An assessment may be made of the geometrical differences between an "open" P–N–P system and a "closed" one that is part of a cyclic ring by comparison of the corresponding parameters in the $[(C_6H_5)_3P \overset{\cdots}{-} N \overset{\cdots}{-} P(C_6H_5)_3]^+$ cation with those in the cyclotriphosphazene molecules, $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3(C_6H_5)_6$, containing $(C_6H_5)_2P–N–P(C_6H_5)_2$ segments. Despite the considerably larger P–N–P bond angles of range 137–142° found in the PPN cation *vs.* those of 124.9 (5)° and 122.1 (3)° in the geometrically constrained $N_3P_3Cl_2(C_6H_5)_4$ and $N_3P_3(C_6H_5)_6$ rings, respectively, the essential invariance of the P–N bond lengths is indicative that the composite effect of inductive σ-bonding and π-bonding character is not appreciably altered in these open and closed P–N–P systems.

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Organometallic Pnicogen Complexes. V. Preparation, Structure, and Bonding of the Tetrameric Antimony–Cobalt Cluster System, $Co_4(CO)_{12}Sb_4$: The First Known (Main Group Element)–(Metal Carbonyl) Cubane-Type Structure[1]

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Abstract: An attempt to prepare the unknown $Co_2(CO)_6Sb_2$ complex (as a pnicogen analog of the recently synthesized $Co_2(CO)_6As_2$) has led instead to the isolation of a new cobalt–antimony cluster $Co_4(CO)_{12}Sb_4$ molecule. Black crystals of this air-stable, insoluble compound were synthesized by the reaction of $Co(OAc)_2 \cdot 4H_2O$ with $SbCl_3$ in methanol (or pentane) solution at 150° under a high-pressure mixture of carbon monoxide and hydrogen. Characterization of this complex by a three-dimensional X-ray diffractometry study revealed a cubane-like architecture comprised of two interpenetrating, concentric nonbonded tetrahedra of cobalt and antimony atoms with the four $Co(CO)_3$ fragments interconnected by triply bridging antimony atoms. The determined structure ideally displays cubic T_d-$\bar{4}3m$ geometry with an average electron-pair Co–Sb distance of 2.614 (2) Å and with acute Sb–Co–Sb and obtuse Co–Sb–Co angles of average values 74.3 (1) and 103.8 (1)°, respectively. This molecule and the related cyclopentadienyliron tetramers, $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ and $Fe_4(h^5\text{-}C_5H_5)_4S_4$, are described in terms of a qualitative molecular orbital model which successfully relates their molecular geometries, including the absence of direct cobalt–cobalt bonding in $Co_4(CO)_{12}Sb_4$, in accord with an observed average nonbonding $Co \cdots Co$ internuclear distance of 4.115 (4) Å. The $Co_4(CO)_{12}Sb_4$ compound crystallizes in the tetragonal system with cell dimensions a = 14.561 (3), c = 10.507 (4) Å, and with centrosymmetric space group symmetry $I4_1/amd$. Each of the four molecules per cell possesses crystallographic site symmetry D_{2d}-$\bar{4}2m$. The application of the symbolic-addition method in space group $I4_1/amd$ to determine this crystal structure is briefly outlined. Full-matrix least-squares refinement of the structure yielded R_1 = 5.0% and R_2 = 5.2% for the 282 independent reflections with $|F_o| > 4\sigma(F_o)$.

The synthesis and study of transition-metal complexes containing metal–metal bonds has shown a meteoric rise in the last few years.[3-7] Prior to about 10 years ago, metal–metal bonding was primarily a curiosity, and the deliberate synthesis of a compound containing a metal–metal bond was virtually unknown.

The recent preparation and characterization of $Co_2(CO)_6As_2$ in our laboratory led to the postulation of the existence of an As–As multiple bond of π order near

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[1] Previous paper in this series: A. S. Foust, M. S. Foster, and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 5633 (1969).

[2] This paper is based in part on a dissertation submitted by A. S. F. to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the Ph.D. degree, Jan 1970.

