made to locate the sulfur atoms from the sharpened Patterson function. A block-diagonal least-squares refinement[17] of the atomic coordinates of the three cobalt atoms was then performed in which an isotropic temperature factor of 2.0 Å^2 was assumed initially for each cobalt atom. After two cycles the usual unweighted reliability factor (R_1) possessed a value of 39.4%. A three-dimensional Fourier synthesis based on the phases of the three cobalt atoms was calculated, and coordinates for five sulfur atoms and two carbonyl groups were acquired. Two cycles of block-diagonal refinement lowered R_1 to 19.6% whereupon a second Fourier map phased on the 12 atoms was calculated. An additional assignment of 12 density peaks as eight ethyl carbon atoms, two carbonyl carbon atoms, and two oxygen atoms was made. Two more cycles of least-squares refinement of the 24 determined atoms decreased R_1 to 12.7%, after which a third computed Fourier synthesis successfully revealed the positional parameters of the remaining two ethyl carbon atoms. Block-diagonal least-squares isotropic refinement of all 26 nonhydrogen atoms resulted after two cycles in $R_1 = 10.6\%$. Further least-squares refinement with a local version of the Busing–Martin–Levy full-matrix program[18] was continued until all individual parameter shifts became less than 28% of the corresponding standard deviations. After correction of two indexing errors, the refinement was terminated after two additional cycles; the final reliability factors are $R_1 = 9.7\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w \cdot |F_o|^2]^{1/2} \times 100 = 10.4\%$. A final difference Fourier synthesis showed no anomalies. No attempt was made to locate the positions of the hydrogen atoms. All 26 nonhydrogen atoms were found to occupy the general

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	0.2894 (5)	0.3528 (3)	0.1520 (2)	3.0 (1)
Co_2	0.4604 (5)	0.2647 (3)	0.0878 (2)	3.0 (1)
Co_3	0.5308 (5)	0.2458 (3)	0.2154 (2)	3.4 (1)
S_4	0.4763 (11)	0.1277 (6)	0.1403 (4)	4.1 (2)
S_5	0.2532 (11)	0.2349 (6)	0.2174 (4)	4.1 (2)
S_6	0.1693 (10)	0.2751 (5)	0.0529 (4)	3.4 (2)
S_7	0.5015 (11)	0.3863 (6)	0.2502 (4)	3.9 (2)
S_8	0.4277 (10)	0.4158 (6)	0.0843 (4)	3.5 (2)
C_9	0.1367 (49)	0.4245 (29)	0.1554 (18)	6.6 (9)
O_{10}	0.0312 (29)	0.4747 (16)	0.1631 (11)	5.9 (6)
C_{11}	0.5193 (35)	0.2434 (21)	0.0176 (14)	3.9 (7)
O_{12}	0.5734 (30)	0.2209 (16)	−0.0292 (12)	6.8 (6)
C_{13}	0.6723 (52)	0.1976 (27)	0.2937 (20)	7.2 (11)
O_{14}	0.7722 (39)	0.1722 (19)	0.3407 (15)	8.9 (8)
C_{15}	0.6752 (44)	0.2833 (22)	0.1611 (16)	4.8 (8)
O_{16}	0.8093 (30)	0.3005 (16)	0.1677 (11)	5.9 (6)
C_{17}	0.6835 (36)	0.0693 (21)	0.1531 (13)	3.3 (6)
C_{18}	0.6634 (43)	0.0035 (24)	0.0895 (16)	6.5 (9)
C_{19}	0.2164 (43)	0.2792 (24)	0.2990 (17)	5.7 (8)
C_{20}	0.2187 (55)	0.1922 (28)	0.3406 (20)	7.5 (10)
C_{21}	0.0522 (40)	0.1750 (20)	0.0646 (16)	4.7 (8)
C_{22}	−0.0144 (53)	0.1316 (29)	−0.0064 (22)	8.5 (11)
C_{23}	0.6616 (44)	0.4667 (25)	0.2383 (16)	6.2 (9)
C_{24}	0.8236 (44)	0.4569 (23)	0.3013 (16)	5.9 (9)
C_{25}	0.2849 (34)	0.4641 (20)	0.0003 (12)	3.4 (7)
C_{26}	0.2261 (39)	0.5579 (23)	0.0108 (14)	5.0 (8)

---

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

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

(16) *Cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structures," G. Bell and Sons, Ltd., London, pp 170–174.

(17) P. W. Sutton, "A Crystallographic Block-Diagonal Least-Squares Program for the CDC 1604 Computer," University of Wisconsin, 1962.

(18) 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.

fourfold positions (4e) of $P2_1/c$: $\pm(x, y, z; -x, {}^1/_2 + y, {}^1/_2 - z)$.[15]

The final atomic parameters with their standard deviations are given in Table I.[19] Bond lengths and angles calculated with the Busing-Martin-Levy function and error program[20] are tabulated in Tables II and III, respectively. All Patterson and Fourier syntheses were computed with the Blount program.[21] The cobalt scattering factors of Thomas and Umeda,[22] the sulfur scattering factors of Dawson,[23] and the carbon and oxygen scattering factors of Berghuis, *et al.*,[24] were used in the structure factor calculations. Table IV gives the "best" molecular planes calculated by sets of specified atoms and the perpendicular distances from these planes.[25]

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

	Distance		Distance
Co_1–Co_2	2.550 (6)	C_{17}–C_{18}	1.57 (4)
Co_1–Co_3	2.553 (7)	C_{19}–C_{20}	1.52 (4)
	2.552 (av)	C_{21}–C_{22}	1.51 (5)
		C_{23}–C_{24}	1.55 (4)
Co_2–Co_3	2.485 (7)	C_{25}–C_{26}	1.49 (4)
Co_1–S_7	2.271 (11)		1.53 (av)
Co_1–S_8	2.241 (9)	$S_4 \ldots S_6$	3.39 (1)
	2.256 (av)	$S_4 \ldots S_5$	3.18 (1)
			3.29 (av)
Co_1–S_5	2.244 (9)		
Co_1–S_6	2.254 (9)	$S_5 \cdots S_6$	3.24 (1)
	2.249 (av)	$S_6 \cdots S_8$	2.89 (1)
		$S_5 \cdots S_7$	2.95 (1)
Co_2–S_8	2.214 (10)		2.92 (av)
Co_3–S_7	2.200 (10)		
		$S_8 \cdots S_7$	3.26 (1)
	2.207 (av)	$S_4 \cdots C_{15}$	2.76 (3)
		$S_8 \cdots C_{15}$	2.90 (3)
Co_2–S_6	2.310 (9)	$S_7 \cdots C_{15}$	3.03 (3)
Co_3–S_5	2.328 (10)		
			2.97 (av)
	2.319 (av)		
		$S_6 \cdots C_9$	3.08 (4)
Co_2–S_4	2.244 (9)	$S_5 \cdots C_9$	3.06 (4)
Co_3–S_4	2.247 (10)		
			3.07 (av)
	2.246 (av)		
		$S_6 \cdots C_{11}$	3.24 (3)
Co_1–C_9	1.66 (4)	$S_5 \cdots C_{13}$	3.40 (4)
Co_2–C_{11}	1.67 (3)		
Co_3–C_{13}	1.80 (4)		3.32 (av)
		$S_4 \cdots C_{11}$	3.11 (3)
	1.71 (av)	$S_4 \cdots C_{13}$	3.20 (4)
			3.16 (av)
Co_2–C_{15}	1.96 (3)		
Co_3–C_{15}	1.94 (3)	$S_8 \cdots C_9$	3.18 (4)
	1.95 (av)	$S_7 \cdots C_9$	3.10 (4)
			3.14 (av)
C_9–O_{10}	1.19 (4)		
C_{11}–O_{12}	1.22 (3)	$S_8 \cdots C_{11}$	3.06 (3)
C_{13}–O_{14}	1.12 (4)	$S_7 \cdots C_{13}$	3.09 (4)
	1.18 (av)		3.08 (av)
		$C_{15} \cdots C_{11}$	2.86 (4)
C_{15}–O_{16}	1.11 (4)	$C_{15} \cdots C_{13}$	2.97 (5)
S_4–C_{17}	1.87 (3)		
S_5–C_{19}	1.89 (3)		2.92 (av)
S_6–C_{21}	1.81 (3)		
S_7–C_{23}	1.84 (4)		
S_8–C_{25}	1.89 (3)		
	1.86 (av)		

