Journal of Organometallic Chemistry, 127 (1977) 209—222
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PREPARATION AND STRUCTURAL CHARACTERIZATION OF $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$: AN ORGANOMETALLIC COMPLEX CONTAINING A TETRAHEDRAL-LIKE ARSENIC ATOM COORDINATED TO FOUR METAL ATOMS

CHARLES F. CAMPANA * and LAWRENCE F. DAHL*
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)

(Received July 14th, 1976)

Summary

The room-temperature reaction of cyclopentadienylcobalt dicarbonyl in benzene solution with arsenic trifluoride has unexpectedly produced in low yield a new tetranuclear metal complex $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$ by the extraction of boron from the Pyrex-glass flask as the tetrafluoroborate anion. This compound has been characterized by physical means including a single-crystal X-ray analysis which not only unambiguously established the actual composition but also revealed an example of an unusual organometallic complex containing a quadruply bridging arsenic atom linking four metal atoms. The entire $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ monocation ideally posesses an $S_4\text{-}\bar{4}$ configuration which consists of two essentially identical $[Co_2(h^5\text{-}C_5H_5)_2(CO)_2]$ fragments joined to each other by a metal-coordinated tetrahedral-like arsenic atom. The central Co_4As core of the diamagnetic monocation, which is structurally related and electronically equivalent to the previously reported $[Fe_2(CO)_8]_2(\mu_4\text{-}Sn)$ molecule, has an approximate $D_{2d}\text{-}\bar{4}2m$ geometry with two electron-pair Co—Co bonding distances of 2.60 Å (av) and four Co···Co nonbonding distances of 4.14 Å (av) and with a mean Co—As bond length of 2.27 Å. The isolated compound crystallizes with two cations, two anions, and one benzene molecule of solvation in a reduced triclinic unit cell of $P\bar{1}$ symmetry and of dimensions a = 9.230(5), b = 18.815(10), c = 8.939(4) Å, α = 100.38(5), β = 95.49(4), and γ = 76.21(5)°. The structure was refined by full-matrix least-squares techniques to an unweighted R_1 value of 4.8% for 1784 independent diffracometry-collected data with $I \geqslant 2\sigma(I)$.

---

* Present address: Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131 (U.S.A.)

Introduction

A number of tetrameric $[M(h^5\text{-}C_5H_5)(\mu_3\text{-}X)]_4^{n}$-type complexes containing triply-bridging sulfur, selenium, or phosphorus atoms bonded to iron or cobalt atoms have recently been synthesized and structurally characterized [1—5]. An X-ray structural determination of the cubane-like $[Co_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}P)_4]$ molecule [5] revealed unusually short P···P separations relative to the corresponding S···S distances in the isoelectronic and similarly distorted cubane-like $[Fe_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4]$ molecule [1]. In order to investigate whether these anomalously short X···X distances (which were later attributed [6] from other work to give rise to distinct bonding forces) were peculiar to phosphorus or whether they might also occur for arsenic, attempts were made to prepare the hitherto unknown $[Co_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_4]$ complex [7] *.

Since arsenic trifluoride has been successfully utilized as a source of "bare" triply-bridging arsenic atoms in the preparation of $[Ni_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_3]^+BF_4^-$ [8] and $Fe_3(CO)_9(\mu_3\text{-}As)_2$ [9], it was thought that the reaction of arsenic trifluoride with cyclopentadienylcobalt dicarbonyl under appropriate conditions might yield the desired cobalt-arsenic tetramer. * This reaction instead produced the $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_3\text{-}As)]^+$ monocation, an unusual spiro-like tetranuclear cobalt complex, whose structure and physicochemical properties are reported here. This tetracobalt-arsenic monocation was found to be of particular stereochemical interest in its being electronically equivalent and structurally analogous to $[Fe_2(CO)_8]_2(\mu_4\text{-}Sn)$ [10] as well as structurally related to $[Fe_2(CO)_6(\mu_2\text{-}SCH_3)]_2(\mu_4\text{-}S)$ [11] and $[Fe_2(CO)_8(\mu_2\text{-}Sn(CH_3)_2)]_2(\mu_4\text{-}Sn)$ [12], which also contain quadruply bridging sulfur or tin atoms.

Experimental

Preparation and properties

$[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$ was prepared from the reaction of arsenic trifluoride with a benzene solution of cyclopentadienylcobalt dicarbonyl in a Pyrex-glass reaction vessel at room temperature. A solution of 5 g (38 mmols) of anhydrous arsenic trifluoride (ROC/RIC Chemical Co.) in 25 ml of freshly distilled benzene was added dropwise to a vigorously stirred solution of 5 g (28 mmols) of cyclopentadienylcobalt dicarbonyl in 25 ml of benzene under a nitrogen atmosphere. The stirring was maintained for 24 h and then discontinued. A slow evaporation of the solution to dryness under a stream of dry nitrogen produced a dark-red, hexane-insoluble residue from which a few dark red crystals were removed and utilized for X-ray analysis. The remainder of the residue was purified by extraction with acetone and filtration through a short silica gel column. An IR spectrum (Beckman IR-8, chloroform solution) of the purified compound exhibited a single carbonyl stretching frequency at 1984 cm^{-1}, as well as bands indicative of cyclopentadienyl and BF_4^- groups. The close similarity of this solution spectrum with a solid-state IR spectrum (KBr disc) of the red crystals provided firm evidence that the compound in solution was unchanged at

---

* The cubane-like $[Co_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_4]$ molecule was subsequently isolated from a different preparative route and structurally characterized by Paquette and Dahl [7].

room temperature from that in the solid state. Its diamagnetic character was established from an EPR solution spectrum (Varian E-3) which showed no resonance and from the line-shape of a proton NMR spectrum (Varian XL-100) which showed only a very sharp singlet at 5.38 ppm corresponding to a single type of cyclopentadienyl proton.

