Organometallic Chalcogen Complexes. XXVI. Synthesis, Structure, and Bonding of the Cubane-Like $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ Tetramers ($n = 0, +1$). Stereochemical Influence Due to Oxidation of a Completely Nonbonding Tetrahedral Metal System[1]

Gary L. Simon and Lawrence F. Dahl*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received October 5, 1972*

Abstract: The cubane-like metal cluster $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ and the hexafluorophosphate salt of the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation have been prepared and structurally characterized by single-crystal X-ray diffraction. The neutral parent tetramer, obtained in a designed synthesis by the reaction of $Co_4(h^5\text{-}C_5H_5)_4S_6$ with triphenylphosphine, fulfilled expectations (which motivated this research) in being the first metal-nonbonding M_4X_4–cubane system successfully oxidized to the monocation. From a detailed comparison of their geometries, important stereochemical information was obtained concerning the antibonding character of the unpaired electron in the metal cluster system. Both $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ complexes ($n = 0, +1$) are comprised of a tetrahedral-like array of cobalt atoms with triply bridging sulfur ligands positioned above the four triangular metal faces and with a *pentahapto*-cyclopentadienyl ring coordinated to each cobalt atom. In the neutral molecule (for which each d^6 Co(III) formally achieves a noble gas electronic configuration without the necessity of any metal–metal electron pair bonds), the Co_4S_4 core of crystallographic site symmetry C_2-2 with six nonbonding Co–Co distances of nonsystematic variation from 3.236 (1) to 3.343 (1) Å and of average length 3.295 Å is presumed in the absence of crystal packing forces to conform to cubic T_d-$\bar{4}3m$ symmetry. Oxidation of the neutral tetramer by $AgPF_6$ produces the tetragonally distorted monocation of crystallographic site symmetry S_4-$\bar{4}$ and of idealized D_{2d}-$\bar{4}2m$ geometry with two long (and presumably nonbonding) Co–Co distances of identical length 3.330 (5) Å and with four significantly shorter Co–Co distances of identical length 3.172 (5) Å. The observed tetragonal distortion of the Co_4S_4 core and the shortening of the latter four Co–Co distances by 0.12 Å (relative to the average Co–Co distance in the neutral parent) are shown to be compatible with a metal cluster MO model in which the oxidized electron primarily originates from a triply degenerate antibonding tetracobalt symmetry combination in the neutral molecule whose geometry, upon removal of one electron, undergoes a Jahn–Teller distortion such that the unpaired electron in the monocation occupies a nondegenerate tetracobalt symmetry combination. On the basis that the two longer Co–Co distances in the monocation still represent nonbonding metal–metal interactions, each of the four shorter Co–Co distances in the monocation is presumed (under the applied metal cluster model) to reflect (in a localized sense) an increase in the individual valence bond order from 0 to 0.125 between the two cobalt atoms resulting in a total limiting cobalt–cobalt valence bond order of 0.5 (*i.e.*, corresponding to 12 bonding and 11 antibonding electrons directly involved in the tetracobalt interactions). Crystals of $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ are monoclinic, space group $C2/c$, with $a = 18.014$ (6) Å, $b = 7.974$ (2) Å, $c = 15.736$ (4) Å, $\beta = 115.281$ (9)°, and $\rho_{obsd} = 2.01$ g cm^{-3} *vs.* $\rho_{calcd} = 2.03$ g cm^{-3} for $Z = 4$. Least-squares refinement gave $R_1(F) = 4.5\%$ and $R_2(F) = 5.7\%$ for 1172 independent diffractometry data with $I > 2\sigma(I)$. Crystals of $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ are tetragonal, space group $I\bar{4}$, with $a = b = 12.777$ (3) Å, $c = 7.815$ (2) Å; $\rho_{obsd} = 2.00$ g cm^{-3} *vs.* $\rho_{calcd} = 2.005$ g cm^{-3} for $Z = 2$. A crystal disordering of each PF_6^- anion occurs between two orientations with the composite possessing crystallographic site symmetry S_4-$\bar{4}$. The preferred least-squares model gave $R_1(F) = 7.0\%$ and $R_2(F) = 6.1\%$ for 402 independent diffractometry data with $I > 2\sigma(I)$.

During the past few years there have been X-ray structural investigations of a variety of organometallic isosteres of the hydrocarbon cubane.[2-11] The molecular architecture of these complexes may be described as two interpenetrating tetrahedra of metal and ligand atoms such that the metal atoms and triply bridging ligands occupy the alternate corners of a cube. With few exceptions these molecules are held together solely by bonding between the metal atoms and triply bridging ligands in that the valence electron requirements of the metal atoms are satisfied without any metal–metal interactions. Examples include $[Mo_4\{(NO)(CO)_2\}_4(OH)_4]$,[4] $[Mo_4\{(H)(CO)_3\}_4(OH)_4]$,[4] $[Re_4(CO)_{12}(SCH_3)_4]$,[5] $[Os_4(CO)_{12}O_4]$,[6] $[Co_4(CO)_{12}Sb_4]$,[7] $[Pt_4(C_2H_5)_{12}Cl_4]$,[8] and $[Pt_4(CH_3)_{12}X_4]$ ($X = Cl$,[9] I,[10] OH[11]).

---

(1) Previous paper in this series: P. D. Frisch and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 5082 (1972).

(2) E. B. Fleischer, *ibid.*, **86**, 3889 (1964); P. Eaton and T. Cole, *ibid.*, **86**, 3157 (1964).

(3) R. S. Nyholm, M R. Truter, and C. W. Bradford, *Nature (London)*, **228**, 648 (1970).

(4) V. Albano, P. Bellon, G. Ciani, and M. Manassero, *Chem. Commun.*, 1242 (1969).

(5) E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *ibid.*, 1531 (1970); W. Harrison, W. C. Marsh, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1009 (1972).

(6) D. Bright, *Chem. Commun.*, 1169 (1970).