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one in order to rationalize the unusually short As–As internuclear separation of 2.273 (3) Å found in an X-ray structural examination of the structurally analogous triphenylphosphine derivative $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$.[1] A comparison of the molecular parameters of $Co_2\{(CO)_5P(C_6H_5)_3\}As_2$ and the structurally and electronically equivalent $Co_2(CO)_6(C_6H_5C_2C_6H_5)$[8,9] molecules with those of $Fe_2(CO)_6S_2$[10] and other iron carbonyl nitrogen analogs[11,12] supports the premise that $Co_2(CO)_6X_2$ molecules should display considerably greater X–X multiple bonding than $Fe_2(CO)_6X_2$ molecules. Thus, it seemed reasonable from energetic considerations that $Co_2(CO)_6Sb_2$ (with the congener Sb substituted in place of As), if it could be made, should likewise display an unusually short X–X bond length in accord with large Sb–Sb multiple bond character. Mother Nature did not smile upon a deliberate synthesis (as is her usual wont in metal carbonyl chemistry) of such a system containing multiple bonding between two atoms of a main group element but instead afforded $Co_4(CO)_{12}Sb_4$. This latter molecule without Sb–Sb bonds is, however, a very interesting one in its own right since it represents the first known (metal carbonyl)–(main group element) cubane-like molecule.

Experimental Section

Preparation of $Co_4(CO)_{12}Sb_4$. The reaction of 10 g of $Co(OAc)_2 \cdot 4H_2O$ with 5 g of $SbCl_3$ in 100 ml of CH_3OH (or pentane) at 150° under 200 atm of CO and 100 atm of H_2 was allowed to proceed 3 days in a Hoke bomb. At the end of this period, the bomb was cooled, vented, and opened. Hundreds of small, shiny black crystals were scraped from the walls of the bomb and the glass liner along with large quantities of yellow-orange material which was not characterized. It has not been possible to dissolve these crystals in common solvents nor to sublime them; the only purification procedure available to date has been mechanical separation with the aid of a microscope. These crystals seem stable in air for at least several weeks. A carbon–hydrogen analysis (Galbraith Laboratories, Inc.) of 4.0 mg of crystals obtained by hand separation under a microscope showed an expected absence of hydrogen and 13.45% of carbon, in good agreement with the calculated value of 13.60% based on the empirical formula $Co(CO)_3Sb$. The tetrameric nature of this compound was established by a single-crystal X-ray examination.

An infrared spectrum of $Co_4(CO)_{12}Sb_4$ was recorded as a Nujol mull on a Beckman IR-8 spectrometer. The spectrum shows two broad absorption bands in the terminal carbonyl region characteristic of a C_{3v} $Co(CO)_3$ group. The nondegenerate A_1 vibration is at 1995 (s) cm^{-1}, and the degenerate E vibration is at 2042 (vs) cm^{-1}.

Mass spectra of $Co_4(CO)_{12}Sb_4$ were attempted without success with an AEI MS-902 spectrometer under a variety of conditions. At a temperature of 150–175° the solid sample loses carbon monoxide as evidenced by the increased relative intensity of the peak at an *m/e* of 28.

Unit Cell and Space Group. The measured lattice constants (25°) and estimated standard deviations for the tetragonal unit cell of $Co_4(CO)_{12}Sb_4$ are: $a = 14.561$ (3), $c = 10.507$ (4) Å; unit cell volume equals 2228 Å^3. The calculated density for four tetrameric molecules per cell is 3.16 g cm^{-3}. The total number of electrons per cell, $F(000)$, is 1920. The systematic absences of $h + k + l$ odd for $\{hkl\}$, h and k both odd for $\{hk0\}$, and $2h + l \neq 4n$ for (hhl) uniquely define the space group as $I4_1/amd$ (D_{4h}^{19}, no. 141).[13] This centrosymmetric space group was successfully utilized in determining the crystal structure which showed the 16 cobalt atoms to occupy one set of 16-fold special positions (16*h*) on mirror planes, the 16 antimony atoms likewise to occupy one set of 16*h* on mirror planes, the 48 carbon atoms to occupy one set of the general 32-fold positions (32*i*) and one set of 16*h*, and the 48 oxygen atoms to occupy one set of 32*i* and one set of 16*h*. With the origin chosen at the center $2/m$ located at $0,-\frac{1}{4},\frac{1}{8}$ from $\bar{4}m2$, these positions are as follows: $32i$ $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) \pm (x,y,z;\ x,\frac{1}{2}-y,z;\ \frac{1}{4}+y,\frac{1}{4}+x,\frac{3}{4}+z;\ \frac{1}{4}+y,\frac{1}{4}-x,\frac{3}{4}+z;\ \bar{x},y,z;\ \bar{x},\frac{1}{2}-y,z;\ \frac{3}{4}-y,\frac{1}{4}+x,\frac{3}{4}+z;\ \frac{3}{4}-y,\frac{1}{4}-x,\frac{3}{4}+z)$; $16h$ $(0,0,0;\ \frac{1}{2},\frac{1}{2},\frac{1}{2}) \pm (0,x,z;\ 0,\frac{1}{2}-x,z;\ \frac{1}{4}+x,\frac{1}{4},\frac{3}{4}+z;\ \frac{3}{4}-x,\frac{1}{4},\frac{3}{4}+z)$.