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

Discussion

General Configuration. The structure of $Co_3(CO)_4(SC_2H_5)_5$ (Figure 1) is the first proven example of a basic $M_3X_6Y_3$ polyhedral structure which for six equivalent atomic X ligands can possess D_{3h} point group symmetry. The three metal atoms in this idealized structure form an equilateral triangular arrangement with three coplanar symmetry-related terminal Y ligands each attached to a metal atom along an internuclear line directed at the centroid of the triangle. The six X ligands are situated in pairs above and below the plane of the triangle of metal atoms but equidistant from each pair of adjacent metal atoms so as to give symmetrically doubly bridging metal-coordinated groups. Each equivalent metal atom is thereby surrounded by one terminal apical Y ligand and four bridging basal X ligands located at the corners of a rectangular pyramid; the resulting stereochemical disposition of nine X and Y ligands about the M_3 triangle formally can be considered to arise from the fusion of the three rectangular pyramids at opposite basal edges. Alternatively, this idealized ligand arrangement of D_{3h} symmetry may be described as a trigonal prism of six X ligands with each of the three Y ligands positioned outside a rectangular face of the prism on a horizontal C_2 axis.[26] Viewed as a symmetrically tricapped trigonal prism, this geometrical array of nine ligands also conforms to the usual nine-coordination about one central atom such as occurs in the $ReH_9{}^{2-}$ anion.[27,28] The three metal atoms in the $M_3X_6Y_3$ structure can also be interconnected by metal-metal interactions (*vide infra*).

In the case of $Co_3(CO)_4(SC_2H_5)_5$ (which according to the above structural type can be designated as $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$), the three cobalt atoms are

---

(19) Calculated and observed structure factor tables for $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ are deposited as Document No. 9957 with the 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.

(20) 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.

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

(22) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

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

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

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

(26) In order for the three MY fragments located at the vertices of an equilateral triangle to be equivalent, it should be realized that six identical X ligands in such a $M_3X_6Y_3$ structure need not necessarily be symmetrically bridging ligands as required by D_{3h} symmetry. The only necessity is that the six X groups be stereochemically oriented such that threefold symmetry is preserved. An example of an equilaterally arrayed triangle of equivalent metal atoms with unsymmetrical bridging groups is given by the $[Fe_4(CO)_{13}]^{2-}$ anion which contains three experimentally equivalent iron atoms with each pair linked by one highly unsymmetrical doubly bridging carbonyl group such that the anion possesses pseudo-threefold symmetry: R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

(27) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(28) For an excellent comprehensive review of higher coordination polyhedra, see E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967).

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

M-M-M	
$Co_1-Co_2-Co_3$	60.9 (2)
$Co_1-Co_3-Co_2$	60.8 (2)
	60.9 (av)
$Co_2-Co_1-Co_3$	58.3 (2)
M-S-M	
$Co_1-S_8-Co_2$	69.8 (3)
$Co_1-S_7-Co_3$	69.6 (3)
	69.7 (av)
$Co_1-S_6-Co_2$	67.9 (3)
$Co_1-S_5-Co_3$	67.8 (3)
	67.9 (av)
$Co_2-S_4-Co_3$	67.2 (3)
S-M-S	
$S_6-Co_1-S_5$	92.3 (3)
$S_4-Co_2-S_6$	96.1 (3)
$S_4-Co_3-S_5$	88.0 (3)
	92.1 (av)
$S_6-Co_1-S_8$	80.2 (3)
$S_5-Co_1-S_7$	81.7 (3)
	81.0 (av)
$S_6-Co_2-S_8$	79.5 (3)
$S_5-Co_3-S_7$	81.3 (3)
	80.4 (av)
$S_8-Co_1-S_7$	92.4 (3)
S-M-M	
$S_6-Co_1-Co_2$	57.1 (2)
$S_5-Co_1-Co_3$	57.6 (3)
	57.4 (av)
$S_6-Co_2-Co_1$	55.0 (2)
$S_5-Co_3-Co_1$	54.5 (3)
	54.8 (av)
$S_4-Co_2-Co_3$	56.5 (3)
$S_4-Co_3-Co_2$	56.3 (2)
	56.4 (av)
$S_8-Co_1-Co_2$	54.6 (3)
$S_7-Co_1-Co_3$	53.9 (3)
	54.3 (av)
S-M-M	
$S_8-Co_2-Co_1$	55.6 (2)
$S_7-Co_3-Co_1$	56.5 (3)
	56.1 (av)
$S_6-Co_1-Co_3$	102.0 (3)
$S_5-Co_1-Co_2$	96.6 (3)
	99.3 (av)
$S_6-Co_2-Co_3$	102.4 (3)
$S_5-Co_3-Co_2$	96.2 (3)
	99.3 (av)
$S_4-Co_2-Co_1$	99.5 (3)
$S_4-Co_3-Co_1$	99.3 (3)
	99.4 (av)
$S_8-Co_1-Co_3$	94.9 (3)
$S_7-Co_1-Co_2$	98.6 (3)
	96.8 (av)
$S_8-Co_2-Co_3$	97.5 (3)
$S_7-Co_3-Co_2$	102.6 (3)
	100.1 (av)
S-M-CO	
$S_6-Co_1-C_9$	102.5 (13)
$S_5-Co_1-C_9$	102.2 (14)
	102.4 (av)
$S_6-Co_2-C_{11}$	107.8 (10)
$S_5-Co_3-C_{13}$	109.9 (12)
	108.9 (av)
$S_4-Co_2-C_{11}$	104.5 (11)
$S_4-Co_3-C_{13}$	103.9 (13)
	104.2 (av)
$S_8-Co_1-C_9$	108.2 (14)
$S_7-Co_1-C_9$	103.1 (13)
	105.7 (av)
$S_8-Co_2-C_{11}$	102.8 (11)
$S_7-Co_3-C_{13}$	100.7 (13)
	101.8 (av)
$S_4-Co_2-C_{15}$	81.7 (9)
$S_4-Co_3-C_{15}$	82.1 (10)
	81.9 (av)
$S_6-Co_2-C_{15}$	148.1 (14)
$S_5-Co_3-C_{15}$	145.1 (14)
	146.6 (av)
S-M-CO	
$S_8-Co_2-C_{15}$	87.8 (14)
$S_7-Co_3-C_{15}$	94.0 (14)
	90.9 (av)
M-M-CO	
$Co_1-Co_2-C_{11}$	152.1 (10)
$Co_1-Co_3-C_{13}$	151.6 (12)
	151.9 (av)
$Co_2-Co_1-C_9$	153.0 (12)
$Co_3-Co_1-C_9$	148.7 (12)
	150.9 (av)
$Co_2-Co_3-C_{13}$	147.2 (12)
$Co_3-Co_2-C_{11}$	146.0 (10)
	146.6 (av)
$Co_1-Co_2-C_{15}$	93.8 (10)
$Co_1-Co_3-C_{15}$	94.1 (10)
	94.0 (av)
$Co_2-Co_3-C_{15}$	50.7 (12)
$Co_3-Co_2-C_{15}$	50.1 (12)
	50.4 (av)
M-CO-M	
$Co_2-C_{15}-Co_3$	79.1 (12)
OC-M-CO	
$C_{11}-Co_2-C_{15}$	103.5 (14)
$C_{13}-Co_3-C_{15}$	105.0 (15)
	104.3 (av)
M-C-O	
$Co_1-C_9-O_{10}$	175.1 (33)
$Co_2-C_{11}-O_{12}$	173.1 (27)
$Co_3-C_{13}-O_{14}$	173.2 (37)
	173.8 (av)
$Co_2-C_{15}-O_{16}$	140.5 (30)
$Co_3-C_{15}-O_{16}$	140.2 (30)
	140.4 (av)
M-S-CH$_2$	
$Co_2-S_4-C_{17}$	112.8 (10)
$Co_3-S_4-C_{17}$	105.6 (10)
$Co_1-S_5-C_{19}$	110.2 (12)
$Co_3-S_5-C_{19}$	115.0 (11)
$Co_1-S_6-C_{21}$	113.4 (10)
$Co_2-S_6-C_{21}$	117.6 (11)
$Co_1-S_7-C_{23}$	114.8 (11)
$Co_3-S_7-C_{23}$	113.1 (12)
$Co_1-S_8-C_{25}$	114.0 (9)
$Co_2-S_8-C_{25}$	115.9 (10)
	113.2 (av)
S-CH$_2$-CH$_3$	
$S_4-C_{17}-C_{18}$	107.6 (20)
$S_5-C_{19}-C_{20}$	103.0 (23)
$S_6-C_{21}-C_{22}$	105.4 (23)
$S_7-C_{23}-C_{24}$	108.2 (23)
$S_8-C_{25}-C_{26}$	110.9 (18)
	107.0 (av)

