cyclopentadienyl carbon ring is tilted such that a line from the molybdenum atom to the centroid of the ring is not parallel with the normal to the ring at the centroid but instead forms an angle of 1.7°. A similar trend in the molybdenum to cyclopentadienyl carbon distances was observed[33] in Mo(π-C₅H₅)(CO)₂(p-CH₃C₆H₄CH₂) where the cyclopentadienyl ring is significantly tipped away from the allylic carbon atoms. Examination of the intramolecular bonding distances indicates that "steric compression" effects can satisfactorily account for the cyclopentadienyl ring tipping in both molecules; in the (π-CH₂SCH₃)-molybdenum complex the S···C₅ and H₂C···C₄ contacts are 3.40 and 3.29 Å, respectively. A similar "tilting" of the π-cyclopentadienyl ring as a general structural feature in the Mo(π-C₅H₅)(CO)₂XY class of compounds was previously noted from a survey by Churchill and Fennessey.[28,31] Since the shortest Mo–C distances were usually observed for the cyclopentadienyl carbon atoms *trans* to the carbonyl groups, Churchill and Fennessey[28,31] attributed the systematic Mo–C variations to steric repulsion and/or a *trans* effect due to the greater π character in the molybdenum–carbonyl bonds. The average Mo–C distance of 2.34 Å and the perpendicular distance from the molybdenum to cyclopentadienyl ring of 2.02 Å in Mo(π-C₅H₅)(CO)₂(CH₂SCH₃) are identical with the corresponding values in Mo(π-C₅H₅)(CO)₂(p-CH₃C₆H₄CH₂) and are close to the corresponding values reported in the other Mo(π-C₅H₅)(CO)₂XY molecules.[28,31]

A view of the environment of the molybdenum atom perpendicular to the cyclopentadienyl ring in Mo(π-C₅H₅)(CO)₂(CH₂SCH₃) (Figure 1) and in Mo(π-C₅H₅)(CO)₂(p-CH₃C₆H₄CH₂) (Figure 3) shows almost the same relative orientation of the cyclopentadienyl ring with respect to the two carbonyls; a similar orientation of the cyclopentadienyl ligand relative to two carbonyl groups is observed in [Mo(π-C₅H₅)(CO)₂]₂-(H)[P(CH₃)₂][32] and in Nb(π-C₅H₅)(CO)₄.[34]

Organometallic Chalcogen Complexes. XVI. Preparation and Structural Characterization of Co₄(π-C₅H₅)₄S₆. A New Mode of Transition Metal Bonding for a Disulfide Group[1]

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Abstract: The reaction of elemental sulfur with Co(π-C₅H₅)(CO)₂ has resulted in the synthesis of a new kind of organometallic sulfur complex, Co₄(π-C₅H₅)₄S₆. This air-stable, relatively insoluble compound was shown to be diamagnetic from its nmr spectrum which revealed four separate, equivalent resonances characteristic of four nonequivalent cyclopentadienyl rings. Its stereochemical characterization as a tetranuclear cobalt complex was ascertained from a three-dimensional X-ray diffraction study carried out on a crystal of stoichiometry Co₄(π-C₅H₅)₄-S₆·½CHCl₃. This solvated crystal contains eight formula species in a monoclinic unit cell of symmetry P2₁/c and dimensions a = 25.618 ± 0.010 Å, b = 10.604 ± 0.004 Å, c = 19.295 ± 0.008 Å, β = 105° 43′ ± 04′. The structure, determined by the application of the Hauptman–Karle symbolic addition method, was refined by rigid-body isotropic least squares of the automatically collected diffractometry data to an unweighted R₁ discrepancy index of 11.7%. The molecular structure consists of a distorted tetrahedral array of C₅H₅Co units interconnected by two triply bridging disulfide S₂ groups and two triply bridging sulfur atoms located above the four triangular faces of the distorted tetrahedron of nonbonding cobalt atoms. This molecular complex supplies a heretofore "missing link" in organometallic chemistry in its exemplification of an S₂ ligand covalently coordinated as a four-electron donor with three metal atoms. The one crystallographically independent chloroform molecule is closely associated by presumed hydrogen bonding with only one of the two crystallographically independent Co₄(π-C₅H₅)₄S₆ molecules. The detailed molecular features are compared with those of related molecular complexes.

Although a wide assortment of cobalt–sulfur atom carbonyl clusters synthesized by Markó, Bor, and coworkers[3-9] have been crystallographically characterized (*e.g.*, Co₃(CO)₉S,[10] [Co₃(CO)₇S]₂S₂,[11] Co₂Fe-

(1) (a) Previous paper in this series: E. R. de Gil and L. F. Dahl, *J. Am. Chem. Soc.*, 91, 3751 (1969); (b) presented in part at the First International Symposium of Inorganica Chimica Acta on "New Aspects of the Chemistry of Metal Carbonyls and Derivatives," Venice, Italy, Sept 2–4, 1968; see *Proc. Inorg. Chim. Acta*, B1 (1969).

(2) This manuscript is based in part on a dissertation submitted by V. A. Uchtman to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, July 1968.

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

(4) L. Markó, 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) E. Klumpp, L. Markó, and G. Bor, *ibid.*, 97, 926 (1964).

$(CO)_9S$,[12] $Co_4(CO)_{10}S_2$,[13] $Co_6(CO)_{11}(S)(SC_2H_5)_4$,[14] Co_6-$(CO)_{15}(S)CS_2$,[15] and $Co_6(CO)_{16}C_2S_3$[16]), no cyclopentadienyl–sulfur complexes of cobalt were known to us prior to the initiation of the work reported in this paper.[17,18] In fact, the metal–sulfur atom cyclopentadienyl clusters (containing more than two metal atoms), which previously had been fully characterized, were $Fe_4(\pi\text{-}C_5H_5)_4S_4$[19,20] and $Ni_3(\pi\text{-}C_5H_5)_3S_2$.[21]

The purpose of this project was to prepare new cobalt–sulfur–cyclopentadienyl complexes in order to augment further the recently developed structural and bonding principles[14,15,21-23] for metal atom carbonyl and cyclopentadienyl cluster systems. The investigation of the reaction of cyclopentadienylcobalt dicarbonyl with elemental sulfur (S_8) instead has led to the preparation of a new kind of "noncluster" cyclopentadienylmetal–sulfur complex, $Co_4(\pi\text{-}C_5H_5)_4S_6$; the stereochemical analysis of this complex was achieved by a single-crystal X-ray diffraction study which revealed the first known example of a disulfide ligand covalently linked to three transition metal atoms.

Experimental Procedure

Preparation and Properties. All reactions were performed in standard glass apparatus in an atmosphere of dry, prepurified nitrogen. The $Co(\pi\text{-}C_5H_5)(CO)_2$ was used as obtained from the supplier (Alfa Inorganics, Inc.). Sulfur (Fischer, precipitated) was used without further purification. All solvents were reagent grade and were dried by standard procedures before use.

