Organometallic Sulfur Complexes. IX. Structure of a Hexanuclear Cobalt Carbonyl Sulfur Complex, $[SCo_3(CO)_7]_2S_2$, Containing a Tetrametal-Coordinated Bridging Disulfide Group[1]

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Abstract: An X-ray analysis of $[SCo_3(CO)_7]_2S_2$ has established the first known case of a disulfide bridging group symmetrically coordinated to four transition metal atoms. The molecular configuration of approximate C_{2v}-2mm symmetry consists of two essentially identical $SCo_3(CO)_7$ moieties linked to each other by a disulfide bridge. This diamagnetic complex crystallizes with two molecules in a reduced triclinic unit cell of symmetry $P\bar{1}$ and of parameters $a = 9.48$ A, $b = 11.78$ A, $c = 13.54$ A, $\alpha = 72° 6'$, $\beta = 78° 31'$, and $\gamma = 69° 37'$. Least-squares refinement based on the three-dimensional photographic data resulted in an unweighted discrepancy factor of 9.0%. A detailed comparison of the structural features of $[SCo_3(CO)_7]_2S_2$ with those of its closely related chemical precursor, $SCo_3(CO)_9$, is made.

The reaction of dicobalt octacarbonyl with either elemental sulfur or a series of sulfur-containing compounds [*e.g.*, H_2S, C_2H_5SH, C_4H_4S, $C_6H_5CH_2SH$, and $Fe_2(CO)_6S_2$] under varying reaction conditions has resulted in a large assortment of organometallic sulfur complexes.[2–7] As part of a systematic structural study of these complexes, a single-crystal X-ray determination of a compound of empirical formula $S_2Co_3(CO)_7$ has been performed. This complex was first prepared by Markó, Bor, and co-workers[5] both by the reaction of dicobalt octacarbonyl with excess sulfur and by the reaction of cobalt tetracarbonyl anion with sodium sulfite. Based on elemental analysis[8] and characterization by solution infrared spectroscopy which revealed seven absorption bands in the terminal carbonyl stretching region, the authors[5] predicted a molecular model for $S_2Co_3(CO)_7$ which consisted of a triangle of cobalt atoms with one sulfur atom bonded symmetrically to all three cobalt atoms and the other sulfur atom bridging two of the three cobalt atoms. A subsequent structural analysis reported here has shown the compound to be a dimeric species in which two $SCo_3(CO)_7$ moieties are linked to each other by a bridging disulfide group.

Experimental Section

Crystals of $[SCo_3(CO)_7]_2S_2$ were kindly supplied to us by Drs. G. Bor and L. Markó of the Hungarian Oil and Gas Research Institute. The black, air-sensitive crystals were mounted in Lindemann thin-walled glass capillaries under an inert atmosphere. A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm, which was mounted about the 0.3-mm rotation axis, was chosen for taking intensity data. Lattice lengths and angles were measured from *h*0*l* and 0*kl* precession photographs.

Multiple-film equiinclination Weissenberg photographs of reciprocal levels *hk*0 through *hk*12 were taken with Zr-filtered Mo Kα radiation by rotation about the *c* axis of an A-centered triclinic unit cell. In order to record all accessible independent reflections on the upper half of the film and thereby eliminate the problem of spot compaction[9] (but not that of spot extension), two separate sets of film data corresponding to a 360° rotation range were obtained for all nonzero reciprocal levels. The relative intensities of the reflections were estimated by comparison with a timed set of standard intensities prepared from the same crystal. The raw intensities were corrected for Lorentz-polarization effects and spot extension[10] but not for absorption ($\mu R_{\max} \leq 0.58$). The two halves of each nonzero Weissenberg layer were then merged *via* least squares[11] on the basis of common reflections to give a total of 1204 independent diffraction maxima. Standard deviations of the observed structure amplitudes were assigned according to the following equations:[12] if $I_0(hkl) \geqslant \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = F_o(hkl)/20$; if $I_0(hkl) < \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = [F_o(hkl)/20][\sqrt{10}I_{\min}/I_0(hkl)]^2$.

The atomic scattering factors used for all atoms were those based on the Hartree–Fock–Slater calculations of Hanson, *et al.*[13] The real and imaginary anomalous contributions to the scattering factors of the cobalt and sulfur atoms were taken from Templeton's tabulation.[14]

Crystal Data

The lattice constants for the A-centered triclinic unit cell of $[SCo_3(CO)_7]_2S_2$ are: $a' = 11.78 \pm 0.03$ A, $b' = 18.00 \pm 0.04$ A, $c' = 14.90 \pm 0.04$ A, $\alpha' = 69° 37' \pm 10'$, $\beta' = 86° 42' \pm 10'$, $\gamma' = 65° 31' \pm 10'$. The lattice constants of the reduced primitive triclinic cell derived[15] from the A-centered cell are: $a = 9.48 \pm 0.04$ A, $b = 11.78 \pm 0.03$ A, $c = 13.54 \pm 0.04$ A, $\alpha = 72° 6' \pm 10'$, $\beta = 78° 31' \pm 10'$, $\gamma = 69° 37' \pm 10'$. All results reported here are given in terms of the A-centered triclinic cell which was used for this structural determination. The reduced primitive cell (unprimed axes) is related to this centered cell (primed axes) by the following transformation: $a = {}^1/_2b'$

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(1) Paper VIII: D. L. Stevenson and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 3721 (1967).

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

(3) C. H. Wei and L. F. Dahl, to be published.