X-Ray data collection

Since attempts to recrystallize the purified residue were unsuccessful, X-ray data were collected on crystals that had been removed from the reaction vessel. A dark-red trigonal prismatic crystal of approximate dimensions 0.04 × 0.20 × 0.56 mm was used for the collection of intensity data. The crystal was glued to the inner wall of an argon-filled Lindemann glass capillary with epoxy cement and oriented along the crystal's longest dimension such that the c axis was nearly parallel to the goniometer axis. This crystal was optically and then X-ray aligned on a Nova-automated Syntex $P\bar{1}$ diffractometer. The angular coordinates of 15 reflections, which were carefully centered with monochromatic Mo-K_α radiation were least-squares refined to yield lattice parameters of $a = 9.230(5)$, $b =$ $= 18.815(10)$, $c = 8.939(4)$ Å, $\alpha = 100.38(5)$, $\beta = 95.49(4)$, and $\gamma = 76.21(5)°$ and a cell volume of 1480(1) Å^3. An experimental density of 1.79 g cm^{-3} (flotation method) is in accord with the calculated density of 1.82 g cm^{-3} based on $Z = 2$ for the subsequently determined formula.

Intensity data were collected via the θ -- 2θ scan mode with a scintillation counter and pulse-height analyzer adjusted to admit 90% of the Mo-K_α peak. The Bragg 2θ angle for the highly-oriented graphite-crystal monochromator was 12.2°, while a take-off angle of 4° was used for the incident-X-ray beam. Variable scan speeds with a minimum of 0.5°/min and variable scan widths based on the overall intensity and width of the peak were employed. A (stationary-crystal)-(stationary-counter) background measurement for one-half of the total scan time was made on each side of a peak. Two standard reflections were measured every 50 reflections to monitor instrument stability as well as crystal alignment and/or decay. Corrections were made for an observed 25% linear decrease in the standard intensities during the data collection period. All independent reflections corresponding to four octants, hkl, $\bar{h}kl$, $hk\bar{l}$, and $\bar{h}k\bar{l}$, of the triclinic reciprocal lattice were collected for $3° \leqslant 2\theta \leqslant 40°$. After correction of the data for background and Lorentz-polarization effects, structure factor amplitudes and corresponding standard deviations were obtained in a manner previously described [13] *. This treatment included the correction of data for absorption effects due to the calculated transmission coefficients varying from 0.50 to 0.85 (based on a μ value of 35.08 cm^{-1} for Mo-K_α radiation). Of the 2145 independent reflections that were sampled, 1784 reflections were considered above background with the criterion $I \geqslant 2.0\sigma(\mathrm{I})$.

Structural determination and refinement

The approximate positions of the arsenic and four cobalt atoms were determined by an interpretation of a Patterson map. The coordinates of the remain-

---

* The programs utilized for the data collection and reduction, the structural determination and refinement, and error analyses are given elsewhere [13], if not otherwise referenced.

ing nonhydrogen atoms in the cation and anion were obtained from subsequent Fourier syntheses. Two cycles of full-matrix least-squares refinement with variation of only the positional parameters followed by two more cycles with variable isotropic temperature factors yielded $R_1 = 16.6\%$ and $R_2 = 19.7\%$ *. The coordinates of the cyclopentadienyl hydrogen atoms were fixed at idealized positions at 1.1 Å from their attached carbon atoms and recalculated after each cycle. At this point all nonhydrogen atoms were assigned anisotropic thermal factors, and block-diagonal least-squares refinement was carried out until apparent convergence at $R_1 = 8.2\%$ and $R_2 = 10.5\%$. A difference Fourier synthesis revealed a planar arrangement of six peaks about a crystallographic center of symmetry with distances corresponding to a benzene molecule. This solvent molecule per cell was refined in subsequent least-squares calculations as a rigid body with anisotropic carbon thermal parameters (and fixed isotropic hydrogen temperature factors) in order to compensate for a slight translational-type ring disorder, as evidenced by the thermal ellipsoids of the six carbon atoms being similarly elongated to a first approximation along one of the in-plane molecular directions. Further block-diagonal least-squares refinement until convergence followed by a final cycle of full-matrix least-squares refinement led to the final discrepancy values of $R_1 = 4.8\%$ and $R_2 = 5.2\%$ with no Δ/σ values on the last cycle being greater than 0.5 and with a final goodness-of-fit value of 1.27. A Fourier difference map showed no unusual features with the largest peak maximum being only 0.7 electron/Å^3. The atomic scattering factors utilized in all structure factor calculations were those of Cromer and Mann [14] for the nonhydrogen atoms and those of Stewart et al. [15] for the hydrogen atoms with corrections applied for real and imaginary anomalous dispersion effects [16] for cobalt and arsenic.

The positional and thermal parameters from the final full-matrix least-squares refinement cycle are presented in Table 1 **. Interatomic distances and bond

(continued on p. 216)

TABLE 1

ATOMIC PARAMETERS FOR $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$ [a]

A. Positional Parameters

	x	y	z
As	0.5583(2)	0.2322(1)	0.3519(2)
Co(1)	0.4589(3)	0.3287(1)	0.2269(2)
Co(2)	0.6125(3)	0.3383(1)	0.4857(2)
Co(3)	0.4602(3)	0.1453(1)	0.4266(3)
Co(4)	0.7010(3)	0.1184(1)	0.2762(3)
C(1)	0.3000(26)	0.3596(11)	0.3304(24)
O(1)	0.1929(18)	0.3820(10)	0.3961(18)
C(2)	0.7634(25)	0.3050(11)	0.3879(23)

(Table to be continued)

---

* $R_1 = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100$ and $R_2 = (\Sigma\omega_i||F_o| - |F_c||^2/\Sigma\omega_i|F_o|^2)^{1/2} \times 100$. All least-squares refinements were based on the minimization of $\Sigma\omega_i||F_o| - |F_c||^2$ with individual weights $\omega_i = (1/\sigma(|F_o|)^2$.

** See NAPS document no. 02951 for supplementary material involving a listing of the observed and calculated structure factors for $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$. Order from ASIS/NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y., 10017. Remit in advance for each NAPS accession number \$1.50 for microfiche or \$5.00 for photocopies up to 30 pages, 15c for each additional page. Make checks payable to Microfiche Publications.