A mixture of $Co(\pi\text{-}C_5H_5)(CO)_2$ (3.0 g, 0.017 mole) and sulfur (0.5 g, 0.015 mole) was stirred in a nitrogen atmosphere at room temperature. Hexane (5-ml portions) was added periodically to maintain a slurry consistency. After 24 hr an additional 50 ml of hexane was added, and the reaction mixture was then filtered. The resulting black residue was washed with another 30-ml portion of hexane and dried *in vacuo* to give approximately 1 g of crude product. This residue then was dissolved in a 20% excess of chloroform and filtered; an equal amount of octane was added and the solution allowed to stand over P_2O_5 in a vacuum desiccator at reduced pressure. Within several hours clusters of lustrous black rod- and needle-shaped crystals (dec $\sim200°$) formed on the walls of the flask. *Anal.* Calcd for $Co_2(C_5H_5)_2S_3$: Co, 34.2; C, 34.9; H, 2.9; S, 27.9. Found:[24] Co, 34.1; C, 35.1; H, 2.9; S, 27.7. Attempts to obtain single crystals (of a size suitable for

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

(8) L. Markó and G. Bor, *ibid.,* 3, 161 (1965).

(9) E. Klumpp, G. Bor, and L. Markó, *Chem. Ber.,* 100, 1451 (1967).

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

(11) D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Am. Chem. Soc.,* 89, 3424 (1967).

(12) D. L. Stevenson, C. H. Wei, and L. F. Dahl, submitted for publication.

(13) C. H. Wei and L. F. Dahl, submitted for publication.

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

(15) J. F. Blount, S. F. Watkins, L. Markó, G. Bor, and L. F. Dahl, submitted for publication.

(16) C. H. Wei and P. A. Agron, submitted for publication.

(17) Subsequently, the preparation of $Co_3(\pi\text{-}C_5H_5)_3S_2$ and $Co_3(\pi\text{-}C_5H_5)_3(CO)(S)$ from the reaction of di-*t*-butylsulfurdiimide with π-cyclopentadienylcobalt dicarbonyl was reported by Otsuka, Nakamura, and Yoshida,[18] but no physical or chemical properties were given for these complexes.

(18) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.,* 7, 261 (1968).

(19) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.,* 5, 892 (1966).

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

(21) H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *J. Am. Chem. Soc.,* 90, 3272 (1968).

(22) C. H. Wei and L. F. Dahl, *ibid.,* 90, 3960, 3969 (1968), and references contained therein.

(23) H. Vahrenkamp and L. F. Dahl, *Angew. Chem.,* 81, 152 (1969); *Angew. Chem. Intern. Ed. Engl.,* 8, 144 (1969).

(24) Alfred Bernhardt Mikroanalytisches Laboratorium in Max-Planck Institut fur Kohlenforschung, 433 Mulheim (Ruhr), Germany.

X-ray diffraction) by prolonged recrystallization (8–10 days) from solutions of greater chloroform concentration led to crystalline samples of stoichiometry $Co_4(\pi\text{-}C_5H_5)_4S_6 \cdot {}^1/_2CHCl_3$, determined from the crystal structure analysis.

$Co_4(\pi\text{-}C_5H_5)_4S_6$ is stable to atmospheric oxygen in the solid state but slowly decomposes in solution. Its solubility in hydrocarbon solvents is very low; it does exhibit slight solubility in halogenated solvents such as chloroform and methylene chloride. The diamagnetism of the complex was indicated by the sharp proton magnetic resonances of saturated $CHCl_3$ and CS_2 solutions. In CS_2 solution four separate resonances of approximately equal intensity were observed at 4.73, 4.77, 4.81, and 4.91 ppm (external TMS as standard), thereby suggesting the presence of four nonequivalent cyclopentadienyl groups. The infrared spectrum (KBr pellet) showed only broad bands at 3075 (w), 1420 (m), 1000 (m), and 800–830 cm⁻¹ (s, very broad), characteristic of metal-coordinated cyclopentadienyl groups; no absorption bands were present in the carbonyl stretching region. Infrared spectra were recorded on a Beckman IR-8 spectrometer, while proton magnetic resonance spectra were obtained from a Varian A-60A spectrometer.

Single-Crystal X-Ray Data. Suitable single crystals were obtained in the manner described above. A rod-shaped crystal of dimensions 0.25 (rotation axis) $\times$ 0.15 $\times$ 0.15 mm was mounted on a glass fiber with epoxy cement. Preliminary oscillation and Weissenberg photographs showed Laue C_{2h}-2/m symmetry characteristic of the monoclinic system. The crystal was optically aligned about the rotation axis (corresponding to the monoclinic *b* symmetry axis) on a General Electric four-circle automated diffractometer, and 31 representative diffraction maxima were carefully centered.[25] The lattice constants (25°), obtained by a least-squares refinement of the measured angle settings of these 31 reflections, were used to generate the angle settings for all data reflections.[26] All intensity data were collected at a take-off angle of 2.0° by the θ-2θ scan technique with symmetric 2θ scans at a 2.0°/min rate over a range of 2.0°. Stationary-crystal-stationary-counter background counts of 15 sec were taken at the beginning and end of each scan. A counter aperture of 2-mm diameter was placed 31 mm from the crystal. Zirconium-filtered Mo Kα radiation was employed with a scintillation detector followed by a pulse-height analyzer adjusted to accept approximately 90% of the Mo Kα pulse distribution.

Intensity data ($hk\bar{l}$, $\overline{hkl}$) were collected for $2\theta \leq 29°$, beyond which there were very few reflections above background. In order to check electronic and crystal stability, the intensities of four standard reflections were measured every 150 reflections. No significant fluctuations in these sets of four standards were observed during the data collection. The intensities were corrected for background and Lorentz–polarization effects by the application of the following relations derivable from counting statistics:[27] $I = CT - t'CB$ and $\sigma^2(I) = (CT + t'^2CB) + EI^2$, where CT = total integrated peak count obtained in scan time t_c; CB = total of both background counts obtained in total time t_B; $t' = t_c/t_B$; and E = instrument instability or "ignorance" factor empirically assigned a value of 0.001. Structure amplitudes were obtained from the following relations: $F^2 = (LP)^{-1}(CT - t'CB) = I(LP)^{-1}$ and $\sigma^2(F) = [0.25(LP)^{-1}(CT + t'^2CB)/(CT - t'CB)] + 0.25F^2E$, where LP is the Lorentz–polarization correction. A given reflection was considered "unobserved" if I was less than $2\sigma(I)$. A total of 1222 observed and 592 unobserved independent reflections originated from this procedure.

No absorption or extinction corrections were applied. The linear absorption coefficient (μ) for Mo Kα radiation of 33.1 cm⁻¹ results in a $\mu R_{max} < 0.5$ for which the change of absorption correction factors with θ is negligible.[28] The relatively small values of the real and imaginary dispersion corrections for Mo Kα radiation (*i.e.,* $\Delta f' = -0.4$, $\Delta f'' = 1.1$ for Co; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for S)[29] were presumed not to have any significant effect on the atomic coordinates in this centrosymmetric crystal.[30] The atomic scat-

(25) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(26) Argonne National Laboratory, "Orientation and Angle Setting Generation Program," Program B-101, 1965.

(27) E. Epstein, Ph.D. Thesis (Appendix), University of Wisconsin, Jan 1969.