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

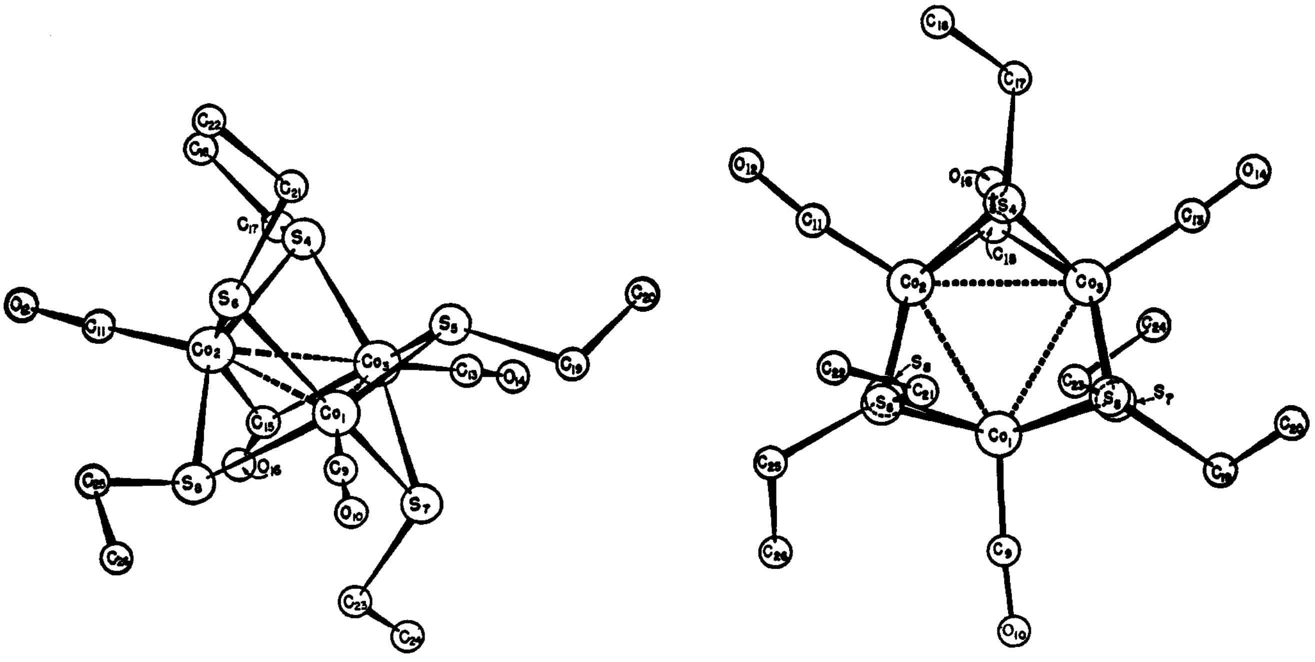


Figure 1. Molecular configuration of $Co_3[(CO)(SC_2H_5)_5](CO)_3$. The view on the right is a projection down the normal to the plane containing the $Co_3(CO)_3$ fragment.

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

(a) Plane through Co$_1$, Co$_2$, and Co$_3$					
$-0.631X - 0.763Y - 0.139Z + 5.246 = 0$					
C$_9$	0.01	C$_{13}$	−0.11	S$_6$	1.37
C$_{10}$	0.02	O$_{14}$	−0.29	S$_7$	−1.36
C$_{11}$	−0.16	S$_4$	1.50	S$_8$	−1.51
C$_{12}$	−0.25	S$_5$	1.58	C$_{15}$	−1.24
(b) Plane through S$_4$, S$_5$, and S$_6$					
$-0.630X - 0.750Y - 0.203Z + 3.888 = 0$					
Co$_1$	−1.48	Co$_3$	−1.57	S$_8$	−2.89
Co$_2$	−1.41	S$_7$	−2.95	C$_{15}$	−2.74
(c) Plane through S$_7$, S$_9$, and C$_{15}$					
$-0.686X - 0.704Y - 0.184Z + 6.639 = 0$					
Co$_1$	1.48	Co$_3$	1.25	S$_5$	2.94
Co$_2$	1.36	S$_4$	2.71	S$_6$	2.89
(d) Plane through Co$_1$, S$_4$, and C$_{15}$					
$0.091X + 0.113Y - 0.989Z + 2.187 = 0$					
O$_{16}$	0.00	S$_6$	1.73	C$_{11}$	2.64
C$_9$	−0.07	S$_5$	−1.51	C$_{13}$	−2.75
O$_{10}$	−0.21	S$_8$	1.54	C$_{12}$	3.56
C$_{17}$	−0.19	S$_7$	−1.71	C$_{14}$	−3.64
Co$_2$	1.25			Centroid (Co$_1$, Co$_2$, Co$_3$)	0.00
Co$_3$	−1.24				
(e) Plane through Co$_2$, S$_5$, and S$_7$					
$-0.592X + 0.641Y - 0.489Z + 0.304 = 0$					
C$_{11}$	−0.09	Co$_3$	−1.25	C$_9$	2.70
O$_{12}$	−0.29	S$_6$	1.73	C$_{13}$	−2.85
C$_{19}$	0.13	S$_4$	−1.65	O$_{10}$	3.64
C$_{23}$	0.03	S$_8$	1.59	O$_{14}$	−3.85
Co$_1$	1.30	C$_{15}$	−1.30	Centroid (Co$_1$, Co$_2$, Co$_3$)	0.01
(f) Plane through Co$_3$, S$_8$, and S$_6$					
$0.693X - 0.510Y - 0.510Z + 1.817 = 0$					
C$_{13}$	0.06	Co$_1$	−1.29	C$_{11}$	2.75
C$_{14}$	0.16	S$_4$	1.63	C$_9$	−2.75
C$_{21}$	−0.10	S$_5$	−1.55	O$_{12}$	3.89
C$_{25}$	0.01	C$_{15}$	1.32	O$_{10}$	−3.84
Co$_2$	1.26	S$_7$	−1.70	Centroid (Co$_1$, Co$_2$, Co$_3$)	−0.01
(g) Plane through S$_5$, S$_6$, S$_7$, and S$_8$					
$0.746X - 0.666Y - 0.019Z + 1.843 = 0$					
S$_5$	0.05	S$_8$	0.04	C$_9$	−2.20
S$_6$	−0.04	Co$_1$	−0.54	O$_{10}$	−3.38
S$_7$	−0.05				
(h) Plane through S$_4$, S$_6$, S$_8$, and C$_{15}$					
$0.488X - 0.212Y - 0.847Z + 1.185 = 0$					
S$_4$	0.00	C$_{15}$	−0.07	C$_{11}$	2.20
S$_6$	0.00	Co$_2$	0.53	O$_{12}$	3.40
S$_8$	0.00				
(i) Plane through S$_4$, S$_5$, S$_7$, and C$_{15}$					
$-0.258X + 0.449Y - 0.855Z + 2.261 = 0$					
S$_4$	−0.02	C$_{15}$	0.26	C$_{13}$	−2.26
S$_5$	0.02	Co$_3$	−0.48	O$_{14}$	−3.34
S$_7$	−0.02				