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

(5) L. Markó, G. Bor, E. Klumpp, B. Markó, and G. Almásy, *Chem. Ber.*, **96**, 955 (1963).

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

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

(8) The empirical formula $S_2Co_3(CO)_7$ was based on the following elemental analysis. Calcd: Co, 40.46; S, 14.67; C, 19.24. Found: Co, 40.45, 40.48; S, 14.93, 15.09; C, 18.95, 19.48.[4]

(9) M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp 227–229.

(10) D. C. Phillips, *Acta Cryst.*, 7, 746 (1954).

(11) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1964.

(12) D. L. Smith, "DACOR—A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

(13) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 17, 1040 (1964).

(14) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(15) L. V. Azároff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, pp 134–136.

$- {}^1/_2c'$, $b = a'$, $c = {}^1/_2b' + {}^1/_2c'$. The calculated density of 2.17 g/cc based on eight species of empirical formula $S_2Co_3(CO)_7$ in the A-centered cell is reasonably near the measured density of 2.07 g/cc (flotation method). The probable space group of the A-centered cell was taken to be $A\bar{1}$ (rather than A1); this choice of the centrosymmetric space group was verified by the subsequent structural analysis. Hence, the crystallographically independent unit consists of two $S_2Co_3(CO)_7$ species which necessitate the location of 6 cobalt, 4 sulfur, 14 carbon, and 14 oxygen atoms in the A-centered (or primitive) unit cell.

Solution of the Structure

A three-dimensional Patterson function calculated with the corrected intensities contained numerous vector peaks due to the 24 cobalt and 16 sulfur atoms in the A-centered unit cell. Although one set of intramolecular vectors consistent with an equilateral triangle of cobalt atoms of approximate side 2.4 A was found, initial efforts to obtain the spatial location of this triangle of cobalt atoms in the centrosymmetric unit cell were unsuccessful. Various structural models involving three to six cobalt atoms were deduced not only from the Patterson map but also from the appropriate scanning of the unit cell with the Blount superposition program,[16] but no self-consistent set of atomic parameters which would converge to the correct molecular structure was obtained by the application of successive Fourier syntheses coupled with least-squares refinement.

The eventual solution of this structural problem was based on the assumption that the actual space group of the compound is A1. Since the choice of origin is arbitrary in this noncentrosymmetric space group, the cobalt triangle was placed in the unit cell in the orientation determined from the Patterson map with the origin situated at one of the cobalt atoms. A Fourier map phased on these three cobalt atoms revealed the positions of two more triangles of cobalt atoms. The fourth triangle of cobalt atoms and the eight sulfur atoms in the asymmetric unit of A1 were determined from a subsequent Fourier map. A ball-and-stick model of the 20 atoms showed that 10 of the atoms (*viz.*, 6 cobalt atoms comprising two triangles and 4 sulfur atoms) were related to the other 10 by a nonimposed center of symmetry. The new atomic coordinates for these 10 atoms, obtained by a transformation of the A-centered acentric cell to a centrosymmetric one with the shift of origin to this determined center of symmetry, were subjected to a full-matrix, least-squares refinement[17] which yielded discrepancy factors of $R_1 = 27.1\%$ and $R_2 = 33.7\%$. Successive Fourier maps revealed the positional parameters of 14 independent carbonyl ligands. Further isotropic least-squares refinement of all atoms with individual atomic temperature factors and a variable scale factor per reciprocal Weissenberg layer resulted in final discrepancy factors of $R_1 = 9.0\%$ and $R_2 = 9.1\%$. No parameter shifted by more than 0.1 of its standard deviation in the final refinement cycle. A difference Fourier map based on the final refinement cycle showed no residual peaks greater than 1.0 e/A^3 or less than -1.0 e/A^3 except for some electron density in the vicinity of the cobalt and sulfur atoms characteristic of anisotropic thermal motion.

The positional and thermal parameters obtained from the final isotropic least-squares cycle are listed in Table I.[18] In order to confirm the over-all correctness of the structure, unobserved but experimentally accessible data (*i.e.*, those reflections either too weak to be judged or actually unobserved) for which $\sin\theta \leqslant 0.45$ were assigned an intensity equal to the minimum observed intensity for the given reciprocal layer. After correction of these intensities for Lorentz-polarization effects and spot extension, comparison of the derived structure factors with the corresponding calculated ones showed no $F_c > 1.5F_o$(min). The bond lengths and angles together with their standard deviations, arranged according to the C_{2v} symmetry of the idealized molecule, are listed in Tables II and III, respectively. Nonbonding *intramolecular* distances, also grouped according to C_{2v} symmetry, are shown in Table IV.