TABLE 1 (continued)

A. Positional Parameters

	x	*y*	*z*
O(2)	0.8701(20)	0.3352(10)	0.3302(18)
C(3)	0.5757(25)	0.1381(11)	0.5908(25)
O(3)	0.6428(17)	0.1302(8)	0.7014(18)
C(4)	0.5927(24)	0.0964(11)	0.1156(29)
O(4)	0.5269(20)	0.0811(9)	0.0020(19)
C(1-1)	0.4839(21)	0.2746(10)	0.0063(20)
C(1-2)	0.3595(21)	0.3293(11)	0.0096(20)
C(1-3)	0.4069(21)	0.3964(10)	0.0627(20)
C(1-4)	0.5590(21)	0.3827(11)	0.0911(20)
C(1-5)	0.6079(20)	0.3053(10)	0.0573(20)
H(1-1)	0.4903	0.2134	—0.0293
H(1-2)	0.2431	0.3250	—0.0223
H(1-3)	0.3283	0.4541	0.0784
H(1-4)	0.6280	0.4223	0.1336
H(1-5)	0.7281	0.2735	0.0670
C(2-1)	0.6209(22)	0.3187(11)	0.7056(20)
C(2-2)	0.7139(24)	0.3656(12)	0.7002(23)
C(2-3)	0.6200(25)	0.4296(12)	0.6536(24)
C(2-4)	0.4749(23)	0.4223(12)	0.6316(22)
C(2-5)	0.4740(22)	0.3497(12)	0.6626(21)
H(2-1)	0.6582	0.2612	0.7382
H(2-2)	0.8341	0.3560	0.7269
H(2-3)	0.6597	0.4802	0.6380
H(2-4)	0.3759	0.4620	0.5944
H(2-5)	0.3750	0.3267	0.6563
C(3-1)	0.2321(23)	0.1891(12)	0.4065(25)
C(3-2)	0.2627(23)	0.1478(13)	0.5155(24)
C(3-3)	0.3249(22)	0.0745(12)	0.4554(24)
C(3-4)	0.3344(22)	0.0718(12)	0.3014(23)
C(3-5)	0.2807(20)	0.1434(11)	0.2710(21)
H(3-1)	0.1834	0.2506	0.4172
H(3-2)	0.2385	0.1674	0.6422
H(3-3)	0.3603	0.0261	0.5186
H(3-4)	0.3809	0.0219	0.2173
H(3-5)	0.2714	0.1607	0.1546
C(4-1)	0.9119(22)	0.1374(12)	0.2782(25)
C(4-2)	0.9020(26)	0.0761(14)	0.1717(26)
C(4-3)	0.8732(24)	0.0238(13)	0.2665(27)
C(4-4)	0.8635(24)	0.0557(13)	0.4105(26)
C(4-5)	0.8872(24)	0.1312(12)	0.4243(24)
H(4-1)	0.9336	0.1903	0.2470
H(4-2)	0.9160	0.0644	0.0523
H(4-3)	0.8591	—0.0332	0.2145
H(4-4)	0.8416	0.0324	0.5094
H(4-5)	0.8877	0.1706	0.5294
B	0.0380(44)	0.2068(18)	—0.1080(38)
F(1)	0.0331(28)	0.2485(12)	—0.2139(23)
F(2)	0.0082(22)	0.2469(9)	0.0195(21)
F(3)	—0.0479(29)	0.1676(16)	—0.1594(38)
F(4)	0.1695(21)	0.1651(12)	—0.1055(18)
BC(1)[b]	—0.0218	—0.4283	—0.0134
BC(2)	—0.0474	0.4772	0.1234
BC(3)	—0.0256	0.5489	0.1367
BH(1)	—0.0389	0.3719	—0.0239
BH(2)	—0.0846	0.4592	0.2203
BH(3)	—0.0457	0.5874	0.2442

(Table to be continued)

TABLE 1 (continued)

B. Anisotropic Temperature Factors ($\times 10^4$) [b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	116(3)	26(1)	120(3)	−9(1)	13(2)	12(1)
Co(1)	173(4)	29(1)	98(4)	−5(2)	9(3)	13(2)
Co(2)	221(5)	32(1)	98(4)	−31(2)	−8(3)	14(2)
Co(3)	122(4)	32(1)	168(4)	−16(2)	29(3)	19(2)
Co(4)	125(4)	29(1)	235(5)	−3(2)	52(4)	16(2)
C(1)	266(46)	36(9)	217(42)	14(16)	−9(35)	61(16)
O(1)	239(31)	89(9)	283(32)	41(13)	82(25)	31(13)
C(2)	233(42)	54(10)	208(38)	−50(17)	13(33)	40(15)
O(2)	340(37)	110(10)	298(34)	−120(17)	56(28)	19(15)
C(3)	254(44)	45(9)	195(39)	−26(16)	30(33)	39(17)
O(3)	278(31)	73(8)	265(31)	−31(12)	−55(25)	76(14)
C(4)	216(42)	27(8)	281(48)	−5(14)	100(37)	−1(17)
O(4)	378(39)	54(7)	263(33)	−51(13)	43(28)	−18(13)
BC(1)	292(68)	44(13)	1501(199)	−48(25)	−370(93)	55(44)
BC(2)	221(59)	164(29)	1552(214)	−121(33)	−533(88)	394(77)
BC(3)	232(63)	125(26)	1528(230)	41(34)	−442(104)	25(63)
B	337(73)	38(13)	191(56)	10(25)	−46(53)	−23(23)
F(1)	843(78)	114(12)	375(40)	92(25)	124(42)	59(19)
F(2)	671(54)	77(8)	392(38)	15(16)	172(36)	−3(15)
F(3)	659(75)	185(19)	1097(105)	−226(34)	−184(64)	−12(37)
F(4)	374(38)	179(15)	356(36)	104(21)	31(29)	24(18)

C. Isotropic Temperature Factors (Å^2)

C(1-1)	6.0(4)	C(3-1)	7.6(5)
C(1-2)	6.1(4)	C(3-2)	7.7(5)
C(1-3)	6.0(4)	C(3-3)	7.3(5)
C(1-4)	6.1(4)	C(3-4)	7.3(5)
C(1-5)	6.0(4)	C(3-5)	6.1(4)
C(2-1)	6.5(5)	C(4-1)	7.3(5)
C(2-2)	7.5(5)	C(4-2)	9.1(6)
C(2-3)	8.0(5)	C(4-3)	8.5(6)
C(2-4)	7.6(5)	C(4-4)	8.5(6)
C(2-5)	6.8(5)	C(4-5)	8.0(5)
H(all) [c]	5.0		

[a] The standard deviations of the last significant figures are given in parentheses after the number in this and the following tables. [b] The benzene molecule of crystallization was refined as a rigid-body molecule of D_{6h} symmetry with C—C and C—H bond distances of 1.394 and 1.096 Å, respectively. [c] The anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [d] All hydrogen thermal parameters were assigned a fixed value of 5.0 Å^2.

