CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CANTERBURY, CHRISTCHURCH, NEW ZEALAND

Structural Studies of Derivatives of Methinyltricobalt Enneacarbonyls. IV.[1] Crystal Structure of Hexacarbonoctacobalt Tetracosacarbonyl, $Co_8(CO)_{24}C_6$

BY R. J. DELLACA AND B. R. PENFOLD*[2]

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The compound $Co_8(CO)_{24}C_6$ is a minor product of the reaction of $ClCCo_3(CO)_9$ with arenes. Its crystal and molecular structure has been determined by three-dimensional X-ray analysis. Crystals are triclinic of space group $P\bar{1}$ with two molecules in a cell of dimensions $a = 15.08$ (1), $b = 15.49$ (1), $c = 9.079$ (4) Å; $\alpha = 92.6$ (1), $\beta = 92.9$ (1), $\gamma = 104.1$ (1)°. X-Ray data were collected by conventional film techniques using Co Kα radiation and the intensities of 1386 reflections above background were measured photometrically. The structure was refined isotropically by full-matrix least-squares procedures to a conventional R factor of 0.068. The structure is composed of discrete molecules of $Co_8(CO)_{24}C_6$ in which three groups of metal atoms are linked in a novel way. At both ends of the molecule are the well-established $-CCo_3(CO)_9$ groups of the parent compound and these are linked by a four-carbon chain containing two acetylene bonds, one of which forms a bridge with a $Co_2(CO)_6$ group. The nonbridging acetylene bond is 1.19 (3) Å long, and the other C–C bonds are in the range 1.36–1.44 (3) Å. The eight independent Co–Co bonds are in the range 2.447–2.490 (7) Å.

Introduction

From the reaction of chloro- or bromomethinyltricobalt enneacarbonyl with *p*-xylene or mesitylene,[3] the compound $Co_8(CO)_{24}C_6$ can be extracted in low yield from the mixture of products if the temperature is controlled suitably.[1] The other products which have been characterized are $[Co_3(CO)_9C]_2CO$,[4] $[Co_3(CO)_9C]_2$,[5] $Co_5(CO)_{15}C_3H$,[6] and $[Co_3(CO)_9C_2]_2$.[1] All of them have one structural feature in common, the $-CCo_3(CO)_9$ or methinyltricobalt enneacarbonyl group which contains a triangle of bonded Co atoms triply bridged by a carbon. This was first characterized by Sutton and Dahl in $CH_3CCo_3(CO)_9$.[7] In each of the products formed along with the Co_8 compound, the $-CCo_3(CO)_9$ group is linked either to a similar group in one of several ways or to a single $Co_2(CO)_6$ unit. The structure of $Co_8(CO)_{24}C_6$ was clearly of great interest in relation to them.

After this paper was submitted we learned of an independent determination of the molecular structure by Seyferth, Spohn, Churchill, Gold, and Scholer.[8] Their sample was however of a different crystalline form, containing benzene of crystallization, and was prepared in an entirely different way from the reaction of $Co_2(CO)_8$ with hexachlorocylopropane. In this context it is also of interest to note that $Co_8(CO)_{24}C_6$ is found in the mixture of products obtained from the reaction of $Co_2(CO)_8$ with alkyl halides.[1]

Experimental Section

Preparation of $Co_8(CO)_{24}C_6$.[9]—The compound was separated by thin layer chromatography from the other hexane-soluble products of the reaction between $YCCo_3(CO)_9$ (Y = Cl, Br) and *p*-xylene or mesitylene at 120–150° as described earlier.[1] Recrystallization from hexane gave the pure compound as long dark needles and thin plates. The compound is soluble without decomposition in common organic solvents and is stable in air. Thermal decomposition occurs above 60° *in vacuo* so it was not possible to obtain a mass spectrum.

Crystallographic Data.[10]—$Co_8(CO)_{24}C_6$, mol wt 1215.8, is triclinic with $a = 15.083$ (12), $b = 15.489$ (12), $c = 9.079$ (4) Å; $\alpha = 92.6$ (1), $\beta = 92.9$ (1), $\gamma = 104.1$ (1)°; $V = 2051$ Å^3; $d_{obsd} = 2.00$ (3) g/cm^3; $Z = 2$; $d_{calcd} = 1.97$ (1) g/cm^3; μ(Co Kα) = 61.8 cm^{-1}.

As there are two molecules per unit cell, no crystallographic symmetry conditions are imposed on the molecule by either space group $P1$ or $P\bar{1}$. The structure has been refined successfully in space group $P\bar{1}$ with all atoms occupying the general twofold set of equivalent positions.

Unit cell dimensions and their estimated standard deviations were obtained from a least-squares refinement on $\sin^2 \theta$. Input data were the distances between Friedel pairs of reflections on calibrated $h0l$ and $0kl$ precession photographs taken with Polaroid film and Mo Kα radiation (λ 0.7107 Å) at room temperature (20°). The real cell angle γ was determined from the difference in spindle settings for these two levels. The experimental density was obtained using a suitably calibrated density gradient tube with CH_3I and CCl_4 as media.

The crystal used for data collection was plate shaped and of approximate dimensions 0.20 mm × 0.037 mm × 0.25 mm normal to (110), (1$\bar{1}$0), and (001), respectively. X-Ray intensities were recorded at room temperature on a two-dimensionally integrating equiinclination Weissenberg camera using Fe-filtered Co Kα radiation. The plateaus of the integrated spots and adjacent background areas were measured using a single-beam photometer and a galvanometer calibrated to indicate intensities directly. The levels (hkn), with $n = 0$ to -5, were recorded and, within these, intensities were assigned to 1386 reflections judged to be above the threshold of observation. Data were measured out to a Bragg angle of 50°; beyond this, very few reflections had an intensity above background. The intensities of reflections on both halves of the Weissenberg films were measured for nonzero levels. Corrections were made for spot extension[11] while spot contraction was assumed to be corrected by the integration process.

The crystal was remounted to oscillate about [110] and a total of 92 nonzero reflections from the zero and first upper levels in this orientation were measured and processed as for the main data set except that no corrections were necessary for spot extension. Interlevel scale factors for the main data set were obtained[12] after both data sets had been corrected, using the Gaussian quadrature method, for the effects of absorption. Transmission factors ranged from 0.35 to 0.79. In view of the

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(2) To whom inquiries should be addressed.

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(8) D. Seyferth, R. J. Spohn, M. R. Churchill, K. Gold, and F. Scholer, *J. Organometal. Chem.*, **23**, 237 (1970).

(9) The compound was prepared by Dr. B. H. Robinson and Mr. J. L. Spencer. For further details see ref 1.

(10) Here and throughout this paper, the figures given in parentheses are estimated standard deviations in the least significant digits quoted.

(11) D. C. Phillips, *Acta Crystallogr.*, **7**, 746 (1954).

(12) A. D. Rae, *ibid.*, **19**, 683 (1965).

small number of data from the crystal in the second orientation, no attempt was made to merge the two data sets.

Only the 1386 observed reflections were used in the refinement process. Following final refinement, structure factor calculations for the 488 unobserved reflections in the reciprocal lattice region investigated showed that 107 F_o values were greater than $F_{\min}$ and that only four of these were greater than $2F_{\min}$.

All calculations except the final stages of the refinement were carried out on an IBM 360/44 computer with 16K words of core storage. For the final refinement a 360/67 with a large core was available. The programs used have been described in part I of this series.[13]

Structure Solution and Refinement

Intensity statistics for the normalized structure factors indicated that the space group was $P\bar{1}$. Eventually, coordinates for the eight independent cobalt atoms were obtained from analysis of vectors in a sharpened three-dimensional Patterson function. Several electron density difference maps preceded by partial least-squares refinement cycles then revealed all carbon and oxygen atoms.