Table I. Final 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)	0.3094 (4)	0.0999 (3)	0.6290 (3)	2.5 (1)
Co(2)	0.2869 (4)	−0.0389 (3)	0.7094 (4)	3.0 (1)
Co(3)	0.0977 (4)	0.1048 (3)	0.6760 (4)	3.2 (1)
Co(4)	0.6384 (4)	−0.0049 (3)	0.7637 (4)	2.9 (1)
Co(5)	0.6179 (4)	−0.1432 (3)	0.8433 (4)	3.1 (1)
Co(6)	0.7286 (4)	−0.0941 (3)	0.9373 (4)	3.2 (1)
S(1)	0.2604 (7)	0.0569 (6)	0.7742 (7)	3.2 (2)
S(2)	0.5347 (8)	−0.0315 (6)	0.8835 (7)	3.1 (2)
S(3)	0.5128 (8)	0.0138 (6)	0.6415 (8)	3.7 (2)
S(4)	0.4965 (7)	−0.1009 (5)	0.7085 (7)	3.2 (2)
C(1)	0.3066 (36)	0.2049 (29)	0.6195 (32)	6.2 (11)
O(1)	0.3115 (27)	0.2665 (22)	0.6220 (24)	8.9 (9)
C(2)	0.2759 (32)	0.1187 (24)	0.5118 (35)	4.7 (10)
O(2)	0.2523 (23)	0.1364 (17)	0.4285 (24)	6.1 (7)
C(3)	0.2539 (31)	−0.1115 (25)	0.8038 (31)	4.7 (9)
O(3)	0.2431 (27)	−0.1677 (21)	0.8713 (26)	8.7 (8)
C(4)	0.2593 (32)	−0.0619 (24)	0.6102 (33)	4.8 (9)
O(4)	0.2451 (23)	−0.0769 (16)	0.5416 (22)	5.8 (6)
C(5)	0.0432 (29)	0.2200 (23)	0.6495 (26)	3.5 (8)
O(5)	0.0055 (21)	0.2952 (18)	0.6289 (20)	6.0 (6)
C(6)	0.0372 (42)	0.1024 (29)	0.5659 (42)	7.2 (12)
O(6)	−0.0121 (26)	0.1086 (18)	0.5001 (25)	7.2 (8)
C(7)	−0.0022 (36)	0.0717 (27)	0.7534 (37)	6.8 (11)
O(7)	−0.0595 (26)	0.0425 (18)	0.8207 (24)	7.7 (8)
C(8)	0.6172 (34)	0.1007 (29)	0.7444 (31)	5.6 (10)
O(8)	0.5932 (25)	0.1763 (21)	0.7287 (24)	8.2 (8)
C(9)	0.7803 (38)	−0.0328 (24)	0.7058 (30)	4.8 (9)
O(9)	0.8733 (25)	−0.0584 (17)	0.6818 (20)	5.7 (6)
C(10)	0.5682 (28)	−0.2169 (22)	0.9255 (29)	3.9 (8)
O(10)	0.5305 (24)	−0.2641 (19)	0.9846 (23)	7.4 (7)
C(11)	0.7504 (38)	−0.2153 (26)	0.8155 (32)	6.1(11)
O(11)	0.8339 (25)	−0.2615 (17)	0.7884 (20)	6.2 (7)
C(12)	0.7494 (34)	−0.0116 (28)	0.9663 (31)	5.9 (10)
O(12)	0.7547 (28)	0.0427 (22)	0.9883 (25)	8.4 (8)
C(13)	0.8798 (39)	−0.1467 (26)	0.9171 (32)	5.6 (10)
O(13)	0.9822 (26)	−0.1880 (17)	0.8975 (20)	6.6 (7)
C(14)	0.7151 (32)	−0.1653 (25)	1.0487 (31)	4.7 (9)
O(14)	0.7270 (26)	−0.2162 (21)	1.1262 (27)	8.5 (8)

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(16) J. F. Blount, "A Superposition Program for the CDC 1604 Computer," University of Wisconsin, 1964.

(17) (a) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS—A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963; (b) 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.

(18) Calculated and observed structure factor tables for $[SCo_3(CO)_7]_2S_2$ are deposited as Document No. 9420 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 $1.25 for photoprints or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

The "best" least-squares molecular planes determined by specified atoms along with the perpendicular distances of these and other atoms from these planes were calculated with the Smith program.[19] The Blount program[20] was used to calculate all Patterson and Fourier maps. The full-matrix, least-squares refinement cycles were carried out with a local version of the Busing–Martin–Levy ORFLS program.[17a] Bond lengths and angles together with their estimated standard deviations were calculated from the full inverse matrix (which included the estimated errors in lattice parameters) with the Busing–Martin–Levy ORFFE program.[17b]

Table II. Bond Lengths (A) with Standard Deviations[a]

Co(1)–Co(2)	2.485 (10)	Co(1)–C(2)	1.70 (5)
Co(4)–Co(5)	2.463 (10)	Co(2)–C(4)	1.75 (5)
		Co(4)–C(9)	1.81 (4)
	2.474 (7)	Co(5)–C(11)	1.72 (4)
Co(1)–Co(3)	2.524 (9)		1.75 (2)
Co(2)–Co(3)	2.521 (12)		
Co(4)–Co(6)	2.531 (12)	Co(3)–C(5)	1.80 (4)
Co(5)–Co(6)	2.544 (9)	Co(3)–C(7)	1.74 (5)
		Co(6)–C(12)	1.79 (5)
	2.531 (5)	Co(6)–C(14)	1.75 (4)
Co(1)–S(1)	2.160 (13)		1.77 (2)
Co(2)–S(1)	2.162 (12)		
Co(4)–S(2)	2.134 (12)	Co(3)–C(6)	1.84 (6)
Co(5)–S(2)	2.122 (12)	Co(6)–C(13)	1.70 (4)
	2.144 (6)		1.75 (4)
Co(3)–S(1)	2.152 (14)	C(1)–O(1)	1.15 (4)
Co(6)–S(2)	2.139 (12)	C(3)–O(3)	1.20 (4)
		C(8)–O(8)	1.20 (4)
	2.145 (9)	C(10)–O(10)	1.20 (3)
Co(1)–S(3)	2.227 (13)		1.19 (2)
Co(4)–S(3)	2.258 (13)		
Co(2)–S(4)	2.253 (12)	C(2)–O(2)	1.18 (4)
Co(5)–S(4)	2.242 (14)	C(4)–O(4)	1.18 (4)
		C(9)–O(9)	1.08 (3)
	2.245 (6)	C(11)–O(11)	1.14 (4)
S(3)–S(4)	2.042 (14)		1.14 (2)
Co(1)–C(1)	1.83 (5)	C(5)–O(5)	1.16 (3)
Co(2)–C(3)	1.70 (4)	C(7)–O(7)	1.26 (4)
Co(4)–C(8)	1.73 (5)	C(12)–O(12)	1.16 (4)
Co(5)–C(10)	1.74 (4)	C(14)–O(14)	1.17 (4)
	1.75 (2)		1.18 (2)
C(6)–O(6)	1.12 (5)		
C(13)–O(13)	1.21 (4)		
	1.18 (3)		

