

lead to the appearance of a peak corresponding to twice the Cu-Cu separation (that is, at $\sim 6 \text{ \AA}$), but no such signal is apparent in the Fourier transform of $\text{Cu}(\text{ClO}_4)_2$. On the other hand, such a peak enhanced by the focusing effect is observed for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and also in the spectra of CuCl_2 and Cu_2O .²¹

The proposed structure resembles that of anhydrous copper sulfate, in which copper atoms are linked in infinite chains, with both short (3.35 Å) and long (4.84 Å) copper-copper distances, except that here two nonequivalent bridging sulfate groups maintain the shorter Cu-Cu separation, one bridge involving two oxygen atoms, Cu-O-S-O-Cu, and the other only one, Cu-O-Cu.²²

A final remark arising from the EXAFS results concerns the short Cu-Cu distance in one chain, suggesting some kind of interaction, but the ESR spectrum shows no evidence of exchange interaction, in particular in the half-field region ($\Delta(ms) = \pm 2$). In most cases for complexes containing copper chains or dimers with copper-copper distances $> 2.8 \text{ \AA}$, the

magnetic interaction proceeds via an exchange mechanism through the bridging ligand, and the relative orientation of the magnetic orbitals is a key factor,²³ not only the inter-metallic distance. In addition, magnetic measurements confirm the absence of any significant exchange coupling between the two copper centers and are thus entirely compatible with the ESR results.²⁴

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Synthesis and Structure of $\text{Co}_6(\mu_6\text{-C}_2)(\mu\text{-CO})_6(\text{CO})_8(\mu_4\text{-S})$: First Example of a Peripheral Dicarbide Metal Carbonyl Cluster

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As the sixth fully characterized member of the $\text{C}_x\text{S}_y\text{Co}_z(\text{CO})_w$ family of cluster carbonyls, the title compound (VI) has been isolated as a new product in the reaction of $\text{Co}_2(\text{CO})_8$ with CS_2 at ambient temperature under an N_2 atmosphere, in low yield (ca. 5% relative to the sum of soluble carbonyl products). Its structure has been characterized by X-ray diffraction analysis and IR spectroscopy. Crystal data: space group $P2_12_12_1$ (D_2^d , No. 19), $a = 18.618$ (5) Å, $b = 13.528$ (5) Å, $c = 9.151$ (4) Å, $Z = 4$, $d_{\text{calcd}} = 2.31 \text{ g cm}^{-3}$. The structure was solved by using a combination of the conventional Patterson method with difference Fourier techniques. Refinement on 1509 reflections for which $F > 6\sigma(F)$ resulted in the final residuals $R = 0.045$ and $R_w = 0.044$. The structure consists of a "boat" array of six cobalt atoms, of which the four basal ones form an essentially regular square, metal-metal bonded along all four edges. The two apical cobalt atoms are connected through a Co-C-C-Co array. The two carbon atoms of the "peripheral" dicarbido unit are bonded also to the four basal cobalt atoms. These four atoms, in turn, are capped also by a face-bridging μ_4 -sulfur atom. Each of the six peripheral Co-Co bonds bears μ -carbonyl ligand, five of them showing different amounts of asymmetry. The solution IR spectrum suggests a dynamic behavior over all six bridges whereas the solid-state IR spectrum reflects the unique situation of the single symmetrical bridge. The apical cobalt atoms bear two of the eight terminal carbonyls, and one CO is terminally bonded to each of the four basal metal atoms. When treated with carbon monoxide, complex VI loses the sulfur atom to yield $(\text{CO})_9\text{Co}_3\text{C}_2\text{Co}_3(\text{CO})_9$, which was also directly observed among the products of the reaction of dicobalt octacarbonyl with CS_2 .

Introduction

Transition-metal carbido clusters have recently been reviewed.¹ The authors divided these clusters into two main classes according to the structural features, i.e. the "cage carbides", in which the metal polyhedron completely encloses the carbido carbon atom, and the "peripheral carbides", in which the carbon atom is bonded at the periphery of the metal polyhedron, generally leaning out of a face of the metal framework.

Even if in the last 2 years there has been an increase in the number of carbido metal clusters reported, reaching at present ca. 100, very few examples among them are dicarbido clusters, i.e. complexes containing two carbido carbon atoms. All the

dicarbido metal carbonyl clusters hitherto reported are cage carbides and can be divided into two types:² (i) where a C_2 unit is encapsulated in a metal polyhedron, as $\text{Rh}_{12}(\text{C}_2)(\text{CO})_{25}$ ⁴ and $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-5}$ and (ii) where two separate carbido

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(2) In principle, the complex $(\text{CO})_9\text{Co}_3\text{C}_2\text{Co}_3(\text{CO})_9$ ³ can belong to the carbido family, as the C_2 unit is bonded only to metal atoms, so being considered the unique member of a third type of dicarbido clusters, in which C_2 links two separate polymetallic entities.

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atoms at a nonbonding distance occupy different cavities of a closed metal polyhedron, as $[\text{Rh}_{15}(\text{C})_2(\text{CO})_{28}]^{-6} \text{H}_x\text{Co}_{13}(\text{C})_2(\text{CO})_{24}$,⁷ $[\text{Rh}_{14}(\text{C})_2(\text{CO})_{33}]^{2-}$,⁸ and $\text{Rh}_{12}(\text{C})_2(\text{CO})_{24}$.⁸

The title compound (VI)⁹ represents the first example of a dicarbido cluster belonging to the "peripheral" class, in which the C_2 unit is part of the framework of a cobalt polyhedron and occupies a peripheral position. It was prepared and identified as one of the $\text{C}_i\text{S}_w\text{Co}_x(\text{CO})_z$ products of the complex reaction between dicobalt octacarbonyl and carbon disulfide at room temperature.¹⁰ Preliminary data have already been reported.¹¹

Experimental Section

Preparation of the Complex. Dicobalt octacarbonyl and carbon disulfide (molar ratio 1:4) were reacted in petroleum ether (40–70 °C) solution at room temperature under a gentle flux of nitrogen: $\text{Co}_2(\text{CO})_8$ disappeared in 2–3 h.

