C27	0.4422 (9)	0.2589 (15)	−0.0049 (14)	0.078 (6)
C28	0.4902 (9)	0.3070 (15)	−0.0068 (14)	0.080 (6)
C29	0.5156 (8)	0.3845 (14)	0.0422 (14)	0.068 (5)
C30	0.4906 (7)	0.4194 (12)	0.0980 (11)	0.055 (4)
C31	0.4332 (5)	0.5275 (10)	0.2125 (9)	0.035 (3)
C32	0.4551 (7)	0.5472 (11)	0.2969 (10)	0.050 (4)
C33	0.4737 (8)	0.6400 (14)	0.3308 (13)	0.069 (5)
C34	0.4686 (7)	0.7119 (13)	0.2688 (12)	0.062 (5)
C35	0.4446 (8)	0.6941 (13)	0.1822 (12)	0.064 (5)
C36	0.4267 (7)	0.5981 (12)	0.1536 (11)	0.058 (4)
C37	0.5143 (5)	−0.0167 (10)	0.3088 (9)	0.036 (3)
C38	0.5579 (6)	−0.0638 (11)	0.2946 (10)	0.048 (4)
C39	0.5950 (7)	−0.1231 (12)	0.3567 (11)	0.057 (4)
C40	0.5862 (8)	−0.1431 (14)	0.4287 (12)	0.065 (5)
C41	0.5418 (7)	−0.1010 (12)	0.4411 (11)	0.057 (4)
C42	0.5039 (6)	−0.0340 (11)	0.3808 (10)	0.044 (4)
C43	0.3037 (6)	−0.0822 (11)	0.1834 (10)	0.043 (3)
C44	0.2477 (7)	−0.1175 (11)	0.1334 (10)	0.046 (4)
C45	0.2315 (7)	−0.2101 (11)	0.1471 (11)	0.052 (4)
C46	0.2715 (7)	−0.2654 (12)	0.2111 (11)	0.053 (4)
C47	0.3252 (8)	−0.2306 (13)	0.2622 (12)	0.061 (5)
C48	0.3408 (7)	−0.1391 (11)	0.2458 (10)	0.050 (4)
C49	0.2602 (6)	0.1017 (10)	0.1085 (10)	0.043 (3)
C50	0.2195 (7)	0.1078 (11)	0.1464 (10)	0.049 (4)
C51	0.1700 (8)	0.1653 (13)	0.1121 (12)	0.062 (5)
C52	0.1619 (7)	0.2188 (13)	0.0400 (11)	0.059 (4)
C53	0.2031 (7)	0.2144 (12)	−0.0010 (11)	0.058 (4)
C54	0.2526 (7)	0.1527 (11)	0.0347 (10)	0.049 (4)
Cl1	0.4174 (3)	−0.1682 (5)	0.4840 (5)	0.111 (2)
Cl2	0.3015 (3)	−0.1663 (5)	0.4767 (5)	0.108 (2)
Cl3	0.1217 (4)	−0.0654 (7)	0.1935 (7)	0.163 (3)
Cl4	0.1438 (4)	−0.1164 (7)	0.3629 (7)	0.165 (4)
C55	0.3740 (11)	−0.1209 (18)	0.5321 (16)	0.103 (8)
C56	0.1513 (20)	−0.1556 (33)	0.2788 (32)	0.225 (20)
B1	0.3608 (4)	0.0656 (7)	0.8486 (6)	0.153 (3)
F1	0.3348 (6)	0.0867 (10)	0.9031 (8)	0.153 (3)
F2	0.4172 (4)	0.0400 (10)	0.8923 (8)	0.153 (3)
F3	0.3321 (6)	−0.0082 (8)	0.7982 (8)	0.153 (3)
F4	0.3592 (6)	0.1439 (8)	0.8007 (8)	0.153 (3)

Table 2. Geometric parameters (Å, °)