[a] Standard deviations of the last significant figures are given in parentheses. For each set of bond lengths the "best value" $\bar{x}$ and the corresponding standard deviation $\sigma(\bar{x})$ were weighted according to the individual estimated standard deviations given in the table.

Discussion

The molecular configuration of $[SCo_3(CO)_7]_2S_2$ (shown in Figure 1) consists of two identical $SCo_3(CO)_7$ moieties linked to each other by a bridging disulfide group such that the dihedral angle between the two planes each formed by the disulfide group and the two adjacent cobalt atoms in each moiety is 119.4°.[21] Although no molecular symmetry is demanded by the space group,[22] the idealized molecule possesses C_{2v}-2mm symmetry. One mirror plane is determined by S(1), S(2), and the midpoint of S(3)–S(4); the other mirror plane passes through S(3), S(4), and the midpoint of S(1)–S(2). The molecular deviations from C_{2v} symmetry primarily involve the carbonyl ligands and presumably arise from packing interactions. The degree of the molecular distortions can be seen from the individual variations in the nonbonding intramolecular distances categorized in Table IV according to C_{2v} symmetry. The average values for these different distances observed in $[SCo_3(CO)_7]_2S_2$ conform closely with the average values for the corresponding intramolecular nonbonding distances reported in $SCo_3(CO)_9$[24] (which possesses an idealized molecular geometry of C_{3v} symmetry) in direct support of the over-all similarity in the molecular structures of these two complexes (*vide infra*).

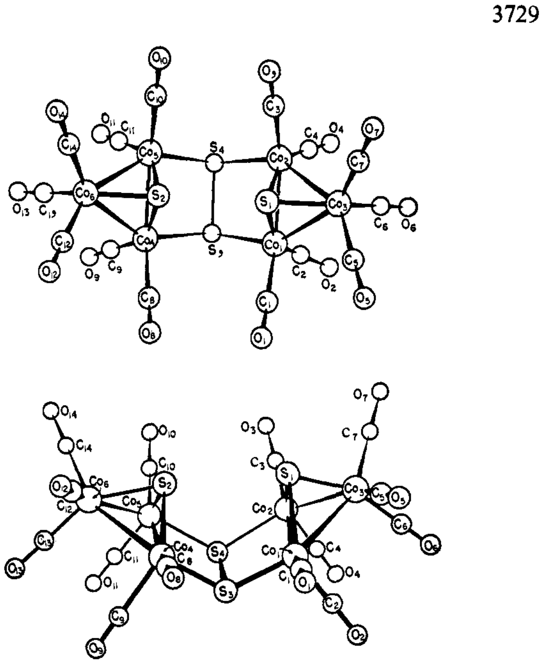

Figure 1. Idealized molecular configuration of $[SCo_3(CO)_7]_2S_2$ corresponding to C_{2v}-2mm symmetry. The view on the top shows the projection down the twofold axis.

The C_{2v} symmetry divides the six cobalt atoms of $[SCo_3(CO)_7]_2S_2$ into two sets: (a) the four cobalt atoms bonded to the disulfide group with each cobalt atom surrounded by two cobalts, two sulfurs, and two carbonyls; (b) the other two cobalt atoms each of which is coordinated with two cobalts, one sulfur, and three carbonyls. The mean values of 2.47 A for the two equivalent Co–Co bonds bridged by the disulfide group and 2.53 A for the remaining four symmetry-related Co–Co bonds can be compared to the Co–Co

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

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

(21) The resulting dihedral angle between the tricobalt plane (Co_1, Co_2, Co_3) and the corresponding Co_2S_2 plane is 174.7° and between the tricobalt plane (Co_4, Co_5, Co_6) and the corresponding Co_2-S_2 plane is 172.7°. All dihedral angles given in this paper are defined as the angles directly between planes rather than as angles between normals to planes.

(22) All atoms in the unit cell of symmetry $A\bar{1}$ occupy the general fourfold set of positions: (0, 0, 0; 0, 1/2, 1/2) ± x, y, z. A Delaunay reduction[23] verified the triclinic symmetry.

(23) L. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958, pp 167–180.

(24) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, 6, 1229 (1967).