The reaction mixture was filtered (the solution contains all the other carbonyl products¹⁰) and the black residue repeatedly washed by small amounts of petroleum ether until the solvent remained colorless. Then chloroform was added to the residue, and the slurry was vigorously stirred at room temperature under nitrogen. Repeated extractions and subsequent filtration gave a dark green solution, from which by slow crystallization at –20 °C black air-stable crystals of complex VI were obtained. The compound is very slightly soluble in hydrocarbon solvents and more soluble in chloroform or carbon tetrachloride. The yield was ca. 5%, with respect to all carbonyl products.

The close structural relationships between complex VI and $(\text{C}-\text{O})_6\text{Co}_3\text{C}_2\text{Co}_3(\text{CO})_9$ (**1**) (vide infra) led us to check the possibility of chemical relationships. In this light, the syntheses of VI starting from **1** and CS_2 or S were attempted but completely failed. The reaction of **1** with CS_2 (reflux in petroleum ether solution under nitrogen for ca. 5 h or with neat CS_2 in a sealed vial at 70 °C for ca. 2 h) or with elemental S (in a sealed vial under vacuum at 100 °C for ca. 10 h) did not lead to other carbonyl compounds but only to decomposition of the starting material. On the other hand, complex VI reacts smoothly and completely with CO (*n*-heptane solution at 45 °C for ca. 30 h), giving rise to **1** (yield ca. 60%), to $\text{Co}_3(\text{CO})_9\text{S}$ (yield ca. 30%), and to small amounts of other unidentified cobalt carbonyl products.

Collection and Reduction of X-ray Data. The crystal and the main experimental data for the structure analysis are reported in Table I. The cell parameters were obtained from the refinement of 25 θ angles. No significant decrease of the intensities of three standard reflections was detected. The absorption correction was made according to the North, Phillips, and Mathews method.¹² Secondary extinction correction has not been made.

Resolution of the Structure. The location of the heavy atoms was obtained by the conventional Patterson method, and subsequent difference Fourier maps supplied the positions of the S, C, and O atoms. The weighting scheme was

$$w = 1/(\sigma(F)^2 + 0.001F^2)$$

where the coefficient was chosen in order to maintain $\sum w\Delta^2$ satisfactorily constant for the amplitudes batched in various ranges of $|F_o|$. In the last cycles of least-squares refinement anisotropic thermal

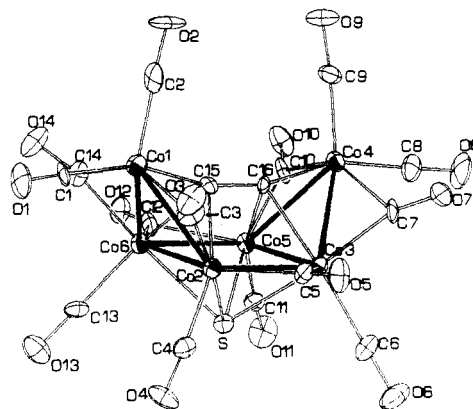


Figure 1. ORTEP plot of $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}$ with 25% probability ellipsoids.

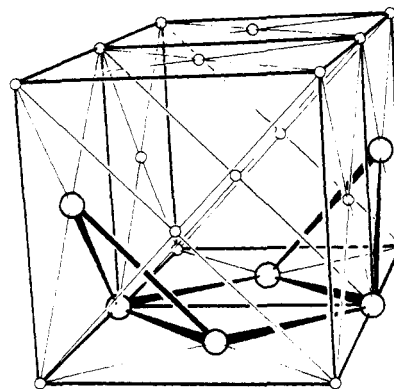


Figure 2. Co_6 "boat" framework inside the face-centered-cubic cobalt lattice.

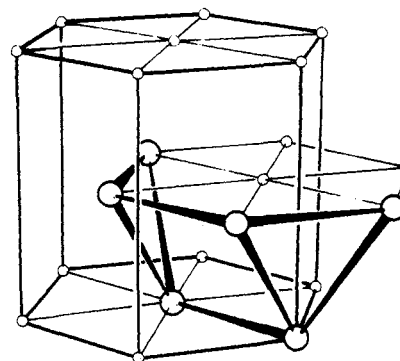


Figure 3. Co_6 "boat" framework inside the hexagonal-close-packed cobalt lattice.

parameters were attributed to all the atoms. Refinement of the enantiomer of the proposed structure converged to residuals ($R = 0.046$, $R_w = 0.045$) which indicate that our model was the correct choice. All the computations were carried out with use of the programs of SHELX 76.¹³ The calculation of the best planes passing through the atoms was made by the method of ref 14.

The final fractional atomic coordinates are listed in Table II and the distance and angle values in Table III. Lists of observed and calculated structure factors and thermal anisotropic parameters are available.¹⁵

Description of the Structure and Discussion

The molecule of $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}$ (Figure 1) has idealized C_{2v} symmetry, with one mirror plane passing through Co(1),

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 (15) Supplementary material.

Table I. Experimental and Crystal Data for X-ray Analysis^a

space group	$P2_12_12_1 (D_2^4, \text{No. } 19)$
a , Å	18.618 (5)
b , Å	13.528 (5)
c , Å	9.151 (4)
V , Å ³	2304.8
mol wt	801.88
Z	4
$d(\text{calcd})$, g cm ⁻³	2.31
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	42.16
approx cryst dimens, mm	$0.10 \times 0.25 \times 0.30$
rel transmission factor	0.712/0.999
diffractometer	Philips PW 1100 (cryst sealed in Lindemann glass capillary)
radiation	Mo K α (graphite monochromatized, $\lambda = 0.7107 \text{ \AA}$)
scan technique	ω
scan width, deg	2.00
scan speed, deg s ⁻¹	0.10
scan range (θ), deg	2.0–25.0
bkgd	each bkgd measd for 5 s
collected reflns	4508
reflns after averaging of equiv ones	2339
reflns with $F > 6\sigma(F)$	1509
final R	0.045
final R_w	0.044

^a Here and in the subsequent tables the esd's are in parentheses.

Co(4), C(15), C(16), and S and the other one bisecting the Co(2)–Co(3) and Co(5)–Co(6) sides of the base. The Co₆ unit is formed by a roughly square-planar Co₄ base with two opposite sides axially bridged by the other Co atoms, to fit a "boat" configuration. The C₂ unit spans between the extreme apexes of the boat, each carbon atom being bonded to all three cobalt atoms of the corresponding triangle. The quadruply bridging S atom symmetrically caps the square base on the opposite side of the C₂ unit. Eight terminal CO groups are bonded to the cluster, two of them to each apical Co atom and one to each Co atom of the base. Finally, six bridging CO groups coordinate the six external sides of the boat.