X-Ray Data Collection. A suitable single crystal of $Co_4(CO)_{12}Sb_4$ whose external features approximated those of a bicapped cube was mounted about the *a* axis with Canada Balsam on the end of a fine glass tube. After preliminary oscillation, Weissenberg, and precession photographs this crystal was centered[14] first optically and then in the X-ray beam of a General Electric four-angle automated diffractometer. Lattice and orientation parameters and instrument constants $2\theta_0$ and χ_0 were calculated from the positions of 20 representative diffraction maxima and were refined by a procedure[15] which minimizes the distance between observed and calculated reciprocal lattice points.

Intensity data were collected[16] at a takeoff angle of 2.0° by the θ–2θ scan technique for $2\theta \leq 40°$ with Zr-filtered Mo Kα radiation (λ 0.7107 Å). Symmetric 2θ scans at a 2.0°/min rate were made over a range of 2.4° for $2\theta < 8°$ and of 2.0° for $8° \leq 2\theta \leq 40°$, and 15-sec background counts were taken at the beginning and end of each scan. Four standard reflections were measured every 70 reflections, and scale factors calculated from these standard reflection intensities did not vary more than ±1%. The observed intensities were corrected for background and Lorentz–polarization effects.[17] The intensities of 2227 reflections corresponding to three octants (hkl, $\bar{h}kl$, $\bar{h}\bar{k}\bar{l}$) were recorded (excluding only those reflections systematically absent due to body centering); and after correction and merging[18] a total of 282 independent reflections was obtained with $|F_o| > 4\sigma(F_o)$. Since the asymmetric reciprocal lattice of intensities for tetragonal D_{4h} Laue symmetry is only one-half of an octant, the intensity of each independent reflection in general was measured six times; the overall excellent agreement in the observed intensity values for a given independent reflection provided strong evidence that the data were of high quality.

An absorption correction was deemed an unnecessary expense, since the extreme values of the absorption correction[19] caused only a ±3.4% fluctuation in F's. The linear absorption coefficient is 75.25 cm^{-1} for Mo Kα radiation, and since the crystal was for all practical purposes spherical,[20] the transmission coefficients ranged from only 0.36 to 0.40. No extinction corrections were made.

Determination of the Structure. The structure was solved by application of the symbolic addition method[21] which obtains phases directly from normalized structure factor amplitudes. The computer programs utilized[22] to facilitate this procedure are limited to orthorhombic and lower symmetry, and so the several *ad hoc* procedures adopted to solve this tetragonal structure are briefly out-

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(20) The spherical nature of this crystal utilized for data collection is apparent from the large number of crystal faces identified [*viz.*, (100), ($\bar{1}$00), (110), (0$\bar{1}$0), (011), (0$\bar{1}$1), (01$\bar{1}$), (0$\bar{1}\bar{1}$), (101), ($\bar{1}$01), (10$\bar{1}$), and ($\bar{1}$0$\bar{1}$)] with the perpendicular distances of these faces from a common origin within the crystal varying from only 0.075 to 0.080 mm.