In all least-squares calculations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where w is the weight assigned to each observation F_o. Initially, all reflections were given unit weights, but in the final stages of refinement, the weights were determined from the empirical formula of Cruickshank[14]

$$w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$$

Coefficients which gave best constancy of average values of the minimized function over the full F_o range at the end of the refinement were $A = 9.3$, $B = 0.7$, $C = -0.005$, and $D = 2.0 \times 10^{-5}$. The usual tabulations of atomic scattering factors[15] for Co, C, and O were used, those for Co only being corrected for anomalous dispersion; values for $\Delta f'$ and $\Delta f''$ of -2.19 and 0.74 electrons, respectively, were interpolated from Cromer's tables.[16]

Because of core storage limitations in our computer, in the initial stages of refinement only 95 parameters could be varied simultaneously so that calculations had to be performed in several blocks. This refinement, with a separate scale factor for each Weissenberg layer, isotropic vibrational parameters, and unit weights converged with R_1 and R_2[17] at 0.091 and 0.101. At this point, the data were corrected for absorption and placed on a common scale as described earlier. With the introduction of the empirical weighting scheme, three cycles of refinement simultaneously varying 248 positional and vibrational parameters and the single scale factor reduced R_1 and R_2 to their final values of 0.068 and 0.088. In the final cycle, maximum parameter shifts as fractions of their esd's were 0.38 for positional parameters and 0.16 for vibrational parameters. A final electron density difference map showed no peak higher than 0.8 e$^-$/Å^3 (roughly one-third of the height of a carbon atom in the structure) and no trough deeper than -0.7 e$^-$/Å^3.

Final positional and vibrational parameters and their esd's (as calculated from the inverse least-squares matrix) are listed in Table I. Observed and calculated structure factor amplitudes for the 1386 reflections used for the refinement are compared in Table II. Examination of these data indicated that a correction for secondary extinction was not warranted.

TABLE I

POSITIONAL AND THERMAL PARAMETERS FOR $Co_8(CO)_{24}C_6$

Atom	x	y	z	B^a
Co(1)	0.4354 (3)	0.2101 (3)	0.3438 (5)	3.4 (1)
Co(2)	0.3820 (3)	0.1787 (3)	0.0834 (5)	3.5 (1)
Co(3)	0.3662 (3)	0.0560 (3)	0.2510 (5)	3.8 (1)
Co(4)	0.1035 (3)	0.1427 (3)	0.1989 (5)	3.6 (1)
Co(5)	0.1546 (3)	0.1760 (3)	0.4614 (5)	3.7 (1)
Co(6)	0.2475 (3)	0.5645 (3)	0.0459 (5)	3.1 (1)
Co(7)	0.3094 (3)	0.6118 (3)	0.3041 (6)	3.8 (1)
Co(8)	0.1425 (3)	0.5695 (3)	0.2440 (5)	3.6 (1)
C(1)	0.313 (2)	0.156 (2)	0.252 (3)	2.8 (6)
C(2)	0.228 (2)	0.175 (2)	0.289 (3)	3.6 (7)
C(3)	0.191 (2)	0.248 (2)	0.292 (3)	2.9 (6)
C(4)	0.211 (2)	0.338 (2)	0.268 (3)	2.2 (6)
C(5)	0.222 (2)	0.415 (2)	0.248 (3)	2.3 (6)
C(6)	0.236 (2)	0.503 (2)	0.224 (3)	3.2 (6)
C(11)	0.437 (2)	0.320 (2)	0.361 (3)	4.8 (8)
C(12)	0.432 (2)	0.187 (2)	0.529 (5)	6.8 (10)
C(13)	0.554 (2)	0.218 (2)	0.320 (4)	6.2 (9)
C(21)	0.366 (2)	0.282 (2)	0.039 (4)	5.3 (8)
C(22)	0.307 (2)	0.114 (2)	−0.063 (4)	5.0 (8)
C(23)	0.491 (3)	0.181 (2)	0.008 (4)	6.4 (9)
C(31)	0.290 (3)	−0.026 (3)	0.139 (5)	8.9 (11)
C(32)	0.337 (3)	0.007 (3)	0.414 (5)	8.1 (11)
C(33)	0.469 (3)	0.022 (3)	0.218 (5)	9.5 (12)
C(41)	0.075 (2)	0.026 (3)	0.189 (4)	6.9 (10)
C(42)	0.118 (2)	0.169 (2)	0.012 (4)	5.6 (9)
C(43)	−0.007 (3)	0.165 (3)	0.213 (5)	8.5 (11)
C(51)	0.063 (3)	0.214 (3)	0.526 (5)	9.7 (13)
C(52)	0.236 (2)	0.236 (2)	0.591 (4)	5.8 (9)
C(53)	0.131 (2)	0.068 (2)	0.526 (4)	6.2 (9)
C(61)	0.352 (3)	0.557 (2)	−0.028 (4)	6.7 (9)
C(62)	0.178 (2)	0.480 (2)	−0.071 (4)	5.1 (8)
C(63)	0.236 (2)	0.663 (2)	−0.035 (4)	4.7 (8)
C(71)	0.424 (2)	0.609 (2)	0.270 (4)	6.4 (9)
C(72)	0.314 (3)	0.578 (3)	0.493 (5)	7.9 (11)
C(73)	0.319 (2)	0.728 (2)	0.309 (4)	5.8 (9)
C(18)	0.116 (2)	0.570 (2)	0.431 (5)	7.3 (11)
C(82)	0.052 (2)	0.481 (2)	0.179 (4)	5.8 (8)
C(83)	0.110 (2)	0.669 (3)	0.196 (4)	7.2 (10)
O(11)	0.434 (1)	0.393 (2)	0.381 (3)	6.8 (6)
O(12)	0.432 (2)	0.171 (2)	0.655 (3)	7.4 (6)
O(13)	0.631 (2)	0.220 (2)	0.309 (3)	8.8 (7)
O(21)	0.354 (1)	0.351 (2)	0.013 (2)	6.0 (5)
O(22)	0.262 (2)	0.076 (2)	−0.158 (3)	7.4 (6)
O(23)	0.559 (2)	0.189 (1)	−0.039 (3)	6.8 (6)
O(31)	0.240 (2)	−0.080 (2)	0.061 (3)	8.9 (7)
O(32)	0.314 (2)	−0.024 (2)	0.528 (3)	8.8 (7)
O(33)	0.537 (2)	0.010 (2)	0.187 (3)	8.7 (7)
O(41)	0.063 (2)	−0.053 (2)	0.188 (3)	9.9 (8)
O(42)	0.129 (2)	0.195 (2)	−0.110 (3)	8.0 (7)
O(43)	−0.077 (2)	0.183 (2)	0.215 (3)	9.7 (8)
O(51)	0.004 (2)	0.246 (2)	0.552 (4)	11.5 (9)
O(52)	0.288 (2)	0.282 (2)	0.679 (3)	7.7 (6)
O(53)	0.115 (2)	−0.005 (2)	0.563 (3)	8.8 (7)
O(61)	0.420 (2)	0.556 (2)	−0.077 (3)	7.5 (6)
O(62)	0.136 (2)	0.423 (2)	−0.152 (3)	6.6 (6)
O(63)	0.225 (1)	0.727 (2)	−0.090 (3)	6.5 (6)
O(71)	0.499 (2)	0.605 (2)	0.253 (3)	7.6 (6)
O(72)	0.314 (2)	0.557 (2)	0.609 (4)	9.2 (8)
O(73)	0.316 (2)	0.803 (2)	0.316 (3)	9.1 (7)
O(81)	0.104 (2)	0.569 (2)	0.552 (4)	9.6 (8)
O(82)	−0.005 (2)	0.420 (2)	0.137 (3)	6.8 (6)
O(83)	0.084 (2)	0.730 (2)	0.159 (3)	8.4 (7)

[a] Isotropic thermal parameter (in Å^2).