The Co₆S Cluster. The boat configuration is unique among the Co₆ clusters reported till now, which usually show octahedral¹⁶ or trigonal-prismatic^{10a,d,17} structures. Only [Co₆P(μ-CO)₂(CO)₁₄]⁻¹⁸ has a metal atom array roughly similar to that of complex VI, and it is formally derived from a trigonal prism in which insertion of a bulk P atom has broken an edge and distorted the remaining square face. The "regular"¹⁹ boat framework of complex VI can be considered to be a finite piece of the lattices of the metallic cobalt (face-centered cubic and hexagonal close packed).²⁰ Figures 2 and 3 show simplified fragments of the two lattices, and the boat configuration is clearly recognized, as part of the cuboctahedron (fccub lattice)

Table II. Fractional Atomic Coordinates of Co₆C₂(CO)₁₄S

atom	x/a	y/b	z/c
Co(1)	1.0359 (1)	0.1157 (2)	0.6284 (3)
Co(2)	0.9596 (1)	0.1852 (2)	0.4242 (3)
Co(3)	0.8405 (1)	0.2717 (2)	0.4989 (3)
Co(4)	0.8098 (1)	0.2724 (2)	0.7719 (3)
Co(5)	0.8010 (1)	0.1120 (2)	0.6395 (3)
Co(6)	0.9213 (1)	0.0283 (2)	0.5666 (3)
S	0.8477 (2)	0.1131 (3)	0.4100 (5)
C(1)	1.1159 (8)	0.0555 (12)	0.5628 (21)
C(2)	1.0716 (9)	0.1736 (15)	0.7880 (24)
C(3)	1.0540 (9)	0.2256 (15)	0.4619 (21)
C(4)	0.9771 (9)	0.1526 (13)	0.2334 (21)
C(5)	0.9301 (9)	0.3201 (15)	0.3941 (19)
C(6)	0.7786 (10)	0.3034 (15)	0.3464 (23)
C(7)	0.8308 (8)	0.3894 (12)	0.5986 (21)
C(8)	0.7259 (10)	0.3348 (14)	0.8052 (23)
C(9)	0.8598 (10)	0.3031 (14)	0.9269 (21)
C(10)	0.7652 (8)	0.1445 (12)	0.8297 (21)
C(11)	0.7143 (9)	0.0558 (13)	0.5909 (19)
C(12)	0.8423 (9)	-0.0209 (15)	0.6935 (22)
C(13)	0.9239 (10)	-0.0779 (13)	0.4452 (19)
C(14)	0.9893 (8)	-0.0231 (15)	0.6940 (21)
C(15)	0.9459 (8)	0.1660 (11)	0.6385 (19)
C(16)	0.8819 (8)	0.2085 (11)	0.6790 (18)
O(1)	1.1667 (7)	0.0235 (12)	0.5153 (18)
O(2)	1.0923 (9)	0.2122 (13)	0.8899 (14)
O(3)	1.1060 (6)	0.2684 (11)	0.4388 (17)
O(4)	0.9857 (8)	0.1246 (12)	0.1183 (15)
O(5)	0.9488 (7)	0.3958 (9)	0.3473 (18)
O(6)	0.7411 (8)	0.3219 (14)	0.2560 (17)
O(7)	0.8287 (7)	0.4719 (9)	0.6134 (15)
O(8)	0.6740 (7)	0.3775 (13)	0.8279 (19)
O(9)	0.8940 (8)	0.3171 (14)	1.0306 (15)
O(10)	0.7362 (6)	0.1177 (10)	0.9328 (15)
O(11)	0.6585 (6)	0.0251 (11)	0.5757 (17)
O(12)	0.8264 (6)	-0.0849 (9)	0.7610 (14)
O(13)	0.9289 (8)	-0.1423 (11)	0.3674 (17)
O(14)	1.0102 (7)	-0.0836 (11)	0.7719 (18)

or of the truncated hexagonal bipyramid of D_{3h} symmetry (hcp lattice).²¹ The similarity between the cluster and the metal lattice is not a geometric formalism, but it is supported by the values of the most relevant crystallographic parameters listed in Table IV. The small differences between the cluster and the lattice arise probably from the greater freedom of arrangement of the cluster necessary to accommodate the ligands without excessive steric crowding. The Co–Co bonds of the base of the "boat" are significant in this light. On the one hand, they are longer than the corresponding Co–Co bond in the metal, because of the absence of the constraint required in an infinite lattice; on the other hand, they are equal (the base is roughly a square),²² because of the presence of bridging groups (Co atoms and CO ligands) on each of them, whereas other Co₄ planar arrays (e.g. Co₄(μ-CO)₂(CO)₈(μ₄-X)₂ (X = S,²³ Te,²⁴ and PC₆H₅²⁴)) are rectangular, the opposite bridged Co–Co bonds being shorter than the unbridged bonds. Moreover, the Co–Co distances are greater than those normally found for bridged Co–Co bonds, probably because the insertion of the C₂ unit causes a small widening of the Co₄ square.