(28) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

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

(30) D. H. Templeton, *Acta Cryst.,* 8, 842 (1955).

tering factors used for all atoms are those based on Hartree–Fock–Slater calculations as compiled by Hanson, *et al.*[31]

Unit Cell and Space Group. The measured lattice constants (25°) and estimated standard deviations for the monoclinic unit cell of $Co_4(\pi\text{-}C_5H_5)_4S_6\cdot{}^1\!/_2CHCl_3$ are: $a = 25.618 \pm 0.010$ Å, $b = 10.604 \pm 0.004$ Å, $c = 19.295 \pm 0.008$ Å, $\beta = 105°\,43' \pm 04'$; unit cell volume $= 5045.3$ Å^3. The experimental density of 1.98 g cm^{-3} (flotation method) agrees well with the value of 1.97 g cm^{-3} calculated on the basis of eight of the above formula species per unit cell. The total number of electrons per cell, $F(000)$, is 2984.

The systematic absences of $\{0k0\}$ for k odd and $\{h0l\}$ for l odd uniquely define the probable space group as $P2_1/c(C_{2h}{}^5$, no. 14). Verification of this centrosymmetric space group was shown by the successful refinement of the structure, the solution of which required the location of 8 cobalt, 12 sulfur, 21 carbon, 3 chlorine, and ideally 21 hydrogen atoms corresponding to two $Co_4(\pi\text{-}C_5H_5)_4S_6$ molecules and one solvated $CHCl_3$ molecule per asymmetric unit. The crystallographically independent atoms were each found from the structural analysis to occupy the following general fourfold set of positions: $\pm(x, y, z; \; x, {}^1\!/_2 - y, {}^1\!/_2 + z).$[32]

Determination of the Structure. Initial attempts to solve a three-dimensional Patterson map were unsuccessful due to the large number of interatomic cobalt and sulfur vectors. Nevertheless, application of the Hauptman–Karle symbolic addition method[33] by use of the computer programs FAME, MAGIC, and LINK[34] led to the successful elucidation of the composition as well as atomic arrangement of the crystal.

A Wilson plot[35] generated from a total of 1686 observed and unobserved reflections provided both an initial scale factor and an over-all isotropic temperature factor from which the observed structure amplitudes were placed on an absolute scale, and normalized structure factor magnitudes $|E|$ were determined. The statistical averages[36] involving the $|E|$, given below, correspond to those for a centrosymmetric crystal in accord with the space group $P2_1/c$.

	Exptl	Theoret for centro-symmetric	Theoret for noncentro-symmetric
$\langle E \rangle$	0.797	0.798	0.886
$\langle |E|^2 \rangle$	1.000	1.000	1.000
$\langle |E|^2 - 1 \rangle$	0.961	0.968	0.736

The set of 11 reflections given in Table I, comprised of three origin-specifying vectors and eight other vectors of large $|E|$ magni-

Table I

h	k	l	$|E|$	Phase	h	k	l	E	Phase
4	$\bar{3}$	$\bar{2}$	3.47	+	4	$\bar{3}$	$\overline{11}$	2.85	D
4	5	11	2.88	+	10	3	10	2.46	E
1	5	2	2.86	+	3	$\bar{5}$	$\bar{9}$	2.96	F
2	$\bar{3}$	$\bar{9}$	2.89	A	4	$\bar{4}$	$\bar{3}$	2.73	G
4	$\bar{5}$	$\bar{4}$	3.48	B	4	$\bar{4}$	$\bar{8}$	2.83	H
4	1	10	3.27	C					

tude to which letter phases were assigned were utilized to initiate the symbolic addition procedure. Approximately 300 reflections, for which $|E| \geq 1.40$, were used in the application of the Hauptman–

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

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

(33) (a) H. Hauptman and J. Karle, 'Solution of the Phase Problem. I. The Centrosymmetric Crystal," American Crystallographic Association Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953; (b) *cf.* I. L. Karle and J. Karle, *Acta Cryst.*, 16, 969 (1963).

(34) R. B. K. Dewar and A. L. Stone, "Fame and Magic, Fortran Computer Programs for Use in the Symbolic Addition Method," University of Chicago, 1966; *cf.* E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts of Papers, American Crystallographic Association Winter Meeting, Atlanta, Ga., 1967, p 20.

(35) M. J. Buerger, "Crystal Structure Analysis," John Wiley and Sons, Inc., New York, N. Y., 1960, p 234.

(36) (a) *Cf.* G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 321; (b) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Cryst.*, 19, 713 (1965).

Karle σ-2 relationship.[33,34] Only signs with a probability factor of $p \geq 0.97$ were accepted. After several cycles, 242 symbolic signs were determined. Of the 256 possible combinations of signs for the eight symbols, that combination of A, B, D, E, G, H as minus and C, F as plus was the most probable (*i.e.*, gave the least number of inconsistencies). A computed three-dimensional Fourier synthesis, based on this sign combination, indicated initial coordinates for eight independent cobalt atoms (as two distorted tetrahedra) together with tentative coordinates for four sulfur atoms. Another Fourier map which utilized all observed data revealed the eight additional independent sulfur atoms. Two cycles of full-matrix least-squares refinement of these cobalt and sulfur atoms with individual isotropic temperature factors gave discrepancy factors

$$R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 26\%$$

$$R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 32\%$$

The refinement was based on the minimization of $\Sigma w_i \Delta F_i^2$, and the weights were assigned according to the relationship $w_i = 1/\sigma_i{}^2(F_o)$. Successive Fourier difference maps located enough carbon atom positions such that the eight cyclopentadienyl rings could be adequately defined as rigid regular pentagonal rings in subsequent least-squares refinements; a description of the rigid-body refinement[37] is outlined in Table IV. Four other peaks, also found on these Fourier difference maps were assigned on the basis of their positions and relative peak heights to the chlorine and carbon atoms of a chloroform molecule of solvation. Four cycles of rigid-body isotropic least-squares refinement, the last of which exhibited no significant positional parameter shifts greater than 0.5σ, resulted in final discrepancy factors of $R_1 = 11.7\%$ and $R_2 = 11.3\%$. A final difference electron density map, calculated from the output of the last refinement cycle, contained no peaks greater than 1.9 e/Å^3; the more intense residual peaks found in the region of the cobalt atoms can be attributed to anisotropic thermal motion. Because of the large number of parameters and the long computing times required for this structural problem, no anisotropic least-squares refinement was carried out. Furthermore, no attempt was made to locate hydrogen atom positions from other positive residual peaks on the final difference synthesis.

Final atomic and rigid-body parameters are given in Tables II and III.[38] Tables IV and V list interatomic distances and angles, respectively. The Blount program[39] was used to carry out all Patterson and Fourier calculations. The full-matrix rigid-body least-squares refinements were carried out with a locally modified version of the Busing–Martin–Levy ORFLS program.[40] Interatomic distances and angles together with estimated standard deviations were calculated with the Busing–Martin–Levy function and error program[41] from the full inverse matrix (which included uncertainties in lattice parameters).