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

Angle	Degrees
M–M–M	
Co(1)–Co(2)–Co(3)	60.6 (3)
Co(3)–Co(1)–Co(2)	60.4 (3)
Co(4)–Co(5)–Co(6)	60.7 (3)
Co(6)–Co(4)–Co(5)	61.2 (3)
	60.7 (2)
Co(2)–Co(3)–Co(1)	59.0 (3)
Co(5)–Co(6)–Co(4)	58.1 (3)
	58.6 (2)
M–S$_{ap}$–M	
Co(1)–S(1)–Co(2)	70.2 (4)
Co(4)–S(2)–Co(5)	70.7 (4)
	70.5 (3)
Co(2)–S(1)–Co(3)	71.5 (4)
Co(3)–S(1)–Co(1)	71.7 (4)
Co(5)–S(2)–Co(6)	73.3 (4)
Co(6)–S(2)–Co(4)	72.6(4)
	72.3 (2)
S$_{ap}$–M–M	
S(1)–Co(1)–Co(2)	54.9 (4)
S(1)–Co(2)–Co(1)	54.9 (3)
S(2)–Co(4)–Co(5)	54.4 (4)
S(2)–Co(5)–Co(4)	54.8 (3)
	54.8 (2)
S(1)–Co(1)–Co(3)	54.0 (4)
S(1)–Co(2)–Co(3)	54.0 (3)
S(2)–Co(4)–Co(6)	53.8 (4)
S(2)–Co(5)–Co(6)	53.7 (4)
	53.9 (2)
S(1)–Co(3)–Co(1)	54.3 (3)
S(1)–Co(3)–Co(2)	54.4 (4)
S(2)–Co(6)–Co(4)	53.6 (4)
S(2)–Co(6)–Co(5)	53.0 (4)
	53.8 (2)
M–S$_{eq}$–M	
Co(1)–S(3)–Co(4)	118.2 (5)
Co(2)–S(4)–Co(5)	118.6 (5)
	118.4 (4)
S$_{eq}$–M–M	
S(3)–Co(1)–Co(2)	84.8 (4)
S(3)–Co(4)–Co(5)	84.9 (4)
S(4)–Co(2)–Co(1)	83.9 (4)
S(4)-Co(5)-Co(4)	84.4 (4)
	84.5 (2)
S(3)–Co(1)–Co(3)	144.8 (4)
S(3)–Co(4)–Co(6)	145.4 (3)
S(4)–Co(2)–Co(3)	144.1 (4)
S(4)–Co(5)–Co(6)	144.4 (4)
	144.7 (2)
M–S$_{eq}$–S$_{eq}$	
Co(1)–S(3)–S(4)	95.9 (5)
Co(4)–S(3)–S(4)	94.6 (6)
Co(2)–S(4)–S(3)	95.5 (5)
Co(5)–S(4)–S(3)	96.1 (6)
	95.5 (3)
S$_{eq}$–M–S$_{ap}$	
S(3)–Co(1)–S(1)	103.3 (5)
S(3)–Co(4)–S(2)	101.9 (4)
S(4)–Co(2)–S(1)	102.5 (4)
S(4)–Co(5)–S(2)	101.7 (5)
	102.3 (3)
M–M–C	
Co(3)–Co(1)–C(1)	107.0 (13)
Co(3)–Co(2)–C(3)	105.1 (12)
Co(6)–Co(4)–C(8)	106.3 (15)
Co(6)–Co(5)–C(10)	107.9 (13)
	106.5 (6)
Co(1)–Co(2)–C(4)	101.2 (13)
Co(2)–Co(1)–C(2)	101.0 (13)
Co(4)–Co(5)–C(11)	101.2 (13)
Co(5)–Co(4)–C(9)	105.5 (12)
	102.3 (6)
Co(1)–Co(3)–C(6)	100.0 (13)
Co(2)–Co(3)–C(6)	94.3 (14)
Co(4)–Co(6)–C(13)	98.0 (15)
Co(5)–Co(6)–C(13)	100.3 (15)
	98.1 (7)
Co(3)–Co(1)–C(2)	94.4 (12)
Co(3)–Co(2)–C(4)	98.5 (12)
Co(6)–Co(4)–C(9)	99.5 (14)
Co(6)–Co(5)–C(11)	96.7 (14)
	97.1 (6)
M–M–C	
Co(1)–Co(2)–C(3)	153.3 (14)
Co(2)–Co(1)–C(1)	155.8 (14)
Co(4)–Co(5)–C(10)	157.3 (11)
Co(5)–Co(4)–C(8)	156.6 (14)
	156.0 (6)
Co(1)–Co(3)–C(7)	153.9 (14)
Co(2)–Co(3)–C(5)	145.8 (10)
Co(4)–Co(6)–C(14)	146.9 (12)
Co(5)–Co(6)–C(12)	152.3 (13)
	149.0 (6)
Co(1)–Co(3)–C(5)	88.4 (10)
Co(2)–Co(3)–C(7)	100.9 (14)
Co(4)–Co(6)–C(12)	98.1 (13)
Co(5)–Co(6)–C(14)	93.0 (13)
	94.1 (6)
S$_{eq}$–M–C	
S(3)–Co(1)–C(1)	103.4 (13)
S(3)–Co(4)–C(8)	102.7 (14)
S(4)–Co(2)–C(3)	105.2 (12)
S(4)–Co(5)–C(10)	102.1 (12)
	103.4 (6)
S(3)–Co(1)–C(2)	97.0 (13)
S(3)–Co(4)–C(9)	95.9 (14)
S(4)–Co(2)–C(4)	93.0 (12)
S(4)–Co(5)–C(11)	96.8 (15)
	95.5 (7)
C–M–C	
C(1)–Co(1)–C(2)	100.6 (19)
C(3)–Co(2)–C(4)	103.3 (19)
C(8)–Co(4)–C(9)	95.9 (17)
C(10)–Co(5)–C(11)	99.6 (17)
	99.6 (9)
C(5)–Co(3)–C(6)	101.8 (19)
C(7)–Co(3)–C(6)	97.9 (22)
C(12)–Co(6)–C(13)	96.8 (19)
C(14)–Co(6)–C(13)	103.2 (18)
	100.2 (10)
C(5)–Co(3)–C(7)	106.4 (18)
C(12)–Co(6)–C(14)	104.2 (19)
	105.3 (13)
S$_{ap}$–M–C	
S(1)–Co(1)–C(1)	100.9 (14)
S(1)–Co(2)–C(3)	98.5 (14)
S(2)–Co(4)–C(8)	102.2 (14)
S(2)–Co(5)–C(10)	102.5 (11)
	101.2 (7)
S(1)–Co(3)–C(5)	99.6 (11)
S(1)–Co(3)–C(7)	101.2 (16)
S(2)–Co(6)–C(12)	102.5 (13)
S(2)–Co(6)–C(14)	97.3 (12)
	100.0 (6)
S(1)–Co(1)–C(2)	146.0 (12)
S(1)–Co(2)–C(4)	149.0 (13)
S(2)–Co(4)–C(9)	151.0 (13)
S(2)–Co(5)–C(11)	147.4 (13)
	148.3 (6)
S(1)–Co(3)–C(6)	145.8 (14)
S(2)–Co(6)–C(13)	147.3 (16)
	146.5 (10)
M–C–O	
Co(1)–C(1)–O(1)	173 (4)
Co(2)–C(3)–O(3)	174 (3)
Co(4)–C(8)–O(8)	176 (4)
Co(5)–C(10)–O(10)	177 (3)
	175 (2)
Co(3)–C(5)–O(5)	177 (3)
Co(3)–C(7)–O(7)	170 (4)
Co(6)–C(12)–O(12)	175 (4)
Co(6)–C(14)–O(14)	169 (3)
	173 (2)
Co(1)–C(2)–O(2)	176 (4)
Co(2)–C(4)–O(4)	178 (3)
Co(4)–C(9)–O(9)	171 (4)
Co(5)–C(11)–O(11)	174 (4)
	175 (2)
Co(3)–C(6)–O(6)	173 (4)
Co(6)–C(13)–O(13)	173 (4)
	173 (3)