(7) A. S. Foust and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7337 (1970).

(8) R. N. Hargreaves and M. R. Truter, *J. Chem. Soc. A*, 90 (1971).

(9) R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, 69, 1561 (1947).

(10) G. Donnay, L. B. Coleman, N. G. Krieghoff, and D. O. Cowan, *Acta Crystallogr., Sect. B*, 24, 157 (1968).

(11) (a) M. N. Hoechstetter and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 400 (1969), and references cited therein; D. O. Cowan, N. G. Krieghoff, and G. Donnay, *Acta Crystallogr., Sect. B*, 24, 287 (1968); (b) T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 7, 2165 (1968); (c) H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organometal. Chem.*, 14, 447 (1968).

At the time of this study, the notable structurally characterized *exceptions* to the "metal nonbonding" tetramers included (1) the cubane-like $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]$ molecule,[12] which contains a completely bonding tetrahedron of iron atoms, and its monocation[13] and (2) $[Fe_4(h^5\text{-}C_5H_5)_4S_4]^n$ (n = 0,[14] +1,[15,16] +2[16,17]) and the $[Fe_4(S_2C_2(CF_3)_2)_4S_4]^{2-}$ anion,[18] which contain distorted cubane-like Fe_4S_4 cores whose deformations from cubic T_d geometry have been ascribed to iron–iron interactions. In this connection it should be noted that the distorted Fe_4S_4 fragment of the $[Fe_4(h^5\text{-}C_5H_5)_4S_4]^{2+}$ cation[17] is analogous in geometry to the distorted Fe_4S_4 core of the electronically equivalent $[Fe_4(S_2C_2(CF_3)_2)_4S_4]^{2-}$ anion.[18] These Fe_4S_4 clusters have been the subject of considerable interest in that X-ray diffraction investigations of the 8-Fe *clostridial* ferredoxin from *micrococcus aerogenes*[19] and the high-potential iron–sulfur protein of *chromatium vinosum*[20] have shown that both of these Fe–S proteins, which are involved in electron transfer redox reactions *in vivo*, contain cubane-like Fe_4S_4 cores. The resulting biochemical implications of the Fe_4S_4 cubane geometry have provided further impetus to the study of both the chemical behavior and structure of inorganic analogs containing the Fe_4S_4 moiety.[21]

This paper reports the designed synthesis of the unknown cobalt analog of $[Fe_4(h^5\text{-}C_5H_5)_4S_4]$, *viz.*, $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ which from electronic considerations would be presumed to belong to the "metal nonbonding" class of cubane-like tetramers. This complex was prepared in the hope that it, in similar fashion, could be successfully oxidized to at least one cationic species without rupture of its atomic framework. A comparison of the geometries of such a neutral tetramer and its monocation was deemed highly desirable in that no previous experimental knowledge existed concerning the stereochemical effect due to removal of a valence electron from a cubane-like system containing a nonbonding tetrahedron of metal atoms. The structural characterizations of the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule and its monocation have provided an opportunity to examine further the nature of the metal–metal interactions in these organometallic complexes.

Experimental Section

Preparation and Characterization of $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ and $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$. The neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ complex was prepared by the reaction of $Co_4(h^5\text{-}C_5H_5)_4S_6$ with excess triphenylphosphine. The production of the triphenylphosphine sulfide adduct *via* cleavage of the disulfide bridges is accompanied by formation of the tetramer, $[Co_4(h^5\text{-}C_5H_5)_4S_4]$. The identification of triphenylphosphine sulfide was accomplished by comparison of its infrared spectrum with that of an authentic sample.[22]

All reactions were run in standard glassware under a nitrogen atmosphere. The $Co_4(h^5\text{-}C_5H_5)_4S_6$ complex was prepared by the method of Uchtman and Dahl[23] with one modification. The crude product was purified by the pouring of a chloroform solution of the complex onto a Florisil column. Elution with $CHCl_3$ followed by evaporation yielded $Co_4(h^5\text{-}C_5H_5)_4S_6$ in 65% yield. The composition of this product was confirmed by comparison of the infrared and nmr spectra with those of an authentic sample.[23]

A solution of 0.250 g (0.36 mmol) of $Co_4(h^5\text{-}C_5H_5)_4S_6$ was dissolved in toluene with 0.250 g (0.95 mmol) of $P(C_6H_5)_3$ and refluxed for 60 hr. The solution was then evaporated to a small volume and poured onto an acid-washed alumina column. Elution with benzene removed the triphenylphosphine sulfide from the reaction product. The reddish black $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ was obtained in 40% yield by elution with $CHCl_3$ and then evaporation of the solvent under vacuum. $[Co_4(h^5\text{-}C_5H_5)_4S_4)$ is insoluble in nonpolar organic solvents and sparingly soluble in polar solvents. Crystals suitable for X-ray diffraction were grown from a chloroform–toluene solution by slow evaporation under nitrogen. The formulation of the complex as $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ was indicated by mass spectral data which are presented in Table I.

$[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ was prepared by the stoichiometric addition of a methanolic solution of $AgPF_6$ to a solution of the neutral tetramer in dichloromethane. Upon the addition of 0.040 g (0.16 mmol) of $AgPF_6$ to 0.100 g (0.16 mmol) of $[Co_4(h^5\text{-}C_5H_5)_4S_4]$, the solution immediately became darker and a finely divided precipitate of metallic silver appeared. The solution was heated in order to increase flocculation and hence the rate of precipitation of the silver metal. Filtration through CELITE removed the silver precipitate from the solution. Crystals of the monocation suitable for X-ray diffraction were grown by slow evaporation under nitrogen of an acetonitrile–toluene solution of the salt. Magnetic susceptibility measurements by the Faraday method[24] at five different field strengths between 5.5 and 8.0 kOe revealed a paramagnetic species with one unpaired electron. The effective magnetic moment of 1.73 BM was corrected for a slight field dependence attributed to a small amount of antiferromagnetic cobalt oxide impurity. Solid-state infrared spectra[25] (KBr pellet) of the neutral tetramer and the hexafluorophosphate salt of the monocation exhibit absorption bands characteristic of the cyclopentadienyl ligands.