Description of Structure and Discussion

In the crystalline state $Co_8(CO)_{24}C_6$ consists of well-separated molecules; the closest intermolecular contact is 3.01 Å. Figure 1 shows a general view of one molecule with all atoms labeled (parentheses have

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[13] M. D. Brice, B. R. Penfold, W. T. Robinson, and S. R. Taylor, *Inorg. Chem.*, **9**, 362 (1970).

[14] D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon, Oxford, 1965, p 114.

[15] "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

[16] D. T. Cromer, *Acta Crystallogr.*, **18**, 511 (1965).

[17] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE II

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES IN ELECTRONS

H	K	OBS	CALC
**** L = 0 ****			
2	0	76	72
4	0	126	129
5	0	60	59
6	0	46	39
7	0	56	55
8	0	47	40
9	0	61	58
10	0	30	31
2	-1	80	76
3	-1	144	150
4	-1	101	109
5	-1	55	46
7	-1	75	74
8	-1	21	22
11	-1	69	67
1	-2	245	297
2	-2	60	54
3	-2	107	107
4	-2	49	44
5	-2	143	160
6	-2	60	55
7	-2	78	79
8	-2	66	68
1	-3	139	155
2	-3	55	47
3	-3	120	117
4	-3	96	93
5	-3	88	81
6	-3	111	108
7	-3	81	79
8	-3	87	81
11	-3	34	32
1	-4	27	25
2	-4	52	52
3	-4	57	50
4	-4	119	120
5	-4	25	24
7	-4	31	30
8	-4	35	37
9	-4	33	33
10	-4	39	42
1	-5	188	202
3	-5	69	72
4	-5	56	57
6	-5	72	77
7	-5	126	133
8	-5	21	19
10	-5	48	45
1	-6	33	35
2	-6	43	44
4	-6	157	162
6	-6	37	38
7	-6	65	62
9	-6	52	58
1	-7	169	155
2	-7	72	72
4	-7	31	36
5	-7	137	144
7	-7	39	38
8	-7	65	70
9	-7	25	26
2	-8	29	29
3	-8	47	55
4	-8	52	57
5	-8	93	94
6	-8	34	37
7	-8	65	74
8	-8	84	85
9	-8	51	52
10	-8	40	45
11	-8	25	20
1	-9	29	26
2	-9	57	57
3	-9	63	50
4	-9	78	78
6	-9	44	47
8	-9	26	30
9	-9	40	41
1	-10	96	99
4	-10	55	52
5	-10	50	51
7	-10	64	70
8	-10	87	95
9	-10	61	66
10	-10	26	29
4	-11	38	35
5	-11	55	56
2	-12	46	48
3	-12	38	37
7	-12	25	27
8	-12	46	59
9	-12	26	28
2	-13	35	32
1	1	119	118
2	1	93	92
3	1	91	84
4	1	33	35
5	1	24	21
6	1	22	23
9	1	23	25
10	1	25	26
11	1	48	45
12	1	45	47
1	2	193	207
2	2	85	87
3	2	57	55
6	2	101	95
7	2	28	29
8	2	32	26
9	2	31	32
10	2	32	33
0	3	151	156
1	3	63	59
2	3	39	37
3	3	45	44
4	3	50	50
6	3	24	22
7	3	35	36
8	3	25	24
10	3	50	44
11	3	29	22
12	3	36	33
1	4	50	52
2	4	92	91
3	4	64	62
4	4	45	37
5	4	70	66
6	4	18	16
7	4	24	16
9	4	63	41
10	4	35	24
11	4	27	23
0	5	245	262
1	5	44	42
2	5	100	101
4	5	50	52
5	5	21	20
6	5	23	25
7	5	22	24
9	5	29	23
11	5	23	24
1	6	55	57
2	6	81	69
3	6	69	64
4	6	35	28
6	6	37	35
9	6	56	52
11	6	45	39
0	7	64	61
1	7	20	19
3	7	77	78
0	8	135	130
4	8	47	47
5	8	25	17
0	9	50	38
2	9	40	40
3	9	33	30
2	10	32	29
2	11	42	33
1	12	61	55
**** L = -1 ****			
-1	0	224	233
-2	0	21	19
-3	0	67	70
-4	0	29	24
-5	0	71	76
-6	0	55	57
-7	0	69	74
-8	0	112	115
1	0	210	215
2	0	51	52
3	0	110	110
4	0	54	59
6	0	91	86
7	0	94	100
8	0	74	75
10	0	28	21
0	-1	100	109
-2	-1	74	81
-3	-1	36	34
-4	-1	98	98
-6	-1	28	34
-7	-1	71	70
-9	-1	27	22
-10	-1	94	94
-11	-1	99	90
-12	-1	44	43
1	-1	50	46
2	-1	126	125
3	-1	124	123
4	-1	172	176
5	-1	278	282
6	-1	115	114
8	-1	80	82
9	-1	38	36
11	-1	42	41
0	-2	130	134
-1	-2	33	31
-2	-2	18	16
-3	-2	16	18
-4	-2	127	130
-5	-2	86	81
-6	-2	100	100
-7	-2	104	103
-8	-2	31	30
-9	-2	61	57
-10	-2	28	24
-12	-2	41	42
1	-2	36	34
2	-2	37	32
3	-2	72	68
4	-2	248	251
5	-2	165	163
6	-2	41	31
7	-2	53	58
8	-2	73	70
9	-2	62	58
10	-2	72	79
0	-3	32	29
-2	-3	23	24
-3	-3	130	134
-4	-3	22	23
-5	-3	25	25
-6	-3	42	40
-8	-3	52	41
-9	-3	37	37
-10	-3	44	45
-11	-3	37	41
1	-3	12	12
2	-3	54	50
3	-3	85	81
4	-3	91	92
5	-3	22	16
7	-3	152	166
8	-3	56	57
9	-3	75	73
10	-3	61	63
0	-4	31	28
-1	-4	67	61
-2	-4	62	60
-3	-4	26	20
-4	-4	114	105
-5	-4	56	53
-6	-4	63	62
-7	-4	22	21
-8	-4	73	71
-9	-4	33	31
-11	-4	77	74
1	-4	32	35
2	-4	16	10
3	-4	28	22
6	-4	33	39
9	-4	85	92
6	-4	32	22
7	-4	41	45
8	-4	25	23
11	-4	78	89
0	-5	20	25
-1	-5	68	66
-2	-5	22	18
-3	-5	27	26
-4	-5	26	28
-6	-5	26	24
-7	-5	66	60
-8	-5	28	21
-9	-5	19	16
1	-5	132	127
2	-5	27	23
3	-5	67	68
4	-5	26	26
5	-5	76	70
6	-5	106	113
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9	-2	68	71
0	-3	93	95
-1	-3	67	65
-3	-3	22	23
-5	-3	62	58
-7	-3	32	37
1	-3	72	70
3	-3	84	86
6	-3	37	47
0	-4	65	75
-1	-4	97	107
-2	-4	42	42
-3	-4	52	45
-5	-4	67	65
1	-4	25	22
2	-4	47	52
3	-4	126	126
4	-4	65	66
5	-4	27	27
7	-4	47	53
0	-5	19	20
-1	-5	35	37
-2	-5	47	43
-3	-5	24	25
-4	-5	30	22
-5	-5	28	32
1	-5	28	29
2	-5	133	146
3	-5	26	26
4	-5	80	87
5	-5	33	34
6	-5	38	38
7	-5	38	38
9	-5	61	62
0	-6	[illegible]	37
-1	-6	47	47
-2	-6	25	24
2	-6	41	40
4	-6	26	28
5	-6	63	65
6	-6	78	92
8	-6	37	40
9	-6	40	39
-1	-7	38	45
-3	-7	35	37
1	-7	47	51
3	-7	113	124
7	-7	49	54
9	-7	37	39
10	-7	44	52
1	-8	29	28
2	-8	37	38
5	-8	35	46
6	-8	44	45
7	-8	61	73
8	-8	31	31
10	-8	34	39
1	-9	32	40
2	-9	49	43
4	-9	53	56
6	-9	38	47
0	-10	42	37
4	-10	48	51
-1	1	27	25
-2	1	129	130
-3	1	18	17
-4	1	42	39
-5	1	51	47
-7	1	34	33
1	1	67	77
2	1	22	23
3	1	82	81
4	1	95	103
5	1	116	119
7	1	53	49
8	1	33	33
0	2	54	61
-1	2	78	66
-2	2	59	47
-3	2	124	117
-6	2	28	32
1	2	118	138
2	2	25	24
4	2	36	29
5	2	60	65
6	2	32	28
7	2	23	23
0	3	88	72
-1	3	76	76
-2	3	92	84
-3	3	41	36
-4	3	60	52
-5	3	83	80
-6	3	106	99
-7	3	41	41
-9	3	30	25
2	3	136	142
4	3	37	37
5	3	24	19
6	3	39	42
-1	4	131	136
-2	4	113	101
-4	4	32	33
-5	4	37	38
-6	4	43	37
-8	4	29	27
2	4	41	41
3	4	25	19
4	4	24	21
6	4	23	27
0	5	49	50
-1	5	19	22
-3	5	46	44
-4	5	42	41
-5	5	84	79
-6	5	89	96
-7	5	32	30
1	5	134	133
2	5	25	30
3	5	57	52
4	5	20	19
5	5	23	22
0	6	20	23
-1	6	78	77
-2	6	81	81
-3	6	68	65
-5	6	24	28
-6	6	57	56
-9	6	67	67
1	6	34	31
2	6	46	46
3	6	23	27
5	6	30	29
6	6	34	34
0	7	35	32
-3	7	45	41
-7	7	53	48
1	7	57	54
3	7	27	27
0	8	90	85
-3	8	38	35
1	8	45	43
2	8	32	26
4	8	30	31
5	8	23	22
6	8	26	20
0	9	47	41
-1	9	50	49
-2	9	88	80
-4	9	74	46
3	9	39	35
5	9	37	34
-3	10	68	65
2	10	55	15
-2	11	50	48
-3	11	66	62
**** L = -5 ****			
-1	0	32	32
-2	0	37	33
-4	0	26	22
-5	0	25	20
-6	0	55	51
2	0	61	63
3	0	61	65
4	0	22	23
5	0	33	43
7	0	55	56
8	0	48	41
9	0	96	95
-2	-1	111	104
-3	-1	35	29
1	-1	21	24
4	-1	91	83
5	-1	44	50
7	-1	60	55
9	-1	71	49
-1	-2	21	27
-2	-2	36	36
-4	-2	18	24
-5	-2	32	29
1	-2	38	17
2	-2	60	54
5	-2	52	51
6	-2	46	40
7	-2	64	66
8	-2	80	79
9	-2	49	51
0	-3	19	24
-2	-3	20	23
-3	-3	52	52
2	-3	66	66
5	-3	44	48
7	-3	28	30
9	-3	77	77
0	-4	57	59
2	-4	31	34
5	-4	23	25
6	-4	65	73
-1	-5	25	23
-3	-5	44	41
-4	-5	54	55
-5	-5	26	21
1	-5	58	58
3	-5	75	80
6	-5	26	25
9	-5	47	45
8	-5	34	41
-2	-6	85	76
4	-6	35	35
5	-6	46	47
6	-6	25	32
7	-6	53	66
8	-6	48	43
-1	-7	32	25
2	-7	52	51
6	-7	57	63
0	-8	31	21
-1	-8	58	54
5	-8	39	41
6	-8	31	39
-1	1	44	54
-2	1	12	16
-3	1	23	19
-6	1	27	26
-7	1	35	34
1	1	12	12
2	1	43	71
3	1	60	53
4	1	59	62
5	1	59	61
6	1	86	89
0	2	103	113
-1	2	60	59
-2	2	52	51
1	2	40	45
2	2	99	97
4	2	47	48
5	2	43	43
6	2	34	28
8	2	56	51
-1	3	22	27
-2	3	76	68
-3	3	39	36
-4	3	47	35
-5	3	55	48
-6	3	37	34
1	3	131	134
2	3	17	18
3	3	24	26
4	3	46	44
5	3	79	75
6	3	30	31
8	3	45	39
0	4	56	56
-2	4	31	20
-3	4	67	59
1	4	49	85
2	4	24	21
4	4	72	71
6	4	24	20
0	5	99	86
-1	5	51	48
-2	5	34	32
-5	5	37	32
-6	5	31	28
-7	5	37	34
2	5	91	94
3	5	24	20
5	5	38	36
6	5	24	25
7	5	42	42
0	6	67	41
-1	6	63	61
-2	6	63	58
-3	6	42	40
3	6	67	66
4	6	28	26
5	6	42	37
6	6	28	26
0	7	78	71
-1	7	67	68
1	7	84	74
4	7	75	69
0	8	60	54
-1	8	66	58
-2	8	46	43
1	8	98	90
4	8	47	41
5	8	39	40
0	9	57	46
-2	9	57	48
-3	9	75	70
1	9	57	54
3	9	45	44
0	10	87	82