Complex VI shows the second example of an S atom quadruply bridging a planar Co₄ framework, the other being

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- (19) The Co–Co basal distances range in the 2.590 (3)–2.619 (3) Å interval and the Co(apical)–Co(basal) distances in the 2.490 (3)–2.562 (3) Å interval; the greatest differences are ca. 10σ in the former case and 24σ in the latter.
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Table III. Interatomic Distances (Å) and Angles (deg)

Co-Co Distances							
Co(1)-Co(2)	2.528 (3)	Co(2)-Co(3)	2.599 (3)	Co(3)-Co(4)	2.562 (3)	Co(4)-Co(5)	2.490 (3)
Co(1)-Co(6)	2.504 (3)	Co(2)-Co(6)	2.590 (3)	Co(3)-Co(5)	2.619 (3)	Co(5)-Co(6)	2.597 (3)
Co-C Distances							
Co(1)-C(1)	1.80 (2)	Co(2)-C(5)	1.93 (2)	Co(4)-C(8)	1.80 (2)	Co(5)-C(12)	2.02 (2)
Co(1)-C(2)	1.79 (2)	Co(2)-C(15)	1.99 (2)	Co(4)-C(9)	1.75 (2)	Co(5)-C(16)	2.02 (2)
Co(1)-C(3)	2.16 (2)	Co(3)-C(5)	2.03 (2)	Co(4)-C(10)	1.99 (2)	Co(6)-C(12)	1.99 (2)
Co(1)-C(14)	2.15 (2)	Co(3)-C(6)	1.86 (2)	Co(4)-C(16)	1.81 (2)	Co(6)-C(13)	1.82 (2)
Co(1)-C(15)	1.81 (2)	Co(3)-C(7)	1.84 (2)	Co(5)-C(10)	1.91 (2)	Co(6)-C(14)	1.86 (2)
Co(2)-C(3)	1.87 (2)	Co(3)-C(16)	2.01 (2)	Co(5)-C(11)	1.84 (2)	Co(6)-C(15)	2.03 (2)
Co(2)-C(4)	1.83 (2)	Co(4)-C(7)	2.27 (2)				
Co-S Distances							
Co(2)-S	2.304 (4)	Co(3)-S	2.299 (5)	Co(5)-S	2.273 (5)	Co(6)-S	2.290 (5)
C-C Distance							
C(15)-C(16)	1.37 (2)						
C-O Distances							
C(1)-O(1)	1.13 (2)	C(5)-O(5)	1.16 (2)	C(9)-O(9)	1.16 (2)	C(12)-O(12)	1.10 (2)
C(2)-O(2)	1.14 (2)	C(6)-O(6)	1.11 (2)	C(10)-O(10)	1.15 (2)	C(13)-O(13)	1.13 (2)
C(3)-O(3)	1.15 (2)	C(7)-O(7)	1.12 (2)	C(11)-O(11)	1.13 (2)	C(14)-O(14)	1.15 (2)
C(4)-O(4)	1.13 (2)	C(8)-O(8)	1.14 (2)				
Co-Co-Co Angles							
Co(2)-Co(1)-Co(6)	62.0 (1)	Co(2)-Co(3)-Co(4)	116.6 (1)	Co(3)-Co(5)-Co(4)	60.1 (1)	Co(1)-Co(6)-Co(2)	59.5 (1)
Co(1)-Co(2)-Co(3)	116.9 (1)	Co(2)-Co(3)-Co(5)	89.8 (1)	Co(3)-Co(5)-Co(6)	89.5 (1)	Co(1)-Co(6)-Co(5)	118.1 (1)
Co(1)-Co(2)-Co(6)	58.6 (1)	Co(4)-Co(3)-Co(5)	57.4 (1)	Co(4)-Co(5)-Co(6)	116.6 (1)	Co(2)-Co(6)-Co(5)	90.5 (1)
Co(3)-Co(2)-Co(6)	90.1 (1)	Co(3)-Co(4)-Co(5)	62.4 (1)				
Co-Co-C Angles							
Co(2)-Co(1)-C(1)	112.8 (6)	Co(3)-Co(2)-C(15)	72.0 (5)	Co(3)-Co(4)-C(7)	44.3 (5)	Co(4)-Co(5)-C(16)	45.8 (4)
Co(2)-Co(1)-C(2)	130.6 (6)	Co(6)-Co(2)-C(3)	113.9 (6)	Co(3)-Co(4)-C(8)	111.1 (7)	Co(6)-Co(5)-C(10)	129.3 (5)
Co(2)-Co(1)-C(3)	46.3 (5)	Co(6)-Co(2)-C(4)	109.4 (6)	Co(3)-Co(4)-C(9)	132.4 (6)	Co(6)-Co(5)-C(11)	120.9 (6)
Co(2)-Co(1)-C(14)	107.7 (5)	Co(6)-Co(2)-C(5)	140.4 (5)	Co(3)-Co(4)-C(10)	110.4 (5)	Co(6)-Co(5)-C(12)	49.1 (5)
Co(2)-Co(1)-C(15)	51.5 (6)	Co(6)-Co(2)-C(15)	50.5 (4)	Co(3)-Co(4)-C(16)	51.3 (5)	Co(6)-Co(5)-C(16)	71.7 (4)
Co(6)-Co(1)-C(1)	114.6 (5)	Co(2)-Co(3)-C(5)	47.2 (5)	Co(5)-Co(4)-C(7)	106.2 (5)	Co(1)-Co(6)-C(12)	131.0 (5)
Co(6)-Co(1)-C(2)	135.2 (6)	Co(2)-Co(3)-C(6)	115.8 (6)	Co(5)-Co(4)-C(8)	115.7 (6)	Co(1)-Co(6)-C(13)	119.3 (6)
Co(6)-Co(1)-C(3)	107.4 (5)	Co(2)-Co(3)-C(7)	127.0 (5)	Co(5)-Co(4)-C(9)	129.6 (7)	Co(1)-Co(6)-C(14)	56.9 (6)
Co(6)-Co(1)-C(14)	46.2 (5)	Co(2)-Co(3)-C(16)	72.3 (4)	Co(5)-Co(4)-C(10)	49.0 (5)	Co(1)-Co(6)-C(15)	45.6 (4)
Co(6)-Co(1)-C(15)	53.2 (5)	Co(4)-Co(3)-C(5)	129.9 (5)	Co(5)-Co(4)-C(16)	53.4 (5)	Co(2)-Co(6)-C(12)	140.5 (6)