Discussion

The crystallographically independent part of the crystal structure of $Co_4(\pi\text{-}C_5H_5)_4S_6\cdot{}^1\!/_2CHCl_3$ consists of two discrete molecules of $Co_4(\pi\text{-}C_5H_5)_4S_6$ (Figure 1) and one chloroform molecule of solvation. In each molecule the cobalt atoms from the four $Co(C_5H_5)$ fragments form a distorted tetrahedron with non-bonding $Co\cdots Co$ distances of range 3.2–3.7 Å. The six sulfur atoms are distributed above the four triangular faces of the tetracobalt unit as two triply bridging sulfur atoms and two triply bridging S_2 groups. The resulting

(37) S. F. Watkins, Ph.D. Thesis (Appendix), University of Wisconsin, 1967, and references cited therein.

(38) A table containing observed and calculated structure factors has been deposited as Document No. NAPS-00335 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by a citing of the document number and by the remitting of $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(39) J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(40) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1962.

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

Table II. Final Atomic Parameters with Their Standard Deviations from Rigid-Body Least-Squares Refinement for $Co_4(\pi-C_5H_5)_4S_6 \cdot \frac{1}{2}CHCl_3{}^a$

		x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
			Molecule I		
	Co(1)	0.1374 (4)	0.0573 (9)	0.9172 (5)	2.5 (3)
	Co(2)	0.0812 (4)	0.2371 (9)	0.0114 (5)	2.8 (3)
	Co(3)	0.0155 (3)	0.2559 (9)	0.8413 (5)	2.5 (3)
	Co(4)	0.1519 (4)	0.4014 (9)	0.8917 (5)	2.6 (3)
	S(1)	0.1243 (7)	0.1267 (17)	0.8065 (10)	3.3 (5)
	S(2)	0.0889 (7)	0.2983 (17)	0.8091 (9)	2.5 (5)
	S(3)	0.0366 (7)	0.3815 (17)	0.9366 (9)	3.1 (5)
	S(4)	0.0912 (7)	0.5133 (17)	0.9251 (9)	3.0 (5)
	S(5)	0.0550 (7)	0.1052 (17)	0.9202 (9)	2.7 (5)
	S(6)	0.1553 (7)	0.2457 (17)	0.9721 (9)	2.3 (5)
$(C_5H_5-1)^b$	C-1	0.14861	−0.0903	0.9943	5.7
	C-2	0.1284	−0.1431	0.9257	5.1
	C-3	0.1659	−0.1195	0.8865	6.3
	C-4	0.2092	−0.0522	0.9310	6.3
	C-5	0.1987	−0.0341	0.9973	2.6
(C_5H_5-2)	C-1	0.0491	0.3135	0.0935	6.5
	C-2	0.1056	0.3239	0.1190	5.9
	C-3	0.1277	0.2028	0.1212	8.7
	C-4	0.0849	0.1175	0.0972	3.6
	C-5	0.0364	0.1857	0.0801	6.9
(C_5H_5-3)	C-1	−0.0674	0.2321	0.8257	5.7
	C-2	−0.0568	0.3443	0.7938	3.4
	C-3	−0.0304	0.3134	0.7414	2.7
	C-4	−0.0248	0.1822	0.7409	4.1
	C-5	−0.0476	0.1318	0.7929	2.7
(C_5H_5-4)	C-1	0.2308	0.4535	0.9409	2.3
	C-2	0.2017	0.5568	0.9048	2.6
	C-3	0.1832	0.5259	0.8322	3.8
	C-4	0.2009	0.4035	0.8231	4.1
	C-5	0.2302	0.3588	0.8901	2.6
			Molecule II		
	Co(1)′	0.3887 (4)	−0.1313 (9)	0.6642 (5)	3.0 (3)
	Co(2)′	0.2729 (4)	−0.0725 (9)	0.6933 (5)	3.0 (3)
	Co(3)′	0.3399 (4)	0.1960 (9)	0.6778 (5)	3.9 (3)
	Co(4)′	0.3971 (4)	−0.0017 (10)	0.8389 (6)	5.0 (3)
	S(1)′	0.4492 (9)	0.0171 (23)	0.7116 (12)	7.2 (7)
	S(2)′	0.4079 (10)	0.1335 (25)	0.7627 (13)	8.9 (8)
	S(3)′	0.2801 (9)	0.1168 (20)	0.7421 (11)	5.8 (6)
	S(4)′	0.3204 (11)	0.1061 (27)	0.8419 (15)	10.6 (9)
	S(5)′	0.3224 (7)	0.0084 (17)	0.6243 (9)	2.6 (5)
	S(6)′	0.3522 (8)	−0.1425 (18)	0.7581 (10)	3.1 (5)
$(C_5H_5-1)′$	C-1	0.3663	−0.2330	0.5662	5.6
	C-2	0.4198	−0.1885	0.5830	5.9
	C-3	0.4482	−0.2443	0.6473	7.3
	C-4	0.4126	−0.3233	0.6706	6.7
	C-5	0.3621	−0.3165	0.6207	2.3
$(C_5H_5-2)′$	C-1	0.1951	−0.0813	0.6215	2.7
	C-2	0.2257	−0.1843	0.6091	3.3
	C-3	0.2408	−0.2556	0.6724	4.3
	C-4	0.2196	−0.1968	0.7239	5.3
	C-5	0.1914	−0.0892	0.6924	1.8
$(C_5H_5-3)′$	C-1	0.3239	0.2864	0.5779	2.3
	C-2	0.2841	0.3117	0.6134	4.3
	C-3	0.3089	0.3740	0.6778	5.9
	C-4	0.3640	0.3874	0.6821	7.9
	C-5	0.3733	0.3333	0.6204	6.3
$(C_5H_5-4)′$	C-1	0.4559	−0.1352	0.8915	3.5
	C-2	0.4817	−0.1785	0.8952	4.7
	C-3	0.4555	0.0661	0.9305	4.9
	C-4	0.4135	0.0009	0.9487	6.1
	C-5	0.4138	−0.1234	0.9246	3.7
			Chloroform		
	C(1)	0.3892 (31)	0.4166 (73)	0.8857 (40)	7.4 (22)
	Cl(1)	0.4472 (10)	0.4813 (23)	0.8742 (13)	10.4 (7)
	Cl(2)	0.3404 (10)	0.5473 (25)	0.8641 (13)	12.8 (8)
	Cl(3)	0.3949 (11)	0.3975 (27)	0.9794 (15)	14.5 (9)

ᵃ Standard deviations of the last significant figures are enclosed in parentheses. ᵇ These individual atomic parameters are based on the refined rigid-body crystallographic coordinates.

molecular geometry arises from the different linkages of the four $Co(\pi-C_5H_5)$ fragments to one another by the triply bridging sulfur and disulfide ligands. Of the six different pairs of cobalt atoms in each molecule

Table III. Final Group Parameters from Least-Squares Rigid-Body Refinement for $Co_4(\pi\text{-}C_5H_5)_4S_6 \cdot {}^1/_2CHCl_3{}^{a,b}$