[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 $Z_k = cz_k \sin\beta$.

bridged in pairs by one carbonyl and five ethylmercapto groups with the other three carbonyl groups stereochemically linked as terminal Y ligands to the cobalt atoms. The presence of the unique carbonyl bridging group destroys the idealized geometry of D_{3h} symmetry for the sulfur–carbon polyhedral framework such that only one vertical mirror plane (passing through Co$_1$, the bridging carbonyl atoms C$_{15}$ and O$_{16}$, S$_4$, and the terminal carbonyl atoms C$_9$ and O$_{10}$) is preserved (Figure 2). The degree of distortion of the sulfur–carbon polyhedron from the full D_{3h} symmetry to C_s-m symmetry is readily seen from an examination of Table IV which shows variations up to 0.3 Å in the perpendicular distances of chemically equivalent atoms (based on D_{3h} symmetry) from the defined least-squares planes a–i. Intramolecular distances and bond angles, grouped according to this remaining idealized mirror plane (Table IVd), are listed along with average values in Table II and III, respectively. Inclusion of even the sulfur-attached methylene carbon atoms further reduces the symmetry to that of C_1-1 for the entire molecule.

The three cobalt atoms form an isosceles triangle which conforms to the observed C_s-m sulfur–carbon polyhedral symmetry. The two chemically equivalent Co–Co bond lengths are both 2.55 *vs.* 2.485 Å (individual esd, 0.007 Å) for the third Co–Co bond length. This significant decrease of 0.065 Å for the distance between the two cobalt atoms bridged by the carbonyl and the mercapto groups compared to the distances between the other two pairs of cobalt atoms bridged only by mercapto groups is also paralleled in the structurally related tricobalt part of the polynuclear cobalt complexes $Co_5(CO)_{10}(SC_2H_5)_5$[10] and $SCo_6(CO)_{11}(SC_2H_5)_4$[29] for which the corresponding Co–Co distances are remarkably similar to those in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$. Both of these latter two complexes possess an identical $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ fragment with the same basic $Co_3X_6Y_3$ structure for the sulfur–carbon polyhedron. However, with *two* carbonyl and *four* mercapto groups functioning as bridging X ligands (rather than the *one* carbonyl and *five* mercapto X ligands contained in the molecular complex $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$), the resulting isosceles triangle of cobalt atoms in the $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ fragment contained in both the pentameric and hexameric cobalt complexes has two equivalent *shorter* Co–Co distances of 2.485 Å (av) (individual esd, 0.007 Å) which are 0.05 Å less than the one *longer* Co–Co distance (of 2.534 and 2.535 Å in the two fragments). The overriding factor leading to a shortening of 0.05–0.06 Å for the Co–Co distance in these three analogous triangular tricobalt systems on replacement of one of the two mercapto sulfur atoms with a bridging carbonyl carbon atom presumably is the "constraining size effect" stereochemically imposed on the coordinated pair of cobalt atoms by the much smaller bridging carbonyl carbon atom. It is noteworthy that a still shorter distance of 2.43 Å (individual esd, 0.006 Å) exists in the dicobalt part of $Co_5(CO)_{10}(SC_2H_5)_5$ for which the two cobalt atoms also are bridged by a carbonyl and a mercapto group.[30] For other dinuclear

---

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

(30) The considerable variation of presumably single-bond Fe–Fe distances observed in certain polynuclear iron carbonyl complexes has been rationalized primarily on the basis of the amount of negative charge localized on each iron atom through coordination with the other ligands; complexes for which the iron atoms appear to have a higher localized negative charge possess greater Fe–Fe distances.[31] Other factors contributing to alterations in metal–metal distances include the different character of the orbitals involved in the metal–metal bond formation, the metal coordination number, as well as steric and electronic effects due to the other metal-coordinated ligands. Recent structural work in our laboratory on binuclear organo (transition metal) complexes containing bridging groups in addition to metal–metal interactions has shown the size of the metal-coordinated bridging atom to have a marked influence on the metal–metal distance.

(31) (a) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84**, 4633 (1962); (b) R. J. Doedens and L. F. Dahl, *ibid.*, **88**, 4847 (1966), and references contained therein.

cobalt carbonyl complexes containing symmetrically bridging carbonyl groups, the observed Co–Co distances are 2.52 Å in $Co_2(CO)_8$,[32] 2.43 Å in the orthorhombic crystal form of $Co_2(CO)_9C_2H_2$,[33] and 2.46 Å in the triclinic crystal form of $Co_2(CO)_9C_2H_2$.[33]

For the unique bridging carbonyl group in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$, the two experimentally equivalent Co–CO distances have an average value of 1.95 Å (individual esd, 0.03 Å) which is one of the longest M–CO distances known for symmetrical doubly bridged carbonyl ligands coordinated to first-row transition metals; the corresponding Co–CO–Co bridging angle of 79° (esd, 1.2°) approaches the minimum known M–CO–M value of 78°.[34] These Co–CO and Co–CO–Co values in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ are not unlike the average M–CO and M–CO–M values observed for triply bridging carbonyl ligands in $[Fe_4(CO)_{13}]^{2-}$ (2.00 Å and 77°),[31b] $[C_5H_5FeCO]_4$ (1.97 Å and 80°),[36] and $(C_5H_5)_3Ni(CO)_2$ (1.93 Å and 77°).[33a] The much shorter normal terminal Co–CO average distance of 1.71 Å (individual esd, 0.04 Å) in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ no doubt reflects the much greater multiple-bond character of a terminal M–CO bond compared to that of a bridging M–CO bond.

