speculations concerning the reasons for the disordering of the Ag atoms based upon silver–aromatic interactions are meaningless.

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The Crystal Structure of Ethylidyneheptacarbonyl-μ-[1,2-bis(dimethylarsino)tetrafluorocyclobutene]-*triangulo*-tricobalt

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The crystal structure of ethylidyneheptacarbonyl-μ-[1,2-bis(dimethylarsino)tetrafluorocyclobutene]-*triangulo*-tricobalt, $Co_3As_2F_4O_7C_{17}H_{15}$, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the monoclinic space group $P2_1/n$; the unit cell contains four molecules and has dimensions a = 10.568 (3) Å, b = 13.462 (5) Å, c = 16.394 (4) Å, β = 90.80 (2)°. The measured density, 2.0 g/cm^3, agrees well with the calculated value, 2.09 g/cm^3. The structure was determined by direct phasing methods and refined by full-matrix least-squares technique to a conventional R index of 0.026 and weighted R of 0.032 for 1673 observed reflections. The cobalt atoms have a triangular arrangement with Co(3)–Co(4), Co(3)–Co(5), and Co(4)–Co(5) being 2.440 (1), 2.479 (2), and 2.470 (2) Å, respectively. A carbon atom in the ethylidyne group is symmetrically placed with respect to this triangle with an average C(18)–Co bond length of 1.903 Å (individual esd 0.007 Å). The ffars ligand bridges Co(3)–Co(4) with As(1)–Co(3) = 2.337 (1) Å and As(2)–Co(4) = 2.358 (1) Å; the cyclobutene ring, As(1), and As(2) are coplanar. Seven carbonyl groups are arranged so that Co(3) and Co(4) have one terminal group while Co(5) has two; three carbonyl groups bridge adjacent cobalt atoms, those bridging Co(3)–Co(5) and Co(4)–Co(5) being asymmetrical.

Introduction

Recently, it has been shown that some of the carbonyl groups in $YCCo_3(CO)_9$ (Y = CF_3, CH_3, Cl) can be replaced by groups containing phosphorus and arsenic, a reaction which had generally been expected to cleave one or more of the metal–metal bonds. Robinson and Tham[1] have synthesized $CH_3CCo_3(CO)_8L$ [L = $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_4H_9)_3P$, $(C_4H_9)_3As$], $CH_3CCo_3(CO)_7L_2$ [L = $(C_6H_5)_3P$, $(C_4H_9)_3As$], and $ClCCo_3(CO)_8(C_6H_5)_3P$. It has been shown by Cullen[2] that 1,2-bis(dimethylarsino)tetrafluorocyclobutene, ffars, will react with $CH_3CCo_3(CO)_9$ (I) and $CF_3CCo_3(CO)_9$ (II), the ffars displacing two carbonyl groups and forming a bridge between adjacent cobalt atoms. The crystal structure[3] of the product with II has indicated that the molecule contains a tetrahedron of cobalt atoms and two ffars ligands. Physical methods indicate that the product with I, $CH_3CCo_3(CO)_7$ffars, has the same three-point linkage of the aliphatic carbon atom to the cobalt atoms as in the parent compound.[4,5] However, the ffars derivative has bridging carbonyl groups in addition to terminal ones.

Experimental Section

Crystals of the compound were red and multifaceted. Weissenberg photographs of the zones $h0l$–$h3l$ and precession photographs of zones $hk0$–$hk2$ and $0kl$–$1kl$, taken with Cu K radiation, established the crystal system as monoclinic and showed the following absences: $h0l$ for $h + l$ odd; $0k0$ for k odd. The space group is therefore $P2_1/n$ [$\pm(x, y, z)$; $\pm(^1/_2 + x, ^1/_2 - y, ^1/_2 + z)$] (a nonstandard orientation of $P2_1/c$).

Crystal Data.—$Co_3As_2F_4O_7C_{17}H_{15}$, mol wt 733.9, crystallizes in the monoclinic space group $P2_1/n$, with a = 10.568 (3) Å, b = 13.462 (5) Å, c = 16.394 (4) Å, β = 90.80 (2)°, and V = 2332 Å^3; d_{obsd} = 2.0 g cm^{-3} (Bermann density balance), d_{calcd} = 2.09 g cm^{-3}, Z = 4, $F(000)$ = 1424, λ(Cu Kα) 1.5418 Å, λ(Mo Kα) 0.7107 Å, λ(Mo Kα_1) 0.70926 Å, and μ(Mo Kα) 52.2 cm^{-1}.

A large crystal was cleaved to an approximate cube and ground to a sphere of diameter 0.3 mm. This sphere was mounted with a general orientation to minimize multiple reflections and was used to measure the cell dimensions and collect the intensity data. Cell dimensions were obtained from the least-squares analysis of 2θ values for 19 high-angle reflections, automatically centered and measured on a Picker four-circle diffractometer using Mo Kα_1 radiation. The errors in the cell dimensions are those determined from the least-squares process. The takeoff angle was 0.8° and the ambient temperature was 23°.