Group	ϕ, deg	θ, deg	ρ, deg
C_5H_5-1	−88 (2)	132 (2)	−60 (2)
C_5H_5-2	−139 (2)	−172 (3)	161 (2)
C_5H_5-3	−83 (2)	133 (3)	179 (3)
C_5H_5-4	73 (1)	101 (2)	38 (1)
C_5H_5-1′	−114 (2)	−126 (3)	−148 (3)
C_5H_5-2′	−162 (2)	−138 (2)	−114 (2)
C_5H_5-3′	11 (1)	−118 (2)	−173 (3)
C_5H_5-4′	24 (1)	−155 (3)	−15 (1)

^{a} The rigid-body group atomic parameters are defined relative to an internal orthonormal axis system (x', y', z') in which carbon C-1 is located at the origin; the $+y'$ direction is along a vector from the midpoint of the C-3–C-4 vector through the origin; the $+x'$ direction is parallel to the C-2–C-5 vector; $+z'$ is the vector product of x' and y'. The cyclopentadienyl carbon ring thus lies in the $x'y'$ plane. A carbon–carbon distance of 1.40 Å was used. The angles ϕ, θ, and ρ define the orientation of the internal rigid-group axial system with respect to an external orthogonal system by rotations about y', x', and z', respectively. In our program the right-handed orthogonal axes a_0, b_0, c_0 are defined relative to the crystal axes as $a_0 = a$, $b_0 = c_0 \times a_0$, $c_0 = a \times b$. ^{b} Estimated individual standard deviations of the last significant figures are given in parentheses.

Table IV. Interatomic Distances of $Co_4(\pi\text{-}C_5H_5)_4S_6 \cdot {}^1/_2CHCl_3$ and Standard Deviations^a

Bond type		Molecule I	Molecule II	Av
	A. Bonding Intramolecular Distances (Å)			
Co–S^3	Co(1)–S(5)	2.19 (2)	2.23 (2)	2.21
	Co(1)–S(6)	2.25 (2)	2.26 (2)	2.25
	Co(2)–S(5)	2.21 (2)	2.24 (2)	2.23
	Co(2)–S(6)	2.23 (2)	2.21 (2)	2.22
	Co(3)–S(5)	2.25 (2)	2.23 (2)	2.24
	Co(4)–S(6)	2.25 (2)	2.24 (2)	2.25
	Av	2.23	2.23	2.23
Co–S^2	Co(2)–S(3)	2.20 (2)	2.20 (2)	2.20
	Co(3)–S(2)	2.18 (2)	2.15 (3)	2.17
	Co(3)–S(3)	2.21 (2)	2.37 (2)	2.29
	Co(4)–S(2)	2.23 (2)	2.12 (3)	2.17
	Av	2.21	2.21	2.21
Co–S^1	Co(1)–S(1)	2.19 (2)	2.23 (3)	2.21
	Co(4)–S(4)	2.19 (2)	2.29 (3)	2.24
	Av	2.19	2.26	2.23
S^1–S^2	S(1)–S(2)	2.04 (2)	2.04 (3)	2.04
	S(3)–S(4)	2.03 (2)	1.93 (3)	1.98
	Av	2.03	1.99	2.01
Av Co to cyclopentadienyl carbon atom distance				
	Co(1)–C(C$_5$H$_5$-1)	2.12 (3)	2.12 (3)	2.12
	Co(2)–C(C$_5$H$_5$-2)	2.13 (3)	2.10 (3)	2.11
	Co(3)–C(C$_5$H$_5$-3)	2.08 (3)	2.09 (3)	2.09
	Co(4)–C(C$_5$H$_5$-4)	2.06 (3)	2.11 (3)	2.09
	Av	2.10	2.11	2.10
Co to cyclopentadienyl centroid distances				
	Co(1)–(C$_5$H$_5$-1)	1.78 (3)	1.73 (3)	1.75
	Co(2)–(C$_5$H$_5$-2)	1.76 (3)	1.73 (3)	1.75
	Co(3)–(C$_5$H$_5$-3)	1.71 (3)	1.71 (3)	1.71
	Co(4)–(C$_5$H$_5$-4)	1.68 (3)	1.73 (3)	1.71
	Av	1.73	1.73	1.73
	Chloroform			
C–Cl	C(1)–Cl(1)	1.71 (7)		
	C(1)–Cl(2)	1.83 (7)		
	C(1)–Cl(3)	1.79 (7)		
	Av	1.78		

Table IV (*Continued*)

Bond type		Molecule I	Molecule II	Av
	B. Nonbonding Intramolecular Distances (<4.0 Å)			
S atoms bonded to Co(1)				
	S(6)…S(1)	3.33 (3)	3.32 (3)	3.33
	S(6)⋯S(5)	2.91 (2)	2.96 (2)	2.93
	S(1)⋯S(5)	3.18 (2)	3.23 (3)	3.20
	Av	3.14	3.17	3.15
S atoms bonded to Co(2)				
	S(6)⋯S(3)	3.27 (3)	3.28 (3)	3.27
	S(6)⋯S(5)	2.91 (2)	2.96 (2)	2.93
	S(3)⋯S(5)	3.00 (2)	3.00 (3)	3.00
	Av	3.06	3.08	3.07
S atoms bonded to Co(3)				
	S(2)⋯S(3)	3.23 (2)	3.19 (3)	3.21
	S(2)⋯S(5)	3.25 (2)	3.24 (3)	3.25
	S(3)⋯S(5)	3.00 (2)	3.00 (2)	3.00
	Av	3.16	3.14	3.15
S atoms bonded to Co(4)				
	S(2)⋯S(6)	3.19 (2)	3.25 (3)	3.22
	S(2)⋯S(4)	3.19 (2)	3.05 (3)	3.12
	S(4)⋯S(6)	3.28 (2)	3.31 (3)	3.29
	Av	3.22	3.20	3.21
	Av for all Co atoms	3.15	3.15	3.15
Co⋯Co				
	Co(1)⋯Co(2)	3.23 (1)	3.22 (1)	3.23
	Co(1)⋯Co(3)	3.72 (1)	3.72 (1)	3.72
	Co(1)⋯Co(4)	3.71 (1)	3.59 (1)	3.65
	Co(2)⋯Co(3)	3.26 (1)	3.38 (1)	3.32
	Co(2)⋯Co(4)	3.73 (1)	3.71 (1)	3.72
	Co(3)⋯Co(4)	3.70 (1)	3.71 (1)	3.71
	Av	3.56	3.55	3.55
Co⋯S				
	Co(3)⋯S(1)	3.33 (2)	3.30 (3)	3.31
	Co(4)⋯S(1)	3.33 (2)	3.10 (3)	3.21
	Co(1)⋯S(2)	3.32 (2)	3.35 (3)	3.33
	Co(3)⋯S(6)	3.78 (2)	3.89 (2)	3.83
	Co(4)⋯S(3)	3.30 (2)	3.32 (2)	3.31
	Co(3)⋯S(4)	3.48 (2)	3.47 (3)	3.47
	Co(2)⋯S(4)	3.41 (2)	3.38 (3)	3.39
	Av	3.42	3.40	3.41
	Chloroform			
Cl⋯Cl				
	Cl(1)⋯Cl(2)	2.78 (4)		
	Cl(1)⋯Cl(3)	2.86 (3)		
	Cl(2)⋯Cl(3)	2.78 (4)		
	Av	2.81		
	C. Intermolecular Distances (<4.0 Å)			
	C(1)⋯S(4)′	3.72 (8)		
	C(1)⋯S(2)′	3.94 (8)		
	Cl(3)⋯S(5)′	3.88 (3)		
	Cl(2)⋯S(6)′	3.92 (3)		

^{a} Standard deviations of the last significant figure are given in parentheses.