TABLE 2

DISTANCES AND ANGLES FOR $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$

A. Intramolecular Distances (Å)

As-Co(1)	2.263(3)	Co(1)-C(1-1)	2.10(2)
As-Co(2)	2.273(3)	Co(1)-C(1-2)	2.06(2)
As-Co(3)	2.271(3)	Co(1)-C(1-3)	2.07(2)
As-Co(4)	2.255(3)	Co(1)-C(1-4)	2.08(2)
	2.266(av)	Co(1)-C(1-5)	2.10(2)
		Co(2)-C(2-1)	2.11(2)
Co(1)-Co(2)	2.596(3)	Co(2)-C(2-2)	2.08(2)
Co(3)-Co(4)	2.607(3)	Co(2)-C(2-3)	2.06(2)
		Co(2)-C(2-4)	2.08(2)
Co(1)-C(1)	1.73(2)	Co(2)-C(2-5)	2.08(2)

(Table to be continued)

TABLE 2 (continued)

A. Intramolecular Distances (Å)

Co(2)-C(2)	1.70(2)	Co(3)-C(3-1)	2.06(2)
Co(3)-C(3)	1.74(2)	Co(3)-C(3-2)	2.07(2)
Co(4)-C(4)	1.71(3)	Co(3)-C(3-3)	2.04(2)
	1.72(av)	Co(3)-C(3-4)	2.09(2)
		Co(3)-C(3-5)	2.11(2)
C(1)-O(1)	1.15(2)	Co(4)-C(4-1)	2.06(2)
C(2)-O(2)	1.16(2)	Co(4)-C(4-2)	2.11(2)
C(3)-O(3)	1.13(2)	Co(4)-C(4-3)	2.06(2)
C(4)-O(4)	1.16(2)	Co(4)-C(4-4)	2.07(2)
	1.15(av)	Co(4)-C(4-5)	2.06(2)
			2.08(av)
B-F(1)	1.32(3)		
B-F(2)	1.26(3)	Co(1)-Cp(1)[a]	1.70
B-F(3)	1.22(3)	Co(2)-Cp(2)	1.71
B-F(4)	1.28(3)	Co(3)-Cp(3)	1.72
	1.27(av)	Co(4)-Cp(4)	1.71
			1.71(av)
C(1-1)-C(1-2)	1.38(2)	C(1-1)-H(1-1)	1.09
C(1-2)-C(1-3)	1.37(3)	C(1-2)-H(1-2)	1.15
C(1-3)-C(1-4)	1.49(3)	C(1-3)-H(1-3)	1.06
C(1-4)-C(1-5)	1.32(3)	C(1-4)-H(1-4)	1.12
C(1-5)-C(1-1)	1.47(3)	C(1-5)-H(1-5)	1.11
C(2-1)-C(2-2)	1.45(2)	C(2-1)-H(2-1)	1.10
C(2-2)-C(2-3)	1.39(2)	C(2-2)-H(2-2)	1.09
C(2-3)-C(2-4)	1.38(2)	C(2-3)-H(2-3)	1.14
C(2-4)-C(2-5)	1.41(3)	C(2-4)-H(2-4)	1.09
C(2-5)-C(2-1)	1.37(3)	C(2-5)-H(2-5)	1.13
C(3-1)-C(3-2)	1.40(2)	C(3-1)-H(3-1)	1.13
C(3-2)-C(3-3)	1.32(2)	C(3-2)-H(3-2)	1.13
C(3-3)-C(3-4)	1.39(3)	C(3-3)-H(3-3)	1.15
C(3-4)-C(3-5)	1.38(2)	C(3-4)-H(3-4)	1.13
C(3-5)-C(3-1)	1.39(2)	C(3-5)-H(3-5)	1.12
C(4-1)-C(4-2)	1.41(2)	C(4-1)-H(4-1)	1.13
C(4-2)-C(4-3)	1.37(2)	C(4-2)-H(4-2)	1.09
C(4-3)-C(4-4)	1.42(2)	C(4-3)-H(4-3)	1.15
C(4-4)-C(4-5)	1.35(2)	C(4-4)-H(4-4)	1.10
C(4-5)-C(4-1)	1.40(2)	C(4-5)-H(4-5)	1.13

B. Bond Angles (Degrees)

Co(1)-As-Co(2)	69.8(1)	As-Co(1)-Cp(1)	128.9
Co(3)-As-Co(4)	70.3(1)	As-Co(2)-Cp(2)	129.0
		As-Co(3)-Cp(3)	131.3
Co(1)-As-Co(3)	133.0(1)	As-Co(4)-Cp(4)	130.5
Co(1)-As-Co(4)	132.2(1)		129.9(av)
Co(2)-As-Co(3)	130.6(1)		
Co(2)-As-Co(4)	132.6(1)	Co(1)-Co(2)-Cp(2)	137.4
	132.1(av)	Co(2)-Co(1)-Cp(1)	136.1
		Co(3)-Co(4)-Cp(4)	136.6
Co(1)-Co(2)-As	54.9(1)	Co(4)-Co(3)-Cp(3)	135.4
Co(2)-Co(1)-As	55.3(1)		136.4(av)
Co(3)-Co(4)-As	55.1(1)		
Co(4)-Co(3)-As	54.5(1)	C(1)-Co(1)-Cp(1)	129.3
	55.0(av)	C(2)-Co(2)-Cp(2)	127.5
		C(3)-Co(3)-Cp(3)	127.8
As-Co(1)-C(1)	95.0(7)	C(4)-Co(4)-Cp(4)	127.8
As-Co(2)-C(2)	95.8(7)		128.1(av)
As-Co(3)-C(3)	95.2(6)		

(Table to be continued)

TABLE 2 (continued)

B. Bond Angles (Degrees)

As-Co(4)-C(4)	95.8(7)	F(1)-B-F(2)	111(3)
	95.5(av)	F(1)-B-F(3)	104(3)
		F(1)-B-F(4)	107(4)
Co(1)-Co(2)-C(2)	88.0(7)	F(2)-B-F(3)	114(4)
Co(2)-Co(1)-C(1)	87.1(7)	F(2)-B-F(4)	112(3)
Co(3)-Co(4)-C(4)	87.0(7)	F(3)-B-F(4)	107(3)
Co(4)-Co(3)—C(3)	87.6(7)		
	87.4(av)		
Co(1)-C(1)-O(1)	177(2)		
Co(2)-C(2)-O(2)	175(2)		
Co(3)-C(3)-O(3)	174(2)		
Co(4)-C(4)-O(4)	176(2)		