X-Ray Data Collection. (a) $[Co_4(h^5\text{-}C_5H_5)_4S_4]$. Preliminary Weissenberg and precession photographs of the neutral tetramer exhibited C_{2h}-$2/m$ monoclinic symmetry. The observed systematic absences for $\{hkl\}$ of $h + k = 2n + 1$ and for $\{h0l\}$ of $l = 2n + 1$ were compatible with two space groups, $C2/c$ and the acentric Cc. The centric $C2/c$ was subsequently shown to be the correct choice by an interpretation of the Patterson vectors and by the successful refinement of the crystal structure. A single crystal of dimensions 0.20 × 0.20 × 0.68 mm along the [100], [001], and [010] directions, respectively, was mounted on a thin glass fiber with epoxy cement. After optical and X-ray alignment[26] on a Datex-controlled, General Electric full-circle diffractometer equipped with a scintillation counter and pulse height analyzer adjusted to admit 90% of the Mo Kα (λ 0.7107 Å) peak, 17 reflections were carefully centered in the X-ray beam by adjustment of the 2θ, χ, and ϕ values so as to maximize the intensities of the diffracted beams. The angle settings

---

(12) M. A. Neuman, Trinh-Toan, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3383 (1972).

(13) (a) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *ibid.*, **94**, 3389 (1972); (b) J. A. Ferguson and T. J. Meyer, *ibid.*, **94**, 3409 (1972).

(14) (a) C. H. Wei, R. G. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966); (b) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966).

(15) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, No. INOR. 130; submitted for publication.

(16) J. A. Ferguson, and T. J. Meyer, *Chem. Commun.*, 623 (1971).

(17) Trinh-Toan, B. K. Teo, J. A. Ferguson, T. J. Meyer, and L. F. Dahl, submitted for publication.

(18) I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972); B. R. Davis, E. F. Epstein, and I. Bernal, private communications to L. F. Dahl, 1972; A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6962 (1969).

(19) L. C. Sieker, E. Adman, and L. H. Jensen, *Nature (London)*, **235**, 40 (1972).

(20) C. W. Carter, Jr., S. T. Freer, Ng. H. Xuong, R. A. Alden, and J. Kraut, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 381 (1972).

(21) The compound $[N(C_2H_5)_4]_2^+[Fe_4S_4(SCH_2C_6H_5)_4]^{2-}$ has been recently prepared and characterized by X-ray diffraction as well as by pmr and Mössbauer spectroscopy, ESCA, electronic spectra, and magnetic susceptibility (T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972); B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, in press.

(22) Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia, Pa., 1964.

(23) V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969).

(24) We wish to thank Mr. James Kleppinger of the University of Wisconsin (Madison) for performing the magnetic susceptibility measurements.

(25) Infrared spectra were recorded (KBr pellets) on a Beckman IR-10 spectrometer.

(26) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

Table I. Mass Spectral Data for $[Co_4(h^5\text{-}C_5H_5)_4S_4]$[a]

Ion	*m/e*	Intensity[b]
$Co_4(C_5H_5)_4S_4^+$	624	0.7
$Co_4(C_5H_5)_3S_4^+$	559	0.5
$Co_3(C_5H_5)_4S^+$	469	0.4
$Co_3(C_5H_5)_3S_3^+$	468	1.6
$Co_3(C_5H_5)_4^+$	437	0.7
$Co_3(C_5H_5)_3S_2^+$	436	3.1
$Co_4(C_5H_5)_3^+$	431	0.4
$Co(C_5H_5)_4S_3^+$	415	1.5
$Co_4(C_5H_5)S_3^+$	397	0.3
$Co_2(C_5H_5)_3S_2^+$	377	0.3
$Co_2(C_5H_5)_2S_4^+$	376	3.1
$Co_3(C_5H_5)_3^+$	372	0.6
$Co_4S_4^+$	364	0.5
$Co(C_5H_5)_4^+$	319	0.4
$Co_3S_4^+$	305	0.4
$Co_2(C_5H_5)_2S^+$	280	1.4
$Co_2(C_5H_5)S_3^+$	279	1.3
$Co(C_5H_5)_3^+$	254	1.2
$Co(C_5H_5)S_4^+$	252	1.1
$Co_2(C_5H_5)S_2^+$	247	9.3
$Co_2S_4^+$	246	0.6
$Co_3(C_5H_5)^+$	242	0.4
$Co_3S_2^+$	241	0.4
$Co(C_5H_5)_2S^+$	221	0.5
$Co(C_5H_5)S_3^+$	220	12.1
$Co_2(C_5H_5)S^+$	215	1.0
Co_3S^+	209	0.3
$Co(C_5H_5)_2^+$	189	49.5
$Co(C_5H_5)S_2^+$	188	3.6
CoS_4^+	187	3.3
$Co_2(C_5H_5)^+$	183	13.7
$Co_2S_2^+$	182	1.3
Co_3^+	177	1.1
$Co(C_5H_5)S^+$	156	0.5
$Co(C_5H_5)^+$	124	7.3
CoS_2^+	123	1.9
Co_2^+	118	1.1
CoS^+	91	58.1
Co^+	59	100.0

[a] Mass spectra were obtained on an AEI MS-902 mass spectrometer at 70 eV with a probe temperature of 160°. Samples were introduced into the ion source by a direct inlet system. [b] Intensity values are presented as relative ion abundances with respect to the peak at *m/e* 59.

were refined by a least-squares procedure[27,28] to yield lattice parameters of $a = 18.014\,(6)$ Å, $b = 7.974\,(2)$ Å, $c = 15.736\,(4)$ Å, and $\beta = 115.281\,(9)°$. The volume of the unit cell is 2044.2 Å^3. The experimental density of 2.01 g cm^{-3} measured by the flotation method agrees well with a calculated one of 2.03 g cm^{-3} based on four molecules per unit cell.