(along the six edges of the distorted cobalt tetrahedron), three pairs of cobalt atoms are connected by an S^3 bridge and a S^1–S^2 bridge, one pair by an S^2 bridge and a S^1–S^2 bridge, one pair by one S^2 bridge and one S^3 bridge, and one pair by two S^3 bridges (where S^1 denotes a sulfur atom bonded to one cobalt atom, S^2 coordinated to two cobalt atoms, and S^3 coordinated to three cobalt atoms). Both independent molecules of point symmetry C_1-1 happen to possess the same handedness (*i.e.*, are superimposable rather than mirror images of each other), but the centrosymmetric space group demands that the unit cell comprised of eight $Co_4(\pi$-

Table V. Bond Angles and Standard Deviations (Deg)[a]

Angle type		Molecule I	Molecule II	Av
S³–Co–S³	S(6)–Co(1)–S(5)	81.8 (7)	82.5 (7)	82.1
	S(6)–Co(2)–S(5)	81.8 (7)	83.3 (7)	82.5
	Av	81.8	82.9	82.3
S³–Co–S¹	S(6)–Co(1)–S(1)	96.8 (7)	95.8 (8)	96.3
	S(5)–Co(1)–S(1)	93.1 (7)	93.0 (9)	93.1
	S(6)–Co(4)–S(4)	95.4 (7)	93.9 (10)	94.7
	Av	95.1	94.2	94.7
S³–Co–S²	S(5)–Co(3)–S(2)	94.3 (7)	95.6 (9)	95.0
	S(6)–Co(2)–S(3)	95.0 (7)	96.1 (8)	95.5
	S(5)–Co(2)–S(3)	85.7 (7)	84.8 (8)	85.3
	S(5)–Co(3)–S(3)	84.4 (7)	81.3 (7)	82.8
	S(6)–Co(4)–S(2)	91.1 (7)	96.1 (9)	93.6
	Av	90.1	90.8	90.4
S²–Co–S²	S(3)–Co(3)–S(2)	94.5 (7)	89.8 (9)	92.1
S²–Co–S¹	S(2)–Co(4)–S(4)	92.4 (7)	87.3 (10)	89.9
Av	S–Co–S angle	90.8	89.0	89.9
Co–S³–Co	Co(2)–S(6)–Co(1)	92.3 (7)	92.5 (8)	92.4
	Co(2)–S(6)–Co(4)	112.7 (8)	113.1 (9)	112.9
	Co(4)–S(6)–Co(1)	111.2 (8)	106.1 (8)	108.6
	Co(1)–S(5)–Co(3)	114.0 (8)	113.2 (9)	113.6
	Co(1)–S(5)–Co(2)	94.6 (8)	92.3 (7)	93.4
	Co(3)–S(5)–Co(2)	94.2 (7)	98.1 (7)	96.1
	Av	103.2	102.5	102.8
Co–S²–Co	Co(4)–S(2)–Co(3)	114.3 (8)	120.4 (12)	117.3
	Co(2)–S(3)–Co(3)	95.3 (8)	95.2 (8)	95.3
	Av	104.8	107.8	106.3
Av	Co–S–Co angle	104.0	105.2	104.5
Co–S¹–S²	Co(1)–S(1)–S(2)	103.1 (9)	103.3 (12)	103.2
	Co(4)–S(4)–S(3)	102.9 (9)	103.5 (13)	103.2
	Av	103.0	103.4	103.2
Co–S²–S¹	Co(2)–S(3)–S(4)	107.5 (10)	109.5 (13)	108.5
	Co(3)–S(3)–S(4)	110.1 (9)	107.3 (13)	108.7
	Co(3)–S(2)–S(1)	104.3 (9)	103.7 (13)	104.0
	Co(4)–S(2)–S(1)	102.4 (9)	96.2 (13)	99.3
	Av	106.1	104.2	105.1
Av	Co–S–S angle	104.5	103.8	104.1
	Chloroform			
Cl–C–Cl				
	Cl(1)–C(1)–Cl(2)	103 (4.2)		
	Cl(2)–C(1)–Cl(3)	100 (3.7)		
	Cl(1)–C(1)–Cl(3)	110 (4.4)		
	Av	104		

[a] Standard deviations of the last significant figure are enclosed in parentheses.

Figure 1. Molecular configuration of $Co_4(\pi\text{-}C_5H_5)_4S_6$.
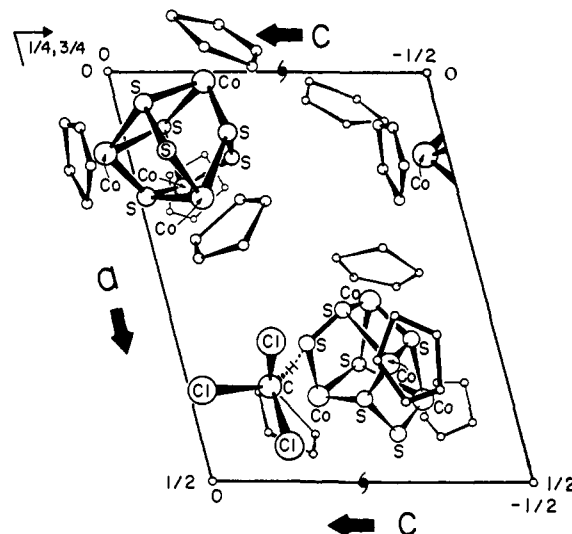
Figure 2. The [010] projection of the asymmetric portion of the unit cell of $Co_4(\pi\text{-}C_5H_5)_4S_6 \cdot \frac{1}{2}CHCl_3$ showing the arrangement of the two tetracobalt molecules and the solvated chloroform molecule.

$C_5H_5)_4S_6$ and four $CHCl_3$ molecules contain the racemate.