Intensities from one quadrant were collected by the θ–2θ scan technique using Mo Kα radiation (niobium filter) and a scintillation counter equipped with pulse height discrimination. The takeoff angle was 4.3°, the detector was positioned 28 cm from the crystal, and the detector aperture was 5.00 mm high and 4.00 mm wide. Each reflection was scanned for 1.8° (extended for the splitting of α_1 and α_2) at a scan rate of 2°/min. For reflections with 2$\theta \leq$ 35°, the background was counted for 10 sec at each end of the scan range while for reflections with 35° < 2$\theta \leq$ 40°, the background counts were for 20 sec. Every 50 reflections, two standard reflections were measured. The maximum deviation of any individual standard from the mean was 1.5%. Several reflections which had a high count rate were remeasured at lower beam intensity and provided no evidence for coincidence losses. In this manner, intensities for 2188 reflections, with 2$\theta \leq$ 40°, were measured.

Intensities were corrected for background, Lorentz–polarization factors, and the absorption for a spherical crystal, μr being 0.78. If the net count for a reflection was less than 2σ, σ = (total count + background)$^{1/2}$, the reflection was considered unobserved. The number of observed reflections was 1673.

Structure Determination.—The phase problem was solved by direct phasing methods.[6,7] E values were determined[8] and the

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[8] All calculations were performed on an IBM 360/50 computer. Programs used were FORDAP, crystallographic Fourier summation and peak searching (A. Zalkin), BUCILS, crystallographic structure factors and full-matrix least squares (University of Canterbury), ORFFE, Fortran crystallographic function and error program (W. R. Busing, K. O. Martin, and H. A. Levy), ORTEP, Fortran thermal-ellipsoid plot program for crystal structure illustrations (C. K. Johnson), MEANPLANE, calculation of weighted mean planes through atom groups with esd's (M. E. Pippy and F. R. Ahmed), and SAP I–IV and DP I–IV, a set of direct phasing programs (S. Hall, F. R. Ahmed, and C. Huber).

TABLE I

(a) Positional (Fractional Coordinates) and Thermal Parameters

Atom	x	y	z	B,[a] Å^2
As(1)	0.1687 (1)[b]	0.0565 (1)	0.35393 (0)	[c]
As(2)	0.3084 (1)	0.0568 (1)	0.12548 (0)	[c]
Co(3)	0.3819 (1)	0.1026 (1)	0.3563 (1)	[c]
Co(4)	0.4681 (1)	0.1054 (1)	0.2190 (1)	[c]
Co(5)	0.5390 (1)	−0.0244 (1)	0.3158 (1)	[c]
C(6)	0.1119 (8)	−0.0635 (6)	0.4070 (5)	3.9 (2)
C(7)	0.0483 (8)	0.1536 (6)	0.3949 (5)	4.1 (2)
C(8)	0.2606 (9)	0.1546 (7)	0.0431 (6)	5.1 (2)
C(9)	0.3265 (9)	−0.0633 (7)	0.0603 (6)	5.3 (2)
C(10)	0.0956 (6)	0.0312 (5)	0.2472 (4)	2.3 (1)
C(11)	0.1435 (6)	0.0311 (5)	0.1709 (4)	2.5 (1)
C(12)	0.0175 (7)	0.0020 (6)	0.1323 (5)	3.3 (2)
C(13)	−0.0346 (7)	0.0018 (6)	0.2195 (4)	2.9 (2)
F(14)	−0.0361 (4)	0.0673 (4)	0.0808 (3)	[c]
F(15)	0.0141 (5)	−0.0877 (4)	0.0950 (3)	[c]
F(16)	−0.0765 (4)	−0.0872 (3)	0.2456 (3)	[c]
F(17)	−0.1284 (4)	0.0670 (4)	0.2327 (3)	[c]
C(18)	0.5524 (6)	0.1167 (5)	0.3214 (4)	2.5 (1)
C(19)	0.6536 (7)	0.1878 (6)	0.3498 (4)	3.3 (2)
C(20)	0.3849 (7)	0.1825 (6)	0.4413 (5)	3.0 (2)
O(21)	0.3886 (6)	0.2332 (4)	0.4965 (3)	[c]
C(22)	0.3509 (7)	0.1959 (6)	0.2702 (4)	2.8 (2)
O(23)	0.2955 (5)	0.2705 (4)	0.2568 (3)	4.3 (1)
C(24)	0.5556 (8)	0.1885 (6)	0.1600 (5)	3.8 (2)
O(25)	0.6161 (7)	0.2407 (5)	0.1213 (4)	[c]
C(26)	0.5693 (8)	−0.0115 (6)	0.1970 (5)	3.5 (2)
O(27)	0.6206 (6)	−0.0544 (5)	0.1464 (3)	[c]
C(28)	0.4981 (8)	−0.1513 (7)	0.3012 (5)	4.0 (2)
O(29)	0.4805 (7)	−0.2353 (5)	0.2954 (4)	[c]
C(30)	0.6847 (8)	−0.0374 (6)	0.3669 (5)	3.1 (2)
O(31)	0.7783 (5)	−0.0430 (4)	0.4032 (3)	[c]
C(32)	0.4208 (7)	−0.0191 (5)	0.4086 (4)	2.8 (2)
O(33)	0.3943 (5)	−0.0728 (4)	0.4624 (3)	3.9 (1)
H(61)[d]	0.165	−0.067	0.462	
H(62)	0.030	−0.041	0.412	
H(63)	0.136	−0.114	0.389	
H(71)	0.069	0.206	0.366	
H(72)	−0.020	0.125	0.400	
H(73)	0.080	0.164	0.455	
H(81)	0.230	0.202	0.071	
H(82)	0.211	0.126	0.028	
H(83)	0.326	0.147	0.023	
H(91)	0.169	0.394	0.410	
H(92)	0.160	0.468	0.463	
H(93)	0.253	0.452	0.469	
H(191)	0.674	0.166	0.401	
H(192)	0.629	0.259	0.342	
H(193)	0.727	0.178	0.315	

