cessible decomposition routes, the weakest bond(s) breaks first. The abundance of fragment ions produced by electron impact is thought to reflect[27] a partitioning of excess energy of the parent ion into the energetically accessible decomposition pathways. Because of the greater excitation energy in mass spectrometry, numerous fragments form; however, the simplest (i.e., highest m/e) fragment usually results from the lowest energy decomposition pathway.

Acknowledgment. We thank the National Science Foundation (Grant 81-050698) and the Air Force Office of Scientific Research (Grant AFOSR-84-0021) for support of this work.

Supplementary Material Available: Tables of mass spectra fragmentation patterns for $Fe(CO)_3[(CH_3)N_4(CH_3)]$, $Fe[P(OCH_3)_3]_3[(CH_3)N_4(CH_3)]$, $(\eta^5\text{-}C_5H_5)Co[(CH_3)N_4(CH_3)]$, $(\eta^5\text{-}C_5H_5)Co[(C_6H_5)N_4(C_6H_5)]$, $(\eta^5\text{-}C_5H_5)Co[(C_6F_5)N_4(C_6F_5)]$, $(\eta^5\text{-}C_5H_5)Co[(2,4\text{-}F_2C_6H_3)N_4(2,4\text{-}F_2C_6H_3)]$, and $(\eta^5\text{-}C_5H_5)Co[(2,6\text{-}(CH_3)_2C_6H_3)N_4(2,6\text{-}(CH_3)_2C_6H_3)]$ (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Biology Division,
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Structural Characterization of a Hexameric Cobalt–Carbonyl–Sulfur Complex, $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$, Consisting of Two Tricobalt Carbonyl Clusters Dissymmetrically Linked by a Bridging SCS Group[1]

CHIN HSUAN WEI

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The reaction of $Co_2(CO)_8$ with CS_2 at room temperature has resulted in the formation of the new hexameric cobalt–carbonyl–sulfur complex $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$ containing a four-electron-donor SCS ligand dissymmetrically linked to two tricobalt clusters, as opposed to the structural isomer $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$, in which the linkage of the CS_2 group to the identical two tricobalt clusters is symmetric. The structure has been unambiguously characterized by X-ray analysis. The crystals contain four formula species in an orthorhombic cell of symmetry *Pnma* and of dimensions $a = 17.067$ (5) Å, $b = 13.074$ (5) Å, and $c = 13.493$ (5) Å. Full-matrix least-squares refinement of 32 independent atoms has yielded discrepancy indexes $R(F) = 0.056$ and $R(F^2) = 0.049$ based on 777 reflections with $F_o^2 \geq \sigma(F_o^2)$. The disordered-crystal model successfully utilized in the refinement assumes a random distribution of each molecule in one of two orientations related to each other by a crystallographic mirror plane. In the $Co_3(CO)_9C$ fragment, which is related to itself by the mirror plane, the Co_3C unit forms a tetrahedron with an idealized $C_{3v}\text{-}3m$ symmetry with its apical carbon being utilized to form a σ bond with one ligand sulfur atom, while in the $Co_3(CO)_7S$ fragment the triangle of basal cobalt atoms takes up an isosceles array due to distortion caused by the formation of cobalt–carbon and cobalt–sulfur bondings. As in other cases of statistically disordered structures, the resulting molecular configuration precludes the accurate determination of molecular parameters, thereby resulting in some anomalous geometries in the molecule.

Introduction

The reactions of dicobalt octacarbonyl with carbon disulfide under varying conditions have resulted in a number of organometallic complexes.[2–7] In addition to the sulfur-free bis(methinyltricobalt enneacarbonyl), $[CCo_3(CO)_9]_2$, the structure of which has been determined,[8] at least eight different sulfur-containing polynuclear complexes of the formula $Co_m(CO)_nC_pS_q$ have been separated by column chromatography[2,3] or by thin-layer chromatography[4–6] and their structures established by X-ray analyses: $SCo_3(CO)_9$,[9] $S_2Co_4(CO)_{10}$,[10] $[Co_3(CO)_8](\mu_5\text{-}CS_2)[Co_3(CO)_7S]$,[11] $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$,[11b] $Co_6C(CO)_{12}S_2$,[4] $SCo_6(C_2)(CO)_{14}$,[5] $Co_8(CO)_{21}C_3S_3$,[6] and $[Co_3(CO)_9C]_2SCO$.[12] The large assortment of these structures provides a dramatic illustration of the importance of metal–metal and metal–ligand interactions in determining the molecular configurations of the polynuclear cobalt carbonyl complexes.