The orientations of the two independent $Co_4(\pi\text{-}C_5H_5)_4S_6$ molecules and one $CHCl_3$ molecule in the asymmetric part of the monoclinic unit cell are illustrated in Figure 2. It can be seen that the chloroform molecule is much closer to one molecule (molecule II) than to the other (molecule I). Whereas all interatomic distances between the CCl_3 part of $CHCl_3$ and molecule I are greater than 4.0 Å, there are considerably shorter contacts (viz., C(1)···S(4)′, 3.72 Å; C(1)···S(2)′, 3.94 Å) between the CCl_3 part of $CHCl_3$ and molecule II. The part of molecule II closest to the inferred position of the chloroform hydrogen atom (Figure 2) is somewhat distorted from its
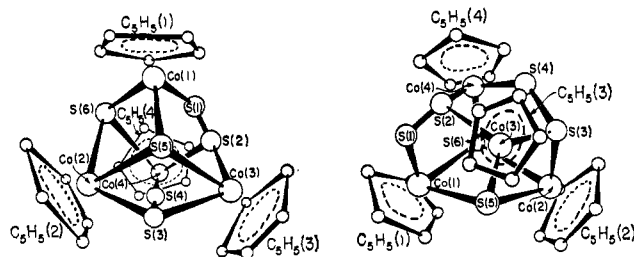
equivalent part in molecule I. The relatively large errors contained in the parameters involving the CCl_3 fragment are presumably a reflection of the inexact positioning of the chloroform molecule due to large thermal effects and/or disorder. If one assumes that the chloroform hydrogen atom of normal C–H bond length 1.1 Å lies along a line between C(1) and S(4)′ (which approximately corresponds to the localized threefold axis of the CCl_3 fragment), then the H···S(4)′ distance is 2.6 Å, considerably less than the sum of the van der Waal radii (1.2 Å for H and 1.85 Å for S).[42] Thus, interaction between the hydrogen atom of $CHCl_3$ and one of the lone pairs of electrons of the disulfide atom S(4)′ is presumably at least partially responsible for the small but highly significant distortions and relatively large thermal parameters of those atoms concerned, namely S(4)′, S(2)′, S(3)′, Co(4)′, and Co(3)′. Because of these deformations in molecule II, the molecular parameters utilized in this discussion will be those from molecule I, unless otherwise specified.

The average cobalt to cyclopentadienyl carbon distance is 2.10 Å. The average cobalt to ring centroid distance of 1.73 Å compares closely with the corresponding average values found in $Co_2(\pi\text{-}C_5H_5)_2\{(t\text{-}C_4H_9N)_2CO\}$ (1.71 Å)[43] and $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$ (1.73 Å)[44] but is somewhat longer than the distances

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(43) Y. Matsu-ura, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, T. Yoshida, and S. Otsuka, Chem. Commun., 1122 (1967).

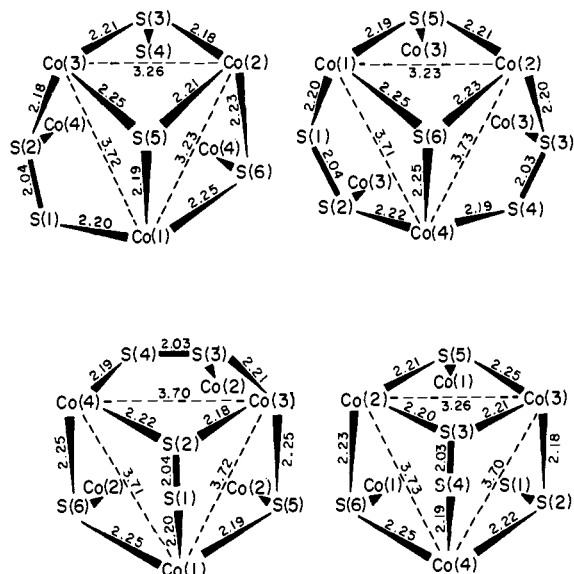(44) V. A. Uchtman and L. F. Dahl, submitted for publication.

Figure 3. The four tricobalt faces of the distorted cobalt tetrahedron in $Co_4(\pi\text{-}C_5H_5)_4S_6$ illustrating the localized environments of the two sulfur and two disulfide ligands linking the cobalt atoms about each face. The bond lengths are those for molecule I.

found in $Co_2(\pi\text{-}C_5H_5)_2\{P(C_6H_5)_2\}_2$ (1.66 Å),[45] $Co(\pi\text{-}C_5H_5)\{(CH_3C_2CH_3)_2CO\}$ (1.67 Å),[46] and $Co(\pi\text{-}C_5H_5)\{(CH_3C_2CH_3)_2(CO)_2\} \cdot 2H_2O$ (1.67 Å).[47]

The different arrangements of the sulfur and disulfide ligands connecting the three cobalt atoms on each of the four faces of the distorted cobalt tetrahedron along with appropriate bond lengths are pictured in Figure 3 for molecule I. The nearly symmetrical bonding of the two triply bridging sulfur atoms positioned above two of the tricobalt faces is shown from the small variation in $Co\text{-}S^3$ bond lengths which range in value from 2.19 to 2.25 Å. The average $Co\text{-}S^3$ distance of 2.23 Å is somewhat longer than that found in other molecules containing a sulfur atom triply bridging a *bonding* triangle of metal atoms (e.g., 2.14 Å in both $Co_3(CO)_9S$[10] and $[Co_3(CO)_7S]_2S_2$,[11] 2.16 Å in $Co_2Fe(CO)_9S$,[12] and $Co_6(CO)_{11}(S)(SC_2H_5)_4$[14]) but is midway between the average values of 2.20 and 2.25 Å found for the two different sets of $Fe\text{-}S^3$ bonds in $Fe_4(\pi\text{-}C_5H_5)_4S_4$[19,20] where the four triply bridging sulfur atoms connect the four faces of a distorted iron tetrahedron which contains only one iron–iron bond on each triangular face.

Disulfide ligands are oriented above the other two faces of the tetracobalt unit in $Co_4(\pi\text{-}C_5H_5)_4S_6$ in such a manner that one of the disulfide sulfur atoms is coordinated to two cobalt atoms of the triangular face, while the other sulfur atom of the S_2 unit is coordinated to the third cobalt atom only. Hence, this complex containing an S_2 ligand bonding to three metal atoms can be considered as supplying a missing structural link in organometallic chemistry in that S_2 groups previously have been shown from X-ray work to bond to one transition metal in $Nb(\pi\text{-}C_5H_5)_2S_2X$ (X = Cl, I),[48,49] to two transition metal atoms in $Fe_2(CO)_6S_2$,[50] and to four

transition metal atoms in $[Co_3(CO)_7S]_2S_2$.[11] The average S–S bond length of 2.03 Å is essentially identical with that found in the latter two complexes. The average $Co\text{-}S^2$ bond length of 2.21 Å is not significantly different from the average $Co\text{-}S^1$ bond length of 2.19 Å. The mean value of 2.20 Å is close to the average $M\text{-}S_2$ values of 2.23 Å in $Fe_2(CO)_6S_2$[50] and 2.24 Å in $[Co_3(CO)_7S]_2S_2$.[11]

The kinds of bridging sulfur ligands linking each pair of cobalt atoms have a pronounced effect on the cobalt–cobalt separation. Of the six independent nonbonding cobalt–cobalt distances of the distorted cobalt tetrahedron of molecule I shown in Figure 3, four distances are close to the average value of 3.71 Å, while the remaining two are much shorter, 3.23 and 3.26 Å. These latter cobalt–cobalt nonbonding separations are those for which the two sulfur ligands directly linking each pair of cobalt atoms are both sulfur atoms. For each of the other four longer cobalt–cobalt tetrahedral edges, one of the two bridging sulfur ligands connecting the two cobalt atoms is of the type Co–S–S–Co, while the other bridging ligand consists of just one sulfur atom. In no case are *both* bridges linking any pair of cobalt atoms of the Co–S–S–Co type.