Data were collected by the θ–2θ scan technique with scan speeds of 2°/min and (stationary-crystal)–(stationary-counter) background measurements of 15 sec on each side of the peak. Symmetric scans of 2.00° for $2\theta \leq 12°$, 1.70° for $12° < 2\theta \leq 20°$, and 1.40° for $20° < 2\theta \leq 45.0°$ were employed. All independent reflections within the sphere $2\theta \leq 45.0°$ were sampled. Four reflections which were sampled at approximately 4-hr intervals were used as standards for crystal alignment, crystal decay, and instrument stability. During the collection of the asymmetric unit no significant changes (>3.5%) were observed in the intensities of these standard reflections. A reflection was considered to be statistically observed if the integrated intensity, I, was greater than twice the esd, $\sigma(I)$, of the intensity. The data reduction formulas are the following: $I = S - B(T/t)$, $\sigma(I) = [S + B(T/t)^2 + (0.05I)^2]^{1/2}$, $|F| = (I/\mathrm{Lp})^{1/2}$, and $\sigma(F) = \sigma(I)/2|F|\mathrm{Lp}$, where S is the scan count for time T, B the total background count measured for time t, and Lp the Lorentz–polarization corrections. Since the transmission coefficients (based on a linear absorption coefficient of 37.05 cm^{-1} for Mo Kα radiation) varied from 0.42 to 0.56, absorption corrections[29] were applied to the individual structure factors. No corrections for extinction were made.

(b) $\mathbf{[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-}$. Oscillation and Weissenberg photographs of $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ revealed tetragonal C_{4h}-$4/m$ Laue symmetry. Systematic absences for $\{hkl\}$ of $h + k + l = 2n + 1$ define a body-centered cell with possible space groups $I4$, $I\bar{4}$, or $I4/m$. A small needle crystal of dimensions $0.10 \times 0.10 \times 0.36$ mm along the [100], [010], and [001] directions, respectively, was mounted on a thin glass fiber with epoxy cement such that the c^* axis was approximately parallel to the spindle axis of the goniometer. After optical and X-ray alignment[26] on a Datex-controlled General Electric full-circle diffractometer equipped with a scintillation counter and pulse height analyzer adjusted to admit 90% of the Mo Kα (λ 0.7107 Å) peak, 18 reflections were carefully centered in the X-ray beam. The 2θ, χ, and ϕ values obtained were least-squares refined[27,28] to yield lattice parameters of $a = b = 12.777\,(3)$ and $c = 7.815\,(2)$ Å. The volume of the unit cell is 1273.6 Å^3. The experimental density of 2.00 (2) g cm^{-3} agrees quite well with the calculated value of 2.005 g cm^{-3} for $Z = 2$. Based on two cubane-type species per cell, considerations of the possible molecular symmetry indicated that the correct space group is $I\bar{4}$. This choice was confirmed by the successful refinement of the structure.

Intensity data were collected *via* the θ–2θ scan technique with scan speeds of 2°/min. Scan widths of 1.8° for $2\theta \leq 10.0°$, 1.6° for $10.0° < 2\theta \leq 20.0°$, and 1.4° for $20.0° < 2\theta \leq 45.0°$ were employed. A (stationary-crystal)–(stationary-counter) background measurement of 20 sec was made on both sides of each peak. Four reflections were sampled at intervals of every 100 reflections as standards of instrument stability, crystal alignment, and crystal decay. No significant changes (>3.0%) were observed for any of these standard reflections. The data were reduced according to the formulas given previously, and 396 independent reflections were considered observed with $I > \sigma(I)$. The subsequent solution and refinement of the structure will be discussed below.

After the initial structural determination, intensity data were recollected with the same crystal on a NOVA-automated Syntex P$\bar{1}$ diffractometer equipped with a scintillation counter, a pulse height analyzer adjusted to admit 90% of the Mo Kα peak ($\lambda(K\alpha_1)$ 0.70926 Å, $\lambda(K\alpha)_2$ 0.71354 Å), and a crystal graphite monochromator set at a Bragg 2θ angle of 12.2°. The orientation matrix was determined by the centering of 15 reflections and a subsequent refinement of the 2θ, ω, ϕ, and χ values. For the data collection, the ω–2θ scan technique was used with variable scan speeds and scan widths based on the relative intensity of each peak. The background was measured on each side of the peak by (stationary-crystal)–(stationary-counter) techniques. The total background time alloted for each peak was equal to two-thirds of the total scan time. Two reflections, which were sampled periodically at intervals of every 50 reflections as standards of instrument stability, crystal alignment, and crystal decay, exhibited no significant changes (*i.e.*, >3%) throughout the experiment. The same data reduction formulas were used with a linear correction to account for the variable scan speeds. All independent data with $\theta \leq 30.0°$ were sampled. The statistical criterion for a datum to be considered observed was that $I \geq 2\sigma(I)$. Corrections for Lorentz–polarization effects as well as polarization of the incident beam due to the crystal monochromator were included in the data reduction which yielded 402 independent observed reflections. Since the calculated transmission coefficients (based on a linear absorption coefficient of 30.90 cm^{-1} for Mo Kα radiation) varied from only 0.73 to 0.76, a correction for absorption was deemed unnecessary. No corrections for extinction were made.

Solution of the Structures. (a) $\mathbf{[Co_4(h^5\text{-}C_5H_5)_4S_4]}$. The structure of the neutral tetramer was determined by the heavy-atom technique. Analysis of the vectors in a three-dimensional Patterson map,[30] based on 1172 observed reflections, revealed the location and orientation of the tetramer about the crystallographic twofold axis. A Fourier synthesis[30] phased on the two independent cobalt and two independent sulfur atoms (which gave discrepancy factors of $R_1 = 24\%$ and $R_2 = 45\%$[31]) did not provide unequivocal infor-

---

(27) A. S. Foust, "ANGSET," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1970.