C. Closest Intermolecular Distances (Å)[b]

C(1)···H(2-3)^{I}	3.08	B···H(1-5)^{IV}	3.26
C(3)···H(3-3)^{II}	3.00	B···H(3-2)^{VIII}	2.92
C(4)···H(3-4)^{III}	3.37	B···H(4-3)^{III}	3.17
O(1)···H(2-3)^{II}	3.27	B···BH(1)	2.99
O(1)···O(2)^{IV}	3.28	F(1)···H(1-2)	2.93
O(2)···H(3-1)^{V}	3.05	F(1)···H(2-1)^{IX}	3.40
O(2)···BH(2)^{V}	2.82	F(1)···H(2-2)^{IX}	2.49
O(2)···F(2)^{V}	3.18	F(1)···H(3-2)^{VIII}	2.44
O(3)···H(1-1)^{VI}	2.91	F(1)···H(4-5)^{IX}	2.89
O(3)···H(3-3)^{VII}	3.24	F(1)···BH(1)	2.60
O(3)···H(3-4)^{VII}	3.14	F(1)···BH(3)^{X}	3.18
O(3)···O(4)^{VI}	3.34	F(2)···H(1-2)	2.98
O(3)···F(3)^{VII}	3.19	F(2)···H(1-5)^{IV}	2.58
O(4)···H(3-4)^{III}	2.55	F(2)···H(3-5)	2.87
O(4)···O(4)^{III}	3.34	F(2)···H(4-1)^{IV}	2.67
C(1-1)···H(2-1)^{VIII}	2.95	F(2)···BH(1)	2.38
C(1-2)···H(2-5)^{VIII}	3.17	F(3)···H(1-5)^{IV}	3.12
C(1-3)···H(2-3)^{I}	3.21	F(3)···H(2-1)^{IX}	3.02
C(1-5)···C(2-1)^{VI}	3.22	F(3)···H(3-2)^{VIII}	3.32
C(1-5)···H(2-1)^{VI}	2.87	F(3)···H(4-2)^{IV}	3.04
C(2-2)···F(1)^{VII}	3.35	F(3)···H(4-3)^{III}	2.70
C(2-2)···BH(1)^{VII}	3.20	F(3)···H(4-5)^{IX}	2.80
C(2-2)···BH(3)^{I}	3.35	F(4)···H(1-2)	3.18
C(2-3)···H(1-3)^{I}	3.02	F(4)···H(3-5)	2.43
C(2-3)···H(2-4)^{I}	3.28	BC(1)···H(1-2)	2.73
C(2-4)···H(1-4)^{I}	3.27	BC(1)···H(1-3)	3.38
C(2-4)···H(2-3)^{I}	3.26	BC(1)···H(2-2)^{IX}	2.85
C(3-1)···C(4-1)^{IV}	3.37	BC(2)···H(1-3)	3.44
C(3-1)···H(4-1)^{IV}	2.98	BC(2)···H(1-4)^{IV}	3.41
C(3-2)···F(1)^{VI}	3.37	BC(3)···H(1-3)	3.37
C(3-3)···H(3-3)^{II}	3.08	BC(3)···H(2-2)^{II}	2.85
C(3-3)···H(4-4)^{II}	2.88		
C(3-5)···H(4-1)^{V}	3.11		
C(4-3)···H(3-3)^{II}	3.41		
C(4-4)···H(3)^{II}	3.03		

---

[a] Cp(*n*) denotes the centroid of the *n*th cyclopentadienyl ring. [b] The superscripts refer to the following symmetry related positions: (I) $1 - x, 1 - y, 1 - z$; (II) $1 - x, -y, 1 - z$; (III) $1 - x, -y, -z$; (IV) $-1 + x, y, z$; (V) $1 + x, y, z$; (VI) $x, y, 1 + z$; (VIII) $x, y, 1 + z$ (IX) $-1 + x, y, -1 + z$; (X) $-x, 1 - y, -z$.

angles (with estimated standard deviations calculated from the variance-covariance matrix) are listed in Table 2. The least-squares planes defined by specific atoms along with perpendicular displacements of these and other atoms from

TABLE 3

DISTANCES OF ATOMS FROM SELECTED LEAST-SQUARES PLANES[a] IN THE $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ CATION AND ANGLES BETWEEN THE NORMALS TO THESE PLANES

A. Distances (Å) from the Plane Formed by Co(1), Co(2), and As.					
$0.869X - 0.104Y - 0.484Z - 3.243 = 0$					
Co(3)	−1.32	C(1)	−1.71	O(1)	−2.84
Co(4)	1.28	C(2)	1.68	O(2)	2.81
B. Distances (Å) from the Plane Formed by Co(3), Co(4) and As.					
$-0.502X + 0.069Y - 0.862Z + 5.366 = 0$					
Co(1)	1.27	C(3)	−1.72	O(3)	−2.82
Co(2)	−1.33	C(4)	1.69	O(4)	2.83
C. Distances (Å) from the Plane Formed by Co(1), Co(2), C(1), and C(2).					
$-0.127X - 0.992Y - 0.015Z + 6.484 = 0$					
Co(1)	0.12	C(1)	−0.12	O(1)	−0.33
Co(2)	0.13	C(2)	−0.13	O(2)	−0.34
As	1.99				
D. Distances (Å) from the Plane Formed by Co(3), Co(4), C(3), and C(4).					
$-0.118X - 0.993Y - 0.006Z - 2.398 = 0$					
Co(3)	0.14	C(3)	−0.13	O(3)	−0.39
Co(4)	0.14	C(4)	−0.14	O(4)	−0.31
As	1.99				
E. Distances (Å) from the Plane Formed by C(1-1), C(1-2), C(1-3), C(1-4), and C(1-5).					
$0.238X + 0.237Y - 0.942Z - 2.483 = 0$					
Co(1)	−1.70	C(1-2)	0.00	C(1-4)	0.01
C(1-1)	0.01	C(1-3)	0.00	C(1-5)	−0.01
F. Distances (Å) from the Plane Formed by C(2-1), C(2-2), C(2-3), C(2-4), and C(2-5).					
$-0.163X - 0.244Y - 0.956Z + 6.021 = 0$					
Co(2)	1.70	C(2-2)	0.00	C(2-4)	−0.01
C(2-1)	−0.01	C(2-3)	0.00	C(2-5)	0.01
G. Distances (Å) from the Plane Formed by C(3-1), C(3-2), C(3-3), C(3-4), and C(3-5).					
$-0.971X - 0.162Y - 0.178Z + 3.683 = 0$					
Co(3)	−1.72	C(3-2)	−0.01	C(3-4)	0.01
C(3-1)	0.02	C(3-3)	0.00	C(3-5)	−0.02
H. Distances (Å) from the Plane Formed by C(4-1), C(4-2), C(4-3), C(4-4), and C(4-5).					
$-0.910X + 0.384Y - 0.157Z + 7.566 = 0$					
Co(4)	1.70	C(4-2)	0.01	C(4-4)	0.00
C(4-1)	−0.01	C(4-3)	−0.01	C(4-5)	0.01
I. Angles (Degrees) Between Normals to the Planes.					
A and B	91.5	A and E	50.4		
A and C	90.0	A and F	51.0		
B and D	89.2	B and G	51.0		
C and D	178.7	B and H	51.8		