The ten crystallographically independent Co–S distances in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ range from 2.20 to 2.33 Å (individual esd, 0.01 Å). Nevertheless, these bond-length variations are such that the previously mentioned mirror plane for the sulfur–carbon polyhedron is essentially retained for the $Co_3\{(S)_5(CO)\}(CO)_3$ fragment. Of the five resulting pairs of common Co–S bond lengths, the largest difference between two members in a given pair is 3σ with the other four differences less than 2σ. The average Co–S value for the symmetrically disposed doubly bridged sulfur atom lying on the mirror plane is 2.25 Å.

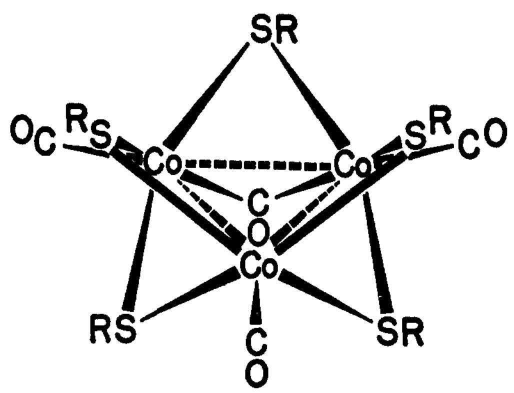


Figure 2. A perspective view of the $Co_3[(CO)(SR)_5](CO)_3$ molecule which clearly shows the vertical mirror plane for the idealized sulfur-carbon polyhedron.

Evidence for an unsymmetrical bonding of each of the other two chemically independent doubly bridged sulfur atoms to its two cobalt atoms is indicated by the corresponding average Co–S values of 2.25 *vs.* 2.32 Å and 2.21 *vs.* 2.26 Å. It is not surprising that these latter doubly bridging mercapto groups connecting two nonrelated cobalt atoms may be unsymmetrically oriented, since there is no symmetry constraint demanding that the two cobalt atoms have the same effective charge density and hence have the same bonding capacity.

Although the five Co–SR–Co bridge angles of range 67–70° are strikingly acute for symmetrically bridging ligands coordinated to two metal atoms by normal electron-pair bridge bonds, these sharp angles are virtually identical with those present in the stereochemically similar $Co_3\{(SC_2H_5)_4(CO)_2\}(CO)_3$ fragment contained in the molecular complexes $Co_5(CO)_{10}(SC_2H_5)_5$ (65–69°)[10] and $SCo_6(CO)_{11}(SC_2H_5)_4$ (66–70°).[29] They also compare favorably with the Fe–SR–Fe bridge angle in $[C_2H_5SFe(CO)_3]_2$ (68° av),[37] with the Co–P$(C_6H_5)_2$–Co bridge angle of 72.5° found in the electronically equivalent and structurally analogous $[(C_6H_5)_2PCoC_5H_5]_2$ complex,[38] and with the Fe–SR–Fe bridge angle in $[CH_3SFe_2(CO)_6]_2S$ (68° av).[39] It has been shown for the dimeric complexes that these unusually acute bridging angles are a consequence of the influence of the metal–metal interaction on the over-all molecular geometry.[38]

The over-all geometrical environment of *two* metal atoms and *one* methylene carbon atom about each doubly bridging sulfur atom in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ and in the other above mercaptoiron carbonyl complexes is similar to that of the *two* cobalt atoms and *either one* of the two phenyl carbon atoms coordinated to each phosphorus atom in $[(C_6H_5)_2PCoC_5H_5]_2$. Hence, it is presumed that the tetrahedral-like orientation of the four σ-bonding electron pairs about each phosphorus atom in $[(C_6H_5)_2PCoC_5H_5]_2$ is not unlike the orientation to a first approximation of the three σ-bonding electron pairs and one localized lone pair about each sulfur atom in the above complexes. Both the mean Co–S–CH_2 angle of 113° (individual esd, 1.2°) and average

---

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

(33) (a) 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; (b) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

(34) An analysis[35] of the structural parameters of a large number of first-row transition metal carbonyl complexes with essentially equivalent symmetrical bridging carbonyl groups (*i.e.*, with the two M–CO distances differing by less than 3.0 esd) showed, with two exceptions discussed below, no M–M distance greater than 2.58 Å; the M–CO distances varied from 1.82 to 1.96 Å and the M–CO–M angles from 78 to 86°. No direct correlation was observed between the size of the bridging angle and the M–CO or M–M bond length. The exceptions are $C_8H_8Fe_2(CO)_5$ (E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, 88, 3158 (1966)) and $[C_8H_4(CH_3)_4]Fe_2(CO)_5$ (F. A. Cotton and M. D. LaPrade, *ibid.*, 90, 2026 (1968)); Fe–Fe distances of 2.742 (3) and 2.724 (4) Å, Fe–CO distances of 1.97 (2) and 1.94 (2) Å, and Fe–CO–Fe angles of 88 (1) and 89 (1)° are found in these two molecular compounds, respectively. The unusually long Fe–Fe distance for a bridging carbonyl group in these essentially identical molecular structures no doubt is dictated by the stereochemical requirements imposed by the particular coordination of the cyclooctatetraene ring with the two iron atoms. An electron-pair, four-center bonding MO can be formulated in these diamagnetic molecules involving the linear combination of a p_π-like cyclooctatetraene orbital for each of two ring carbon atoms and a σ-like iron orbital for each iron atom in that geometrical considerations show both cyclooctatetraene ring carbon orbitals to be directed toward the midpoint of the Fe–Fe internuclear line. This kind of localized electron-pair interaction enables each iron atom (also bonded to the one bridging and two terminal carbonyl groups and to a π-allylic fragment of the cyclooctatetraene ring) to achieve a closed-shell electronic configuration without the necessity for any additional Fe–Fe electron-pair interaction.

(35) J. Molin-Case and L. F. Dahl, unpublished research.

(36) M. A. Neuman, L. F. Dahl, and R. B. King, submitted for publication; R. B. King, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 22–O; R. B. King, *Inorg. Chem.*, 5, 2227 (1966).

(37) L. F. Dahl and C. H. Wei, *ibid.*, 2, 328 (1963).

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

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

S–CH_2 distance of 1.86 Å (individual esd, 0.03 Å) in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ agrees within expectations with the corresponding average values in the other thioethylmetal carbonyls and with the average Co–P–C_6H_5 angle of 121° and average P–C_6H_5 distance of 1.84 Å in $[(C_6H_5)_2PCoC_5H_5]_2$.

All intermolecular contacts in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ are found to be greater than 3.2 Å, which supports the premise that the molecules are held together in the crystalline state primarily by van der Waals cohesive forces.

Structural and Bonding Relationship with the $[Re_3Cl_{12}]^{3-}$ Metal Cluster. This $M_3X_6Y_3$-type structure found for $Co_3\{(CO)(SC_2H_5)_5\}(CO)_3$ can be related to another basic triangular metal structural unit of general formula $M_3X_9Y_3$ (written as such for comparative purposes) which occurs for a large number of trinuclear rhenium(III) halogeno anions.[40] The prototype of this triangular metal cluster system (which for nine identical X and three identical Y atomic ligands also ideally possesses D_{3h} symmetry) is the $[Re_3Cl_{12}]^{3-}$ anion[41] (*i.e.*, $[Re_3Cl_9Cl_3]^{3-}$) shown in Figure 3. The close structural relationship of these two types of triangular metal clusters is apparent in that the polyhedral structure of $M_3X_6Y_3$ can be formally derived from that of $M_3X_9Y_3$ by a rotation of 45° about each of the three M–Y internuclear axes which thereby causes the six out-of-plane terminal X ligands and three in-plane bridging X ligands of $M_3X_9Y_3$ to coalesce into the six bridging ligands of $M_3X_6Y_3$.