In addition to the above-quoted complexes, another complex, initially formulated as $Co_4(CO)_{10}CS_2$ on the bases of its elementary analyses and IR absorption bands, was considered to be an isomer of $[Co_3(CO)_8](\mu_5\text{-}CS_2)[Co_3(CO)_7S]$[11,13] and was designated Ia.[2,3] Markó et al.[2] further reported that this complex contains no bridging carbonyl group and that the CS_2

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(13) It should be pointed out that this compound was also initially proposed to have a molecular formula $Co_4(CO)_{10}CS_2$ and hence was assigned isomer Ib. The most pronounced difference between Ia and Ib was that in their IR absorption patterns in the bridging carbonyl stretching region the former showed no band while the latter showed a band at 1838 cm^{-1}. The molecular weight for either compound, however, was not reported.[2,3]

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Table I. Crystal Data and Intensity Collection for $[Co_3(CO)_9C](\mu_3\text{-SCS})[Co_3(CO)_7S]$

fw: 921.988
space group: D_{2h}^{16}-*Pnma*
$a = 17.067$ (5) Å
$b = 13.074$ (5) Å
$c = 13.493$ (5) Å
$V = 3010.75$ Å^3
$Z = 4$

$D_{\text{calcd}} = 2.034$ g cm^{-3}
$D_{\text{obsd}} = 2.02$ (2) g cm^{-3} [a]
$F(000) = 1784$
cryst dimens: 0.08 × 0.15 × 0.25 mm
μ(Mo Kα) = 36.15 cm^{-1}
temp: 24 °C

radiation: Mo Kα
takeoff angle: 1.0–1.5° (ω scan), 3.0° (θ–2θ scan)
2θ limits: 1–50°
scan type: ω scan (2θ 1–35°), θ–2θ scan (2θ 34–50°)
scan step: 0.025°/step (ω scan), 0.05°/step (θ–2θ scan)
time per step: 2 s (ω scan), 10 s (θ–2θ scan)
2θ offset: 0.4–0.635° (ω scan)[b]
bkgd count time: 56–80 s (ω scan), 200 s (θ–2θ scan)
no. of unique nonzero reflcns collected: 938
reflcns with $F_o^2 \geqslant \sigma(F_o^2)$: 777
no. of variables: 241
data-to-variables ratio: 3.22

[a] Crystal density measured by flotation in mixtures of carbon tetrachloride and diiodomethane. [b] Aperture widths varied depending on the 2θ range.

group is attached to cobalt atoms through pure σ bondings.

As part of a systematic structural investigation of polynuclear cobalt chalcogen complexes including trimeric,[9,14,15] tetrameric,[10,16] pentameric,[17] and hexameric complexes,[18,19] a single-crystal X-ray determination of complex Ia was undertaken. The structural analysis reported here has shown the compound to be a hexameric species in which a $Co_3(CO)_7S$ fragment is linked dissymmetrically to a sulfur and the carbon atoms of CS_2 with the remaining sulfur atom being σ bonded to the apical carbon atom of a $Co_3(CO)_9C$ moiety. The compound is hence a structural isomer of $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$,[11b] in which the coordination of CS_2 to the two tricobalt clusters is symmetrical. Furthermore, the space group requirements of the title compound necessitate the hexameric molecule to be orientated in two alternative configurations (of opposite chirality) in the crystalline space, in a way somewhat similar to that for a disordered structure reported for $Co_3(CO)_{10}BH_2N(C_2H_5)_3$.[20]

Experimental Section

The preparation of the compound was reproduced by allowing 15.6 g of $Co_2(CO)_8$ and 25 mL of CS_2 (mole ratio $Co_2(CO)_8$:CS_2 = 1:9) to react at room temperature (24 °C) according to procedures similar to those described by Klumpp et al.[3] After 1 day the crude product was digested in 30 mL of hexane and filtered. The black residue was further separated by silica gel chromatography (column diameter 23 mm, length 63 cm) using hexane as an eluent. The portion containing Ia was recrystallized from a hexane solution, and approximately 0.45 g was obtained. The IR absorption spectrum in hexane solution gave essentially the same absorption bands as reported[3] in the region of 2000–2100 cm^{-1}, and the X-ray diffraction patterns were identical with those of the crystalline sample generously furnished by Drs. L. Markó and G. Bor, then of the Hungarian Oil and Gas Research Institute (Veszprém).