(28) The uncertainties (given in parentheses) of the lattice parameters obtained from ANGSET are estimates of precision and are unrealistically small on account of the large number of reflections used in the least-squares determination.

(29) J. F. Blount, "DEAR," based on a method given by W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(30) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

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

mation about the locations of the cyclopentadienyl carbon atoms. However, isotropic least squares[32] coupled with Fourier difference maps eventually revealed the positions of all ten crystallographically independent carbon atoms. Refinement of this model with isotropic thermal parameters reduced the residuals to $R_1 = 9.8\%$ and $R_2 = 13.6\%$. At this point idealized coordinates for the cyclopentadienyl hydrogen atoms were calculated with the program MIRAGE.[33] These idealized positions for the hydrogen atoms were not allowed to vary during the least-squares refinement but were recalculated after each cycle so as to take into account the shifts in positions of the carbon atoms. The hydrogen thermal parameters were constrained to an isotropic value of 3.0 Å^2. Anisotropic full-matrix refinement of all nonhydrogen atoms reduced the residuals to $R_1 = 4.5\%$ and $R_2 = 5.7\%$ at convergence. In the latter stages of refinement real and imaginary corrections to the scattering factors due to anomalous dispersion were applied for cobalt (*viz.*, $\Delta f' = 0.4$, $\Delta f'' = 1.1$) and sulfur (*viz.*, $\Delta f' = 0.1$, $\Delta f'' = 0.2$).[34] A final Fourier difference map revealed no peak greater than 0.5 e/Å^3. The final goodness-of-fit parameter was 1.89 which indicates an underestimation of the standard deviation of an observation of unit weight.

(b) $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$. The structure of the monocation was also determined by the heavy atom technique. Interpretation of a three-dimensional Patterson map[30] yielded the locations of the independent cobalt and sulfur atoms. A Fourier synthesis[30] phased on these two atoms (which gave reliability indices of $R_1 = 32\%$ and $R_2 = 36\%$)[31] provided initial coordinates for the independent phosphorus atom. Further Fourier syntheses coupled with isotropic least-squares[32] refinement provided positional parameters for the cyclopentadienyl carbon atoms. In addition, six octahedrally disposed peaks around the phosphorus atom were interpreted as being fluorine atoms. Least-squares refinement of this model for the PF_6^- anion was unsuccessful, however, in that the fluorine atomic positions would not converge at chemically reasonable sites. Furthermore, the inordinately high isotropic thermal parameters for the phosphorus atom (~15 Å^2) and six fluorine atoms (~20 Å^2) indicated that the chosen model did not accurately reflect the electron distribution of the anion. In the hopes that a more accurate determination of the phases would provide the true location and orientation of the PF_6^- anion, an anisotropic refinement of the atom in the cation was undertaken. This resulted in residuals of $R_1 = 16\%$ and $R_2 = 21\%$ and correctly revealed *via* a Fourier difference map a twofold disorder of each of the two PF_6^- anions in the unit cell. The independent phosphorus atom sits on a crystallographic $\bar{4}$ axis (corresponding to one set of twofold special positions 2c of $I\bar{4}$) with 12 half-weighted fluorine atoms (of which three are crystallographically independent) located such that the two orientations of the PF_6^- anion are related to each other by a rotation of 90° about the $\bar{4}$ axis (Figure 1[35]).

Before final refinement, the absolute configuration of the molecule in the space group was determined by an inclusion in the structure factor calculations of both the real and imaginary corrections for anomalous dispersion (*viz.*, $\Delta f' = 0.4$, $\Delta f'' = 1.1$ for cobalt; $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for sulfur; and $\Delta f' = 0.1$, $\Delta f'' = 0.2$ for phosphorus).[34] The reliability indices of $R_1 = 13.3\%$ and $R_2 = 6.9\%$ obtained for x, y, z, as opposed to the values of $R_1 = 13.6\%$ and $R_2 = 10.9\%$ obtained for $\bar{x}, \bar{y}, \bar{z}$, established the enantiomorph at the 0.5% level of confidence.[36] As in the neutral tetramer, idealized coordinates were determined[33] for each hydrogen atom after each least-squares cycle; isotropic temperature factors of 3.0 Å^2 were assigned to each hydrogen atom and were not varied in the least-squares refinements. Three different least-squares refinements were done in an attempt to determine a "best" model for the monocation. The first refinement (A) utilized the initial data set (from the General Electric diffractometer) and anisotropic thermal parameters for all nonhydrogen atoms. At convergence the final residuals were $R_1 = 7.4\%$ and $R_2 = 7.0\%$, the goodness-of-fit parameter was 1.68, and the data-to-parameter ratio was 4.35:1; the largest parameter shifts during the last cycle were less than half the esd. The last two refinements utilized the second data set (from the Syntex diffractometer). In the second refinement (B) the thermal motion of each of the three half-weighted fluorine atoms was treated isotropically, while all other nonhydrogen atoms were allowed to vibrate anisotropically. At convergence the final residuals were $R_1 = 7.0\%$ and $R_2 = 6.1\%$, the goodness-of-fit parameter was 1.54, and the data-to-parameter ratio was 5.1:1; the large isotropic thermal parameters of the fluorine atoms (*viz.*, 14.5, 10.0, and 16.5 Å^2) indicated, however, that these atoms (as found in other previously reported refinements of PF_6^- anions) were experiencing considerable nonspherical thermal motion which would be best handled by an anisotropic thermal model. A third refinement (C) with anisotropically varying thermal parameters for all nonhydrogen atoms converged with final residuals of $R_1 = 6.7\%$ and $R_2 = 5.8\%$, and with a goodness-of-fit parameter of 1.49; the data-to-parameter ratio for this model was 4.3:1. The fact that the changes in corresponding R values are significant at the 0.01 level of confidence[36] is not surprising since it is only reasonable to expect that anisotropically varying thermal parameters will better reflect the extensive thermal motion of the fluorine atoms. However, the relatively small decrease of 0.3% in the R values indicates that (with consideration of the 20% decrease in the data-to-parameter ratio) the parameters obtained in the isotropic refinement, especially those of the cation, are perhaps equally accurate. Final Fourier difference maps revealed no residual electron density greater than 0.5 e/Å^3.