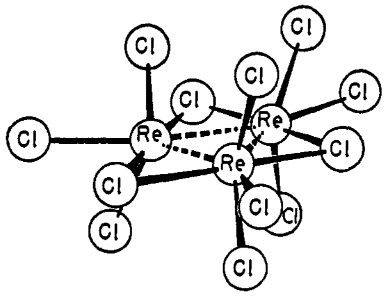


Figure 3. Molecular configuration of the $[Re_3Cl_{12}]^{3-}$ anion of chemically equivalent D_{3h}-$\bar{6}$2m symmetry.[41]

Of stereochemical importance to a qualitatively pleasing and conceptually digestable picture of the nature of the metal–metal interactions in $Co_3\{(SC_2H_5)_5)CO\}(CO)_3$ is the similar localized square-pyramidal environment of the five X and Y ligands about each metal atom in both $[Re_3Cl_{12}]^{3-}$ and $Co_3\{(SC_2H_5)(CO)\}(CO)_3$ which allows the simple molecular orbital approach applied semiquantitatively by Cotton and Haas[42] to the trirhenium fragment of $[Re_3Cl_{12}]^{3-}$ to be invoked for the tricobalt part of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$. Each rhenium atom in the $[Re_3Cl_{12}]^{3-}$ anion was assumed to use the $d_{x^2-y^2}$, s, p_x, p_y, and p_z orbitals in forming localized σ bonds with the four attached basal chlorine atoms and the apical in-plane terminal chlorine atom. The four remaining atomic d orbitals (*viz.* d_{xy}, d_{z^2}, d_{xz}, and d_{yz}) of each rhenium atom were combined to give six bonding and six antibonding rhenium symmetry orbitals classified according to the irreducible representations of D_{3h} symmetry. On the basis of the calculated ordering of one-electron energy levels for the trirhenium symmetry orbital combinations,[43] Cotton and Haas[42] showed the 12 electrons in the trirhenium cluster system to occupy all six of the bonding metal symmetry orbitals but none of the six antibonding ones.

In order that the d-orbital types and transformational scheme involved in the metal–metal interactions in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ be analogous to those utilized in $[Re_3Cl_{12}]^{3-}$, local right-handed coordinate systems were chosen at each cobalt atom with the *z* axis directed along the Co–CO line toward the centroid of the cobalt triangle, the *x* axis located in the plane of the cobalt triangle, and the *y* axis perpendicular to this cobalt plane.[44] The simplifying assumption of D_{3h} symmetry for the tricobalt cluster[45] is reasonable in that the observed variations in the Co–Co bond lengths are not sufficient to indicate any significant change in the bonding interactions from a qualitative viewpoint. In our analogous case we also assumed that five of the nine valence orbitals of each cobalt atom are primarily utilized to form localized σ bonds with the five X and Y ligands and hence are not available to bond with the other cobalt atoms. For the above particular choice of local cobalt coordinate axes, the cobalt–ligand σ bonding was assumed to involve the d_{xy} s, $(1/\sqrt{2})(p_x + p_y)$, $(1/\sqrt{2})(p_x - p_y)$, and p_z orbitals of each cobalt atom; the four d orbitals excepting d_{xy} then are available for cobalt–cobalt interactions. The transformation properties of the d_{z^2}, d_{xz}, and d_{yz} orbitals of each cobalt atom are identical with those derived by Cotton and Haas[42] for the corresponding d orbitals of the rhenium atoms in the $[Re_3Cl_{12}]^{3-}$ anion. The salient difference in the energy-level ordering of metal symmetry orbitals between these two trimeric cluster systems is due to the different irreducible representations spanned by the $d_{x^2-y^2}$ orbitals on the three cobalt atoms compared to those spanned by the d_{xy} orbitals on the three rhenium atoms.[46] The $d_{x^2-y^2}$ orbitals of

(40) For the latest leading references, see (a) F. A. Cotton, *Quart. Rev.* (London), 20, 389 (1966); (b) F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, 6, 223 (1967); (c) B. R. Penfold and W. T. Robinson, *ibid.*, 5, 1758 (1966); (d) M. Elder and B. R. Penfold, *ibid.*, 5, 1763 (1966).

(41) (a) W. T. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.* 116 (1963); (b) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, 85, 1349 (1963); *Inorg. Chem.*, 2, 1166 (1963).

(42) F. A. Cotton and T. E. Haas, *ibid.*, 3, 10 (1964).

(43) This particular MO treatment of a metal halide cluster system, for which only the individual metal valence orbitals assumed to be involved in metal–metal interactions are transformed into symmetry orbitals, has an implicit first-order presumption that a perfect pairing approximation allows separability with regard to metal–halogen interactions. Possible metal–halogen π bonding is neglected. Furthermore, the energy changes produced by the trirhenium symmetry orbital combinations of the appropriate atomic d orbitals (taken to have the same energy prior to the metal–metal interaction) are assumed to be sufficiently large to give qualitatively the correct electron distribution patterns invariant to the use of possible rhenium hybrid orbitals.

(44) An alternative orientation of the local coordinate system for each cobalt atom with the *x* and *y* axes instead directed along the Co–X bonds (rather than parallel to the two diagonals of the idealized square formed by the four basal X ligands) obviously alters the labeling of the orbital types belonging to the irreducible representations of the metal symmetry orbitals, and hence is less convenient for making a direct comparison of the relevant orbitals involved in the metal atom cluster bonding of the $[Re_3Cl_{12}]^{3-}$ anion with those of the $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ molecule.

(45) The small breakdown of the symmetry classifications for the resulting degenerate symmetry orbitals of the tricobalt fragment due to the observed idealized molecular geometry of C_s-m for $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ is ignored for these rationalizations.

(46) These qualitative symmetry arguments stress the fact that the orientation of the metal-coordinated ligands relative to the metal cluster fragment plays a vital role in determining the number of bonding and

the three cobalt atoms combine to give *one bonding* cobalt symmetry orbital, $d_{x^2-y^2}(a_1')$, and *two* degenerate *antibonding* cobalt symmetry orbitals, $d_{x^2-y^2}(e'^*)$, whereas the d_{xy} orbitals of the three rhenium atoms transform to give *two* degenerate *bonding* rhenium symmetry orbitals, $d_{xy}(e'')$, and *one antibonding* rhenium symmetry orbital, $d_{xy}(a_1''^*)$. Based on reasonable metal orbital overlap considerations tempered by the partial qualitative applicability of the Cotton–Haas energy-level diagram for the trirhenium cluster to the tricobalt part of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$, the 20 valence electrons for the tricobalt system would not only occupy all five of the metal bonding symmetry orbitals ($d_{z^2}(a_1')^2$, $d_{xz}(e')^4$, $d_{yz}(a_2'')^2$, $d_{x^2-y^2}(a')^2$, but also five metal antibonding orbitals—either the levels $d_{x^2-y^2}(e'^*)^4$, $d_{yz}(e'^*)^4$, and $d_{z^2}(e'^*)^2$ for which case there would be two unpaired electrons, or the levels $d_{x^2-y^2}$-$(e'^*)^4$, $d_{yz}(e'^*)^4$, and $d_{xz}(a_2'^*)^2$ for which case the complex would be diamagnetic. The observed diamagnetism of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ conforms only to the latter possible electronic configuration (unless there is sufficient breakdown of the degenerate $d_{z^2}(e'^*)$ orbitals due to the actual chemically equivalent molecular symmetry of C_s-m to give spin-pairing of the two least stable electrons).[45]

Application of the Coulson definition[47] of MO bond order to the easily derivable normalized LCAO–metal symmetry orbitals in their various representations (not given here to conserve space) gives between any pair of adjacent metal atoms in the equilateral metal array an MO order of $+^2/_3$ for a completely occupied bonding representation (*i.e.*, containing either two electrons in a nondegenerate level or four electrons in a doubly degenerate level) and $-^2/_3$ for a completely occupied antibonding representation. For the *diamagnetic* tricobalt electronic configuration (given above) involving the *four* bonding and *three* antibonding occupied representations, the net MO Co–Co bond order is $+^2/_3$.