For the purpose of valence-bond electron counting, each sulfur atom may formally be considered as possessing four tetrahedrally oriented localized electron pairs about it. The terminally bonded sulfur atoms (S^1) of the disulfide group and the triply bridging sulfur atoms (S^3) each have one nonbonding and three bonding electron pairs, while the doubly bridging sulfur atoms (S^2) of the disulfide group have two nonbonding and two bonding electron pairs. With the assumption of a normal electron-pair bond between the sulfur atoms of the disulfide group in accord with the observed single-bond S–S distance (in molecule I), it readily follows that the disulfide group, as well as the triply bridging S atom, is a four-electron donor to the three cobalt atoms of each triangular face of the distorted cobalt tetrahedron. Thus, each cobalt atom conforms to a closed-shell electronic configuration without the necessity of any Co–Co interactions.

Each of the four cobalt atoms in the $Co_4(\pi\text{-}C_5H_5)_4S_6$ molecule has a different localized environment of three bonded sulfur ligands. The different kinds of sulfur atoms attached to each cobalt atom are of the following types: Co(1), S^3, S^3, S^1; Co(2), S^3, S^3, S^2; Co(3), S^3, S^2, S^2; Co(4), S^3, S^2, S^1. This different asymmetry for each of the cobalt atoms presumably influences the four cyclopentadienyl groups sufficiently such that the proton nmr spectrum of a CS_2 solution exhibits four separate cyclopentadienyl hydrogen resonances. No correlation between proton resonance frequency and sulfur environment about a given cobalt atom is readily apparent. The nonbonding distances between two sulfur atoms coordinated to the same cobalt fall within a wide range of values from 2.91 to 3.33 Å. The average value of 3.15 Å is midway between the two nonbonding sets of average sulfur $\cdots$ sulfur values (3.33 and 2.88 Å) observed in $Fe_4(\pi\text{-}C_5H_5)_4S_4$[19,20] where the tetrahedron of iron atoms is distorted by the necessity of only two iron–iron bonds from an idealized cubic configuration of T_d symmetry (*with* or *without* six metal-metal bonds) to the observed configuration of tetragonal D_{2d} symmetry.

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With the assumption that the π-cyclopentadienyl ligand is regarded as formally tridentate by the occupation of three coordination sites, each cobalt atom may be regarded as possessing an octahedral-like coordination. The S-Co-S bond angles vary from 81 to 97° with an average value of 90°. All the Co-S distances in molecule I vary from only 2.18 to 2.25 Å with an average value of 2.21 Å. The average values for Co-S³ (2.23 Å), Co-S² (2.21 Å), and Co-S¹ (2.19 Å) are not significantly different from one another. As expected, the observed Co-S-Co and Co-S-S bond angles in molecule I reflect considerable distortion of the tetrahedral-like (or pyramidal) character of each sulfur atom. The Co-S-Co bond angles vary in molecule I from 92 to 114° with an average value of 103°; the Co-S-S angular range is from 102 to 110° with an average value of 105°.

With no direct metal-metal interactions present in this complex, the molecular geometry is dictated primarily by the stereochemical requirements of the sulfur and disulfide ligands interconnecting the four [Co₄(π-C₅H₅)₄(S₂)ₓ(S)₄₋ₓ]. In view of the structure and stability of this complex, one is led to postulate the possible isolation of the other four related complexes [(C₅H₅)₄-Co₄(S₂)ₓ(S)₄₋ₓ] (where x has the values 0, 1, 3, 4), each of which would also achieve a closed-shell electronic configuration for each metal atom without the need of cobalt-cobalt bonds. Nevertheless, the existence of such complexes must certainly depend upon the steric requirements of the resulting cobalt-sulfur fragment such that nonbonding repulsions, especially those between metal atoms, are minimized.

Organometallic Chalcogen Complexes. XVII. Preparation and Structural Characterization of a Metal–Oxygen Atom Cluster System, $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$[1]

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Abstract: A new metal-oxygen cluster system, $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$, has been isolated in very low yield from prolonged ultraviolet irradiation of a $Co(\pi\text{-}C_5H_5)(CO)_2$ solution. The compound presumably arises by oxidative and/or photolytic decomposition of the King compound $Co_3(\pi\text{-}C_5H_5)_3(CO)_3$. The characterization of this complex was achieved from the X-ray structural determination. The molecular configuration of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ consists of an equilateral triangle of cobalt atoms with triply bridging carbonyl and oxygen ligands symmetrically positioned above and below the tricobalt plane on the principal threefold molecular axis. The three cyclopentadienyl rings are perpendicularly disposed about the tricobalt plane such that with the assumption of cylindrical symmetry for each ring the molecule approximates C_{3v}-3m symmetry. A stereochemical consequence of the necessity of electron-pair cobalt-cobalt bonds in order for each cobalt atom to attain a closed-shell electronic configuration is a single-bond Co-Co distance of 2.365 ± 0.004 Å which is similar to the metal-metal bond length of 2.358 ± 0.002 Å in the electronically equivalent and structurally analogous complex $Ni_2Co(\pi\text{-}C_5H_5)_3(CO)_2$. The structural features of $Co_3(\pi\text{-}C_5H_5)_3(CO)(O)$ are also compared with those of the geometrically related $Ni_3(\pi\text{-}C_5H_5)_3(CO)_2$ and $Ni_3(\pi\text{-}C_5H_5)_3S_2$ complexes. Despite complications caused by a twinning of the hexagonal crystals and by a horizontal mirror plane crystal disordering of the cyclopentadienyl, carbonyl, and oxygen ligands, the structure was successfully elucidated by application of the Wei technique and refined by least squares to a final $R_1(F^2)$ value of 6.4% and $R_2(F^2)$ value of 10.4% for the diffractometry-collected intensity data. The single-crystal component contains two formula species in a hexagonal unit cell of symmetry $P6_3/m$ and dimensions $a = 9.077 ± 0.006$ Å and $c = 10.235 ± 0.006$ Å; the calculated and observed densities are both 1.89 g cm⁻³.

The pyrolysis or photolysis of mononuclear and dinuclear cyclopentadienylmetal carbonyl complexes has given rise to a number of unusual polynuclear cyclopentadienylmetal carbonyl complexes. The pyrolysis of $Fe_2(\pi\text{-}C_5H_5)_2(CO)_4$ yields the very stable tetranuclear iron derivative $[Fe(\pi\text{-}C_5H_5)CO]_4$,[3] while the pyrolysis of $Ni_2(\pi\text{-}C_5H_5)_2(CO)_2$ gives the stable paramagnetic trinuclear nickel complex $Ni_3(\pi\text{-}C_5H_5)_3$-$(CO)_2$.[4] Of considerable interest is the photolysis of $Rh(\pi\text{-}C_5H_5)(CO)_2$ which not only produces the dinuclear rhodium derivative $Rh_2(\pi\text{-}C_5H_5)_2(CO)_3$ but also on prolonged irradiation yields a mixture of two geo-

(1) Previous paper in this series: V. A. Uchtman and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 3756 (1969).

(2) This manuscript is based in part on a dissertation submitted by V. A. Uchtman to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, July 1968.

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