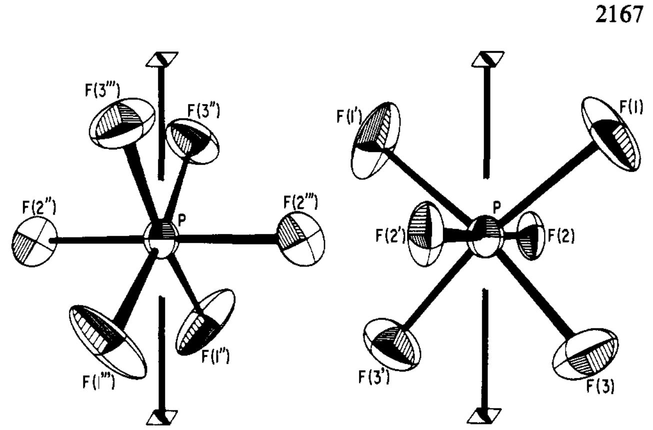

Figure 1. The two orientations of the crystal *disordered* PF_6^- anion related to each other by a 90° rotation about the crystallographic S_4-$\bar{4}$ axis. The atoms are represented by thermal ellipsoids of 5% probability.

A comparison of the atomic positional and thermal parameters as well as the interatomic distances and bond angles for the cation reveals that the corresponding parameters of refinements B and C are identical within 2σ. Refinement A is not in quite such good agreement with refinements B and C in that wider variations ($<6\sigma$) were exhibited among the corresponding thermal parameters. However, the only interatomic distance in the cation which differs by more than 2σ between refinement A and refinements B and C is the Co–C(5) distance which is 1.91 (4) Å in refinement A, 2.05 (3) Å in refinement B, and 2.08 (3) Å in refinement C. All corresponding bond angles in the cation agree within 2σ for all three refinements. Although the individual atomic positional and thermal parameters for the anion agree within 2σ for all three refinements, several of the F–P–F bond angles show much wider discrepancies.

The lower R values obtained from the second set of data *vs.* those from the first set are indicative of the different statistical criteria used. In the first data set a reflection was considered observed and included in the structural determination if $I > \sigma(I)$, while in the second set a stricter requirement was employed, *viz.*, $I > 2\sigma(I)$. The net result is that the weak and relatively less reliable intensities play a more dominant role in refinement A. *For the purposes of the discussion, the parameters of refinement B will be utilized* in deference to both the relatively low esd's found for the cation and to the more chemically reasonable geometry obtained for the PF_6^- anion.

The atomic scattering factors used in all refinements for the nonhydrogen atoms were those of Hanson, *et al.*,[37] while the hydrogen

---

(32) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(33) J. C. Calabrese, "MIRAGE," Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1971.

(34) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215.

(35) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(36) W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

(37) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *ibid.*, 17, 1040 (1964).

Table II. Final Positional and Thermal Parameters for $[Co_4(h^5\text{-}C_5H_5)_4S_4]$[a]

A. Positional Parameters

Atom	x	y	z
Co(1)	0.07813 (4)	0.13836 (10)	0.22070 (5)
Co(2)	0.06978 (5)	0.42852 (10)	0.36009 (5)
S(1)	0.06637 (9)	0.41694 (19)	0.21711 (10)
S(2)	0.05854 (9)	0.14942 (19)	0.35139 (10)
C(1)	0.1784 (3)	−0.0280 (8)	0.2809 (4)
C(2)	0.1147 (4)	−0.1082 (8)	0.2057 (5)
C(3)	0.1004 (4)	−0.0131 (12)	0.1237 (5)
C(4)	0.1555 (5)	0.1235 (11)	0.1510 (6)
C(5)	0.2023 (4)	0.1144 (9)	0.2472 (6)
C(6)	0.1013 (4)	0.6776 (7)	0.4096 (5)
C(7)	0.1701 (4)	0.5975 (9)	0.4105 (5)
C(8)	0.1876 (5)	0.4593 (10)	0.4703 (6)
C(9)	0.1271 (6)	0.4575 (11)	0.5065 (5)
C(10)	0.0751 (5)	0.5935 (10)	0.4687 (5)
H(1)[b]	0.2021	−0.0665	0.3477
H(2)	0.0853	−0.2125	0.2091
H(3)	0.0587	−0.0389	0.0587
H(4)	0.1599	0.2121	0.1085
H(5)	0.2461	0.1956	0.2855
H(6)	0.0751	0.7804	0.3725
H(7)	0.2021	0.6316	0.3746
H(8)	0.2336	0.3779	0.4845
H(9)	0.1225	0.3742	0.5515
H(10)	0.0270	0.6242	0.4816

B. Anisotropic Thermal Parameters[c]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co(1)	27.4 (4)	106.2 (17)	38.9 (5)	7.4 (5)	10.8 (3)	8.6 (6)
Co(2)	33.0 (4)	101.0 (16)	35.0 (5)	−8.5 (5)	6.8 (3)	−1.6 (6)
S(1)	36.0 (7)	104.2 (27)	41.3 (9)	−3.5 (10)	11.9 (6)	6.4 (11)
S(2)	31.0 (7)	107.2 (28)	40.6 (9)	−0.8 (10)	10.9 (6)	6.2 (11)
C(1)	29 (2)	142 (12)	50 (4)	24 (4)	11 (2)	20 (5)
C(2)	36 (3)	148 (12)	62 (5)	20 (5)	11 (3)	−12 (6)
C(3)	42 (3)	330 (21)	47 (4)	61 (7)	8 (3)	−25 (8)
C(4)	54 (4)	330 (21)	80 (6)	77 (8)	45 (4)	92 (9)
C(5)	30 (3)	203 (14)	82 (5)	4 (5)	22 (3)	31 (7)
C(6)	44 (3)	123 (11)	51 (4)	−19 (5)	17 (3)	−17 (6)
C(7)	33 (3)	172 (13)	63 (4)	−27 (5)	10 (3)	−22 (6)
C(8)	44 (3)	183 (16)	78 (6)	4 (6)	−19 (4)	−22 (8)
C(9)	86 (5)	247 (19)	33 (4)	−85 (8)	1 (4)	−3 (7)
C(10)	56 (4)	197 (15)	54 (4)	−40 (6)	22 (3)	−47 (7)