Pt2—Pt1	2.867 (1)	C31—P1	1.835 (14)
P1—Pt1	2.211 (4)	C18—P2	1.870 (16)
P3—Pt1	2.312 (4)	C43—P2	1.808 (15)
O1—Pt1	2.137 (8)	C49—P2	1.840 (15)
C8—Pt1	2.063 (13)	C1—P3	1.830 (14)
P2—Pt2	2.206 (4)	C13—P3	1.805 (14)
P4—Pt2	2.318 (3)	C19—P3	1.845 (15)
O1—Pt2	2.153 (9)	C7—P4	1.833 (14)
C2—Pt2	2.062 (13)	C16—P4	1.809 (15)
C15—P1	1.862 (15)	C37—P4	1.837 (14)
C25—P1	1.814 (15)		
P1—Pt1—Pt2	128.4 (1)	O1—Pt2—Pt1	47.8 (2)
P3—Pt1—Pt2	83.0 (1)	O1—Pt2—P2	173.2 (2)
P3—Pt1—P1	94.3 (1)	O1—Pt2—P4	88.3 (2)
O1—Pt1—Pt2	48.3 (2)	C2—Pt2—Pt1	93.2 (4)
O1—Pt1—P1	176.0 (2)	C2—Pt2—P2	93.2 (4)
O1—Pt1—P3	87.7 (2)	C2—Pt2—P4	168.9 (4)
C8—Pt1—Pt2	93.6 (4)	C2—Pt2—O1	82.4 (4)
C8—Pt1—P1	91.8 (4)	C1—P3—Pt1	112.6 (4)
C8—Pt1—P3	173.9 (4)	C7—P4—Pt2	114.2 (5)
C8—Pt1—O1	86.2 (4)	Pt2—O1—Pt1	83.9 (3)
P2—Pt2—Pt1	127.8 (1)	C2—C1—P3	120.2 (10)
P4—Pt2—Pt1	84.8 (1)	C8—C7—P4	121.4 (10)
P4—Pt2—P2	96.7 (1)		

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55990 (36 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1032]

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Structure of the Trigonal Phase of Bis(methinyltricobaltenneacarbonyl), [CCo₃(CO)₉]₂

Urs Geiser and Aravinda M. Kini

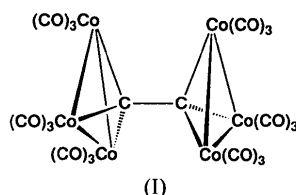Chemistry and Materials Science Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA

Abstract

A second, trigonal, phase of $[CCo_3(CO)_9]_2$, μ_6-dicarbide-$1{:}2{:}3\kappa^3 C^1;4{:}5{:}6\kappa^3 C^2$-hexakis(tricarbonylcobalt)-(6 Co—Co), has been found, in addition to the monoclinic one reported earlier [Brice & Penfold (1972). Inorg. Chem. 11, 1381-1384]. The intermolecular geometry of the molecule in the two crystallographic modifications is virtually the same. The two Co_3 triangles are twisted by ca 28° with respect to each other, indicating a conformation between staggered and eclipsed. Optically active crystals of the trigonal phase form by spontaneous resolution of the enantiomorphic conformers.

Comment

One of the methods of preparing substituted tetra-thiafulvalenes as precursors for the electrochemical synthesis of organic conductors or superconductors consists of the coupling of the corresponding substituted 1,3-dithiole-2-thione with a metal carbonyl [for a recent overview, see Williams, Ferraro, Thorn, Carlson, Geiser, Wang, Kini & Whangbo (1992)]. In such an attempt to couple 1,2,5-thiadiazolo[3,4-d]-[1,3]dithiole-2-thione to form bis(1,2,5-thiadiazolo)-tetrathiafulvalene with $Co_2(CO)_8$ in refluxing toluene (Le Coustumer & Mollier, 1980), black distorted-octahedral crystals were formed. A crystal structure analysis was undertaken in order to identify the product, which proved to be a new crystallographic modification of $[CCo_3(CO)_9]_2$ (I). None of the desired tetrathiafulvalene product formed, indicating that $Co_2(CO)_8$ either reacts directly with the thia-diazole side group, or that the π-electron withdrawing nature of the thiadiazole group leads to a shift in the stability of the reaction intermediates and thus to different products. $[CCo_3(CO)_9]_2$ was first synthesized by Allegra, Mostardini Peronaci & Ercoli

(I)

(1966), who pointed out its sparingly soluble nature and great stability. The crystal structure of the monoclinic (space group $C2/c$) phase of $[CCo_3(CO)_9]_2$ was described by Brice & Penfold (1972).