(b) Anisotropic Temperature Factors[e]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	0.0267 (5)	0.0377 (5)	0.0207 (4)	−0.0017 (4)	0.0002 (4)	0.0007 (3)
As(2)	0.0355 (5)	0.0404 (5)	0.0219 (4)	−0.0002 (4)	0.0012 (4)	−0.0005 (3)
Co(3)	0.0279 (6)	0.0350 (6)	0.0236 (5)	−0.0001 (4)	−0.0015 (4)	−0.0022 (4)
Co(4)	0.0320 (6)	0.0412 (6)	0.0244 (5)	−0.0029 (5)	0.0010 (4)	0.0031 (4)
Co(5)	0.0320 (6)	0.0327 (6)	0.0340 (5)	0.0018 (5)	−0.0023 (4)	−0.0019 (4)
F(14)	0.055 (3)	0.097 (4)	0.042 (3)	0.005 (3)	−0.013 (2)	0.020 (3)
F(15)	0.068 (3)	0.073 (3)	0.046 (3)	−0.021 (3)	−0.001 (2)	−0.029 (3)
F(16)	0.055 (3)	0.061 (3)	0.049 (3)	−0.024 (2)	−0.001 (2)	0.001 (2)
F(17)	0.036 (2)	0.080 (3)	0.054 (3)	0.009 (3)	−0.001 (2)	−0.011 (2)
O(21)	0.093 (5)	0.056 (4)	0.044 (4)	0.001 (3)	−0.004 (3)	−0.015 (3)
O(25)	0.104 (5)	0.071 (5)	0.086 (5)	−0.023 (4)	0.043 (4)	0.017 (4)
O(27)	0.088 (5)	0.097 (5)	0.045 (4)	0.039 (4)	0.013 (3)	−0.015 (3)
O(29)	0.106 (6)	0.045 (4)	0.114 (6)	−0.009 (4)	−0.021 (4)	−0.010 (4)
O(31)	0.040 (3)	0.078 (4)	0.060 (4)	0.010 (3)	−0.007 (3)	−0.006 (3)

[a] Isotropic temperature factor. [b] In this table, and all subsequent tables, the figure in parentheses is the esd in the least significant digit. [c] Atom has an anisotropic temperature factor. [d] H(61)–H(93) were given a B of 7.0 Å^2 whereas H(191)–H(193) were given a value of 6.0 Å^2. [e] Expression of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ with the units of U_{ij} being squared ångströms.

reflections 5,3,11 ($E = 3.708$), 3,12,2 ($E = 3.553$), and 2,7,10 ($E = 2.791$) were each assigned a phase angle of 0° and used as starting phases in the symbolic addition procedure. Initially, only reflections with $E \geq 1.8$ were used in the Σ_2 relationship and the phases for all these reflections could be unambiguously assigned. Later, the sign-determining process was extended to reflections with $E \geq 1.5$ resulting in 299 phased values. An electron density synthesis, using F_o values instead of E's, yielded the positions of the arsenic and cobalt atoms. Two cycles of least-squares refinement with these five atomic posi-

TABLE IIA

INTERATOMIC DISTANCES (Å)