Co(1)-Co(2)-C(3)	56.3 (6)	Co(4)-Co(3)-C(6)	126.4 (6)	Co(3)-Co(5)-C(10)	110.8 (5)	Co(2)-Co(6)-C(13)	109.4 (5)
Co(1)-Co(2)-C(4)	121.0 (5)	Co(4)-Co(3)-C(7)	59.5 (6)	Co(3)-Co(5)-C(11)	117.9 (5)	Co(2)-Co(6)-C(14)	115.8 (6)
Co(1)-Co(2)-C(5)	128.2 (5)	Co(4)-Co(3)-C(16)	44.6 (4)	Co(3)-Co(5)-C(12)	138.4 (5)	Co(2)-Co(6)-C(15)	49.3 (5)
Co(1)-Co(2)-C(15)	45.3 (4)	Co(5)-Co(3)-C(5)	136.7 (5)	Co(3)-Co(5)-C(16)	49.3 (4)	Co(5)-Co(6)-C(12)	50.1 (5)
Co(3)-Co(2)-C(3)	128.4 (6)	Co(5)-Co(3)-C(6)	112.7 (6)	Co(4)-Co(5)-C(10)	51.8 (5)	Co(5)-Co(6)-C(13)	121.7 (6)
Co(3)-Co(2)-C(4)	120.8 (5)	Co(5)-Co(3)-C(7)	116.2 (6)	Co(4)-Co(5)-C(11)	122.4 (5)	Co(5)-Co(6)-C(14)	126.2 (6)
Co(3)-Co(2)-C(5)	50.8 (5)	Co(5)-Co(3)-C(16)	49.8 (4)	Co(4)-Co(5)-C(12)	129.2 (5)	Co(5)-Co(6)-C(15)	73.2 (4)
C-Co-C Angles							
C(1)-Co(1)-C(2)	99.3 (7)	C(3)-Co(2)-C(5)	91.0 (8)	C(7)-Co(4)-C(8)	86.7 (7)	C(10)-Co(5)-C(12)	96.6 (7)
C(1)-Co(1)-C(3)	87.0 (8)	C(3)-Co(2)-C(15)	88.7 (7)	C(7)-Co(4)-C(9)	108.0 (8)	C(10)-Co(5)-C(16)	87.1 (7)
C(1)-Co(1)-C(14)	91.8 (7)	C(4)-Co(2)-C(5)	98.2 (8)	C(7)-Co(4)-C(10)	149.5 (7)	C(11)-Co(5)-C(12)	91.4 (7)
C(1)-Co(1)-C(15)	162.2 (8)	C(4)-Co(2)-C(15)	158.3 (7)	C(7)-Co(4)-C(16)	83.0 (6)	C(11)-Co(5)-C(16)	164.3 (7)
C(2)-Co(1)-C(3)	102.6 (8)	C(5)-Co(2)-C(15)	103.2 (7)	C(8)-Co(4)-C(9)	102.3 (9)	C(12)-Co(6)-C(16)	104.3 (6)
C(2)-Co(1)-C(14)	107.7 (9)	C(5)-Co(3)-C(6)	94.6 (8)	C(8)-Co(4)-C(10)	90.0 (7)	C(12)-Co(6)-C(13)	96.4 (8)
C(2)-Co(1)-C(15)	98.0 (7)	C(5)-Co(3)-C(7)	92.0 (8)	C(8)-Co(4)-C(16)	161.3 (8)	C(12)-Co(6)-C(14)	90.7 (7)
C(3)-Co(1)-C(14)	149.5 (8)	C(5)-Co(3)-C(16)	102.1 (6)	C(9)-Co(4)-C(10)	102.3 (8)	C(12)-Co(6)-C(15)	106.6 (6)
C(3)-Co(1)-C(15)	85.5 (7)	C(6)-Co(3)-C(7)	96.4 (8)	C(9)-Co(4)-C(16)	95.7 (8)	C(13)-Co(6)-C(14)	94.0 (9)
C(14)-Co(1)-C(15)	86.6 (6)	C(6)-Co(3)-C(16)	162.0 (8)	C(10)-Co(4)-C(16)	91.0 (7)	C(13)-Co(6)-C(15)	156.7 (7)
C(3)-Co(2)-C(4)	94.5 (8)	C(7)-Co(3)-C(16)	89.9 (7)	C(10)-Co(5)-C(11)	90.6 (7)	C(14)-Co(6)-C(15)	89.2 (8)
Co-Co-S Angles							
Co(1)-Co(2)-S	113.1 (2)	Co(2)-Co(3)-S	55.7 (1)	Co(3)-Co(5)-S	55.5 (1)	Co(1)-Co(6)-S	114.5 (2)
Co(3)-Co(2)-S	55.5 (1)	Co(4)-Co(3)-S	111.2 (2)	Co(4)-Co(5)-S	114.8 (2)	Co(2)-Co(6)-S	55.9 (1)
Co(6)-Co(2)-S	55.4 (1)	Co(5)-Co(3)-S	54.6 (1)	Co(6)-Co(5)-S	55.6 (1)	Co(5)-Co(6)-S	55.0 (1)
S-Co-C Angles							
S-Co(2)-C(3)	169.3 (6)	S-Co(3)-C(5)	94.9 (5)	S-Co(5)-C(10)	166.3 (5)	S-Co(6)-C(12)	95.2 (6)
S-Co(2)-C(4)	90.3 (5)	S-Co(3)-C(6)	89.2 (7)	S-Co(5)-C(11)	96.6 (5)	S-Co(6)-C(13)	91.7 (6)
S-Co(2)-C(5)	97.8 (5)	S-Co(3)-C(7)	170.7 (6)	S-Co(5)-C(12)	94.9 (6)	S-Co(6)-C(14)	171.3 (6)
S-Co(2)-C(15)	83.4 (4)	S-Co(3)-C(16)	82.6 (4)	S-Co(5)-C(16)	82.9 (5)	S-Co(6)-C(15)	83.0 (5)
Co-C-C Angles							
Co(1)-C(15)-C(16)	166.7 (1.4)	Co(6)-C(15)-C(16)	106.0 (1.0)	Co(4)-C(16)-C(15)	166.0 (1.3)	Co(5)-C(16)-C(15)	109.1 (1.1)
Co(2)-C(15)-C(16)	108.8 (1.2)	Co(3)-C(16)-C(15)	106.8 (1.2)				
Co-C-Co Angles							
Co(1)-C(3)-Co(2)	77.4 (7)	Co(4)-C(10)-Co(5)	79.2 (7)	Co(1)-C(15)-Co(2)	83.1 (7)	Co(3)-C(16)-Co(4)	84.1 (6)
Co(2)-C(5)-Co(3)	82.0 (8)	Co(5)-C(12)-Co(6)	80.8 (8)	Co(1)-C(15)-Co(6)	81.2 (6)	Co(3)-C(16)-Co(5)	80.9 (6)
Co(3)-C(7)-Co(4)	76.1 (6)	Co(1)-C(14)-Co(6)	76.8 (7)	Co(2)-C(15)-Co(6)	80.2 (6)	Co(4)-C(16)-Co(5)	80.8 (6)