been omitted from atom labels for greater diagram clarity but the numbering scheme is the same as in Table I). A different view of the molecule is presented in the form of a stereopair in Figure 2. Bond lengths and angles with their esd's are listed in Tables III and IV, with selected nonbonded contacts in Table V. Although $Co_8(CO)_{24}C_6$ possesses no crystallographic symmetry, there is idealized molecular symmetry C_s-*m* which is well illustrated in Figure 1.

The molecular structure established in our study is essentially the same as for $Co_8(CO)_{24}C_6 \cdot 0.5C_6H_6$ reported by Seyferth, *et al.*,[8] and the only individual bond lengths and angles which differ significantly are those (such as the Co–C(carbonyl) and C–O lengths) which are members of a large chemically equivalent set whose average values do agree. Apart from these the largest individual discrepancy is for the bond length of C(1)–C(2) [1.44 (3) Å in this analysis compared with the 1.37 (3) Å of Seyferth, *et al.*]. We shall not therefore undertake a point by point comparison of the two structures but do include averaged dimensions for each in the comparative Tables VI and VII. (We note that, on the basis of internal consistency of chemically equivalent bond lengths, our structural parameters are generally of higher precision than those reported for $Co_8(CO)_{24}C_6 \cdot 0.5C_6H_6$). In the subsequent discussion our main concern is to relate the $Co_8(CO)_{24}C_6$ structure to other structures containing the $-CCo_3(CO)_9$ group, in general, and to the compounds $[Co_3(CO)_9C_2]_2$[1] and $Co_5(CO)_{15}C_3H$,[6] in particular.