[a] In this and subsequent tables the estimated standard deviations of the last significant figures are given in parentheses. [b] The positional parameters for the hydrogen atoms are recalculated after each least-squares cycle and fixed at 1.0 Å from their attached carbon atoms. Their thermal parameters were fixed at an isotropic value of 3.0 Å². [c] The anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

scattering factors were from Stewart, *et al.*[38] The atomic parameters from the output of the last least-squares cycle for $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ are given in Table II,[39] while those from refinements A, B, and C for $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ are supplied in Table III.[39] Interatomic distances and bond angles with estimated standard deviations, calculated[40] from the full inverse matrix containing the estimated uncertainties in lattice parameters, are documented in Tables IV and V. Least-squares planes[41] of interest were calculated.

Results and Discussion

General Description of the Structure (a) $[Co_4(h^5\text{-}C_5H_5)_4S_4]$. The neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ compound crystallizes as discrete molecules with a cubane-like molecular geometry comprised of two interpenetrating nonbonded tetrahedra (Figures 2 and 3[35]). The four $Co(C_5H_5)$ fragments are interconnected by triply bridging sulfur atoms such that the cobalt and sulfur atoms lie at alternate corners of a distorted cube. In the absence of any net metal–metal interactions, an isolated neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule would be expected to possess a $T_d\text{-}\bar{4}3m$ cubic geometry (with the assumption of cylindrical symmetry for the cyclopentadienyl rings).

The crystallographic site symmetry of the tetramer is C_2-2 with the twofold axis coincident with one of the three *pseudo*-S_4-$\bar{4}$ molecular axes. However, an examination of the molecular parameters reveals a small but crystallographically significant nonsystematic distortion which may be attributed to crystal packing forces (*vide infra*). Although the 12 Co–S distances (of which six are crystallographically independent) show very little deviation (*i.e.*, ≤0.008 Å), the six nonbonding Co···Co distances (of which four are crystallographically independent) show a large variation of 0.107 Å

---

(38) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(39) Observed and calculated structure factors for the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule and $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ (refinement B) 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 code number JACS-73-2164. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(40) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(41) D. L. Smith, "PLANES," Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

Table III. Final Positional and Thermal Parameters for $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$. Refinements A, B, and C

A. Positional Parameters

Atom	x	y	z	Atom	x	y	z
Cobalt				C(3)			
(A)	0.5725 (2)	0.6076 (3)	0.3639 (4)	(A)	0.7079 (24)	0.6949 (29)	0.3436 (49)
(B)	0.5732 (2)	0.6078 (2)	0.3640 (4)	(B)	0.7086 (22)	0.6951 (25)	0.3474 (38)
(C)	0.5732 (2)	0.6078 (2)	0.3640 (4)	(C)	0.7087 (22)	0.6954 (25)	0.3467 (36)
Sulfur				C(4)			
(A)	0.5629 (4)	0.5956 (4)	0.6458 (5)	(A)	0.6319 (39)	0.7631 (19)	0.3599 (49)
(B)	0.5642 (5)	0.5949 (4)	0.6463 (7)	(B)	0.6300 (35)	0.7609 (19)	0.3686 (46)
(C)	0.5640 (5)	0.5951 (4)	0.6461 (7)	(C)	0.6267 (34)	0.7609 (18)	0.3673 (43)
Phosphorus				C(5)			
(A)	0	$^1/_2$	$^1/_4$	(A)	0.5657 (33)	0.7348 (29)	0.2363 (56)
(B)	0	$^1/_2$	$^1/_4$	(B)	0.5620 (25)	0.7421 (26)	0.2222 (47)
(C)	0	$^1/_2$	$^1/_4$	(C)	0.5613 (24)	0.7427 (26)	0.2158 (43)
F(1)[a]				H(1)[b]			
(A)	0.0931 (138)	0.5284 (81)	0.3724 (257)	(A)	0.5667	0.6434	0.0148
(B)	0.0937 (43)	0.5301 (35)	0.3598 (83)	(B)	0.5738	0.6404	0.0139
(C)	0.0995 (56)	0.5400 (61)	0.3224 (123)	(C)	0.5771	0.6377	0.0110
F(2)[a]				H(2)			
(A)	0.1076 (42)	0.5407 (48)	0.2484 (184)	(A)	0.7442	0.5868	0.1526
(B)	0.1179 (29)	0.5423 (32)	0.2267 (64)	(B)	0.7488	0.5858	0.1575
(C)	0.1164 (63)	0.5323 (68)	0.2096 (155)	(C)	0.7492	0.5868	0.1632
F(3)[a]				H(3)			
(A)	0.0741 (124)	0.5264 (84)	0.1103 (170)	(A)	0.7691	0.6895	0.4232
(B)	0.0679 (43)	0.5155 (41)	0.0948 (68)	(B)	0.7680	0.6896	0.4308
(C)	0.0570 (61)	0.5096 (99)	0.0911 (63)	(C)	0.7685	0.6895	0.4295
C(1)				H(4)			
(A)	0.5997 (32)	0.6695 (25)	0.1227 (34)	(A)	0.6261	0.8162	0.4537
(B)	0.6047 (27)	0.6676 (22)	0.1227 (32)	(B)	0.6204	0.8110	0.4647
(C)	0.6062 (27)	0.6663 (22)	0.1203 (32)	(C)	0.6151	0.8106	0.4633
C(2)				H(5)			
(A)	0.6950 (27)	0.6411 (24)	0.1997 (42)	(A)	0.4947	0.7679	0.2210
(B)	0.6981 (22)	0.6392 (21)	0.2015 (33)	(B)	0.4937	0.7773	0.1963
(C)	0.6976 (21)	0.6404 (21)	0.2041 (35)	(C)	0.4939	0.7788	0.1864