As(1)–Co(3)	2.337 (1)				
As(2)–Co(4)	2.358 (1)				
Co(3)–Co(4)	2.440 (1)				
Co(3)–Co(5)	2.479 (2)				
Co(4)–Co(5)	2.470 (2)				
Co(3)–C(18)	1.907 (7)				
Co(4)–C(18)	1.895 (7)				
Co(5)–C(18)	1.907 (7)				
C(19)–C(18)	1.50 (1)				
As(1)–C(6)	1.934 (8)	As(2)–C(8)	1.947 (9)		
As(1)–C(7)	1.950 (8)	As(2)–C(9)	1.949 (10)		
As(1)–C(10)	1.933 (7)	As(2)–C(11)	1.936 (7)		
Co(3)–C(20)	1.761 (9)	Co(4)–C(24)	1.752 (9)	Co(5)–C(28)	1.778 (10)
Co(3)–C(22)	1.915 (7)	Co(4)–C(22)	1.937 (7)	Co(5)–C(30)	1.751 (9)
Co(3)–C(32)	1.892 (7)	Co(4)–C(26)	1.940 (9)	Co(5)–C(32)	1.983 (7)
				Co(5)–C(26)	1.986 (8)
C(20)–O(21)	1.134 (8)	1.196[a]			
C(24)–O(25)	1.146 (10)	1.216[a]			
C(28)–O(29)	1.150 (10)	1.222[a]			
C(30)–O(31)	1.150 (9)	1.213[a]			
C(22)–O(23)	1.182 (8)				
C(26)–O(27)	1.153 (9)	1.219[a]			
C(32)–O(33)	1.178 (8)				
C(10)–C(11)	1.36 (1)				
C(10)–C(13)	1.50 (1)				
C(11)–C(12)	1.52 (1)				
C(12)–C(13)	1.54 (1)				
C(12)–F(14)	1.340 (9)	1.397[a]			
C(12)–F(15)	1.354 (9)	1.354[a]			
C(13)–F(16)	1.348 (8)	1.399[a]			
C(13)–F(17)	1.345 (8)	1.397[a]			

[a] Corrected for riding motion.

tions resulted in a conventional R index[9] of 0.25. Individual, isotropic temperature factors were allowed for the atoms while observations were given unit weight. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$.

All nonhydrogen atoms except C(9) and C(12) were revealed in an electron density difference synthesis. After another least-squares refinement cycle and difference Fourier summation, the remaining two carbon atoms were accounted for and there was evidence of anisotropic motion of cobalt and arsenic atoms. With all these atomic parameters included, refinement reduced R to 0.041 and wR to 0.046.[10] At this stage, the weighting scheme was altered to $\sigma = A$ for $B \leq F_o \leq C$, $\sigma = (A^2B/F_o)^{1/2}$ for $B > F_o$, and $\sigma = (A^2F_o/C)^{1/2}$ for $C < F_o$, where A is a constant which reduces the error of fit to unity. Further least-squares refinement and electron density difference syntheses indicated anisotropic motion for the fluorine atoms, O(21), O(25), O(27), O(29), and O(31) and led to an R index of 0.031 and wR of 0.039. All hydrogen atoms were located and when included in the structure factor calculations, but not refined, the refinement converged to R equal to 0.026 and wR equal to 0.032. The final values of the weighting scheme parameters were A = 1.95, B = 35.0, and C = 55.0 and the error of fit was 1.01. This weighting scheme gave constant values of $w\Delta^2/n$ for ranges of F_o and $(\sin\theta)/\lambda$. No unobserved reflections were used in the refinement. There was no evidence for extinction.

A final electron density difference synthesis showed, as its major features, four peaks of height $\sim$0.4 e Å^{-3} near the heavy atoms and a peak of height 0.3 e Å^{-3} near As(1). On the same scale, carbon atoms had peak heights of 5–5.5 e Å^{-3}.

Scattering factors for the nonhydrogen atoms were taken from the tables of Cromer and Waber[11] while those for hydrogen were from a table of Stewart, Davidson, and Simpson.[12a] Anomalous dispersion corrections, f' and f'', for the arsenic and cobalt atoms were those listed in ref 12b.

Results

The parameters for all the atoms obtained from the last least-squares refinement cycle are listed in Table I.[13] Errors in interatomic distances and angles include contributions from the correlation coefficients between atomic parameters and the errors in the cell dimensions. These distances and angles are tabulated in Table II. The group of atoms As(1), As(2), C(10), C(11), C(12), and C(13) defines a plane which makes an angle of 111.9° with the plane of the cobalt atoms. The equation of these planes and the deviations of selected atoms from them are listed in Table III.

Figure 1 is a diagram of the molecule and indicates the numbering used. The way in which the molecules pack in the unit cell is illustrated in Figure 2.

Discussion

Three seven-coordinate cobalt atoms form a triangular cluster which is capped by an aliphatic carbon atom

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[9] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

[10] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

[11] D. T. Cromer and J. T. Waber, *Acta Crystallgr.*, **18**, 104 (1965).

[12] (a) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965); (b) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 213.