Anal. Calcd for $Co_6S_3C_{18}O_{16}$: Co, 38.35; S, 10.43; C, 23.45. Found:[21] Co, 39.44; S, 10.29; C, 23.82. The molecular weight determination using $CHCl_3$ as the solvent[21] gave the value 893 ± 44 (vs. 921.988 calculated).[22]

X-ray Data Collection. Preliminary photographs showed that the crystals belong to the orthorhombic system, with space group either *Pnma* or $Pn2_1a$.[23] Five strong reflections in the 2θ range 27–35° were centered with an Oak Ridge computer-controlled diffractometer[26] with Nb-filtered Mo Kα_1 (λ = 0.7093 Å) radiation, and the cell parameters were refined by the least-squares method.

In general, the crystals were of poor diffracting quality. Attempts to obtain crystals of high quality using solvents other than hexane, however, were fruitless. The selected crystal of dimensions 0.08 × 0.15 × 0.25 mm was mounted in a thin-walled capillary with a tiny amount of grease. The maximum mosaic spread of the crystal was estimated to be 0.6°. A summary of crystal data and intensity collection is given in Table I.

Up to a 2θ limit of 35°, the intensities were measured by an ω step-scan technique, in which three scans were performed for each reflection: a main scan with the detector set at the computed 2θ and two backgroun scans with the detector offset lower and higher in 2θ. The time spent on each background measurement was equal to the time spent on the main scan. For the higher 2θ range (34–50°), the data collection program PEAKTOP was modified to select[27] strong reflections. Only those accepted were then measured by a θ–2θ step-scan technique, in which backgrounds were measured at the beginning and end of each scan. During the course of data collection, no significant change in the intensities of the standard reflection was observed.

Of the 938 unique nonzero reflections with $2\theta \leq 50°$ (equivalent to a minimum spacing 0.84 Å), the 777 reflections with $F_o^2 \geq \sigma(F_o^2)$ were utilized in the refinements of the structure. No absorption corrections were applied ($\mu R_{\max} = 0.54$). Variances $\sigma^2(F_o^2)$ for use in least-squares weighting were estimated in a manner similar to that given elsewhere.[28]

Solution and Refinement of the Structure. Attempts to interpret large peaks in a three-dimensional sharpened Patterson function in terms of the proposed molecular formula $Co_4(CO)_{10}CS_2$ were unsuccessful. Instead, two independent sets of triangular arrays of cobalt atoms could be assigned. Initially, one of them was placed on the crystallographic mirror plane ($y = {}^1/_4$) and the other related by the mirror plane passing through Co(2) and the midpoint of Co(1) and Co(1′) (primed atoms represent mirror-related corresponding atoms). Least-squares refinement[29] of this partial structure using isotropic thermal parameters and the centrosymmetric space group *Pnma* yielded an $R(F)$ value of 0.44. From the subsequent difference-Fourier maps interpretation of large peaks enabled the assignment of three sulfur atoms. From the successive Fourier syntheses and least-squares refinements it then became apparent that the two cobalt atoms (Co(4) and Co(5)) of the Co_3S fragment were off the mirror plane, necessitating this portion of the molecule to have two alternative orientations related to each other by the crystallographic mirror plane. After the refinement of this disordered partial model ($R(F)$ down to 0.27), a new difference-Fourier synthesis was computed. Interpretation of this map combined with stereochemical knowledge eventually enabled

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(22) These results show the mole ratio Co/S = 2, in agreement with the finding of Klumpp et al.[3] The molecular weight determined suggests the plausible molecular formula $Co_6(CO)_{15}C_3S_3$, which agrees with the X-ray-derived formula of $Co_6(CO)_{16}C_2S_3$ within experimental errors.

(23) After the structure was solved, the application of the program NORMAL (part of the program MULTAN[24]) for the data set up to $2\theta = 50°$ (1108 reflections) revealed that the statistical averages of $|E^2 - 1|$ and $|E|$ were 1.058 and 0.753, corresponding to those for a centrosymmetric crystal (theoretical values for centrosymmetric 0.968, 0.798 and for acentric 0.736, 0.886, respectively[25]). This supports the centrosymmetric space group chosen in this study (see below).

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(27) The criteria used were as follows. With a 5° takeoff angle and a wide counter slit (6 mm), each reflection to be tested was measured at the calculated 2θ value for 10 s followed by a background measurement for 10 s with the detector offset 1.5° lower than in 2θ. If the time required to achieve the $\sigma(N)/N$ ratio of 0.3 was less than 50 s, the reflection was accepted. This ratio, where N is the net count, decreases as the counting time is increased.