Table III (Continued)

		Co-S-Co Angles					
Co(2)-S-Co(3)	68.8 (1)	Co(2)-S-Co(6)	68.6 (1)	Co(3)-S-Co(6)	106.3 (2)	Co(5)-S-Co(6)	69.4 (1)
Co(2)-S-Co(5)	107.2 (2)	Co(3)-S-Co(5)	69.9 (1)				
		Co-C-O Angles					
Co(1)-C(1)-O(1)	175.0 (1.8)	Co(2)-C(5)-O(5)	143.2 (1.3)	Co(4)-C(8)-O(8)	177.5 (1.8)	Co(5)-C(12)-O(12)	137.1 (1.4)
Co(1)-C(2)-O(2)	177.7 (1.8)	Co(3)-C(5)-O(5)	134.7 (1.3)	Co(4)-C(9)-O(9)	175.6 (2.0)	Co(6)-C(12)-O(12)	142.1 (1.5)
Co(1)-C(3)-O(3)	127.6 (1.5)	Co(3)-C(6)-O(6)	179.3 (1.9)	Co(4)-C(10)-O(10)	133.7 (1.4)	Co(6)-C(13)-O(13)	176.5 (1.8)
Co(2)-C(3)-O(3)	154.9 (1.7)	Co(3)-C(7)-O(7)	156.9 (1.8)	Co(5)-C(10)-O(10)	147.1 (1.4)	Co(1)-C(14)-O(14)	130.9 (1.4)
Co(2)-C(4)-O(4)	174.1 (1.7)	Co(4)-C(7)-O(7)	126.9 (1.6)	Co(5)-C(11)-O(11)	172.3 (1.7)	Co(6)-C(14)-O(14)	152.3 (1.6)

$\text{Co}_4(\text{CO})_{10}\text{S}_2$.²³ The distance of S from the Co_4 plane is identical in both cases (1.37 Å) whereas the Co-S bonds are little longer in complex VI than in $\text{Co}_4(\text{CO})_{10}\text{S}_2$ (2.29 (average) vs. 2.26 Å (average)).

The C_2 Unit. The dicarbido C_2 unit is bonded to the Co_6 cluster via two short (1.81 Å (average)) bonds to the apical Co atoms and four long (2.01 Å (average)) bonds to the basal Co atoms. The long bond distance is greater than the mean Co-C value reported for Co_3C clusters²⁵ and lies in the range of the formally single Co-CH₃ bond in methylcobaloximes (1.990–2.026 Å).²⁶ The short bond distance has the same order of magnitude as the Co-CO (terminal) distance, indicating a partial double-bond character.

The C-C distance (1.37 Å) is close to the mean C-C double-bond value (1.33 Å) and significantly shorter than the dicarbido distance reported for $\text{Rh}_{12}(\text{C}_2)(\text{CO})_{25}$ (1.48 Å)⁴ and for $[\text{Co}_{11}(\text{C}_2)(\text{CO})_{22}]^{3-}$ (1.62 Å).³ In the last complexes, however, the C_2 unit is encapsulated in a cavity of the metal cluster and the C-C bond is elongated to allow efficient metal-carbon bonding interactions.

The four-atom chain $\text{Co}_{\text{ap}}\text{-C-C-Co}_{\text{ap}}$ lies on a plane²⁷ with significant π -electron delocalization, showing a formal resemblance to the C_4 *cis*-butadiene chain. The plane is inclined (81°) with respect to the Co_4 plane as a consequence of the slight asymmetry of the cluster.¹⁹

The Co_6C_2 framework could be viewed as deformation of two well-known Co_6 structures, i.e. of a trigonal-prismatic array in which a C_2 unit is inserted by breaking an edge, or of an eclipsed rotamer of **1** in the way that the Co_3C pyramids tilt to bring two pairs of their cobalt atoms into a bonding distance, to form a new Co_4 square. The latter view is supported by the close relationships between VI and **1** (e.g.: C-C bond length, 1.37 Å (VI) vs. 1.37 Å (1); Co-C bond length, 1.94 Å (average) (VI) vs. 1.96 Å (average) (1), etc.), which indicate very similar bonding interactions. However, as the C_2 unit is bonded only to cobalt atoms, complex VI, according to the suggested nomenclature,¹ appears to be the first example of an exposed metal carbonyl dicarbido cluster, and on the basis of the structure of the Co_6 framework, it can be a proper model of a surface defect in which a C_2 unit is adsorbed. Furthermore, the observation that the only source of carbon atom to form VI are C_1 molecules (CO or CS_2) suggests that the formation of C_2 bonded to a metal array can be seen as a model of the initial step of reaction paths in a Fischer-Tropsch synthesis by which carbon is deposited on the catalyst surface.²⁸

The CO Groups. The eight terminal CO groups have the normal values of the C-O and Co-C bond distances and of the Co-C-O bond angles, whereas the six bridging CO's show a variety of arrangements. The bridging CO groups are

usually divided into symmetric, asymmetric, and semibridging types, on the basis of the difference in M-C bond lengths and in M-C-O angles. Even though these types are not distinct but rather merge into one another, the use of well-documented criteria²⁹ would allow us to classify CO(12) as symmetric, CO(5) and CO(10) as asymmetric, and CO(3), CO(7), and CO(14) as semibridging carbonyl groups. Two suggestions, not necessarily opposed to each other, have been made to explain the absence of symmetry in the CO coordination. On one hand, the importance of the asymmetric CO groups to neutralize unequal charge distribution between electronically nonequivalent metal atoms has been pointed out.³⁰ On the other hand,²⁹ the effect of crystal-packing forces on the configuration of the bridging CO's has been cited.

In our compound CO(5) and CO(12) are bonded to a pair of electronically equivalent Co atoms and are expected to be symmetric, but only CO(12) is so, CO(5) showing a small distortion, which could just be the result of packing forces as well as minor electronic differences. The other CO's are bonded to nonequivalent cobalt atoms and have the same local asymmetry, i.e. the bond to the apical Co is longer than that to the corresponding basal Co. Nevertheless the distortion of CO(10) is markedly lower than that of the others, being comparable to that of CO(5). We conclude that the electronic factors may have some bearing on the shape of the bridging CO's but that the effect of the packing steric forces is also present, in particular to explain the degree of asymmetry of CO(5) and CO(10). We return to this point in the paragraph dealing with the infrared spectra of the bridging CO region.