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lined. A reciprocal lattice octant of $|F|$ values corresponding to an orthorhombic D_{2h} asymmetric unit was then produced from the tetragonal half-octant of $|F|$ values corresponding to the D_{4h} holohedral asymmetric unit. The first step in the direct solution of this crystal structure involved the use of all reflections in the generated orthorhombic asymmetric unit to obtain a Wilson plot[23] which enabled the calculation of a normalized structure factor $|E|$ for each reflection. The expanded data were processed by the computer program FAME,[22] which assigns symbols for selected reflections on the basis of interactions. Complete program autonomy is generally acceptable for orthorhombic or lower symmetry, but for this case of tetragonal space group symmetry the following steps were followed to provide additional constraints. The space group *Imma* is the proper orthorhombic subgroup of $I4_1/amd$, and hence all of the limitations on the phases and amplitudes of reflections imposed by *Imma* are contained in the limitations for $I4_1/amd$. In addition, this tetragonal space group requires for $h + k + l = 4n$ that $F(hkl) = F(khl)$ with $h + k = 2n$ and that $F(hkl) = -F(khl)$ with $h + k = 2n + 1$; for $h + k + l = 4n + 2$, $F(hkl) = -F(khl)$ with $h + k = 2n$ and $F(hkl) = F(khl)$ with $h + k = 2n + 1$. By application of the above tetragonal constraints, the following seven reflections involving four symbols may be chosen to comprise the initial list of knowns: (1,10,5), A; (10,1,5), −A; (4,11,1), B; (11,4,1), −B; (1,5,8), C; (5,1,8), −C; and (4,4,4), D.

Five cycles of symbolic addition were performed with the program MAGIC,[22] and this procedure led to 313 phase determinations. These phases yielded an E map[24] which contained ambiguities but was interpretable. In retrospect, it would have been better to start with four symbols involving a uug reflection and either a guu reflection or a ugu reflection from each of the $h + k + l = 4n$ and $h + k + l = 4n + 2$ classes.

Initial coordinates of the independent Co and Sb atoms were obtained from an interpretation of the E map. An electron-density map[24] phased on these Co and Sb coordinates revealed the positions of the two independent carbonyl groups. Four cycles of full-matrix least-squares refinement[25–27] with all atoms isotropic lowered the conventional residuals from $R_1 = 26.7$ and $R_2 = 27.9\%$ to $R_1 = 6.6$ and $R_2 = 7.6\%$. Two further cycles of full-matrix least-squares refinement[25] with all atoms anisotropic lowered the residuals to $R_1 = 5.0$ and $R_2 = 5.2\%$. A final three-dimensional difference Fourier map verified the structural analysis in that it showed no anomalies; no residual peaks were greater than +1.2 electrons/Å^3 or less than −1.0 electron/Å^3. Further unambiguous evidence for the complete identification of the compound's stoichiometry from the X-ray structural investigation (in accord with the C–H analysis and the compound's ir spectrum) is provided not only from the reasonable values of the determined molecular parameters but also from the resulting rational thermal coefficients (as represented in Figure 1 by the expected size and shape of the thermal ellipsoid of each kind of atom), which are very sensitive to the atomic scattering factors assigned in the least-squares refinements.

The output parameters from the final cycle of refinement are listed in Table I.[28] Table II gives both the interatomic distances and bond angles.

Table I. Atomic Parameters for $Co_4(CO)_{12}Sb_4$[a]

A. Atomic positional parameters[b]

	x	y	z
Sb	0.0000	0.3582 (1)	−0.0183 (1)
Co	0.1416 (2)	0.2500	0.0126 (3)
C(1)	0.1249 (16)	0.2500	0.1822 (27)
O(1)	0.1201 (12)	0.2500	0.2921 (17)
C(2)	0.2204 (12)	0.3440 (14)	−0.0053 (14)
O(2)	0.2736 (9)	0.4020 (9)	−0.0202 (12)

B. Anisotropic temperature factors (×10^4)[b,c]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	36 (1)	38 (1)	58 (2)	0	0	1 (1)
Co	25 (2)	28 (2)	39 (3)	0	−4 (2)	0
C(1)	34 (16)	30 (14)	89 (31)	0	7 (18)	0
O(1)	63 (13)	78 (14)	71 (22)	0	7 (14)	0
C(2)	41 (9)	56 (11)	36 (16)	13 (10)	−8 (12)	0 (11)
O(2)	56 (7)	44 (7)	141 (17)	−14 (7)	21 (10)	−6 (9)