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Table II. Positional and Isotropic Thermal Parameters for $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$[a,b]

	x	y	z	B_{eq} or B, Å^2
Co(1)	0.2360 (1)	0.1566 (3)	0.7085 (2)	8.1 (1)
Co(2)	0.3574 (2)	$^1/_4$	0.6713 (2)	9.0 (2)
Co(3)	0.1304 (2)	$^1/_4$	0.3014 (2)	6.0 (1)
Co(4)	0.0160 (3)	0.2012 (4)	0.1882 (3)	6.4 (2)
Co(5)	0.0088 (2)	0.1914 (4)	0.3756 (3)	6.4 (2)
S(1)	0.2541 (3)	$^1/_4$	0.4757 (4)	8.2 (3)
S(2)	0.0837 (8)	0.0985 (17)	0.2833 (8)	6.5 (5)
S(3)	0.0898 (4)	0.1970 (7)	0.5061 (5)	6.4 (3)
C(A)	0.259 (1)	$^1/_4$	0.605 (1)	6.6 (8)
C(B)	0.163 (1)	$^1/_4$	0.435 (2)	7.1 (8)
C(1)	0.258 (2)	0.040 (3)	0.647 (2)	12.3 (14)
C(2)	0.132 (1)	0.138 (2)	0.717 (2)	11.7 (8)
C(3)	0.258 (1)	0.131 (3)	0.835 (2)	16.5 (12)
C(4)	0.408 (1)	0.148 (3)	0.617 (1)	13.5 (14)
C(5)	0.399 (1)	$^1/_4$	0.795 (2)	13.0 (15)
C(6)	0.117 (3)	0.375 (5)	0.297 (4)	7.0 (17)
C(7)	0.222 (1)	$^1/_4$	0.236 (2)	8.3 (11)
C(8)	−0.064 (1)	0.110 (2)	0.173 (1)	10.7 (9)
C(9)	−0.029 (3)	0.319 (4)	0.188 (4)	9.7 (20)
C(10)	0.073 (2)	$^1/_4$	0.076 (2)	22.5 (30)
C(11)	−0.069 (1)	0.107 (2)	0.420 (1)	9.5 (8)
C(12)	−0.040 (2)	0.306 (3)	0.406 (2)	5.4 (9)
O(1)	0.273 (2)	−0.030 (2)	0.604 (2)	15.7 (11)
O(2)	0.068 (8)	0.129 (1)	0.727 (1)	16.0 (8)
O(3)	0.275 (1)	0.114 (2)	0.913 (1)	21.9 (12)
O(4)	0.442 (1)	0.090 (2)	0.575 (1)	15.5 (10)
O(5)	0.427 (1)	$^1/_4$	0.871 (1)	22.4 (20)
O(6)	0.100 (2)	0.473 (3)	0.314 (3)	9.8 (12)
O(7)	0.281 (1)	$^1/_4$	0.199 (2)	12.1 (9)
O(8)	−0.116 (2)	0.073 (3)	0.148 (2)	10.2 (12)
O(9)[c]	−0.064 (1)	0.390 (2)	0.173 (1)	10.7 (9)
O(10)	0.105 (1)	$^1/_4$	0.003 (2)	23.7 (21)
O(11)	−0.102 (2)	0.026 (3)	0.445 (2)	11.6 (14)
O(12)[d]	−0.069 (1)	0.393 (2)	0.420 (1)	9.5 (8)

[a] The estimated standard deviations are given in all tables and in the text. The digits in parentheses correspond to the least significant digits of the parameters. [b] The equivalent isotropic temperature factors were calculated by the relation given by Hamilton (Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609) $B_{eq} = 8\pi^2(U_{11} + U_{22} + U_{33})/3$, where $U_{ii} = \beta_{ii}/2\pi^2 a_i^{*2}$ (a_i^* values are the reciprocal cell parameters). [c] Related to C(8) by the crystallographic mirror plane at $y = {}^1/_4$. [d] Related to C(11) by the crystallographic mirror plane at $y = {}^1/_4$.

the location of 16 terminal carbonyl ligands and two additional carbons, of which one atom, C(A), was equally coordinated to three cobalt atoms to form a Co_3C cluster.

A close examination of the geometry surrounding the resulting $Co_3(CO)_7S$ fragment revealed that C(8), O(9) and C(11), O(12) were nearly related to the corresponding partners by the mirror plane. Hence, only the average positions for C(8), O(9) and C(11), O(12) were taken as independent. Several cycles of the refinement, in which only cobalt and sulfur atoms were assigned anisotropic thermal parameters, resulted in the $R(F)$ value 0.113. In the final refinement all atoms except for C(6), C(9), and C(12) were assigned anisotropic thermal parameters, and the refinement was carried out until all parameter shifts became less than 1% of the corresponding esd's. The final figures for $R(F)$, $R(F^2)$, and $R_w(F^2)$ (defined as $[\sum w|\Delta F^2|^2/wF_o^4]^{1/2}$) were 0.056, 0.049, and 0.076, respectively. The standard deviation of an observation of unit weight, defined as $[w|\Delta F^2|^2/(n-p)]^{1/2}$, where n is the number of observations and p the number of variables fitted to the data set, was 1.199. A final difference-Fourier synthesis showed no residual peak greater than 0.44 or less than −0.35 e/Å^3.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