[13] A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE IIB
INTERATOMIC ANGLES (DEG)

Co(4)–Co(3)–Co(5)	60.28 (4)	As(1)–Co(3)–Co(4)	111.19 (5)		
Co(3)–Co(4)–Co(5)	60.65 (4)	As(1)–Co(3)–Co(5)	117.50 (5)		
Co(3)–Co(5)–Co(4)	59.07 (4)	As(2)–Co(4)–Co(3)	108.80 (5)		
		As(2)–Co(4)–Co(5)	115.43 (5)		
Co(3)–C(18)–C(19)	129.9 (5)	As(1)–Co(3)–C(18)	159.4 (2)		
Co(4)–C(18)–C(19)	130.4 (5)	As(2)–Co(4)–C(18)	157.2 (2)		
Co(5)–C(18)–C(19)	134.4 (5)	As(1)–Co(3)–C(20)	100.5 (2)		
Co(3)–C(18)–Co(4)	78.9 (3)	As(1)–Co(3)–C(22)	90.4 (2)		
Co(3)–C(18)–Co(5)	81.1 (3)	As(1)–Co(3)–C(32)	88.9 (2)		
		As(2)–Co(4)–C(22)	90.0 (2)		
Co(4)–C(18)–Co(5)	81.0 (3)	As(2)–Co(4)–C(24)	101.3 (3)		
		As(2)–Co(4)–C(26)	92.6 (2)		
Co(3)–As(1)–C(6)	121.3 (2)	Co(4)–As(2)–C(8)	116.1 (3)		
Co(3)–As(1)–C(7)	116.7 (2)	Co(4)–As(2)–C(9)	120.8 (3)		
Co(3)–As(1)–C(10)	115.8 (2)	Co(4)–As(2)–C(11)	116.1 (2)		
C(6)–As(1)–C(7)	101.3 (3)	C(8)–As(2)–C(9)	102.0 (4)		
C(6)–As(1)–C(10)	97.9 (3)	C(8)–As(2)–C(11)	99.3 (3)		
C(7)–As(1)–C(10)	100.1 (3)	C(9)–As(2)–C(11)	99.1 (3)		
Co(4)–Co(3)–C(20)	135.9 (2)	Co(3)–Co(4)–C(24)	136.6 (3)	Co(4)–Co(5)–C(28)	121.5 (3)
Co(4)–Co(3)–C(22)	51.1 (2)	Co(3)–Co(4)–C(22)	50.3 (2)	Co(4)–Co(5)–C(30)	129.4 (2)
		Co(3)–Co(4)–C(26)	111.9 (2)	Co(3)–Co(5)–C(26)	108.7 (2)
Co(4)–Co(3)–C(32)	110.5 (2)			Co(4)–Co(5)–C(32)	106.2 (2)
Co(4)–Co(3)–C(18)	49.9 (2)	Co(3)–Co(4)–C(18)	50.3 (2)	Co(4)–Co(5)–C(18)	49.3 (2)
Co(5)–Co(3)–C(20)	128.9 (2)	Co(5)–Co(4)–C(24)	130.5 (3)	Co(3)–Co(5)–C(28)	122.4 (3)
Co(5)–Co(3)–C(22)	111.3 (2)	Co(5)–Co(4)–C(22)	110.9 (2)	Co(3)–Co(5)–C(30)	121.9 (2)
		Co(5)–Co(4)–C(26)	51.9 (2)	Co(4)–Co(5)–C(26)	50.2 (2)
Co(5)–Co(3)–C(32)	51.9 (2)			Co(3)–Co(5)–C(32)	48.6 (2)
Co(5)–Co(3)–C(18)	49.5 (2)	Co(5)–Co(4)–C(18)	49.7 (2)	Co(3)–Co(5)–C(18)	49.6 (2)
C(20)–Co(3)–C(22)	100.6 (3)	C(24)–Co(4)–C(22)	100.6 (3)	C(28)–Co(5)–C(30)	100.3 (4)
		C(24)–Co(4)–C(26)	96.8 (4)	C(28)–Co(5)–C(26)	89.6 (4)
C(20)–Co(3)–C(32)	99.7 (3)			C(28)–Co(5)–C(32)	89.0 (3)
C(20)–Co(3)–C(18)	99.8 (3)	C(24)–Co(4)–C(18)	101.1 (3)	C(28)–Co(5)–C(18)	169.0 (3)
		C(22)–Co(4)–C(26)	161.5 (3)	C(30)–Co(5)–C(26)	108.9 (3)
C(22)–Co(3)–C(32)	159.5 (3)			C(30)–Co(5)–C(32)	101.1 (3)
C(22)–Co(3)–C(18)	82.3 (3)	C(22)–Co(4)–C(18)	82.0 (3)	C(30)–Co(5)–C(18)	90.7 (3)
				C(26)–Co(5)–C(32)	149.5 (3)
		C(26)–Co(4)–C(18)	88.7 (3)	C(26)–Co(5)–C(18)	87.0 (3)
C(32)–Co(3)–C(18)	91.3 (3)			C(32)–Co(5)–C(18)	88.6 (3)
Co(3)–C(20)–O(21)	178.8 (9)	Co(3)–C(22)–O(23)	140.7 (6)		
Co(4)–C(24)–O(25)	177.7 (8)	Co(4)–C(22)–O(23)	140.6 (6)		
Co(5)–C(28)–O(29)	174.4 (8)	Co(4)–C(26)–O(27)	143.7 (7)		
Co(5)–C(30)–O(31)	176.7 (7)	Co(5)–C(26)–O(27)	138.3 (7)		
		Co(3)–C(32)–O(33)	145.0 (6)		
		Co(5)–C(32)–O(33)	135.4 (6)		
		Co(3)–C(22)–Co(4)	78.6 (3)		
		Co(3)–C(32)–Co(5)	79.5 (3)		
		Co(4)–C(26)–Co(5)	78.0 (3)		
As(1)–C(10)–C(11)	133.3 (5)	As(2)–C(11)–C(10)	134.7 (5)		
As(1)–C(10)–C(13)	132.5 (5)	As(2)–C(11)–C(12)	132.4 (5)		
C(11)–C(10)–C(13)	94.2 (5)	C(10(–C(11)–C(12)	92.8 (6)		
C(11)–C(12)–C(13)	86.4 (5)				
C(12)–C(13)–C(10)	86.6 (5)				
C(11)–C(12)–F(14)	117.0 (6)	C(10)–C(13)–F(16)	116.3 (6)		
C(11)–C(12)–F(15)	115.9 (6)	C(10)–C(13)–F(17)	117.1 (6)		
C(13)–C(12)–F(14)	115.7 (6)	C(12)–C(13)–F(16)	114.8 (6)		
C(13)–C(12)–F(15)	114.2 (6)	C(12)–C(13)–F(17)	115.0 (6)		
F(14)–C(12)–F(15)	107.0 (6)	F(16)–C(13)–F(17)	106.5 (6)		