[a] The standard deviation of the last significant figure is given in parentheses following the number. [b] The Sb, Co, C(1), and O(1) atoms lie on crystallographic mirror planes, and the appropriate parameters have been constrained. [c] The anisotropic thermal parameters are of the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\cdot\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

Table II. Interatomic Distances and Bond Angles for $Co_4(CO)_{12}Sb_4$[a]

A. Bonding Intramolecular Distances (Å)			
Co–Sb	2.616 (3)	Co–C	1.80 (3)
	2.612 (3)		1.80 (3)
	2.614 (av)		1.80 (av)
C–O	1.16 (3)		
	1.16 (2)		
	1.16 (av)		
B. Nonbonding Intramolecular Distances (Å)			
Co···Co	4.124 (6)	Sb···Sb	3.152 (3)
	4.106 (5)		3.161 (3)
	4.115 (av)		3.156 (av)
Sb···C	3.19 (2)	C···C	2.77 (3)
	3.21 (2)		2.73 (3)
	3.20 (av)		2.75 (av)
C. Intramolecular Angles (deg)			
Sb–Co–Sb	74.1 (1)	Co–C–O	176 (2)
	74.4 (1)		177 (1)
	74.3 (av)		176 (av)
Co–Sb–Co	104.1 (1)	C–Co–C	101 (1)
	103.5 (1)		99 (1)
	103.8 (av)		100 (av)

[a] The standard deviation of the last significant figure is given in parentheses following the number.

Discussion

Crystalline $Co_4(CO)_{12}Sb_4$ consists of tetrameric molecules with a cubane-like architecture in which the cobalt and antimony atoms occupy the alternate corners of a distorted cube (Figure 1). The four $Co(CO)_3$ fragments are interconnected by triply bridging antimony atoms located above the four faces of a regular tetrahedron of nonbonding cobalt atoms. The crystallographic site symmetry of the $Co_4(CO)_{12}Sb_4$ molecule is tetragonal D_{2d}-$\bar{4}2m$, and the local symmetry of each of the cobalt and antimony atoms is strictly C_s-m. Within the error limits of this determination, however, the geometry of the $Co_4(CO)_{12}Sb_4$ molecule conforms to cubic T_d-$\bar{4}3m$ symmetry with the localized site symmetry of each

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(26) Least-squares refinement was based on the minimization of $\Sigma w_i \Delta F_i^2$, and the weights were assigned according to the estimated standard deviations[16] of the observed structure factors. The unweighted and weighted discrepancy factors used are $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]\cdot 100$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}100$.

(27) The scattering factor tables used are those of H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964). No anomalous dispersion corrections were made since these corrections involve real and imaginary terms for Co of 0.4 and 1.1, respectively, and real and imaginary terms for Sb of −0.6 and 2.0, respectively. Relatively small dispersion corrections have been found in our laboratories not to affect significantly the atomic coordinates of centrosymmetric structures (*cf.* D. H. Templeton, *ibid.*, **8**, 842 (1955)).

(28) Calculated and observed structure factors utilized in the least-squares refinement are deposited as Document No. NAPS-01148 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and remitting $2.00 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC–NAPS.

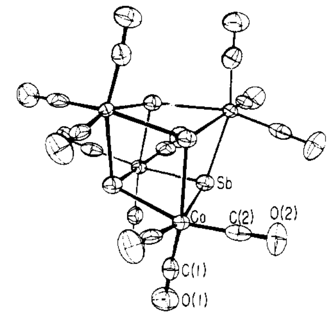

Figure 1. The 50% probability thermal ellipsoids of $Co_4(CO)_{12}Sb_4$. The molecule of idealized T_d-$\bar{4}3m$ geometry has crystallographic site symmetry D_{2d}-$\bar{4}2m$.

cobalt and antimony atom being C_{3v}-$3m$. The localized environment about each cobalt atom may be described as trigonally distorted octahedral with three coordination sites occupied by terminal carbonyl ligands and the other three coordination sites occupied by antimony atoms. Similarly, each antimony atom may be considered as trigonal pyramidal with three coordination sites occupied by cobalt atoms and the fourth site occupied by a lone pair of electrons.