The molecule contains two $-CCo_3(CO)_9$ units of idealized symmetry C_{3v}-$3m$ linked by a chain of four carbon atoms. Within this chain, the acetylene bond

TABLE III

BOND DISTANCES (Å)[a]

Co(1)-Co(2)	2.447 (7)	Co(6)-Co(7)	2.490 (7)
Co(1)-Co(3)	2.453 (7)	Co(6)-Co(8)	2.466 (7)
Co(2)-Co(3)	2.462 (7)	Co(7)-Co(8)	2.468 (7)
	2.454 (7)		*2.475* (*11*)
Co(1)-C(1)	1.95 (4)	Co(6)-C(6)	1.90 (3)
Co(2)-C(1)	1.89 (3)	Co(7)-C(6)	1.87 (3)
Co(3)-C(1)	1.91 (3)	Co(8)-C(6)	1.95 (3)
	1.92 (*3*)		*1.91* (*3*)
Co(1)-C(11)	1.70 (5)	Co(6)-C(61)	1.77 (4)
Co(1)-C(12)	1.74 (4)	Co(6)-C(62)	1.73 (3)
Co(2)-C(21)	1.74 (4)	Co(7)-C(71)	1.78 (4)
Co(2)-C(22)	1.79 (4)	Co(7)-C(72)	1.82 (5)
Co(3)-C(31)	1.74 (4)	Co(8)-C(81)	1.76 (5)
Co(3)-C(32)	1.72 (5)	Co(8)-C(82)	1.74 (3)
	1.74 (*3*)		*1.77* (*3*)
Co(1)-C(13)	1.79 (4)	Co(6)-C(63)	1.76 (3)
Co(2)-C(23)	1.80 (4)	Co(7)-C(73)	1.76 (4)
Co(3)-C(33)	1.79 (5)	Co(8)-C(83)	1.79 (4)
	1.79 (4)		*1.77* (4)
Co(4)-Co(5)	2.461 (8)	C(1)-C(2)	1.44 (3)
Co(4)-C(41)	1.75 (4)	C(2)-C(3)	1.37 (3)
Co(4)-C(42)	1.77 (4)		
Co(4)-C(43)	1.80 (4)	C(3)-C(4)	1.38 (3)
Co(5)-C(51)	1.75 (5)		
Co(5)-C(52)	1.72 (4)	C(4)-C(5)	1.19 (3)
Co(5)-C(53)	1.76 (4)		
	1.76 (*3*)	C(5)-C(6)	1.36 (3)
Co(4)-C(2)	1.95 (3)		
Co(4)-C(3)	1.95 (3)	C-O	1.12-1.20 (4)
Co(5)-C(2)	1.97 (3)	Mean of 24 values	*1.16* (*3*)
Co(5)-C(3)	1.96 (3)		
	1.96 (*3*)		

[a] Mean values of bonds assumed to be chemically equivalent are italicized and their associated uncertainties are rms deviations given by the expression $(\Sigma_n(x_i - \bar{x})^2/n)^{1/2}$ where there are n observations. The estimated standard deviations of individual bonds were calculated using variances and covariances in positional parameters and variances only in cell parameters.

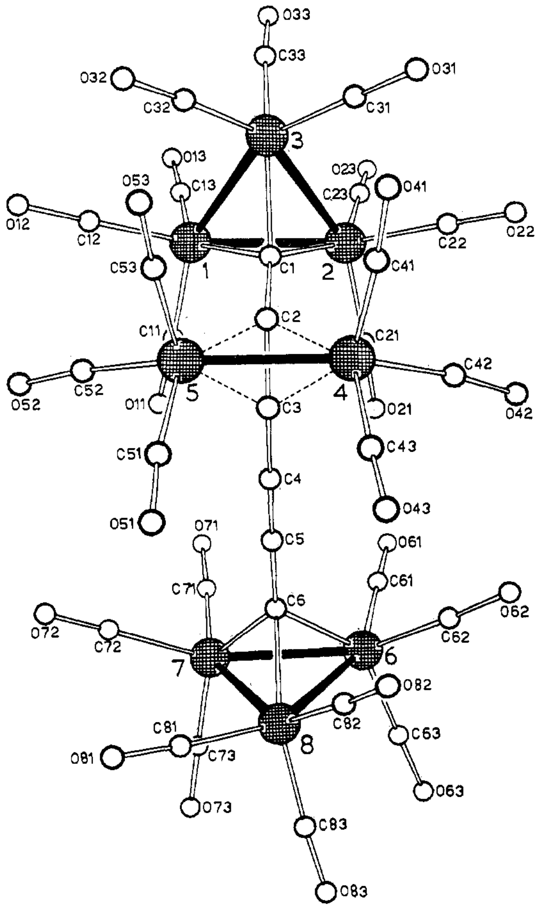

Figure 1.—One molecule of $Co_8(CO)_{24}C_6$ viewed down the pseudomirror plane.

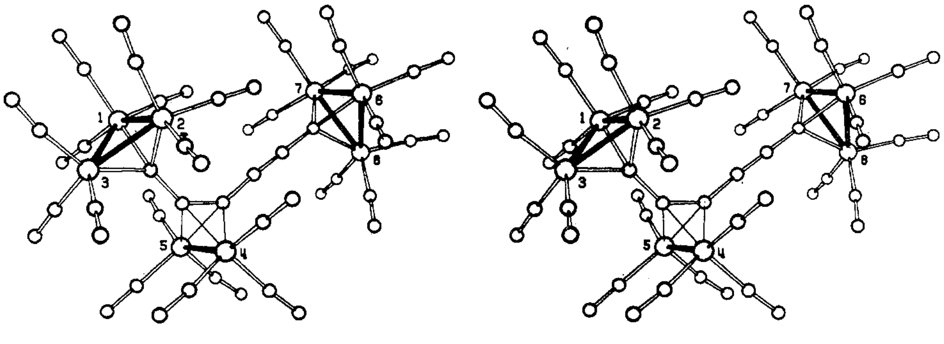

Figure 2.—A general stereoscopic view of one molecule of $Co_8(CO)_{24}C_6$.

C(2)-C(3) bridges a $Co_2(CO)_6$ unit, an arrangement which has previously been observed in complexes of $Co_2(CO)_6$ with diphenylacetylene[18] and with the cyclic acetylene C_6F_6[19] and also in a related complex of $Ni(C_5H_5)_2$ with diphenylacetylene.[20] There is an identical arrangement in $Co_5(CO)_{15}C_3H$.[6] C(4)-C(5) is another acetylene bond, uncoordinated and attached to the bridge carbon atom of one of the terminal $-CCo_3(CO)_9$ units just as in $[Co_3(CO)_9C_2]_2$.[1] Overall, $Co_8(CO)_{24}C_6$ may be considered as a structural combination of $Co_5(CO)_{15}C_3H$ and $[Co_3(CO)_9C_2]_2$ and in Figure 3 the skeletons of these three compounds are oriented so as to illustrate their interrelationship. Whereas in $[Co_3(CO)_9C_2]_2$ a single triple bond has been inserted between two $-CCo_3(CO)_9$ groups, in $Co_8(CO)_{24}C_6$ two conjugated triple bonds have been inserted and one of them is coordinated to an additional $Co_2(CO)_6$ group.

The $-CCo_3(CO)_9$ units are similar to those which have been found in $CH_3CCo_3(CO)_9$,[7] $CH_3CCo_3(CO)_8P(C_6H_5)_3$,[13] $[Co_3(CO)_9C]_2CO$,[4] $Co_3(CO)_{10}BH_2N(C_2H_5)_3$,[21] $Co_5(CO)_{15}C_3H$,[6] $[Co_3(CO)_9C_2]_2$,[1] and $[Co_3$-

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[19] N. A. Bailey and R. Mason, *J. Chem. Soc. A*, 1293 (1968).

[20] O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, **11**, 595 (1968).

[21] F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2265 (1968).