As in the earlier crystallographic study, the molecules possess approximately 32 symmetry, but are located on a twofold rotation axis. In the trigonal modification, all molecules in the crystal adopt the same handedness; thus the system exhibits spontaneous resolution of the conformational enantiomers. The intramolecular geometry of both modifications is virtually the same, considering the somewhat limited accuracy of the earlier structure determination (see Tables 2 and 3). The central C—C bond is somewhat shorter than a single bond, indicating limited hybridization. However, it is 0.06 Å longer than that found in the other modification. The apparent difference may result from the better experimental data and the fully anisotropic refinement of the present structure, rather than reflect a true chemical difference.

The axial Co—CO bonds are slightly longer than the equatorial ones; a result of the *trans* position of the axial ligands with respect to the Co—C(bridge)

bond. As in the monoclinic modification, the conformation of the Co_3 triangles is neither eclipsed (torsion angles 0°) nor staggered (torsion angles 60°): the non-equivalent *cis*-torsion angles are 29.5 (6) and 26.4 (1.1)° for Co1—C—C—Co3 and Co2—C—C—Co2, respectively. No such angles are given by Brice & Penfold (1972), but from their Fig. 2, a similar value of *ca* 30° can be deduced.
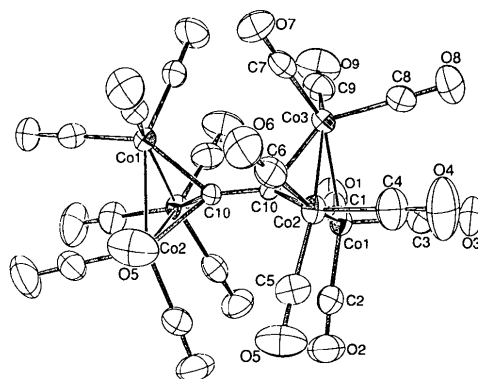

Fig. 1. View of $[CCo_3(CO)_9]_2$ showing 50% probability ellipsoids for all atoms. Atomic labels are shown for one unique half of the molecule and for a few selected atoms for the other half. A twofold rotation axis approximately along the normal to the drawing plane intersects the molecule.

Experimental

Crystal data

$[Co_6(C_2)(CO)_{18}]$	Mo $K\alpha$ radiation
$M_r = 881.8$	$\lambda = 0.7107$ Å
Trigonal	Cell parameters from 25
$P3_121$	reflections
$a = 9.710$ (2) Å	$\theta = 10$–12°
$b = 9.710$ (2) Å	$\mu = 3.546$ mm^{-1}
$c = 25.746$ (6) Å	$T = 295$ (2) K
$V = 2102.2$ (8) Å^3	Distorted octahedron
$Z = 3$	$0.3 \times 0.3 \times 0.3$ mm
$D_x = 2.090$ Mg m^{-3}	Black