From a valence-bond formalism, $Co_3\{(SC_2H_5)_5$-$(CO)\}(CO)_3$ is an exception to the "noble gas" rule in that (with the assumption of Co–Co electron-pair bonds as indicated by the observed bonding distances) the entire molecule contains two electrons in excess of the closed-shell krypton configuration for each cobalt atom. The MO metal–metal bond order corresponding to a closed-shell configuration for each cobalt atom can be obtained by the consideration of the tricobalt electronic configuration without the two highest energy electrons in the antibonding $d_{xz}(a_2'^*)$ level. The resulting *net* MO cobalt–cobalt order is $+^4/_3$ which in valence-bond terminology conforms to a cobalt–cobalt single bond. Hence, the effect of antibonding electrons in excess of the noble-gas configuration of the metal atom is to reduce the valence-bond metal–metal order to less than 1.0. The observed Co–Co bond lengths in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ conform approximately to expected single-bond distances, but obviously it is impossible to correlate metal–metal distances with bond orders for ligand-bridged complexes due to the inseparability of the effects of the bridging atoms and the metal–metal interactions.

It is noteworthy that the estimated valence-bond Re–Re order in $[Re_3Cl_{12}]^{3-}$ is *two*.[48–51] The corresponding MO Re–Re order in $[Re_3Cl_{12}]^{3-}$ based on the 12 bonding electrons in the trirhenium fragment occupying two nondegenerate and two doubly degenerate representations is $+^8/_3$. As expected, this value is twice the above MO metal–metal order of $+^4/_3$ corresponding to a valence-bond metal–metal order of *one*.

This comparison of the electronic structures for the analogous trimetal cluster systems in $Co_3\{(SC_2H_5)_5$-$(CO)\}(CO)_3$ and $[Re_3Cl_{12}]^{3-}$ provides a rationale for the observation that metal halide and oxide clusters are known in general for only the earlier members of the transition metal series[52,53] in contrast to the metal carbonyl cluster systems which primarily exist for the latter elements of the transition series. The stability of the metal carbonyl cluster systems (which by the Cotton–Haas MO model accommodate valence electrons in antibonding metal symmetry orbitals) no doubt is due largely to the back-bonding ability of the carbonyl ligands and to a lesser degree to that of the mercapto sulfur atoms (relative to the essentially nonexistent back-bonding ability of either the halogen or oxygen ligands); hence, by means of π-bonding MO combinations the electrons placed by the Haas–Cotton MO model in the bonding and antibonding symmetry orbitals of the metal atoms are considerably delocalized over the molecule.

Geometry of the Sulfur–Carbon Polyhedron. A comparison of the dimensions of the trigonal prism formed by the six sulfur and carbonyl carbon bridging X ligands in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ (Figure 4a) and in the $Co_3\{(SC_2H_5)_4(CO)_2)\}(CO)_3$ fragment of both $Co_5(CO)_{10}(SC_2H_5)_5$ (Figure 4b) and $SCo_6(CO)_{11}(SC_2H_5)_4$ (Figure 4c) with the dimensions of the trigonal-prismatic array of sulfur atoms in $V\{S_2C_2(C_6H_5)_2\}_3$,[54] $Mo\{S_2C_2H_2\}_3$,[55] and $Re\{S_2C_2(C_6H_5)_2\}_3$[56] is informative.

---

antibonding metal symmetry orbitals as well as their arrangement. The difference of five bonding and seven antibonding metal symmetry orbitals in the tricobalt part of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ *vs.* six bonding and six antibonding ones in the trirhenium part of $[Re_3Cl_{12}]^{3-}$ is solely due to the availability for the metal–metal interaction of a d_{xy} orbital for each metal atom rather than a $d_{x^2-y^2}$ one. This observation was earlier noted by Cotton and Haas[42] in their bonding treatment of $[M_6X_8]^{4+}$ and $[M_6X_{12}]^{2+}$ systems. For these two octahedral metal clusters, an identical variation in the metal basis sets (also comprised of four atomic orbitals for each metal atom), which differ from each other only by a $\pi/4$ rotation of one d orbital on each metal atom about the local *z* axis, completely accounts for the $[M_6X_8]^{4+}$ possessing 12 bonding metal symmetry orbitals compared to 8 for $[M_6X_{12}]^{2+}$.

(47) C. A. Coulson, *Proc. Roy. Soc.* (London), **A169**, 413 (1938).

(48) F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

(49) J. E. Fergusson, B. R. Penfold, M. Elder, and B. H. Robinson, *J. Chem. Soc.*, 5500 (1965).

(50) S. F. A. Kettle, *Theoret. Chim. Acta*, **3**, 211 (1965).

(51) A conceptual conversion from the MO symbolism to a valence-bond picture for the Re–Re bonding is readily made once it is recognized that of the four available d orbitals for each rhenium the hybrid combinations ($d_{z^2} \pm d_{xz}$) give rise to the two equivalent rhenium orbitals which can form localized electron-pair Re–Re σ bonds by overlap with the corresponding identical orbitals on the other two rhenium atoms. The other two combinations ($d_{yz} \pm d_{xy}$) lead to the two equivalent d_π rhenium orbitals which can form localized electron-pair Re–Re π bonds by overlap with the corresponding d_π orbitals on the other rhenium atoms. No doubt the bonding in these metal atom clusters more nearly conforms to the multicenter MO model with delocalized metal symmetry orbitals extending over the entire metal framework.

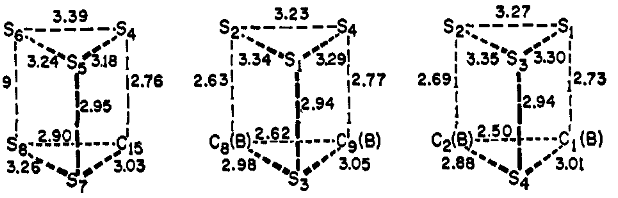
(52) Similar MO treatments of the metal–metal interactions in $[M_6X_8]^{4+}$ (M = Mo, W) and $[M_6X_{12}]^{2+}$ (M = Nb, Ta) by Cotton and Haas[42] showed that these octahedral metal clusters also have electrons in all of their bonding symmetry orbitals but none in their antibonding symmetry orbitals.

(53) One obvious exception to this generalization is Pt_6Cl_{12}: K. Brodersen, G. Thiele, and H. G. Schnering, *Z. Anorg. Allgem. Chem.*, **337**, 120 (1965).

(54) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2874 (1966).

(55) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

(56) R. Eisenberg and J. A. Ibers, *ibid.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).