TABLE IV

BOND ANGLES (DEG)[a]

Co(1)–Co(2)–Co(3)	60.0 (2)	Co(6)–Co(7)–Co(8)	59.6 (2)
Co(1)–Co(3)–Co(2)	59.7 (2)	Co(7)–Co(8)–Co(6)	60.6 (2)
Co(3)–Co(1)–Co(2)	60.3 (2)	Co(8)–Co(6)–Co(7)	59.7 (2)
	60.0		*60.0*
C(11)–Co(1)–C(12)	99 (1)	C(61)–Co(6)–C(62)	96 (2)
C(21)–Co(2)–C(22)	97 (1)	C(71)–Co(7)–C(72)	96 (2)
C(31)–Co(3)–C(32)	95 (2)	C(81)–Co(8)–C(82)	97 (2)
	97		*96*
C(11)–Co(1)–C(13)	100 (1)	C(61)–Co(6)–C(63)	99 (2)
C(12)–Co(1)–C(13)	99 (1)	C(62)–Co(6)–C(63)	103 (1)
C(21)–Co(2)–C(23)	102 (1)	C(71)–Co(7)–C(73)	100 (1)
C(22)–Co(2)–C(23)	99 (1)	C(72)–Co(7)–C(73)	109 (2)
C(31)–Co(3)–C(33)	98 (2)	C(81)–Co(8)–C(83)	99 (2)
C(32)–Co(3)–C(33)	101 (2)	C(82)–Co(8)–C(83)	106 (2)
	100		*103*
C(11)–Co(1)–C(1)	103 (1)	C(61)–Co(6)–C(6)	108 (1)
C(12)–Co(1)–C(1)	107 (1)	C(62)–Co(6)–C(6)	98 (1)
C(21)–Co(2)–C(1)	102 (1)	C(71)–Co(7)–C(6)	106 (1)
C(22)–Co(2)–C(1)	104 (1)	C(72)–Co(7)–C(6)	96 (1)
C(31)–Co(3)–C(1)	105 (2)	C(81)–Co(8)–C(6)	107 (1)
C(32)–Co(3)–C(1)	105 (2)	C(82)–Co(8)–C(6)	95 (1)
	104		*102*
C(11)–Co(1)–Co(2)	99 (1)	C(61)–Co(6)–Co(7)	97 (1)
C(12)–Co(1)–Co(3)	95 (1)	C(62)–Co(6)–Co(8)	100 (1)
C(21)–Co(2)–Co(1)	100 (1)	C(71)–Co(7)–Co(6)	95 (1)
C(22)–Co(2)–Co(3)	95 (1)	C(72)–Co(7)–Co(8)	101 (1)
C(31)–Co(3)–Co(2)	98 (1)	C(81)–Co(8)–Co(7)	93 (1)
C(32)–Co(3)–Co(1)	100 (1)	C(82)–Co(8)–Co(6)	99 (1)
	98		*98*
C(11)–Co(1)–Co(3)	152 (1)	C(61)–Co(6)–Co(8)	155 (1)
C(12)–Co(1)–Co(2)	153 (1)	C(62)–Co(6)–Co(7)	146 (1)
C(21)–Co(2)–Co(3)	151 (1)	C(71)–Co(7)–Co(8)	153 (1)
C(22)–Co(2)–Co(1)	152 (1)	C(72)–Co(7)–Co(6)	145 (1)
C(31)–Co(3)–Co(1)	154 (1)	C(81)–Co(8)–Co(6)	152 (1)
C(32)–Co(3)–Co(2)	153 (1)	C(82)–Co(8)–Co(7)	143 (1)
	153		*149*
C(13)–Co(1)–C(1)	142 (1)	C(63)–Co(6)–C(6)	144 (1)
C(23)–Co(2)–C(1)	145 (1)	C(73)–Co(7)–C(6)	142 (1)
C(33)–Co(3)–C(1)	143 (2)	C(83)–Co(8)–C(6)	144 (1)
	143		*143*
C(2)–C(1)–Co(2)	131 (2)	C(5)–C(6)–Co(7)	138 (2)
C(2)–C(1)–Co(3)	138 (2)	C(5)–C(6)–Co(6)	132 (2)
C(2)–C(1)–Co(1)	127 (2)	C(5)–C(6)–Co(8)	124 (2)
	132		*131*

C(13)–Co(1)–Co(2)	97 (1)	C(63)–Co(6)–Co(7)	105 (1)
C(13)–Co(1)–Co(3)	101 (1)	C(63)–Co(6)–Co(8)	96 (1)
C(23)–Co(2)–Co(1)	98 (1)	C(73)–Co(7)–Co(6)	102 (1)
C(23)–Co(2)–Co(3)	102 (1)	C(73)–Co(7)–Co(8)	95 (1)
C(33)–Co(3)–Co(1)	99 (1)	C(83)–Co(8)–Co(6)	98 (1)
C(33)–Co(3)–Co(2)	100 (1)	C(83)–Co(8)–Co(7)	107 (1)
	100		*100*
C(1)–Co(1)–Co(2)	49 (1)	C(6)–Co(6)–Co(7)	48 (1)
C(1)–Co(1)–Co(3)	50 (1)	C(6)–Co(6)–Co(8)	51 (1)
C(1)–Co(2)–Co(1)	52 (1)	C(6)–Co(7)–Co(6)	49 (1)
C(1)–Co(2)–Co(3)	50 (1)	C(6)–Co(7)–Co(8)	51 (1)
C(1)–Co(3)–Co(1)	51 (1)	C(6)–Co(8)–Co(6)	49 (1)
C(1)–Co(3)–Co(2)	49 (1)	C(6)–Co(8)–Co(7)	48 (1)
	50		*49*
Co(1)–C(1)–Co(2)	79 (1)	Co(6)–C(6)–Co(7)	83 (1)
Co(1)–C(1)–Co(3)	79 (1)	Co(7)–C(6)–Co(8)	80 (1)
Co(2)–C(1)–Co(3)	81 (1)	Co(8)–C(6)–Co(6)	80 (1)
	80		*81*
C(41)–Co(4)–C(43)	101 (2)	C(42)–Co(4)–C(43)	98 (2)
C(51)–Co(5)–C(53)	101 (2)	C(51)–Co(5)–C(52)	97 (2)
C(41)–Co(4)–C(42)	103 (2)	C(2)–Co(4)–C(3)	41 (1)
C(52)–Co(5)–C(53)	103 (1)	C(2)–Co(5)–C(3)	41 (1)
C(41)–Co(4)–C(3)	143 (1)	C(43)–Co(4)–C(2)	142 (2)
C(53)–Co(5)–C(3)	145 (1)	C(51)–Co(5)–C(2)	142 (2)
C(41)–Co(4)–C(2)	104 (1)	C(43)–Co(4)–C(3)	105 (1)
C(53)–Co(5)–C(2)	107 (1)	C(51)–Co(5)–C(3)	104 (2)
C(42)–Co(4)–C(3)	98 (1)	C(42)–Co(4)–C(2)	104 (1)
C(52)–Co(5)–C(3)	99 (1)	C(52)–Co(5)–C(2)	101 (1)
C(2)–Co(4)–Co(5)	51 (1)	C(3)–Co(4)–Co(5)	51 (1)
C(2)–Co(5)–Co(4)	51 (1)	C(3)–Co(5)–Co(4)	51 (1)
C(41)–Co(4)–Co(5)	101 (1)	C(43)–Co(4)–Co(5)	97 (1)
C(53)–Co(5)–Co(4)	101 (1)	C(51)–Co(5)–Co(4)	100 (1)
C(3)–C(2)–Co(4)	69 (2)	C(2)–C(3)–Co(4)	70 (2)
C(3)–C(2)–Co(5)	69 (2)	C(2)–C(3)–Co(5)	70 (2)
C(1)–C(2)–Co(4)	134 (2)	C(4)–C(3)–Co(4)	134 (2)
C(1)–C(2)–Co(5)	139 (2)	C(4)–C(3)–Co(5)	135 (2)
Co(4)–C(2)–Co(5)	78 (1)	C(42)–Co(4)–Co(5)	149 (1)
Co(4)–C(3)–Co(5)	78 (1)	C(52)–Co(5)–Co(4)	148 (1)
C(1)–C(2)–C(3)	138 (2)	Co–C–O	171–179 (3)
		Mean of 24 values	*176*
C(2)–C(3)–C(4)	142 (2)		
C(3)–C(4)–C(5)	176 (3)		
C(4)–C(5)–C(6)	179 (3)		

[a] See footnote to Table III. Rms deviations are not given for mean values of angles assumed to be chemically equivalent because these usually far exceed the esd's of individual values.

(CO)$_9$C]$_2$.[5] Corresponding bond lengths in this series of compounds are compared in Table VI.