[a] Standard deviations of the last significant figures are given in parentheses. For each set of bond angles the "best value" $\bar{x}$ and the corresponding standard deviation $\sigma(\bar{x})$ were weighted according to the individual estimated standard deviations given in the table.

bond lengths of 2.52 A in $Co_2(CO)_8$,[25] 2.49 A in $Co_4(CO)_{12}$,[26] 2.46 A in $Co_3(CO)_9CCH_3$,[27] and 2.64 A in $SCo_3(CO)_9$.[24] The average Co–S_{ap} bond length of 2.14 A in the same as that in $SCo_3(CO)_9$.[24] The average Co–S_{eq} (*i.e.*, Co-disulfide group) bond distance of 2.24 A closely conforms to the average Fe–(bridging disulfide) distance in $[SFe(CO)_3]_2$ (2.23 A)[28] and the doubly bridging Co–mercapto distances in $Co_3(CO)_4(SC_2H_5)_5$ (2.26 A),[29] $Co_5(CO)_{10}(SC_2H_5)_5$ (2.24 A),[29] and $SCo_6(CO)_{11}(SC_2H_5)_4$ (2.21 A).[29] Pauling's covalent radii of 1.16 A for both iron and cobalt and 1.04 A for sulfur give a calculated distance of 2.20 A for the Fe–S and Co–S bonds. The S–S bond length of 2.04 A is essentially identical with that of 2.01 A in the disulfide bridge in $[SFe(CO)_3]_2$.[28] The average terminal Co–C and C–O distances of 1.76 and 1.17 A, respectively, are not unlike those in other cobalt carbonyl complexes; the terminal Co–C–O angles are all approximately linear.

The [010] projection of the unit cell of $[SCo_3(CO)_7]_2S_2$ (Figure 2) depicts the orientation of two centrosymmetrically related dimeric molecules. For the sake of clarity, the other two molecules in the unit cell are not shown. The closest intermolecular approaches of 2.9 A for O···O contacts, 3.25 A for C···O contacts, and 3.4 A for O···S contacts indicate that the intermolecular crystal forces are primarily of the van der Waals type.

A detailed comparison of the structural features of $[SCo_3(CO)_7]_2S_2$ with those of the closely related mo-

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Table IV. Nonbonding Intramolecular Distances (A)[a]