The overall molecular geometry of $Co_4(CO)_{12}Sb_4$ may be viewed in terms of a set of four cobalt atoms and a set of four antimony atoms positioned at the vertices of two regular interpenetrating, concentric tetrahedra. The sizes of these two nonbonding tetrahedra are appreciably different from each other (*i.e.*, the average Co···Co distance is 4.115 (4) Å *vs.* the average Sb···Sb distance of 3.156 (2) Å) as reflected in the sharply acute Sb–Co–Sb angle of 74.3 (1)° (av) compared to the obtuse Co–Sb–Co angle of 103.8 (1)° (av). The average Co–Sb bond length was found to be 2.614 (2) Å. Since all intermolecular contact distances are greater than 2.9 Å, it is evident that the crystalline forces holding the molecules together are primarily of the van der Waals type.

$Co_4(CO)_{12}Sb_4$ is the first proven (metal carbonyl)–(main group element) member of the small but rapidly growing family of cubane-like molecules. This general type structure has been demonstrated from X-ray studies to occur for the hydrocarbon cubane C_8H_8,[29] $[Pt(CH_3)_3Cl]_4$,[30] $[Pt(CH_3)_3(OH)]_4$,[31–33] $[PtX(C_3H_6)X]_4$ (X = Cl, Br),[34] $[Cu\{As(C_2H_5)_3\}X]_4$ (X = Br, I),[35] $[Zn(CH_3)(OCH_3)]_4$,[36] $[M\{OC(CH_3)_3\}]_4$ (M = K, Rb, Cs),[37] $[M\{OSi(CH_3)_3\}]_4$ (M = K, Rb, Cs),[38] $[M(CH_3)\{OSi(CH_3)_3\}]_4$ (M = Be,[39] Zn,[40] Cd,[40] Hg[41]), $[Al(C_6H_5)\{N(C_6H_5)\}]_4$,[42] the triphenylphosphine adduct of $[M\{(CO)_2(NO)\}(OH)]_4$ (M = Mo, W),[43] and of $[M\{(H)(CO)_3\}(OH)]_4$ (M = Mo, W),[43] $Si_8R_8O_{12}$ (R = CH_3, C_2H_5, H),[44] $[Tl(OCH_3)]_4$,[45a] $[Pb_4(OH)_4]^{4+}$,[45b] $[Li(CH_3)]_4$,[46] and $[Fe(h^5\text{-}C_5H_5)(CO)]_4$.[47]

The valence bonding requirements of both the cobalt and antimony atoms in $Co_4(CO)_{12}Sb_4$ are satisfied. Since the $Co(CO)_3$ fragment and Sb are electronically equivalent, the formation of electron-pair Sb–Co bonds allows the cobalt and antimony atoms each to attain a closed-shell electronic configuration. It is also useful to consider the molecular orbitals involved in the bonding of $Co_4(CO)_{12}Sb_4$. Under localized C_{3v} site symmetry the nine valence orbitals of each cobalt atom transform as follows: five 3d(a_1 + 2e); one 4s(a_1), and three 4p(a_1 + e). A similar classification of the appropriate orbitals of the three carbonyl groups gives three σ-bonding orbitals (a_1 + e), six π (a_1 + a_2 + 2e), and six π^* (a_1 + a_2 + 2e). The relevant orbitals for each antimony atom likewise transform under C_{3v} localized site symmetry as three σ-bonding orbitals (a_1 + e) and an unshared electron pair (a_1). For purposes of convenience without detracting from the conclusions based on these symmetry arguments, the nine cobalt valence orbitals ($3a_1$ + 3e) may be hybridized into one a_1 + e orbital set which gives maximum overlap with the three carbonyl σ-bonding orbitals (a_1 + e), into a second (a_1 + e) orbital set which gives maximum overlap with the σ-bonding orbitals from three triply bridging antimony atoms, and into a third (a_1 + e) orbital set which may interact with the other three cobalt atoms. By the formation of bonding and antibonding symmetry combinations between each cobalt atom and its six attached ligands (*viz.*, the three carbonyl groups and three antimony atoms) with only the relatively low-energy bonding combinations occupied, the cobalt–carbonyl and cobalt–antimony electron-pair σ bonds are separated under the assumed perfect-pairing approximation from the possible cobalt–cobalt interactions. Under T_d molecular symmetry the remaining set of 3 orbitals per metal atom combine to give 12 metal symmetry combinations of a_1 + e + t_1 + $2t_2$ representations, of which, from reasonable metal orbital overlap considerations, the a_1 + t_2 + e ones are bonding (relative to the isolated metal orbitals at the same energy) and the t_1 + t_2 ones are antibonding. In the case of $Co_4(CO)_{12}Sb_4$, which has a total of 24 electrons available for metal–metal interactions, both the bonding and antibonding metal symmetry combinations are occupied, thereby resulting in no net cobalt–cobalt bond stability, in agreement with the observed nonbonding average