Infrared Spectra

I. Vibrations of the $\text{Co}_6\text{C}_2\text{S}$ Cluster Core. The nine-atom cluster $\text{Co}_6\text{C}_2\text{S}$ has 21 normal modes, of which 4 belong to the IR-inactive species A_2 , according to the species distribution

$$\Gamma = 7 A_1 + 4 A_2 + 6 B_1 + 4 B_2$$

These modes can roughly be divided into the following categories: C-C stretches, Co-C stretches, Co-S stretches, and Co-Co stretches. All "stretching" displacements are inevitably connected with some kind of deformation, due to the closed polyhedron structure, which does not allow "pure" stretching modes of "separated" bonds. The only pure stretching mode could be envisaged as a "breathing" of the entire cluster; this type of vibration, surely existing with homoatomic clusters, cannot, however, occur in this case without angle deformation, owing to the difference in mass of atoms that cause one or another type of bond to dominate the vibration in different frequency regions.

A precise and correct vibrational analysis that could have given a quantitative picture about the real form of the vibrational modes of the cluster is precluded not only because of the lack of Raman data (since we did not succeed in obtaining the Raman spectrum of the greenish black crystalline substance) but also as a consequence of the overlap of a part of the cluster skeletal vibrations with the carbonyl vibrations

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(27) The equation of the plane is $6.12X + 11.83Y - 3.26Z - 5.66 = 0$ for fractional coordinates, and the distances (Å) from the plane are respectively as follows: Co(1), -0.0004 (43); Co(4), 0.0005 (43); C(15), 0.011 (27); C(16), -0.011 (27) with $\chi^2 = \sum(d/\sigma)^2 = 0.33$.

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Table IV. Comparison between $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}$ and Metallic Cobalt Lattice (Fccub and Hcp): Bond Lengths (Å) and Angles (deg) in the Co_6 "Boat"

structural parameters ^a	complex	metallic Co
Co(b)-Co(b) dist	2.60 (av)	2.50 (av)
Co(b)-Co(a) dist	2.52 (av)	
Co(b)-Co(a)-Co(b) angle	62.2 (av)	60.0
Co(b)-Co(b)-Co(b) angle	90.0 (av)	90.0
Co(a)-Co(b)-Co(b) angle	58.9 (av)	60.0
dihedral angle between triangular and square planes	122 (av)	125

^a Co(a) and Co(b) indicate the apical and the basal Co atoms of the "boat", respectively.

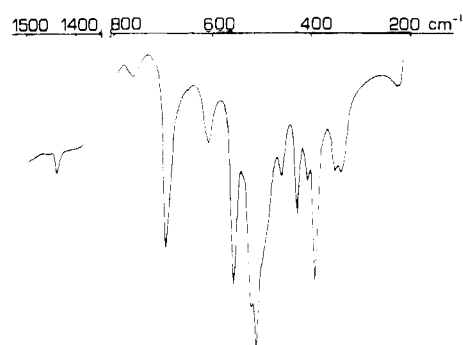


Figure 4. IR spectrum of $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}$ in the 1500–200- cm^{-1} region (CsI disk).

in the 600–300- cm^{-1} region, which renders the calculational separation of these modes futile.

With these limitations in mind we propose the following assignments for the bands observed in the spectral region between 1500 and 200 cm^{-1} .

There is a weak band at 1444 cm^{-1} (Figure 4), which we assign to the C–C stretching vibration (species A_1). This mode has, of course, also some admixture of $\nu(\text{Co}-\text{C})$ character, and in this way it can have a slight dipole moment component in the direction of the z axis. The frequency value is intermediate between the zones of the single and double C–C bonds. The same type of vibration in **1** is Raman active only, and its frequency is unknown. Unfortunately, we did not succeed either in obtaining the Raman spectrum of **1**; hence there is, at the moment, no basis for the comparison of the $\nu(\text{C}-\text{C})$ frequency of the title compound with those of other related compounds.

As we proceed with the assignment of the bands toward decreasing energies, the weak broad band at 760 cm^{-1} is probably a combination band (or, less probably a Co–C stretching mode). The strong band at 698 cm^{-1} surely belongs to a vibration of dominating $\nu(\text{Co}-\text{C})$ character. The high intensity suggests that it should be assigned to a B_1 mode in which an essentially rigid C_2 entity vibrates longitudinally relative to the "boat". Also, the band of medium intensity at 610 cm^{-1} must belong to a $\nu(\text{Co}-\text{C})$ mode. It could belong to either species A_1 or B_2 . (The species distribution of the "Co–C stretching" modes is $2 A_1 + 2 B_1 + A_2 + B_2$. Hence we see, with certainty, only two of the five IR-active modes of this character.)

The bands of $\delta(\text{Co}-\text{C}-\text{O})$ character between 557 and 337 cm^{-1} surely mix and overlap strongly with the absorptions belonging to the other Co–C stretching modes and even with those belonging to the $\nu(\text{Co}-\text{CO})$ modes, owing to the presence of different types of CO bridges (vide infra).

The very weak band at ca. 230 cm^{-1} is one of the $\nu(\text{Co}-\text{S})$ stretching modes, presumably the A_1 mode. This value is lower than most of the Co–S stretching frequencies reported for M_3S pyramids,³¹ but this is in agreement with the higher Co–S

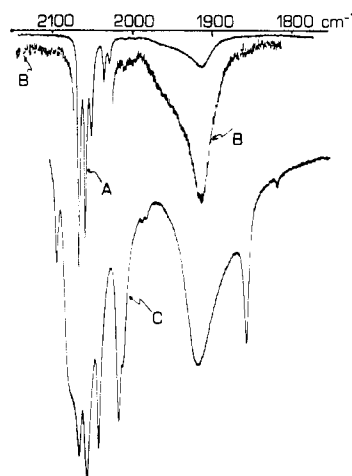


Figure 5. IR spectra of $\text{Co}_6\text{C}_2(\text{CO})_{14}\text{S}$ in the CO stretching region: (A) *n*-heptane saturated solution, 1 mm KBr, background subtracted; (B) as in (A), with 5-fold ordinate expansion; (C) KBr disk.

distances found in this compound.