(a) (b) (c)

Figure 4. Dimensions of the trigonal prism formed by the six bridging X ligands in the basic $M_3X_6Y_3$ structure where (a) X equals one CO and five SC_2H_5 groups in the molecular complex $Co_3[(SC_2H_5)_5(CO)](CO)_3$; (b) X equals two CO and four SC_2H_5 groups in the $Co_3[(SC_2H_5)_4(CO)_2](CO)_3$ fragment of the molecular complex $Co_6(CO)_{10}(SC_2H_5)_5$;[10] (c) X equals two CO and four SC_2H_5 groups in the $Co_3[(SC_2H_5)_4(CO)_2](CO)_3$ fragment of the molecular complex $SCo_6(CO)_{11}(SC_2H_5)_4$.[29]

For the latter three monomeric molecular complexes with the uncommonly occurring trigonal-prismatic coordination, both the average inter- and intraligand S···S distances are strikingly equivalent with values that range only from 3.03 to 3.11 Å. These presumably short S···S distances (*i.e.*, the tabulated van der Waals radius of sulfur is 1.85 Å) together with the essentially identical M–S distances for these three monomeric molecular complexes led to the prediction[54] that the stabilization of the trigonal-prismatic coordination with respect to octahedral coordination is partly a consequence of direct interligand S···S bonding interactions. Examination of the lengths of the trigonal prisms for the three polynuclear cobalt carbonyl sulfur complexes (Figure 4) reveals *longer* average S···S distances (*viz.* 3.27 Å in a, 3.29 Å in b, and 3.31 Å in c) for pairs of doubly bridging mercapto sulfur atoms located on a given side of the triangular plane of cobalt atoms but considerably *shorter* average S···S distances (*viz.* 2.92 Å in a, 2.94 Å in b, and 2.94 Å in c) for pairs of sulfur atoms situated above and below the tricobalt plane. A similar trend of longer and shorter average S···C(B) distances for the corresponding triangular and vertical rectangular sides of the prism (*viz.* 2.96 *vs.* 2.76 Å in a, 3.02 *vs.* 2.70 Å in b, and 2.94 *vs.* 2.71 Å in c) is also observed. The essential invariance of these short intramolecular distances between the adjacent X ligands, especially those involving *cis*-equatorial X ligands bonded to a given cobalt atom, emphasizes the relative atomic close packing of the M_3X_6 fragment in the three cobalt complexes. To what extent these close contacts imply the presence of interdonor-atom bonding forces resulting in molecular stabilization cannot be estimated with any certainty.

As presented in Table IVg–i for the trimeric cobalt complex, each of the three cobalt atoms is 0.5 Å out of the "mean" plane of its coordinated equatorial X atoms in the direction of the terminal carbonyl Y ligands. This perpendicular displacement is at least 0.1 Å greater than the corresponding average directional displacement of the iron atoms from their respective basal planes of sulfur and carbonyl carbon atoms in $[C_2H_5SFe(CO)_3]_2$ (0.38 Å for both iron atoms),[37] $[SFe(CO)_3]_2$ (0.32 and 0.34 Å),[57] and in $[CH_3SFe_2(CO)_6]_2S$ (0.36 Å (av) for the four iron atoms).[39] Nevertheless, in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ the average nonbonding X···Y distances of 3.15 Å for the S···CO contacts and 2.92 Å for the C(B)···CO contacts are considerably longer than the corresponding interligand prism distances. These observations indicate that this increased deformation of each cobalt atom out of its basal plane is not due to steric pressure of the X ligand atoms on the Y carbonyl carbon atoms. In contrast, the closest Cl···Cl contacts in the structurally related $[Re_3Cl_{12}]^{3-}$ anion (previously described) occur between the out-of-plane terminal X chlorine atoms and the in-plane terminal Y chlorine atoms; presumably these particular nonbonding interactions are responsible for the unusual length of the three in-plane terminal Re–Cl bonds, which are 0.16 Å (av) longer than the six out-of-plane terminal Re–Cl bonds.[41]

Stereochemistry of Methylene Carbon Atoms and Resulting Chemical Implications. Of prime chemical significance is that the X-ray analyses of $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ and the other two previously mentioned mercaptocobalt carbonyl complexes, $Co_6(CO)_{10}(SC_2H_5)_5$[10] and $SCo_6(CO)_{11}(SC_2H_5)_4$,[29] show that the stoichiometry in these three polynuclear cobalt complexes is governed by the stereochemical disposition of the methylene groups attached to the bridging sulfur atoms. Hence, the steric compression of the methylene groups not only provides a rational explanation for the nonisolation of a $Co_3\{SR_6\}(CO)_3$ molecular complex (with six bridging mercapto groups)[58,59] but also accounts for the trimer being a final product in the reaction of dicobalt octacarbonyl with excess ethyl mercaptan.

The particular arrangement of the methylene carbon atoms attached to the mercapto sulfur atoms in $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$ provides a minimum of intramolecular nonbonding repulsion. Figure 1 shows only *one* CH_2 group on each side of the $Co_3\{(S)_5(CO)\}(CO)_3$ fragment (*viz.* the methylene carbon atoms C_{21} and C_{23}) to be in an axial position while the other three S–CH_2 bonds are equatorially oriented. The fact that the two sulfur atoms which form the axial S–CH_2 bonds are an average distance of 0.27 Å nearer the plane of the three cobalt atoms than the other three sulfur atoms which form equatorial S–CH_2 bonds (*i.e.*, the perpendicular distances in Table IVa give 1.365 Å (av) for S_6 and S_7 *vs.* 1.53 Å (av) for S_4, S_5, and S_8) indicates bending deformations of the cobalt–sulfur skeleton in order to increase the closest nonbonding distances of the axial ethyl groups with the other bridging ligands.

Even with the allowance of a drastic skeletal deformation, geometrical considerations show that in order to minimize the large steric requirements of the

---

(57) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 4, 1 (1965).

(58) It is noteworthy that the D_{3h} $M_3X_6Y_3$ structure with six bridging X atoms has been suggested as one of the possibilities for the iron–oxygen polyhedron in the recently prepared trimeric *n*-alkoxides of iron(III), $[Fe_3(OR)_9]$.[59] However, magnetic susceptibility data which indicate a cooperative spin coupling between the three iron atoms have been interpreted for a preferred iron–oxygen polyhedral model involving FeO_4 tetrahedra linked through corners to give a cyclic structure with only one OR bridging group between each pair of iron atoms.[59] Our stereochemical arguments for the nonexistence of the $M_3X_6Y_3$ structure containing six symmetrically bridging thioalkoxide groups would also eliminate a similar D_{3h} configuration for the iron–oxygen polyhedron in $[Fe_3(OR)_9]$. Nevertheless, the D_{3h} structure would be expected to occur for the kind of metal complexes $M_3\{halogen\}_6(CO)_3$ where electronically equivalent halogen atoms (containing no sterically hindering substituents) have been inserted in place of bridging three-electron SR or OR donors.

(59) R. W. Adams, C. G. Barraclough, R. L. Martin, and G. Winter, *Inorg. Chem.*, 5, 346 (1966).

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$_2$H$_5$ 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]

Acknowledgments. We are particularly indebted to Drs. L. Markó, G. Bor, and their colleagues for kindly supplying a sample of the compound and for their interest in this work. We also are grateful to Mr. Alan Foust and Dr. Heinrich Vahrenkamp of our laboratories for making the magnetic measurements. We wish to thank Professor R. F. Fenske of the University of Wisconsin for helpful discussions on the bonding. This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant No. 518-66. The use of the CDC 1604 and 3600 computers at the University of Wisconsin Computing Center was made available through partial support of NSF and WARF through the University Research Committee.

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

Chin Hsuan Wei and Lawrence F. Dahl

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received August 31, 1967*

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–

---

[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).

[3] C. H. Wei and L. F. Dahl, *ibid.*, 4, 1 (1965).

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

[5] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, 83, 1761 (1961).

[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.