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Co···Co internuclear distance of 4.115 (4) Å. No doubt, the charge density accumulation on the cobalt atoms due to the occupation of both the bonding and antibonding cobalt symmetry combinations (which at the equilibrium Co···Co distance are all essentially nonbonding) is dissipated to a considerable extent onto the carbonyl groups by the use of the π^* carbonyl orbitals.

This molecular orbital model may be extended to rationalize the observed molecular configurations of the related $[\text{Fe}(h^5\text{-C}_5\text{H}_5)(\text{CO})]_4$[47] and $[\text{Fe}(h^5\text{-C}_5\text{H}_5)\text{S}]_4$[48,49] tetramers which possess triply bridging carbonyl groups and sulfur atoms, respectively, bonded to $\text{Fe}(h^5\text{-C}_5\text{H}_5)$ fragments. With the assumption that the metal–ligand interactions in these latter complexes can likewise be treated in an analogous fashion and separated from the metal–metal interactions, the above symmetry arguments when applied to $[\text{Fe}(h^5\text{-C}_5\text{H}_5)(\text{CO})]_4$, which has 12 electrons available for metal–metal interactions, lead to the conclusion that the $a_1 + e + t_2$ metal symmetry bonding combinations are filled but the antibonding $t_1 + t_2$ ones are empty. A T_d-cubane structure (*i.e.*, this symmetry classification assumes cylindrical symmetry for each cyclopentadienyl ring) containing six electron-pair Fe–Fe bonds is predicted, in harmony with the observed diamagnetism and molecular dimensions.[47] On the other hand, the same above energy-level scheme would predict under T_d molecular symmetry that the $[\text{Fe}(h^5\text{-C}_5\text{H}_5)\text{S}]_4$ molecule, which has available 20 electrons for metal–metal interactions, would possess a ^3T ground state which would lead to a Jahn–Teller distortion. A tetragonal deformation would account for the observed diamagnetism and $D_{2d}\text{-}\bar{4}2m$ geometry of $[\text{Fe}(h^5\text{-C}_5\text{H}_5)\text{S}]_4$ containing two electron-pair iron–iron bonding distances of 2.650 (6) Å (av) and four iron–iron nonbonding distances of 3.365 (6) Å (av).[49] One interesting prediction that arises from this MO model is that the $[\text{Fe}(h^5\text{-C}_5\text{H}_5)\text{S}]_4{}^{2+}$ cation ideally should possess a regular tetrahedron of iron atoms with an Fe–Fe valence bond order of 0.5.

Other bonding arguments[1,50] have emphasized that substitution of Co(CO)_3 groups in place of arsenic atoms in yellow As_4 to give $\text{Co(CO)}_3\text{As}_3$ and $\text{Co}_2(\text{CO})_6\text{As}_2$ affects a stabilization of the As_4 structure by partial removal of electron density from the electron-rich As atoms to the more electronegative Co(CO)_3 system. The marked decrease in the average As–As bond length on replacement of arsenic atoms with Co(CO)_3 groups (*viz.*, from 2.44 Å in As_4 to 2.372 (5) Å in $\text{Co(CO)}_3\text{As}_3$ to 2.273 (3) Å in $\text{Co}_2\{(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3\}\text{As}_2$) is in complete accord with delocalized MO arguments[1,50] which predict a lowering of antibonding orbital character between the bonded arsenic atoms with increased substitution of Co(CO)_3 groups. The structure of $\text{Co}_4(\text{CO})_{12}\text{Sb}_4$ illustrates a second mechanism for the stabilization of these tetrahedral $(\text{Pn})_4$ molecules (Pn = P, As, Sb). The placement of a triply bridging Co(CO)_3 fragment over each of the four faces of a Sb_4 molecule would retain a closed-shell configuration for each antimony by substitution of Co–Sb bonds in place of Sb–Sb bonds, to give the $\text{Co}_4(\text{CO})_{12}\text{Sb}_4$ geometry with a nonbonded Sb–Sb equilibrium separation. Very high-temperature–high-pressure reactions[51] of $\text{Co}_2(\text{CO})_8$ with SbCl_3 often produced pale yellow solutions of a compound which infrared analysis indicated might be $\text{Co(CO)}_3\text{Sb}_3$. Since this compound, which appeared to be light sensitive, has not been positively identified as yet, no detailed comparisons of relative stability should be made.