In the first $-CCo_3(CO)_9$ unit, containing the triangle Co(1)Co(2)Co(3), the average Co–Co bond length is 2.454 (7) Å. The average Co–CO(axial) bond length of 1.79 (4) Å is longer than the average Co–CO(equatorial) length of 1.74 (3) Å as previously observed (see Table VI). The C–C–Co bond angles of 127, 131, and 138 (2)° at the bridge carbon C(1) show a similar spread to those we found for $Co_5(CO)_{15}C_3H$ (126, 128, 140°). However, in contrast to the latter compound the Co(4)–Co(5) vector is not twisted with respect to the Co(1)–Co(2) vector. Consequently, nonbonded contacts between oxygen atoms of the $Co_3(CO)_9$ and $Co_2(CO)_6$ portions of the molecule are of similar length and are all greater than 3.0 Å (in $Co_5(CO)_{15}C_3H$ they ranged from 2.95 to 3.24 Å). The dihedral angles between the Co_3 plane and the planes formed by each Co atom and its equatorial CO groups are 27, 28, and 26° for Co(1), Co(2), and Co(3), respectively (values for $Co_5(CO)_{15}C_3H$ are 30, 27, and 22°). Bond lengths and angles in the $Co_2(CO)_6$ fragment are in good agreement with those observed for $Co_5(CO)_{15}C_3H$; the Co(4)–Co(5) bond length is 2.461 (8) Å (2.447 (4) Å in $Co_5(CO)_{15}C_3H$).

The second $-CCo_3(CO)_9$ group is somewhat distorted from ideal C_{3v} symmetry and this, coupled with its orientation with respect to the rest of the molecule, is mainly responsible for destroying the mirror symmetry of the whole molecule. This may be seen to some extent in Figure 1 and in the bond angles about Co(6), Co(7), and Co(8) in Table IV. The C–C–Co bond angles at the bridge carbon C(6) are 132, 138, and 124 (2)° and the dihedral angles between the Co_3 triangle and the planes formed by each Co atom and its equatorial CO groups are 31, 34, and 37° for

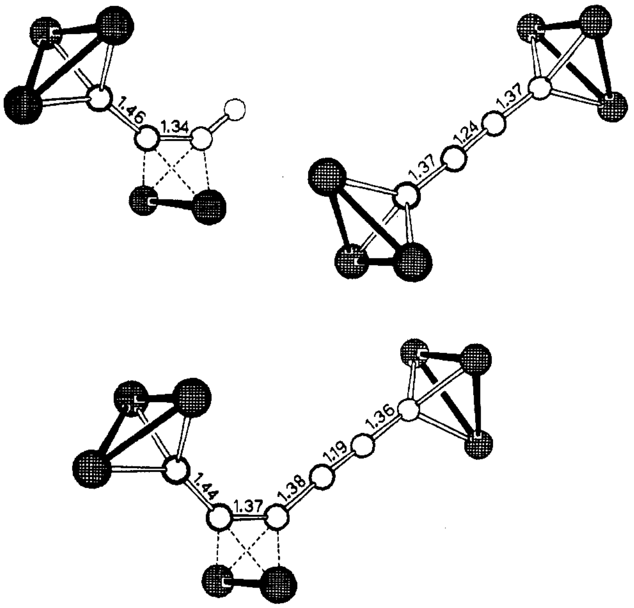

Figure 3.—The cobalt–carbon skeletons of $Co_5(CO)_{15}C_3H$, $[Co_3(CO)_9C_2]_2$, and $Co_8(CO)_{24}C_6$, with carbon chain bond lengths, illustrating the interrelation of the three molecular structures.

TABLE V

SELECTED NONBONDED CONTACTS (Å)

C(11)···C(12)	2.61	C(61)···C(62)	2.60
C(21)···C(22)	2.64	C(71)···C(72)	2.66
C(31)···C(32)	2.56	C(81)···C(82)	2.63
C(11)···C(21)	3.04	C(61)···C(71)	2.86
C(12)···C(32)	2.93	C(62)···C(72)	3.03
C(22)···C(31)	2.87	C(72)···C(81)	2.98
C(11)···C(13)	2.67	C(61)···C(63)	2.68
C(12)···C(13)	2.69	C(62)···C(63)	2.74
C(21)···C(23)	2.74	C(71)···C(73)	2.72
C(22)···C(23)	2.74	C(72)···C(73)	2.91
C(31)···C(33)	2.68	C(81)···C(83)	2.69
C(32)···C(33)	2.71	C(82)···C(83)	2.81
C(13)···C(23)	2.93	C(63)···C(73)	3.32
C(13)···C(33)	3.08	C(63)···C(83)	2.91
C(23)···C(33)	3.14	C(73)···C(83)	3.17
C(41)···C(42)	2.76	C(51)···C(52)	2.59
C(41)···C(43)	2.75	C(51)···C(53)	2.71
C(42)···C(43)	2.69	C(52)···C(53)	2.72
C(41)···C(53)	3.14	C(51)··C(43)	2.98
O(12)···O(52)	3.09	O(21)···C(61)	3.24
O(22)···O(42)	3.08	O(11)···O(71)	3.43
O(31)···O(41)	3.07		
O(32)···O(53)	3.12		
	Intermolecular		
O(13)···O(63)	3.01	O(31)···O(63)	3.18
O(51)···O(83)	3.06		

the planes containing Co(6), Co(7), and Co(8), respectively. (The average value for these dihedral angles in $[Co_3(CO)_9C_2]_2$, in which the $-CCo_3(CO)_9$ units are in a similar environment, is 28°.) The average Co–C(bridge) bond length for this triangle is 1.91 (3) Å (1.92 (3) Å for the other triangle) and the average Co–Co bond length is 2.475 (11) Å.

TABLE VI

BOND LENGTHS (Å) IN THE $-CCo_3(CO)_9$ GROUP IN RELATED COMPOUNDS[a]

	Co–Co	Co–C (bridge)	Co–CO (axial)	Co–CO (equatorial)	Ref
$CH_3CCo_3(CO)_9$	2.467 (5)	1.90 (2)	1.81 (2)	1.80 (2)	*b*
$[Co_3(CO)_9C]_2CO$	2.47 (1)	1.89 (5)	1.85 (4)	1.81 (5)	*c*
$Co_3(CO)_{10}BH_2N(C_2H_5)_3$	2.495 (3)	1.92 (1)	1.83 (2)	1.77 (2)	*d*
$CH_3CCo_3(CO)_8P(C_6H_5)_3$	2.498 (8)	1.91 (2)	1.79 (1)	1.74 (1)	*e*
$Co_5(CO)_{15}C_3H$	2.47 (1)	1.92 (2)	1.79 (2)	1.75 (2)	*f*
$[Co_3(CO)_9C_2]_2$	2.47 (1)	1.92 (1)	1.82 (1)	1.78 (2)	*g*
$Co_8(CO)_{24}C_6$	2.46 (1)	1.92 (3)	1.78 (4)	1.76 (4)	*h*
$Co_8(CO)_{24}C_6 \cdot 0.5C_6H_6$	2.47 (1)	1.93 (3)	1.82 (5)	1.78 (6)	*i*
$[Co_3(CO)_9C]_2$	2.457 (2)	1.96 (1)	1.78 (1)	1.79 (1)	*j*

[a] Structurally equivalent distances have been averaged. Uncertainties quoted are rms deviations. [b] Reference 7. [c] Reference 4. [d] Reference 21. [e] Reference 13. [f] Reference 6. [g] Reference 1. [h] This work. [i] Reference 8. [j] Reference 5.