Co(1)–Co(1′)	2.441 (7)	Co(3)–S(2)	2.15 (2)
Co(1)–Co(2)	2.457 (4)	Co(4)–S(2)	2.19 (2)
Co(1)–C(A)	1.89 (1)	Co(5)–S(2)	2.16 (1)
Co(2)–C(A)	1.90 (2)	Co(3)–C(B)	1.88 (2)
Co(3)–Co(4)	2.560 (5)	Co(5)–S(3)	2.240 (7)
Co(4)–Co(5)	2.534 (6)	C(A)–S(1)	1.75 (2)
Co(5)–Co(3)	2.427 (5)	S(1)–C(B)	1.65 (2)
		C(B)–S(3)	1.72 (2)

Co(1)–Co(2)–Co(1′)	59.6 (2)	Co(4)–Co(3)–S(2)	54.5 (3)
Co(2)–Co(1)–Co(1′)	60.2 (1)	Co(3)–Co(4)–S(2)	53.1 (6)
Co(1)–C(A)–Co(1′)	80.3 (7)	Co(5)–Co(4)–S(2)	53.8 (3)
Co(1)–C(A)–Co(2)	80.9 (6)	Co(4)–Co(5)–S(2)	54.8 (4)
Co(1)–Co(2)–C(A)	49.5 (4)	Co(3)–Co(5)–S(2)	55.5 (6)
Co(2)–Co(1)–C(A)	49.6 (5)	Co(5)–Co(3)–S(2)	55.8 (3)
Co(1′)–Co(1)–C(A)	49.9 (4)	Co(3)–Co(5)–S(3)	77.7 (2)
Co(1)–C(A)–S(1)	136.5 (5)	S(2)–Co(5)–S(3)	96.2 (4)
Co(2)–C(A)–S(1)	120.9 (11)	Co(5)–Co(3)–C(B)	81.7 (6)
Co(3)–Co(4)–Co(5)	56.9 (1)	S(2)–Co(3)–C(B)	102.6 (4)
Co(4)–Co(5)–Co(3)	62.1 (2)	Co(3)–C(B)–S(1)	126.4 (12)
Co(5)–Co(3)–Co(4)	61.0 (1)	Co(3)–C(B)–S(3)	108.8 (10)
Co(3)–S(2)–Co(4)	72.4 (7)	Co(5)–S(3)–C(B)	91.2 (8)
Co(4)–S(2)–Co(5)	71.4 (5)	S(1)–C(B)–S(3)	119.9 (11)
Co(5)–S(2)–Co(3)	68.6 (6)	C(A)–S(1)–C(B)	112.3 (10)

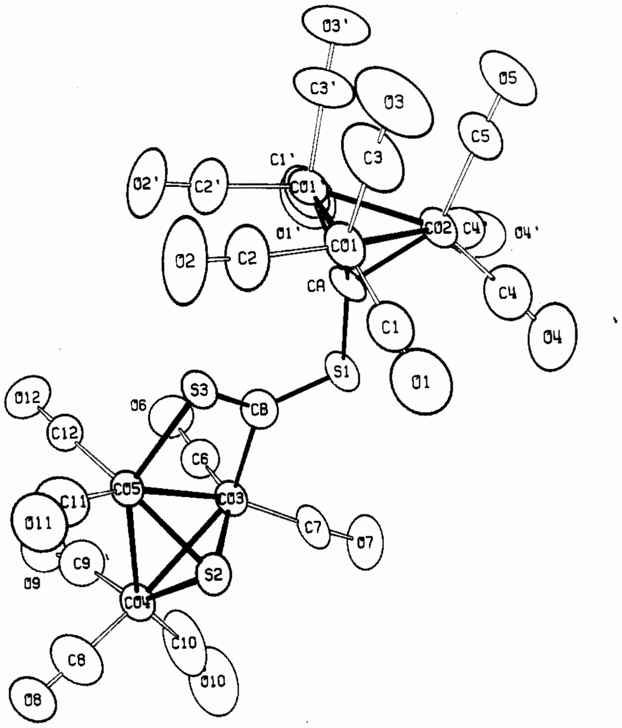

Figure 1. Perspective view of the molecule $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$, showing the μ_3-SCS bridging group connected to the two tricobalt clusters, $CCo_3(CO)_9$ and $SCo_3(CO)_7$. All atoms are labeled. Primed atoms are related to the corresponding nonprimed atoms by the crystallographic mirror plane.