Data collection

Nicolet $P3/F$ diffractometer	$R_{int} = 0.035$
ω scans of width 1.2° and	$\theta_{max} = 25.0°$
rate 2–12° min^{-1}	$h = -11 \rightarrow 5$
Absorption correction:	$k = -5 \rightarrow 11$
by integration from crystal	$l = -2 \rightarrow 30$
shape	3 standard reflections
$T_{min} = 0.487$, $T_{max} =$	monitored every 96
0.533	reflections
4789 measured reflections	intensity variation: <2%
1475 independent reflections	
1268 observed reflections	
$[F > 4\sigma(F)]$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.10$
Final $R = 0.025$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
$wR = 0.023$	$\Delta\rho_{min} = -0.26$ e Å^{-3}
$S = 0.948$	Atomic scattering factors
1268 reflections	from *International Tables*
199 parameters	*for X-ray Crystallography*
$w = \sigma^{-2}(F)$	(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co1	0.71565 (9)	0.11919 (10)	0.64571 (3)	0.0363 (3)
Co2	0.86331 (9)	0.01154 (9)	0.59985 (3)	0.0385 (3)
Co3	0.92161 (9)	0.28451 (9)	0.58225 (3)	0.0387 (3)
C1	0.6994 (7)	0.2716 (8)	0.6797 (2)	0.050 (3)
O1	0.6870 (6)	0.3664 (6)	0.7012 (2)	0.087 (3)
C2	0.6251 (8)	−0.0285 (8)	0.6954 (2)	0.048 (3)
O2	0.5608 (6)	−0.1212 (6)	0.7262 (2)	0.074 (2)
C3	0.5493 (7)	0.0513 (8)	0.6000 (2)	0.049 (3)
O3	0.4493 (5)	0.0122 (6)	0.5708 (2)	0.068 (2)
C4	0.7246 (9)	−0.0912 (9)	0.5472 (2)	0.069 (3)
O4	0.6385 (7)	−0.1563 (7)	0.5139 (2)	0.124 (4)
C5	0.8108 (8)	−0.1541 (8)	0.6415 (2)	0.056 (3)
O5	0.7750 (7)	−0.2619 (6)	0.6666 (2)	0.095 (3)
C6	1.0383 (8)	0.0239 (7)	0.5716 (2)	0.054 (3)
O6	1.1460 (6)	0.0298 (7)	0.5532 (2)	0.083 (3)
C7	1.1140 (8)	0.3590 (8)	0.5521 (2)	0.049 (3)
O7	1.2345 (5)	0.4099 (6)	0.5329 (2)	0.069 (2)
C8	0.7981 (8)	0.2410 (8)	0.5241 (2)	0.057 (3)
O8	0.7221 (6)	0.2137 (7)	0.4879 (2)	0.094 (3)
C9	0.9395 (9)	0.4726 (9)	0.5994 (2)	0.063 (3)
O9	0.9489 (7)	0.5903 (6)	0.6081 (2)	0.101 (3)
C10	0.9424 (6)	0.1929 (6)	0.6463 (2)	0.028 (2)

Table 2. Geometric parameters (Å, °)