at the apex of a distorted trigonal pyramid. This carbon atom forms a bond of equal length to each cobalt atom, a structural feature which is also present in $CH_3CCo_3(CO)_9$ (III)[5] and $CH_3CCo_3(CO)_8P(C_6H_5)_3$ (IV).[14] The ffars group is attached to Co(3) and Co(4) in an orientation "axial" with respect to the plane of the cobalt atoms—planes I and II make a dihedral angle of 111.9°—an attachment different from that found in IV where the phosphine group is bonded equatorially.

Each pair of adjacent cobalt atoms is bridged by a carbonyl group, the carbonyl group in every case being bonded "equatorially." Co(3) and Co(4) each have one terminal group whereas Co(5) has two such groups.

Co(3)–Co(4), 2.440 (1) Å, is different from the other cobalt–cobalt bonds and is significantly shorter than Co(3)–Co(5), 2.479 (2) Å, and Co(4)–Co(5), 2.470 (2) Å. Such results are consistent with Co(3)–Co(4) being bridged by three groups whereas the other cobalt–cobalt bonds are only associated with two bridging groups. Similar observations were found in cobalt clusters where carbonyl and thio groups act as bridging

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

TABLE III

EQUATIONS TO PLANES OF FORM $AX + BY + CZ + D = 0$[a]

Plane	Atoms defining plane	*A*	*B*	*C*	*D*	χ^2
I	Co(3), Co(4), Co(5)	−0.7370	−0.5960	−0.3189	5.600	0
II	As(1), As(2), C(10), C(11), C(12), C(13)	−0.2345	0.9675	−0.0948	0.213	4.77
III	Co(5), midpoint Co(3)–Co(4), midpoint As(1)–As(2)	0.3697	0.0076	−0.9291	2.734	0

Plane	Atom	Dev from planes, Å
II	As(1)	0.0000 (7)
	As(2)	−0.0001 (8)
	C(10)	0.011 (7)
	C(11)	0.006 (7)
	C(12)	−0.003 (8)
	C(13)	−0.008 (8)
	Co(3)	0.0677 (9)[b]
	Co(4)	0.0972 (9)[b]

[a] *X*, *Y*, and *Z* refer to orthogonal axes, along *a*, *b*, and *c**, respectively, and are in angströms. [b] Atom not used to define plane.

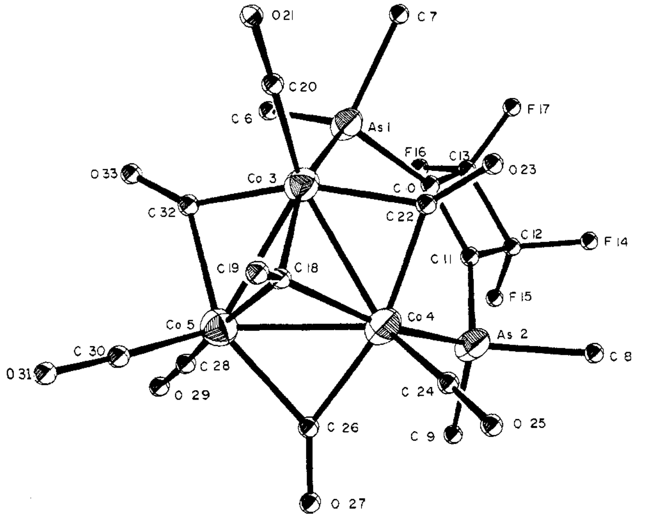

Figure 1.—A diagram of a molecule of $Co_3As_2F_4O_7C_{17}H_{15}$.