The least-squares refinements were carried out on F^2. Atomic scattering factors used were those of Thomas and Umeda[30] for cobalt, those of Dawson[31] for sulfur, and those of Berghuis et al.[32] for carbon and oxygen. The real and imaginary dispersion corrections of cobalt and sulfur for Mo Kα radiation by Cromer[33] were also included. The final positional and isotropic temperature factors (or their equivalents) are listed in Table II. Some selected bond lengths and angles, calculated with the Busing–Martin–Levy program,[34] are given in Table III. All figures were prepared by use of the Johnson program.[35] Lists of observed and calculated structure amplitudes and of anisotropic thermal parameters, a complete listing of bond lengths and angles, and two stereoscopic views of the molecule are available as supplementary material.

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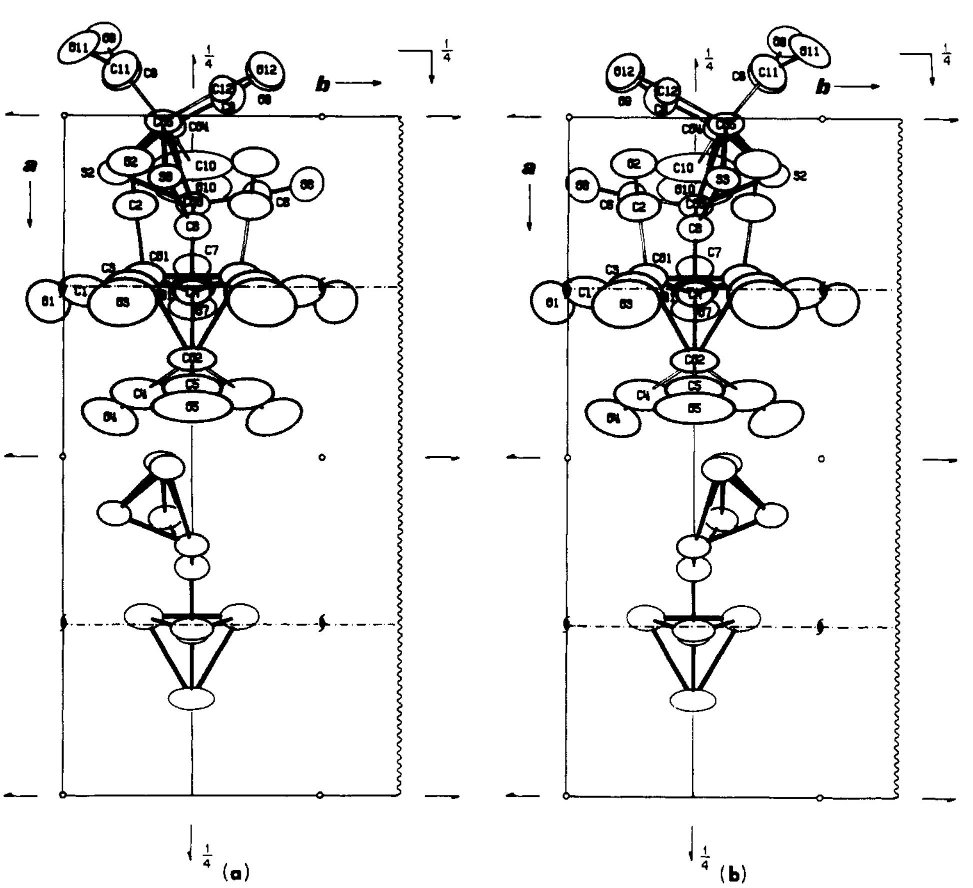

Figure 2. Two alternative molecular orientations viewed down the *c* axis. For the sake of clarity, carbonyl groups for the symmetry-related molecules (lower portion of the figure) are not shown. Postional parameters for the atoms in (a) are given in Table II.

Results and Discussion

The crystal structure of $[Co_3(CO)_9C](\mu_3\text{-}SCS)[Co_3(CO)_7S]$ consists of discrete molecules of a hexacobalt species as shown in Figure 1. The two tricobalt carbonyl clusters, $Co_3(CO)_9C$ and $Co_3(CO)_7S$, are linked by a tridentate bridging SCS group in a dissymmetrical fashion through the bondings of S(1) to the apical carbon atom C(A) of $Co_3(CO)_9C$ and of C(B) and S(3) to the two cobalt atoms Co(3) and Co(5) of $Co_3(CO)_7S$. The $Co_3(CO)_9C$ fragment of the molecule is related to itself by the crystallographic mirror plane, which also relates the remaining portion of the molecule. The resulting consequence is the existence of two alternative configurations with respect to the mirror plane, as illustrated in Figure 2.