II. C–O Stretching Vibrations. (a) Terminal Region. We have the following representation for the eight *terminal* C–O stretching modes:

$$\Gamma = 3 A_1 + A_2 + 3 B_1 + B_2$$

i.e., there are seven IR-active modes. The spectrum obtained in a hexane solution (Figure 5) shows that five of them have high or medium intensities, at 2065.5, 2057.5, 2050.0, 2034.5, and 2028.0 (± 0.5) cm^{-1} . A sixth terminal C–O stretching frequency at 2094 cm^{-1} can be added from the solid-state spectrum and assigned, with confidence, to the totally symmetric in-phase (A_1) mode. It is known from previous studies³² that (a) the frequency of this mode is varied only very slightly when the solid-state and solution values are compared and (b) crystal effects increase the intensity of this band or even make it IR active in several cases when idealized molecular point group symmetry predicts an inactive species for this mode.

There is, in addition, a very weak band at ca. 2008 cm^{-1} , observed only with ordinate expansion (demanded by the very low solubility of the title compound in alkanes). However, this is presumably a ^{13}C -isotopic band.

There are two vibrational forms that are probable candidates for being assigned to the two strongest bands at 2065.5 and 2057.7 cm^{-1} : (i) an A_1 mode in which the four apical CO groups stretch in phase and the four basal ones stretch out of phase and (ii) a B_1 mode in which the four CO groups of half of the molecule vibrate in phase, but opposite to the groups of the other half. (The plane of symmetry dividing the molecule into halves is, in this case, the one passing through the S atom and the midpoint of the C–C bond, perpendicular to this bond.)

There is a certain analogy between these vibrational forms with those found in a detailed vibrational study of some $\text{M}_4(\text{CO})_{12}$ cluster compounds of C_{3v} symmetry.³³

The third band in the central group, at 2050 cm^{-1} , can be assigned to the single B_2 mode, in which only the basal CO groups vibrate, in an antisymmetric manner relative to the plane passing through the S and the two apical Co atoms (and their corresponding four CO groups, which, however, are not involved in this mode, for symmetry reasons).

The two lower energy weaker bands, plus the seventh mode (which probably has near-zero intensity according to a dipole

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moment canceling mechanism discussed previously³⁴), then share the remaining three modes.

The shoulder at about 2077 cm⁻¹ shown by the solid-state spectrum is the consequence of a crystal effect, similar to the analogous features observed for the M₃(CO)₁₂ (M = Ru, Os) compounds. The explanation of its origin is not yet clear.

(b) CO Bridges. The region 1990–1800 cm⁻¹ of the spectrum of complex VI shows a very peculiar pattern. In solution we obtain an extremely broad asymmetric band centered at ca. 1913 cm⁻¹, with a shoulder around 1950 cm⁻¹. For alkane solutions a broad band like this is very unusual. It slightly reminds us of the band in the spectrum of Fe₃(CO)₁₂; however, in that case the intensity of the broad band relative to that the terminal bands is considerably lower than in the present case.³⁵

The bridging region of the spectrum in the solid state is, to our best knowledge, unprecedented in its pattern (Figure 5). Besides a broad band centered at 1918 cm⁻¹, there is also a sharp band present (of a "normal" metal carbonyl band shape) at 1858 cm⁻¹. A weak isotopic band at 1819 cm⁻¹ completes the pattern. The ratio of the integrated intensities of the two bands is approximately 5:1, and the frequency ratio 1819/1858 = 0.979 differs only by 0.2% from the "practical" isotopic frequency ratio of a monocarbonyl.³⁶ Hence the spectrum suggests a CO-bridge system in which one particular bridge is a "regular" one (concerning band form and frequency) whereas the other five bridges are in some sort of asymmetric or semibridging form,²⁹ exerting probably a fast fluctuation or another "averaging" mechanism from which the broadness of the absorption arises.

In this way the IR spectrum confirms the structural results in which only one bridging ligand, viz. CO(12), has been found to be in an essentially symmetrical position. The ligand CO(5), which should be the mirror-plane-related counterpart of CO(12) in an idealized C_{2v} symmetry, shows substantial distortions from the symmetrical position: there is a difference of 8.5°

of the two Co–C–O angles and of 0.10 Å of the two Co–C distances. (The corresponding values in the "symmetric" CO(12) are 5° and 0.03 Å, respectively). In the case of the four strongly asymmetric bridges bonded between the apical cobalt atoms and the basal ones, the degree of asymmetry expressed in terms of differences of the two Co–C–O angles and Co–C distances (in parentheses) associated with each bridge is as follows: Co(3), 27.3° (0.29 Å); CO(7), 30.9° (0.43 Å); CO(10), 13.4° (0.08 Å); CO(14), 21.4° (0.29 Å).

If we keep these peculiarities in mind, a comparison of the IR spectroscopic data with the structural ones suggests the following statements:

(1) The difference of ca. 9° between the two geminal Co–C–O angles, plus a difference of 0.1 Å of the Co–C distances, puts a CO bridge into the category of asymmetric bridges whereas a difference of ca. 5° (combined with essentially equal Co–C distances) does not.

(2) The difference between symmetric and asymmetric CO bridges shows a continuous transition in terms of X-ray diffraction structural data, but the same difference represents qualitatively distinct categories with characteristic frequency differences for the infrared absorption.

(3) If there are differently asymmetric CO bridges in the same molecule, these do not give rise to separate, distinct absorption bands reflecting the great differences in the asymmetry, but rather the absorption owing to asymmetric bridges merge together into an extremely broad band.

(4) The present structure seems to be the first example for two distinctly different types of origin for CO-bridge asymmetry in the same molecule, viz. the one due to the electronic nonequivalence of bridged metal atoms and the one due to the asymmetry imposed by crystal-packing effects upon one of the two bridges that are in electronically equivalent positions.^{29,30}

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Supplementary Material Available: Listings of observed and calculated structure factors and thermal anisotropic parameters and a figure of the packing in an unit cell (11 pages). Ordering information is given on any current masthead page.

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