---

[a] The equations of the planes are given in an orthogonal Ångstrom coordinate system (XYZ) which is related to the fractional triclinic unit cell coordinate system (xyz) as follows: $X = xa + yb\cos\gamma + zc\cos\beta$, $Y = yb\sin\gamma + zc\cos\mu$, $Z = zc\cos\sigma$, where $\cos\mu = (\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$, and $\sin\sigma = (1 - \cos^2\beta - \cos^2\mu)^{1/2}$.

these planes and the angles between the normals to these planes are presented in Table 3.

Results and discussion

The $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4(\mathrm{CO})_4(\mu_4\text{-}\mathrm{As})]^+$ monocation with the $\mathrm{BF_4^-}$ counterion was obtained in low yield from the reaction of arsenic trifluoride with a benzene solution of cyclopentadienylcobalt dicarbonyl in a Pyrex-glass reaction vessel at room temperature. The presence of only terminal carbonyl ligands was indicated from the analogous solution and solid-state IR spectra. The diamagnetism of the monocation was established in solution from the lack of an EPR resonance and from the nature of a ^{1}H NMR spectrum which showed only one sharp singlet characteristic of the equivalence of all cyclopentadienyl protons. The X-ray crystallographic study, which was undertaken to determine the actual composition as well as the molecular configuration of this new type of metal—arsenic complex, disclosed the presence of a tetrahedral-like arsenic atom linking two bis(cyclopentadienylcobalt carbonyl) moieties to each other by its participation as a common bridging ligand in each moiety.

Crystalline $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4(\mathrm{CO})_4(\mu_4\text{-}\mathrm{As})]^+\mathrm{BF_4^-}\cdot\frac{1}{2}\mathrm{C_6H_6}$ is composed of discrete cations and anions packed as shown in Fig. 1 and 2. Each primitive triclinic unit cell contains two $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4(\mathrm{CO})_4(\mu_4\text{-}\mathrm{As})]^+$ cations, two $\mathrm{BF_4^-}$ anions, and one benzene molecule of crystallization which is located on a crystallographic center of symmetry at $(0, \frac{1}{2}, 0)$. The closest intermolecular contacts are normal thereby suggesting no unusual intermolecular interactions.

The configuration of the $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4(\mathrm{CO})_4(\mu_4\text{-}\mathrm{As})]^+$ monocation depicted in Figs. 3 and 4 consists of two identical $[\mathrm{Co_2}(h^5\text{-}\mathrm{C_5H_5})_2(\mathrm{CO})_2]$ moieties joined to a unique arsenic atom such that this arsenic atom is tetrahedrally coordinated to four cobalt atoms. Although no special symmetry is demanded by the space

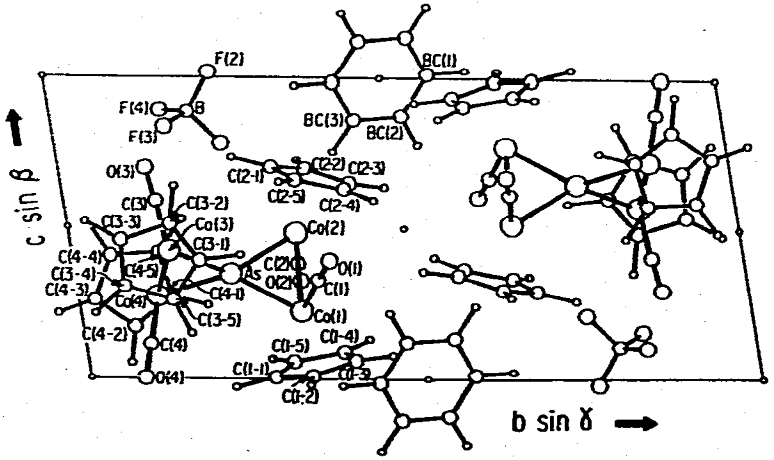

Fig. 1. [100] projection showing two $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4(\mathrm{CO})_4(\mu_4\text{-}\mathrm{As})]^+$ cations, two $\mathrm{BF_4^-}$ anions, and one benzene molecule in the reduced triclinic unit cell of $P\bar{1}$ symmetry.

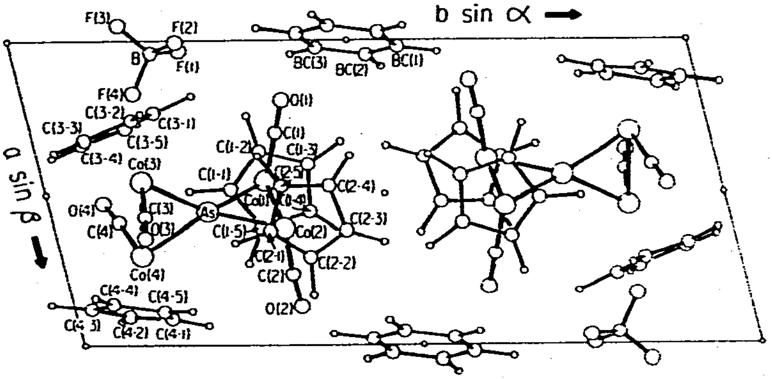

Fig. 2. [001] projection showing two $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ cations, two BF_4^- anions, and one benzene molecule in the centrosymmetric unit cell.