The Co_3 plane of the $Co_3(CO)_9C$ fragment is seen in Figure 2 to tilt relative to the *c* axis by 13.62 (9)°, and its plane normal makes an angle of 10.7 (7)° with the C(A)–S(1) vector. The other Co_3 plane of the $Co_3(CO)_7S$ fragment has its plane normal forming angles of 109.5 (1), 19.5 (1), and 88.2 (2)° with *a*, *b*, and *c* axes, respectively. Eleven atoms (Co(2), Co(3), S(1), C(A), C(B), C(5), C(7), C(10), O(5), O(7), and O(10)) are constrained to lie on the crystallographic mirror plane. Minimum intermolecular distances (excluding those between mirror-related, disordered portions of the molecule) of 3.00 (4) Å for S···O contacts, 3.06 (4) Å for C···O contacts, and 2.92 (3) Å for O···O contacts suggest no abnormal interactions among molecules. In view of the disorder, however, it is conceivable that not all molecular parameters are normal, which in turn gives rise to deformation for some molecular geometries. This can be further visualized by the inspection of Figure 2, in which many thermal ellipsoids (particularly those on the mirror plane) have the individual principal axis that corresponds to the largest root-mean-square component of thermal displacement nearly coincident with the *b* axis, suggesting that the molecule as a whole could be slightly off the mirror plane and that it is not unlikely that the positional parameters for the atoms of the $Co_3(CO)_9C$ fragment and those lying on the mirror plane represent the average of a pair of positions.[36]

The geometry of the $Co_3(CO)_9C$ moiety is analogous to those found in the structures of $[Co_3(CO)_9C](\mu_3\text{-}CS_2)[Co_3(CO)_7S]$,[11b] $[Co_3(CO)_9C]_2SCO$,[12] $Co_3(CO)_{10}BH_2N(C_2H_5)_3$,[20] $Co_3(CO)_9CCH_3$,[37] $[Co_3(CO)_9C]_2CO$,[38] $Co_5(CO)_{15}C_3H$,[39] $C_6(CO)_{18}C_4$,[40] $Co_8(CO)_{24}C_6$,[41] $[CCo_3(CO)_9]_2$,[42] $C_6H_5C(O)CCo_3(CO)_9$,[43] and $(CO)_9Co_3CCl$,[44] in which each apical carbon is symmetrically bonded to a basal $Co_3(CO)_9$ fragment to result in an idealized C_{3v}-$3m$ symmetry. The three cobalt atoms of the Co_3C core in this structure form a roughly equilateral triangular array with 2.441 (7) and 2.457 (4) Å for Co(1)–Co(1′) and Co(1)–Co(2); the apical C(A) atom is nearly equidistant from the three cobalt atoms (average Co–C(A) distance 1.89 (1) Å), and it has the average value 49.7 (3)° for C(A)–Co–Co angles. Furthermore, the dihedral angle between the plane of the three cobalt atoms and the plane defined by one cobalt atom and its two equatorial carbonyl

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(36) It is noteworthy that atoms C(10) and O(5) have the two largest root-mean-square components of thermal displacement along the *b* axial direction, being 0.849 (7) and 0.834 (4) Å, respectively. The ratios of the largest and the smallest displacements along the corresponding principal axes for these two atoms were calculated to be usually large, being 4.0 (8) and 3.5 (5), respectively, with the remaining atoms having the ratios ranging from 1.3 (2) for O(6) to 3.1 (5) for C(4).

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Table IV. Comparison of Selected Bond Distances (Å) and Angles (deg) for [$Co_3(CO)_9C$](μ_3-SCS)[$Co_3(CO)_7S$] and $SCo_3(CO)_7(CSNMe_2)$[48]

	this work	ref 48
Co(3)–Co(5)	2.427 (5)	2.440 (1)
Co(3)–C(B)	1.88 (2)	1.958 (5)
Co(5)–S(3)	2.240 (7)	2.260 (2)
S(3)–C(B)	1.72 (2)	1.695 (5)
S(3)–Co(5)–Co(3)	77.7 (2)	77.11 (5)
C(B)–Co(3)–Co(5)	81.7 (6)	82.39
Co(5)–S(3)–C(B)	91.2 (8)	93.9 (2)
Co(3)–C(B)–S(3)	108.8 (10)	106.6 (3)

carbon atoms was calculated to be 27 (1)° with respect to Co(1) and 27 (1)° with respect to Co(2), in agreement with the average value of 30° given by Penfold and Robinson.[45]