C(2)···C(6)	3.00 (6)	S(1)···C(1)	3.08 (4)
C(4)···C(6)	2.92 (6)	S(1)···C(3)	2.94 (4)
C(9)···C(13)	3.07 (6)	S(2)···C(8)	3.02 (4)
C(11)···C(13)	3.05 (6)	S(2)···C(10)	3.02 (4)
	3.01 (av)		3.02 (av)
C(2)···C(4)	3.15 (5)	S(1)···C(5)	3.03 (4)
C(9)···C(11)	3.28 (5)	S(1)···C(7)	3.02 (4)
		S(2)···C(12)	3.07 (4)
	3.22 (av)	S(2)···C(14)	2.93 (4)
C(1)···C(2)	2.72 (7)		
C(3)···C(4)	2.70 (7)		3.01 (av)
C(8)···C(9)	2.63 (6)	S(3)···C(1)	3.19 (5)
C(10)···C(11)	2.65 (6)	S(3)···C(8)	3.13 (5)
		S(4)···C(3)	3.16 (4)
	2.67 (av)	S(4)···C(10)	3.12 (4)
C(5)···C(6)	2.83 (7)		
C(7)···C(6)	2.70 (8)		3.15 (av)
C(12)···C(13)	2.61 (7)	S(3)···C(2)	2.96 (5)
C(14)···C(13)	2.70 (6)	S(3)···C(9)	3.03 (4)
		S(4)···C(4)	2.92 (4)
	2.71 (av)	S(4)···C(11)	2.99 (4)
C(5)···C(2)	3.60 (5)		
C(7)···C(4)	4.07 (6)		2.98 (av)
C(12)···C(9)	4.02 (7)	S(1)···S(3)	3.44 (2)
C(14)···C(11)	3.85 (6)	S(1)···S(4)	3.44 (2)
		S(2)···S(3)	3.41 (2)
	3.89 (av)	S(2)···S(4)	3.38 (2)
C(5)···C(7)	2.83 (6)		
C(12)···C(14)	2.80 (6)		3.42 (av)
	2.81 (av)	S(1)···S(2)	3.19 (2)
C(1)···C(5)	3.03 (5)		
C(3)···C(7)	3.30 (6)		
C(8)···C(12)	3.28 (6)		
C(10)...C(14)	3.18 (5)		
	3.20 (av)		
C(1)···C(8)	3.60 (6)		
C(3)···C(10)	3.62 (5)		
	3.61 (av)		

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

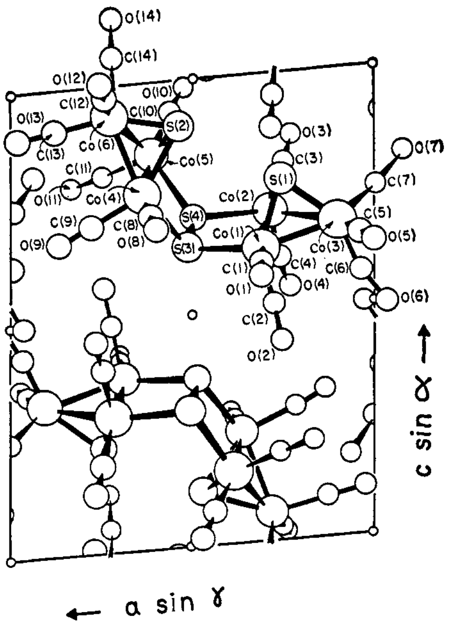

Figure 2. View down the [010] direction depicting the orientation of two centrosymmetrically related molecules in the triclinic unit cell of symmetry $A\bar{1}$. The other two molecules in the unit cell which are related to those in the drawing by A-centering are not shown.

lecular complex $SCo_3(CO)_9$ is informative. The formation of $[SCo_3(CO)_7]_2S_2$ can be considered formally to arise from the replacement of two *cis* equatorial carbonyl ligands in each of two $SCo_3(CO)_9$ molecules with a bridging disulfide group.[30] The displacement of the two electron-pair carbonyl donors by the three-electron disulfide donor results in a closed-shell electronic configuration for each cobalt atom in the dimeric species in contrast to $SCo_3(CO)_9$ in which the whole molecule possesses one electron in excess of the number required to permit each cobalt atom to attain the "krypton" configuration.

The stereochemical consequence of the substitution of the disulfide group for the two carbonyl groups in $SCo_3(CO)_9$ is a definite symmetrical deformation of the resulting dimeric molecule, $[SCo_3(CO)_7]_2S_2$, due primarily to the fixed geometrical requirements of the chelating disulfide bridge. The influence of this imposed steric constraint of the disulfide linkage on the localized environment of each of the four adjacent cobalt atoms (designated as Co_A) in $[SCo_3(CO)_7]_2S_2$ as contrasted to the localized environment of each of the cobalt atoms (designated as Co_B), both in the two $Co(CO)_3$ groups of $[SCo_3(CO)_7]_2S_2$ and in the three equivalent $Co(CO)_3$ groups of $SCo_3(CO)_9$, is best seen from a comparison of the various metal-metal-ligand angles. As expected, the average value of 84° for the four Co_A–Co_A–S(equatorial) angles is considerably less than both the average value of 94° for the four Co_A–Co_B–CO(equatorial) angles in $[SCo_3(CO)_7]_2S_2$ and the average value of 97° for the six corresponding Co–Co–CO(equatorial) angles in $SCo_3(CO)_9$. This average angular decrease of 10° for the acute Co_A–Co_A–S(equatorial) angles is counterbalanced by a corresponding angular increase of 12° for the Co_B–Co_A–CO(equatorial) angles in $[SCo_3(CO)_7]_2S_2$ to an average value of 106°. These changes in the metal-metal-ligand angles in $[SCo_3(CO)_7]_2S_2$ primarily result from a rotation of each of the four Co_A-dicarbonyl groups about its axial carbonyl direction by approximately 11° such as to permit maximum overlap (*i.e.*, maximum bond strength) of the appropriate bonding orbitals of the Co_A and sulfur atoms. Since the axial Co_A–CO direction is inclined to the tricobalt plane such that the average Co_B–Co_A–CO (axial) angle is 97° and the average Co_A–Co_A–CO(axial) angle is 102°, this rotation increases the upward Co–CO tilt of the carbonyl group attached to each Co_A from the basal cobalt plane in a given half of the $[SCo_3(CO)_7]_2S_2$ molecule to an average value of 22° from the average value of 15° for the two equatorial carbonyl groups bonded to each Co_B and of 16° for the carbonyl groups attached to each cobalt atom in $SCo_3(CO)_9$. The average upward tilt of the Co_A–S ligands with respect to the triangular cobalt plane is correspondingly decreased to 6° by this rotation. This twisting deformation results in the ligand-metal-ligand angles being essentially unaltered. The average equatorial-equatorial S–Co_A–CO angle of 103° is very similar to the corresponding