group, (i.e., all atoms are in general positions), the independent monocation ideally possesses S_4-$\bar{4}$ symmetry with the $\bar{4}$ axis passing through the unique arsenic atom and through the midpoints of the Co(1)—Co(2) and Co(3)—Co(4) bond vectors. A consideration of each of the two $[Co_2(h^5\text{-}C_5H_5)_2(CO)_2As]$ fragments as an edge-bridged bioctahedron is consistent with the localized environment about each cobalt atom being viewed conceptually as pseudooctahedral with the bridging arsenic atom and terminal carbonyl ligand each occupying a coordination site, the cyclopentadienyl ligand occupying three more sites, and a distinct "bent" Co—Co bond occupying the sixth coordination site [17,18] *. The approximate conformity of each $[Co_2(h^5\text{-}C_5H_5)_2(CO)_2As]$ fragment to a C_2 geometry with the twofold axis coincident with the S_4-$\bar{4}$ axis of the monocation is shown from a calculation of its Co_2As plane (Table 3, A and B). The pairs of corresponding atoms related by the twofold axis are essentially equidistant from these symmetry planes. The closeness of the two Co_2As planes to being perpendicular, which is required under S_4 symmetry, is evidenced by their dihedral angle of 91.5°. The resulting $[CO_4As]^+$ species formally containing a quadruply bridging arsenic cation, which donates one valence electron to each of the four cobalt atoms, is considerably distorted from a regular tetrahedral T_d arrangement toward a tetragonal D_{2d}-$\bar{4}2m$ geometry due to the six intramolecular Co—Co distances being divided into two electron-pair bonding ones of 2.60 Å (av.) and four nonbonding ones of 4.14 Å (av.). The disposition of the cyclopentadienyl and carbonyl ligands about the central Co_4As core reduces the symmetry from D_{2d} for the core toward the observed S_4 symmetry for the entire monocation.

The mean Co—As distance of 2.266 Å is similar to the mean Co—As distance of 2.288 Å found in $[Co_3(CO)_8(\mu_4\text{-}As)]_3$ [19,20], which also contains arsenic atoms tetrahedrally coordinated to four cobalt atoms. The mean Co—CO and

---

* A face-bridged bioctahedral description with a distinct "bent" metal—metal bond conceptually envisioned as completing an octahedral-like coordination about each metal atom was proposed [17] for the $Fe_2(CO)_6X_2$-type dimers. Although nonparameterized molecular orbital calculations [18] on representative complexes indicate in general that the Fe—Fe bond is not as "bent" as that assumed from a regular octahedral-like environment, nevertheless, this overall representation of the metal valency as octahedral-like is found not to be inappropriate in these complexes.

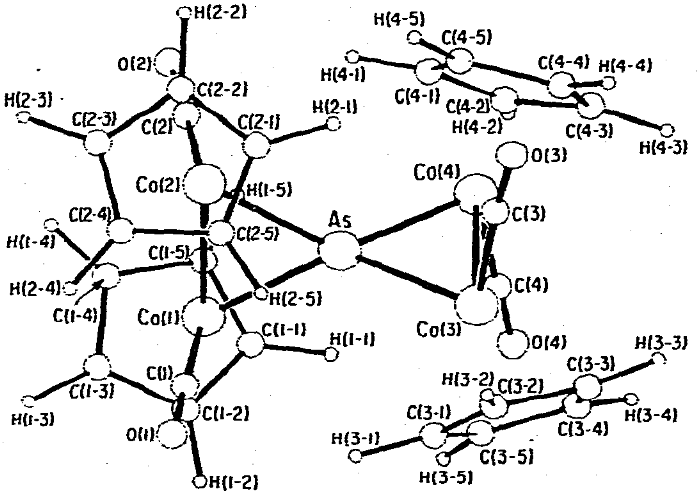

Fig. 3. Configuration of the $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ monocation showing the atom labeling scheme used.

C—O distances are 1.72 and 1.15 Å, respectively, with the approximately linear Co—C—O bonds being nearly perpendicular to the attached Co_2As triangles. The cyclopentadienyl rings form dihedral angles of 51° with the Co_2As triangles. The average Co—C(cyclopentadienyl) distance is 2.08 Å, while the average distance from the centroid of a cyclopentadienyl ring to its attached cobalt atom is 1.71 Å.

The $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ monocation is structurally analogous and electronically equivalent to the air-stable $[Fe_2(CO)_8]_2(\mu_4\text{-}Sn)$ molecule [10] which has a spiro-like Fe_4Sn core resulting from the bonding of four $Fe(CO)_4$ groups to a tetrahedrally distorted tin atom. The entire molecule closely con-

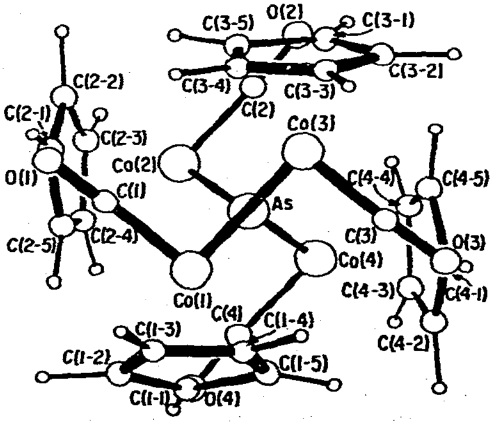

Fig. 4. The $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ monocation viewed down the pseudo $S_4\text{-}\bar{4}$ axis.

forms to tetragonal D_{2d}-$\bar{4}2m$ symmetry with two bonding Fe—Fe distances of 2.87 Å and four nonbonding Fe···Fe distances of 4.65 Å. The large tetragonal D_{2d} distortion from a cubic T_d geometry containing a regular tetrahedral tin atom is also a consequence of the formation of the two electron-pair metal—metal bonds enabling each octahedral-like iron atom to attain a closed-shell electronic configuration in accord with the observed diamagnetism of the compound. Two other structurally related tetrairon cluster molecules are the $[Fe_2(CO)_6(\mu_2\text{-}SCH_3)]_2(\mu_4\text{-}S)$ molecule [11] with its spiro-like Fe_4S core and the $[Fe_2(CO)_8(\mu_2\text{-}Sn(CH_3)_2)]_2(\mu_4\text{-}Sn)$ molecule [12] with its spiro-like Fe_4Sn core. The $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ monocation represents the first example (to our knowledge) of a discrete organometallic complex with a spiro-like metal cluster core containing a central arsenic or phosphorus atom. The prior existence of "bare" arsenic and phosphorus atoms tetrahedrally coordinated to four transition metals in a discrete metal cluster system was established from structural studies of the trimeric $[Co_3(CO)_8(\mu_4\text{-}As)]_3$ and $[Co_3(CO)_7(\mu_4\text{-}P)]_3$ complexes [19,20] in which the arsenic and phosphorus atoms are each tetrahedrally linked to three metal atoms in one bonding triangular array and to a fourth metal atom in another triangular metal array.