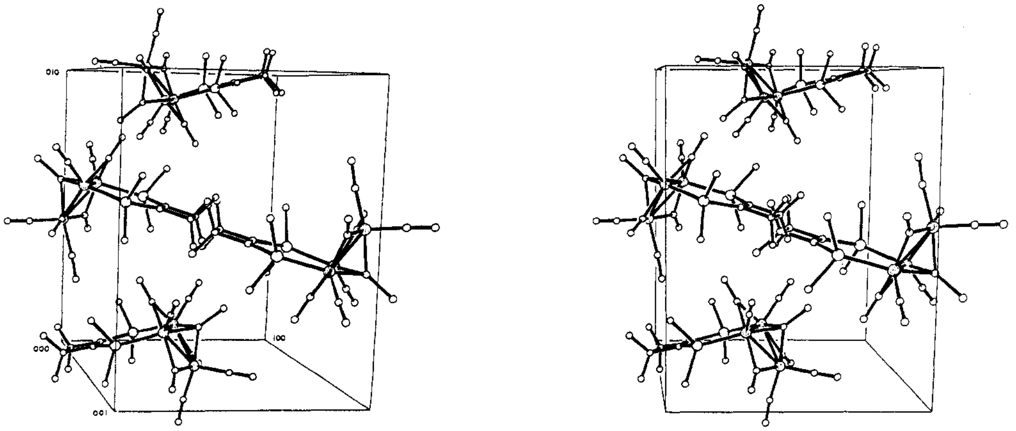

Figure 2.—A stereodiagram of $Co_3As_2F_4O_7C_{17}H_{15}$, showing the manner of packing in the unit cell.

ligands.[15a,b,c] The values do, however, fall within the range found for other cobalt–cobalt bonds.[3,5,14,15] Each cobalt atom attains a closed-shell configuration.

Because of the small interatomic angles Co–Co–Co and Co–Co–C(18), imposed by the distorted trigonal pyramid, valence-bond descriptions of the bonding will have serious shortcomings; in particular, bent bonds are necessary and electronic spectra cannot be explained. A molecular orbital approach was introduced by Cotton and Haas[16] to explain the bonding in $[Re_3Cl_{12}]^{3-}$ and this approach was also successfully applied by Wei and Dahl[15a] to $Co_3[(SC_2H_5)_5Co](CO)_3$. A feature of both compounds is that a metal atom lies in the basal plane of a square pyramid of donor atoms. Wei and Dahl assumed the use of d_{xy}, s, p_x, p_y, and p_z orbitals on the cobalt atom in forming five localized σ bonds to the five ligands, the remaining four d orbitals being used in another set of molecular orbitals for cobalt–cobalt interactions. As(1), C(18), C(22), and C(32) are approximately planar and, with C(20), determine a distorted square pyramid with Co(3) being about 0.3 Å out of the basal "plane." Similarly, As(2), C(18), C(22), C(26), and C(24) and C(18), C(26), C(28), C(32), and C(30) are corners of distorted square pyramids about Co(4) and Co(5), respectively. This suggests that a bonding scheme, similar to that proposed for $Co_3[(SC_2H_5)_5Co](CO)_3$, can be applied here.

Significant differences occur in the two arsenic–cobalt bond lengths; Co(3)–As(1) is 2.337 (1) Å and Co(4)–

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(15) (a) C. H. Wei and L. F. Dahl, *J. Amer. Chem.*, **90**, 3960 (1968); (b) *ibid.*, **90**, 3969 (1968); (c) *ibid.*, **90**, 3977 (1968); (d) C. H. Wei, *Inorg. Chem.*, **8**, 2384 (1969); (e) P. Corradini, *J. Chem. Phys.*, **31**, 1679 (1959); (f) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967); (g) D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3727 (1967); (h) R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2197 (1970); (i) R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *ibid.*, **9**, 2204 (1970); (j) G. Allegra and S. Valle, *Acta Crystallogr.*, *Sect. B*, **25**, 107 (1969); (k) F. Klanberg, W. B. Askew, and L. J. Guggenberger, *Inorg. Chem.*, **7**, 2265 (1968); (l) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

(16) F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

As(2) is 2.358 (1) Å; *cf.* the sum of covalent radii of 2.342 Å.[17] The reasons for this are not readily apparent. However, the different lengths are consistent with the distribution of "short" and "long" bonds about Co(3) and Co(4). It is of interest to note that calculation has shown that the lone pair on each arsenic is directed along the cobalt–arsenic vector which rules out explanations involving "bent bonds."