The archetypal $\text{Co}_4(\text{CO})_{12}\text{Sb}_4$ structure suggests that it should be possible to prepare other isosteric tetramers of T_d symmetry containing triply bridging main group atoms without metal–metal bonds such as $\text{Fe}_4(\text{CO})_{12}\text{X}_4$ (X = S, Se, Te), $\text{Co}_4(h^5\text{-C}_5\text{H}_5)_4\text{X}_4$ (X = S, Se, Te), and $\text{Ni}_4(h^5\text{-C}_5\text{H}_5)_4\text{X}_4$ (X = P, As, Sb, Bi). To date the only iron carbonyl chalcogenides isolated are $\text{Fe}_2(\text{CO})_6\text{X}_2$ (X = S, Se)[10,52] and $\text{Fe}_3(\text{CO})_9\text{X}_2$ (X = S, Se, Te).[53–55] The recently prepared tetrameric $\text{Co}_4(h^5\text{-C}_5\text{H}_5)_4\text{S}_6$ complex,[16] which consists of a distorted tetrahedral array of $\text{Co}(h^5\text{-C}_5\text{H}_5)$ fragments interconnected by two triply bridging disulfide S_2 groups and by two triply bridging sulfur atoms located above the four triangular faces of the distorted tetrahedron of nonbonded cobalt atoms, is electronically equivalent and structurally analogous to the unknown $\text{Co}_4(h^5\text{-C}_5\text{H}_5)_4\text{S}_4$ complex in that each triply bridging disulfide group as well as each triply bridging sulfur atom is a four-electron donor to the three cobalt atoms. These structural data together with the fact that arsenic, unlike its congener element antimony, forms different cobalt carbonyl clusters indicate that the existence of the tetrameric complexes may be critically dependent upon the steric requirements and effective electronegativities of the bridging main group atoms such that the most likely candidates for tetrameric species analogous to $\text{Co}_4(\text{CO})_{12}\text{Sb}_4$ are $\text{Ni}_4(h^5\text{-C}_5\text{H}_5)_4\text{Sb}_4$ and the corresponding tellurium complexes $\text{Fe}_4(\text{CO})_{12}\text{Te}_4$ and $\text{Co}_4(h^5\text{-C}_5\text{H}_5)_4\text{Te}_4$. Efforts are underway in an attempt to synthesize these and related molecules.[56]

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(56) NOTE ADDED IN PROOF. Since submission of our paper, a communication by D. Bright [*Chem. Commun.*, 1169 (1970)] has appeared on the crystal structure of $\text{Os}_4(\text{CO})_{12}\text{O}_4$ [B. F. G. Johnson, J. Lewis, I. G. Williams, and J. Wilson, *ibid.*, 391 (1966); C. W. Bradford and R. S. Nyholm, *ibid.*, 384 (1967)]. The X-ray diffraction study revealed another example of a cubane-type structure for a metal carbonyl complex with four oxygen and four Os(CO)_3 groups situated at alternate corners of a distorted cube. This tetrameric molecule is electronically equivalent to the $\text{Co}_4(\text{CO})_{12}\text{Sb}_4$ molecule; the fact that direct metal–metal bonds again are not necessary in order for each metal to obtain a closed-shell diamagnetic state is in agreement with the reported two independent nonbonding Os···Os distances of 3.253 (4) and 3.190 (4) Å. The experimentally observed distortion of the geometry of $\text{Os}_4(\text{CO})_{12}\text{O}_4$ from cubic $T_d\text{-}\bar{4}3m$ symmetry (as exemplified by the significant difference in the above two Os···Os distances) is attributed by Bright to crystal packing.