The presence of the tetrafluoroborate anions was indicated by the IR spectra and substantiated by the X-ray analysis. The independent BF_4^- anion was found to be a nearly regular tetrahedron with B—F bond lengths of range 1.22(3)—1.32(3) Å and with F—B—F angles varying from 104(3)° to 112(3)°. Although the average B—F distance of 1.27 Å is considerably shorter than those previously reported for KBF_4 (1.40 Å) [21], $RbBF_4$ (1.43 Å) [22], and NH_4BF_4 (1.43 Å) [22], it is essentially identical with that determined for $[Ni_3(h^5\text{-}C_5H_5)_3(\mu_3\text{-}(t\text{-}NC_4H_9))]^+BF_4^-$ [23] and for $[Ni_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_3]^+BF_4^-$ [8]. This short value may be attributed to unusually large anisotropic thermal motion of the monoanion in the $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+BF_4^- \cdot \frac{1}{2}C_6H_6$ crystal, which results in the observed B—F distances being systematically reduced from their true values. The boron atom in the BF_4^- anion apparently originates from the Pyrex-glass of the reaction vessel, in that similar extractions of boron from Pyrex glass with fluorine-containing reagents to give the tetrafluoroborate anion have been observed previously in the reaction of perfluoroethylene with *trans*-$Pt(P(C_2H_5)_3)_2HCl$ to produce $[Pt(P(C_2H_5)_3)_2Cl(CO)]^+BF_4^-$ [24] and in the reaction of arsenic trifluoride with nickelocene to give $[Ni_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}As)_3]^+BF_4^-$ [8].

The detection of the benzene solvent molecule in the unit cell was revealed from a Fourier difference map which unequivocally showed a planar arrangement of six atoms about a crystallographic center of symmetry. As indicated from Figs. 1 and 2, the solvent molecule fits easily into its space in the unit cell with no anomalously short contacts involving either the $[Co_4(h^5\text{-}C_5H_5)_4(CO)_4(\mu_4\text{-}As)]^+$ cations or the BF_4^- anions. The shortest H···H and H···F contacts are 2.41 and 2.38 Å, respectively.

Acknowledgments

This research was financially supported by the National Science Foundation. The use of the UNIVAC 1110 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation administered through the University Research Committee.

References

1 (a) R.A. Schunn, C.J. Fritchie, Jr. and C.T. Prewitt, Inorg. Chem. 5 (1966) 892; (b) C.H. Wei, R.G. Wilkes, P.M. Treichel and L.F. Dahl, Inorg. Chem. 5 (1966) 900.
2 (a) Trinh-Toan, W.P. Fehlhammer and L.F. Dahl, J. Amer. Chem. Soc., in press; (b) Trinh-Toan, B.K. Teo, J.A. Ferguson, T.J. Meyer and L.F. Dahl, J. Amer. Chem. Soc., in press.
3 (a) R.M. Roder and L.F. Dahl, submitted for publication; (b) R.M. Roder, Ph.D. Thesis, University of Wisconsin-Madison, 1973.
4 T.M. Burger, C.H. Wei and L.F. Dahl, to be published.
5 G.L. Simon and L.F. Dahl, J. Amer. Chem. Soc., 95 (1973) 2164, 2175.
6 R.C. Ryan and L.F. Dahl, J. Amer. Chem. Soc., 97 (1975) 6904.
7 M.S. Paquette and L.F. Dahl, to be published.
8 (a) J.D. Sinclair and L.F. Dahl, to be published; (b) J.D. Sinclair, Ph.D. Thesis, University of Wisconsin-Madison, 1972.
9 L.T.J. Delbaere, L.J. Kruczynski and D.W. McBride, J. Chem. Soc. Dalton (1973) 307.
10 P.F. Lindley and F. Woodward, J. Chem. Soc., A, (1967) 382.
11 J.M. Coleman, A. Wojcicki, P.J. Pollick and L.F. Dahl, Inorg. Chem., 6 (1967) 1236.
12 R.M. Sweet, C.J. Fritchie, Jr. and R.A. Schunn, Inorg. Chem., 6 (1967) 749.
13 (a) C.F. Campana, Ph.D. Thesis, University of Wisconsin-Madison, 1975; (b) J.L. Petersen and L.F. Dahl, J. Amer. Chem. Soc., 97 (1975) 6422.
14 D.T. Cromer and J.F. Mann, Acta Crystallogr., Sect. A, 24 (1968) 321.
15 R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys., 42 (1965) 3175.
16 International Tables for X-Ray Crystallography, Vol. III, the Kynoch Press, Birmingham, England, 1962, p. 215.
17 (a) C.H. Wei and L.F. Dahl, Inorg. Chem., 4 (1965) 1; (b) L.F. Dahl and C.H. Wei, Inorg. Chem., 2 (1968) 328.
18 B.K. Teo, M.B. Hall, R.F. Fenske and L.F. Dahl, Inorg. Chem., 14 (1975) 3103.
19 R.S. Gall, Ph.D. Thesis, University of Wisconsin-Madison, 1973.
20 R.S. Gall, A.S. Foust, P.J. Pollick, A. Wojcicki and L.F. Dahl, Abstracts of the American Crystallographic Association Berkeley, California, March, 1974.
21 A. Bellanco and F. Sgarlata, Rend. Soc. Mineralog. Ital., 7 (1951) 42.
22 J.L. Hoard and V. Blair, J. Amer. Chem. Soc., 57 (1935) 1985.
23 P.D. Frisch, Ph.D. Thesis, University of Wisconsin-Madison, 1972.
24 H.C. Clark, P.W.R. Corfield, K.R. Dixon and J.A. Ibers, J. Amer. Chem. Soc., 89 (1967) 3360.