The average carbon–arsenic bond length is 1.942 (7) Å which is close to the average value found in $Co_4(CO)_8(ffars)_2$,[3] 1.93 Å, individual esd 0.02 Å. Angles of type C–As–C are smaller than the tetrahedral angle whereas those of type M–As–C, M = metal, are larger. This effect is probably due to the carbon–arsenic bonds having more p-orbital character than cobalt–arsenic bonds which have a high s-orbital character, a distribution due to cobalt being more electropositive than carbon.[18]

In the ethylidyne group, the C(18) forms equal bonds to each cobalt atom of lengths 1.907 (7), 1.895 (7), and 1.907 (7) Å to Co(3), Co(4), and Co(5), respectively; *cf.* 1.90 Å in III and 1.91 (2) Å in IV. The angles involving C(18) are also consistent with those with a similar CH_3CCo_3– grouping. A normal, single carbon–carbon bond of length 1.50 (1) Å joins C(18) and C(19).

The different environment of Co(5) from Co(3) and Co(4) is reflected in the bridging carbonyl groups. C(22), which spans Co(3) and Co(4), has essentially equal cobalt–carbon bond lengths whereas those bridging Co(3), Co(5) and Co(4), Co(5) are asymmetric; in each case, the longer cobalt–carbon bond involves Co(5) (see Table II). The values may be compared with the value of 1.92 Å found in $Co_2(CO)_8$[15l] where the bridge is symmetrical. Cobalt–carbon bonds involving terminal groups are normal, mean 1.76 (1) Å. It is observed that the carbon–oxygen bond lengths for terminal groups are consistently shorter than those for bridging groups. This trend is also true for $Co_5(CO)_{10}(SC_2H_5)_5$[15b] and $SCo_6(CO)_{11}(SC_2H_5)_4$[15c] whereas the reverse situation is found for $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$.[15a] It is expected that the bridging groups should have the shortest carbon–oxygen bond length but Cotton[19] pointed out that this bond length is very insensitive to bond order change.

The molecule has approximately C_s symmetry with the largest deviations (~0.04 Å) from the plane (Table III) in the carbonyl groups. However these deviations are not considered to be chemically significant.

Within the ffars ligand, C(10)–C(11) is a double bond (1.36 (1) Å), while other carbon–carbon bonds have the single-bond value. The carbon–fluorine distances are equal, average 1.347 Å, individual esd 0.009 Å, which are near the published value, 1.344 (4) Å.[20]

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[17] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

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[19] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 729.

[20] Reference 12b, p 275.

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Structure and Bonding of the Lithium Rhodium Hydrides Li_4RhH_4 and Li_4RhH_5[1]

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The structure and bonding of the lithium rhodium hydrides Li_4RhH_4 and Li_4RhH_5 have been studied using single-crystal X-ray diffraction and magnetic susceptibility techniques. X-Ray intensities were measured with a scintillation counter. Li_4RhH_4 has a = 6.338 (5) and c = 4.113 (8) Å, probable space group $I4/m$, Z = 2, and calculated density 2.707 g/cm³. The rhodium atom is surrounded by four lithium atoms at 2.83 (2) Å, eight lithium atoms at 2.84 (3) Å, and four hydrogen atoms at about 1.9 Å. The final values for R_w are 0.0625 with hydrogen and 0.0718 without hydrogen. Li_4RhH_5 has a = 3.880 (3), b = 9.020 (5), and c = 8.895 (6) Å, probable space group $Cmcm$, Z = 4, and calculated density 2.895 g/cm³. The rhodium atom position was derived from the X-ray data. The remainder of the structure was inferred from packing considerations and from its relation to the structure of Li_4RhH_4. For the refinement with rhodium alone, R_w = 0.126; with all atoms in their presumed positions, but without further refinement, R_w = 0.145. In the proposed structure of Li_4RhH_5, Rh–Li distances are 2.55 and 2.79 Å, Li–Li distances range from 2.46 to 2.75 Å, Rh–H distances are 1.81–1.96 Å, and Li–H distances range from 1.82 to 1.97 Å. Both lithium rhodium hydrides were found to possess weak, temperature-independent paramagnetism over the temperature range 51–297°K. The molar susceptibilities, in cgs units, were determined to be 1.2×10^{-6} for Li_4RhH_4 and 2.1×10^{-6} for Li_4RhH_5. These data indicate that the spins of the electrons are paired in both compounds. Both compounds appear to be related to LiH, suggesting ionic bonding between hydrogen and both of the metals. There is also some indication of metallic bonding between lithium and rhodium. The structure rules out the presence of localized rhodium–rhodium bonding.

Introduction

When lithium hydride and rhodium metal are heated together to approximately 600° in an inert atmosphere, a black liquid forms which changes to a brittle black solid upon cooling to room temperature. Farr's[2] original work on this reaction established the existence of two compounds, Li_4RhH_4 and Li_4RhH_5. These formu-

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission, presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, and based on a dissertation submitted by L. B. Lundberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Denver, May 1968.

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