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(30) The structural determination of $[SCo_3(CO)_7]_2S_2$ accounts for the experimentally observed fact[5] that $SCo_3(CO)_9$ is a reaction intermediate from which the dimeric species is formed by the addition of excess sulfur. One possible mechanism leading to the formation of the dimeric species involves the displacement of a carbonyl group of an $SCo_3(CO)_9$ molecule by one sulfur atom of an S_x species followed by replacement of a second *cis* equatorial carbonyl group bonded to another cobalt atom with an adjacent sulfur atom of the polysulfide chain. The resulting reactive species then gives the dimeric product on interaction with a second $SCo_3(CO)_9$ molecule.

equatorial–equatorial OC–Co–CO angles of 105° in the two $Co(CO)_3$ groups of $[SCo_3(CO)_7]_2S_2$ and of 101° in $SCo_3(CO)_9$; the average equatorial–axial $S–Co_A–CO$ angle of 96° is comparable to the identical average equatorial–axial $OC–Co_A–CO$ and $OC–Co_B–CO$ angles of 100° in $[SCo_3(CO)_7]_2S_2$ and to the corresponding average equatorial–axial OC–Co–CO angle of 101° in $SCo_3(CO)_9$.

The salient structural difference between $[SCo_3(CO)_7]_2S_2$ and $SCo_3(CO)_9$ is that the average value of 2.64 A for the three equivalent Co–Co bond lengths in $SCo_3(CO)_9$ is more than 0.1 A longer than either of the average values of 2.47 and 2.53 A for two sets of Co–Co bonds in $[SCo_3(CO)_7]_2S_2$, whereas the average $Co–S_{ap}$ bond lengths are identical for the two compounds. Clearly, this difference in Co–Co bond lengths must be a consequence of the effect of the disulfide bridge in $[SCo_3(CO)_7]_2S_2$ and/or the influence of the unpaired electron in $SCo_3(CO)_9$. In order to ascertain the relative importance of these two effects, an X-ray study of $SFeCo_2(CO)_9$ was carried out; the results of this structural determination will be reported in a future paper.[31]

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The Formation of and Interrelation between Some Peroxo Binuclear Cobalt Complexes. I[1]

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Abstract: The interrelations between Werner's green and red μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} salts, $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_4$ and $[(en)_2Co(NH_2)(O_2)Co(en)_2]H(NO_3)_4 \cdot 2H_2O$, respectively, have been reexamined. A brown, diamagnetic complex $[(en)_2Co(NH_2)(O_2)Co(en)_2](NO_3)_3 \cdot 2.5H_2O$ has been obtained from ammoniacal solutions of the green salt, and similarly from the red salt; the brown complex is thought to be the reduced counterpart of the paramagnetic green salt, rather than a complex containing the ion $[(en)_2Co^{III}(NH)(O_2)Co^{IV}(en_2)]^{3+}$, as previously assumed by Werner. The red salt is not simply a protonation product of the brown salt, but rather is a secondary (probably isomeric) product thereof, as is shown by quantitative optical measurements of transformation rates and equilibrium concentrations.

The objective of the present series of studies is to clarify the formation process of and interrelations between various peroxo–dicobalt complexes. The present paper is particularly concerned with the acid–base and oxidation behavior, primarily of Werner's[2a] green and red ethylenediamine series of such compounds.

By the measurement of magnetic susceptibilities, Malatesta[2b] ascertained the presence of one unpaired electron per two cobalt atoms in a series of green μ-peroxo compounds including Werner's green μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} complex. Epr studies by Ebsworth and Weil[3] indicated that such an odd electron is equally distributed with respect to the two cobalt nuclei.

On the other hand, Thompson and Wilmarth[4] studied the red μ-amido-μ-peroxo-bis{bis(ethylenediamine)cobalt} complex, once thought by Werner to be isomeric with the analogous paramagnetic green compound mentioned above, and found it to be diamagnetic and transformable by one-electron oxidation to the green form. Furthermore, they found that the red form contains one molecule of acid per dicobalt complex, and thereby accounted for the fact that both green and red compounds had the same number of anions (*e.g.*, four univalent anions) per binuclear complex cation in spite of the difference in the oxidation states.

The present study has unveiled further complications in the relation between compounds of this series, as well as among the corresponding ammonia complexes. Specifically, kinetic and equilibrium studies of the interchange between these compounds made it evident that a certain kind of isomerism also is intermingled with the redox and protonation phenomena. A short description of these studies has appeared elsewhere.[5]

Results and Discussion

I. On the Constitution of the Dibridged Peroxo–Dicobalt–Ethylenediamine Complexes. Although Thompson and Wilmarth inferred that Werner's red dibridged peroxo–dicobalt–ethylenediamine complex

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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