Co1—C2	1.791 (6)	Co3—C8	1.832 (6)
Co1—C1	1.792 (6)	Co3—C10	1.932 (5)
Co1—C3	1.834 (6)	C1—O1	1.132 (7)
Co1—C10	1.946 (5)	C2—O2	1.126 (7)
Co1—Co3	2.457 (1)	C3—O3	1.134 (6)
Co1—Co2	2.458 (1)	C4—O4	1.142 (7)
Co2—C5	1.782 (7)	C5—O5	1.127 (7)
Co2—C6	1.796 (7)	C6—O6	1.123 (7)
Co2—C4	1.818 (7)	C7—O7	1.130 (7)
Co2—C10	1.941 (5)	C8—O8	1.134 (7)
Co2—Co3	2.460 (1)	C9—O9	1.123 (8)
Co3—C9	1.801 (8)	C10^i—C10	1.426 (9)
Co3—C7	1.807 (7)		
C2—Co1—C1	95.9 (3)	C9—Co3—C7	98.2 (3)
C2—Co1—C3	100.3 (3)	C9—Co3—C8	98.9 (3)
C2—Co1—C10	107.5 (3)	C9—Co3—C10	106.1 (2)
C2—Co1—Co3	155.8 (2)	C9—Co3—Co1	97.7 (2)
C2—Co1—Co2	99.2 (2)	C9—Co3—Co2	154.3 (2)
C1—Co1—C3	100.6 (3)	C7—Co3—C8	99.6 (3)
C1—Co1—C10	104.1 (2)	C7—Co3—C10	103.1 (2)
C1—Co1—Co3	99.4 (2)	C7—Co3—Co1	152.7 (2)
C1—Co1—Co2	153.7 (2)	C7—Co3—Co2	98.4 (2)
C3—Co1—C10	140.3 (2)	C8—Co3—C10	143.1 (3)
C3—Co1—Co3	95.2 (2)	C8—Co3—Co1	99.7 (2)
C3—Co1—Co2	97.8 (2)	C8—Co3—Co2	97.5 (2)
C10—Co1—Co3	50.4 (1)	C10—Co3—Co1	50.9 (2)
C10—Co1—Co2	50.7 (1)	C10—Co3—Co2	50.7 (1)
Co3—Co1—Co2	60.07 (3)	Co1—Co3—Co2	59.99 (3)
C5—Co2—C6	97.9 (3)	O1—C1—Co1	179.1 (6)
C5—Co2—C4	98.9 (3)	O2—C2—Co1	176.3 (6)
C5—Co2—C10	104.6 (2)	O3—C3—Co1	178.0 (5)
C5—Co2—Co1	97.5 (2)	O4—C4—Co2	179.2 (7)
C5—Co2—Co3	153.0 (2)	O5—C5—Co2	177.9 (6)
C6—Co2—C4	98.7 (3)	O6—C6—Co2	178.7 (6)

C6—Co2—C10	104.9 (3)	O7—C7—Co3	177.9 (6)
C6—Co2—Co1	154.1 (2)	O8—C8—Co3	179.6 (7)
C6—Co2—Co3	98.8 (2)	O9—C9—Co3	177.2 (6)
C4—Co2—C10	143.7 (3)	C10^i—C10—Co3	133.5 (4)
C4—Co2—Co1	99.3 (2)	C10—C10—Co2	133.3 (2)
C4—Co2—Co3	99.3 (2)	C10—C10—Co1	132.2 (5)
C10—Co2—Co1	50.9 (2)	Co3—C10—Co2	78.8 (2)
C10—Co2—Co3	50.4 (1)	Co3—C10—Co1	78.6 (2)
Co1—Co2—Co3	59.94 (3)	Co2—C10—Co1	78.4 (2)

Symmetry code: (i) $2 - x, 1 - x + y, \tfrac{4}{3} - z$.

Table 3. Average lengths of chemically equivalent bonds (Å)

Carbonyl groups 3, 4 and 8 are axial, the remainder are equatorial.

Bond type	Average	R.m.s. deviation	Range	Monoclinic phase (Brice & Penfold, 1972)
Co—Co	2.458	0.001	2.457–2.460	2.457 (1)
Co—C(bridge)	1.940	0.006	1.932–1.946	1.96 (1)
Co—CO(eq.)	1.795	0.008	1.782–1.807	1.79 (1)
Co—CO(ax.)	1.828	0.007	1.818–1.834	1.79 (1)
C—O(eq.)	1.127	0.003	1.123–1.132	1.13 (1)
C—O(ax.)	1.137	0.004	1.134–1.142	1.15 (1)

The absolute configuration of the data crystal was tested by the following method: the observed data were averaged in the point group 321, to yield 2492 unique allowed reflections [R_{int} = 0.031, 2176 reflections with $F > 4\sigma(F)$]; refinement of 199 variables was carried out in both enantiomorphic space groups:

Space group	R	wR	S
$P3_121$	0.0298	0.0278	1.011
$P3_221$	0.0305	0.0282	1.027

Based on the slightly better agreement factors, space group $P3_121$ was assigned to the chosen data crystal. The achiral synthesis mixture is expected to yield crystals of each space group in equal amounts.

The *UCLA Crystallographic Program Package* (Strouse, 1985) was employed for the data reduction, structure solution and refinement.

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