TABLE VII

COMPARISON OF CARBON CHAIN DIMENSIONS (Å AND DEG) IN COMPOUNDS CONTAINING LINKED $-CCo_3(CO)_9$ GROUPS

Description	$Co_5(CO)_{15}C_3H$[a]	$[Co_3(CO)_9C_2]_2$[b]	$Co_8(CO)_{24}C_6$[c]	$Co_8(CO)_{24}C_6 \cdot 0.5C_6H_6$[d]
Co bridge to coordinated acetylene	1.46 (2)		1.44 (3)	1.37 (4)
Co bridge to acetylene		1.37 (1)	1.36 (3)	1.36 (4)
Coordinated acetylene	1.34 (2)		1.37 (3)	1.37 (4)
Acetylene		1.24 (2)	1.19 (3)	1.20 (4)
Angle at coordinated acetylene	146 (1)		140 (2)[e]	144 (4)[e]

[a] Reference 6. [b] Reference 1. [c] This work. [d] Reference 8. [e] Mean of two values.

Determination of the $Co_8(CO)_{24}C_6$ structure provides independent assessment of the lengths of bonds in the carbon chains of $Co_5(CO)_{15}C_3H$ and $[Co_3(CO)_9C_2]_2$. Comparative values are listed in Table VII. See also Figure 3. All the corresponding bond lengths agree within 2σ, while the average of the two angles C(1)–C(2)–C(3) and C(2)–C(3)–C(4) in $Co_8(CO)_{24}C_6$ differs by less than 3σ from the corresponding angle in $Co_5(CO)_{15}C_3H$. The bond C(3)–C(4), linking the coordinated acetylene and acetylene bonds, is unique to the $Co_8(CO)_{24}C_6$ structure but its value of 1.38 (3) Å compares well with the 1.36 (4) Å observed for $Co_8(CO)_{24}C_6 \cdot 0.5C_6H_6$.[8]

In terms of their lengths, all bonds in the carbon chains of $Co_5(CO)_{15}C_3H$, $[Co_3(CO)_9C_2]_2$, and $Co_8(CO)_{24}C_6$ appear to have multiple character. In particular the C–C bonds formed by the carbon atom which triply bridges the Co_3 triangle are overall significantly shorter than expected for a single bond. Thus the bonds of type C(1)–C(2) (1.46 (2) and 1.44 (3) Å) are each 2.5σ shorter than 1.51 Å, the value expected for an sp^3 to sp^2 link, and the bonds of type C(5)–C(6) (1.37 (1) and 1.36 (3) Å) are more than 3σ shorter than 1.46 Å, the value expected for an sp^3 to sp link.[22] It would follow that the Co–C(bridge) bonds have an order less than unity and one would expect a correlation between a lengthening of these bonds and the multiplicity of the C(bridge)–C bonds. As there are three Co–C bonds to release electrons, the lengthening in each one will be small and variations so far reported (see Table VI) are not significant. However, in the structure of $[Co_3(CO)_9C_2]_2$ recently determined[5] in this laboratory, the Co–C bonds are significantly lengthened to 1.96 (1) Å while the connecting C–C bond is 1.37 Å. The significance of these observations will be discussed in a forthcoming paper in this series.

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CONTRIBUTION FROM THE LASH MILLER CHEMICAL LABORATORIES,
UNIVERSITY OF TORONTO, TORONTO 181, ONTARIO, CANADA

The Crystal and Molecular Structure of μ-Oxalato-bis(tetrapyridineruthenium(II)) Fluoroborate

BY P.-T. CHENG, B. R. LOESCHER, AND S. C. NYBURG*

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The crystal structure of μ-oxalato-bis(tetrapyridineruthenium(II)) fluoroborate, $[Ru(C_5H_5N)_4C_2O_4Ru(C_5H_5N)_4](BF_4)_2$, has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 10.926 (5), b = 16.740 (7), c = 13.732 (5) Å, and β = 116.51 (1)° with two molecules per unit cell. ρ_{obsd} = 1.60 and ρ_{calcd} = 1.62 g cm^{-3} for Z = 2. Least-squares refinement of 3165 observed reflections collected by counter methods has yielded a final conventional R factor of 0.071 and a weighted R factor of 0.069. The two ruthenium atoms of the molecule are linked to a centrosymmetric planar tetradentate oxalate ligand. The coordinating ligands form slightly distorted octahedra about each ruthenium atom consisting of two oxygen atoms from the oxalate ligand and four nitrogen atoms from the pyridine ligands. Several features of the structure indicate that the arrangement of four pyridine molecules in the cis configuration causes significantly greater steric interaction than in comparable *trans*-tetrapyridine complexes. This result is in accord with the observed experimental difficulties in preparing *cis*-tetrapyridine complexes. The fluoroborate anion is disordered about one of the threefold B–F axes of the tetrahedron. The unique undisordered fluorine atom is probably held in position by means of a hydrogen bond to an α hydrogen of one of the pyridine rings. The bond lengths and angles of the oxalate ligand are not significantly different from those of the oxalate ion in potassium oxalate monohydrate. The average Ru–N bond distance of 2.08 Å is significantly shorter than that of 2.13 Å in chlorotetraammine(sulfur dioxide)ruthenium(II) chloride.

Introduction

Dinuclear transition metal complexes containing a bridging tetradentate oxalate ligand have been known for several years. The first conclusive evidence was presented in 1938[1] when a partial X-ray analysis of the tri-n-butylphosphine complex $(C_4H_9)_3P(Cl)PdC_2O_4Pd(C_4H_9)_3P(Cl)^0$ revealed the Pd···Pd distance to be 5.48 Å. This is quite close to the required distance of 5.3 Å for a bridging oxalate. This result refuted the earlier postulate of bridging chloro ligands which would require a Pd···Pd separation of only 3.4 Å.

The first complete structure analysis of a molecule containing a bridging oxalate was that of the mineral humboltine, $FeC_2O_4 \cdot 2H_2O$, in 1957.[2] The iron atoms are linked by planar bridging tetradentate oxalate ligands, forming planar polymeric chains with the two water molecules completing the octahedron about each iron. Preliminary reports on the structures of the complexes $Cu(NH_3)_2C_2O_4$,[3] $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$,[4] and $Ti_2(C_2O_4)_3 \cdot 10H_2O$[5] have also shown the oxalate ligand to be four-coordinate. In the uranyl complex, two-thirds of the oxalates are tridentate. Tetradentate oxalate complexes have also been claimed for several other transition metals.[6–8]

Almost every two- or three-valent transition metal which supports an octahedral configuration of ligands forms complexes with the stoichiometry $M(C_5H_5N)_4X_2^{n+}$ where X is an anionic ligand and n is 0 or 1.[9,10] Despite several attempts and claims of preparation,[11–13] only one of these complexes displays cis–trans isomerism: dichlorotetrapyridineiridium(III) chloride.[11]

In an attempt to prepare *cis*-tetrapyridine complexes of ruthenium(II), hexapyridineruthenium(II) salts were treated with oxalic acid. Since ruthenium(II) has a low affinity for oxygen donor ligands it was hoped that oxalate could be readily displaced under mild conditions forming cis complexes. Physical data indicated that the complex formed was probably $[(C_5H_5N)_4RuC_2O_4Ru(C_5H_5N)_4](BF_4)_2$.[14] The oxalate could not be displaced from this complex without employing reaction conditions which brought about accompanying loss of pyridine.

It was decided that an X-ray structural analysis of this complex would present an excellent opportunity to study both the bridging tetradentate oxalate ligand and the configuration and interactions of four pyridine ligands in the cis octahedral configuration.

Experimental Section

The complex crystallizes overnight from methanol solution as large, deep-red parallepipeds. The crystals are invariably twinned but after partial re-solution in methanol single-crystal fragments can be obtained.

Anal. Calcd for $C_{42}H_{40}N_8O_4Ru_2B_2F_8$: C, 45.99; H, 3.65; N, 10.22; Ru, 18.45. Found: C, 46.34; H, 3.76; N, 10.13; Ru, 18.68.

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