Many structures of cobalt carbonyl complexes containing the Co_3S moiety with the sulfur located at the apical position have been reported, and a comparison of Co–Co and Co–S_{ap} distances for this family of complexes has been made.[11b] It is well understood that the $Co_3(CO)_7S$ fragment can be considered to arise from the replacement of two cis equatorial carbonyl groups in the $SCo_3(CO)_9$[9] molecule with a bidentate bridging ligand. The triply bridging metal-coordinated apical sulfur in the $Co_3(CO)_7S$ entity shares four of its valence electrons with the metals, and the displacement of the two electron-pair carbonyl donors by the three-electron-donor ligand results in a closed-shell electronic configuration for each cobalt atom. The situation is similar to those observed in the structures of [$Co_3(CO)_8$](μ_5-CS_2)[$Co_3(CO)_7S$],[11] [$Co_3(CO)_9C$](μ_3-CS_2)[$Co_3(CO)_7S$],[11b] [$SCo_3(CO)_7]_2S_2$,[46] $SCo_3(CO)_7$(μ-$CH_3CNC_6H_{11}$),[47] and $SCo_3(CO)_7(CSNMe_2)$,[48] in which the substitution of the bidentate bridging ligand for the two carbonyl groups invariably leads to significant deformations of the molecule. In the present structure, the three basal cobalt atoms are constrained to possess an isosceles triangular array, as shown by a considerably short Co(3)–Co(5) distance of 2.427 (5) Å as compared to 2.560 (5) and 2.534 (6) Å for the other two Co(3)–Co(4) and Co(4)–Co(5) distances. Since S(2) is nearly equidistant from the basal cobalt atoms (average Co–S distance 2.17 (1) Å), the deformation of the triangular Co_3 unit entails distortions of the Co_3S fragment, leading to a smaller angle, 68.6 (6)°, for Co(3)–S(2)–Co(5) than the other two Co–S–Co angles (72.4 (7) and 71.4 (5)°).

The bonding of the bridging SCS ligand to the two tricobalt clusters and the resulting alteration in its geometry are of chemical interest. Through the σ bondings to Co(3) and Co(5), the two bidentate atoms S(3) and C(B) form a four-membered ring system that is found to be planar to within 0.062 (5) Å. This ring system is nearly in the same plane defined by Co(3), Co(4), and Co(5) (dihedral angle 7.2 (3)°). A bookkeeping account of electrons shows that the bridging CS_2 ligand in the structural isomer [$Co_3(CO)_9C$](μ_3-CS_2)[$Co_3(CO)_7S$][11b] also donates four electrons, except that the symmetric bondings of the two sulfur atoms to the $Co_3(CO)_7S$ fragment results in a formation of a five-membered ring system that was reported to be strictly planar. In the present molecule, the three angles subtended by the neighboring atoms of C(B) are 126.4 (12), 108.8 (10), and 119.9 (11)° for Co(3)–C(B)–S(1), Co(3)–C(B)–S(3), and S(1)–C(B)–S(3), respectively, and the C(B) atom is out of the plane defined by the surrounding three atoms by 0.223 (6) Å (due in part to the displacement of S(3) from the crystallographic mirror plane). The near-planarity of the C(B) atom and the central angles with the three bonded neighbors unequivocally establishes that the C(B) atom possesses trigonal-orbital character. Although the bond length 1.72 (2) Å for S(3)–C(B) can be compared with 1.696 (11) and 1.674 (10) Å for [$Co_3(CO)_9C$](μ_3-CS_2)[$Co_3(CO)_7S$],[11b] 1.695 (5) Å for $SCo_3(CO)_7(CSNMe_2)$,[48] and 1.711 (8) Å for $Fe_4(CO)_{12}S(CSNMe_2)(CNMe_2)$,[49] the S(1)–C(B) distance of 1.65 (2) Å is noticeably shorter than that for the S(3)–C(B) bond.[50] Unfortunately, the relatively large esd's associated with these bond lengths (due to the crystal disorder and to a small data-to-variable ratio of 3.22) do not permit a precise assessment of the degree of π-electron delocalization within the S(1)–C(B)–S(3) fragment.

The stereochemical environment surrounding the chelation of carbon and sulfur atoms to the $Co_3(CO)_7S$ entity in this structure is analogous to that found in the structure of $SCo_3(CO)_7(CSNMe_2)$.[48] A comparison of the pertinent molecular parameters for the four-membered rings formed is given in Table IV, from which a close agreement between the corresponding pairs of parameters can be seen.

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Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic thermal parameters, and intramolecular distances and angles and two stereoscopic views of the molecule (9 pages). Ordering information is given on any current masthead page.

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