B. Thermal Parameters[c]

Atom		$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	(A)	91 (3)	121 (3)	127 (4)	−24 (2)	−10 (4)	−10 (4)
	(B)	83 (2)	96 (3)	119 (4)	−23 (2)	−8 (4)	−16 (4)
	(C)	82 (2)	98 (3)	120 (4)	−23 (3)	−9 (4)	−15 (4)
S	(A)	166 (7)	78 (5)	125 (8)	8 (5)	−11 (8)	−15 (10)
	(B)	116 (6)	76 (5)	131 (9)	3 (4)	−6 (9)	−35 (8)
	(C)	117 (6)	76 (5)	131 (8)	4 (4)	−13 (9)	−32 (8)
P[d]	(A)	120 (20)	120	384 (57)	0	0	0
	(B)	107 (17)	107	382 (45)	0	0	0
	(C)	102 (17)	102	393 (51)	0	0	0
F(1)	(A)	400 (147)	250 (104)	1214 (407)	−107 (99)	593 (218)	−180 (152)
	(B)	14.5 (13)[e]					
	(C)	149 (53)	171 (61)	611 (217)	12 (42)	−50 (101)	−111 (120)
F(2)	(A)	122 (42)	166 (50)	687 (239)	66 (36)	37 (106)	46 (113)
	(B)	10.0 (9)[e]					
	(C)	151 (52)	183 (52)	674 (274)	−11 (38)	39 (115)	−143 (123)
F(3)	(A)	391 (162)	241 (133)	554 (175)	−20 (85)	−222 (168)	3 (144)
	(B)	16.5 (14)[e]					
	(C)	199 (57)	536 (168)	327 (103)	−110 (108)	79 (65)	104 (107)
C(1)	(A)	194 (35)	172 (35)	172 (51)	−91 (31)	−40 (46)	114 (39)
	(B)	174 (30)	140 (27)	141 (39)	−79 (25)	7 (41)	63 (34)
	(C)	174 (30)	147 (28)	151 (40)	−74 (25)	37 (42)	45 (36)
C(2)	(A)	134 (28)	159 (34)	264 (72)	−53 (26)	101 (41)	−3 (40)
	(B)	97 (22)	165 (29)	194 (56)	−37 (20)	37 (31)	54 (32)
	(C)	81 (20)	163 (29)	252 (66)	−29 (19)	23 (31)	73 (34)
C(3)	(A)	180 (33)	139 (31)	309 (79)	−35 (23)	−123 (47)	44 (50)
	(B)	129 (25)	164 (31)	198 (54)	−69 (20)	−84 (37)	−7 (41)
	(C)	136 (25)	171 (31)	149 (48)	−86 (21)	−75 (35)	−5 (37)
C(4)	(A)	361 (57)	34 (17)	351 (77)	−96 (25)	119 (67)	−78 (40)
	(B)	297 (52)	53 (18)	295 (69)	−55 (23)	91 (61)	−44 (39)
	(C)	311 (51)	50 (17)	266 (64)	−42 (22)	124 (60)	−41 (37)
C(5)	(A)	221 (50)	166 (39)	577 (116)	−27 (34)	93 (62)	−200 (59)
	(B)	153 (32)	109 (27)	392 (88)	−19 (24)	82 (43)	12 (44)
	(C)	161 (32)	131 (29)	288 (76)	−24 (24)	96 (40)	54 (42)

---

[a] Corresponds to crystalline disordered site with occupancy factor of $^1/_2$. [b] Footnote *b*, Table II. [c] Footnote *c*, Table II. [d] For the phosphorus atom located on a special position (2c) on a $\bar{4}$ axis, β_{11} and β_{22} are required by symmetry to be equal, and β_{12}, β_{13}, and β_{23} to be zero. [e] Isotropic thermal parameter.

Table IV. Interatomic Distances (Å) and Angles (deg) for $[Co_4(h^5\text{-}C_5H_5)_4S_4]$

A. Intramolecular Distances			
Co(1)···Co(1′)	3.315 (2)	Co(1)–S(1)	2.230 (2)
Co(1)···Co(2)	3.236 (1)	Co(1)–S(2)	2.232 (2)
Co(1)···Co(2′)	3.343 (1)	Co(1)–S(2′)	2.230 (2)
Co(2)···Co(2′)	3.299 (2)	Co(2)–S(1)	2.226 (2)
	3.295 (wtd av)	Co(2)–S(2)	2.234 (2)
		Co(2)–S(1′)	2.226 (2)
S(1)···S(1′)	2.984 (3)		2.230 (av)
S(1)···S(2)	3.048 (2)		
S(1)···S(2′)	2.950 (2)	C(1)–C(2)	1.401 (9)
S(2)···S(2′)	2.980 (3)	C(2)–C(3)	1.422 (10)
	2.990 (wtd av)	C(3)–C(4)	1.411 (12)
		C(4)–C(5)	1.386 (11)
Co(1)–C(1)	2.111 (6)	C(5)–C(1)	1.396 (9)
Co(1)–C(2)	2.118 (6)	C(6)–C(7)	1.388 (9)
Co(1)–C(3)	2.114 (6)	C(7)–C(8)	1.395 (10)
Co(1)–C(4)	2.113 (7)	C(8)–C(9)	1.431 (11)
Co(1)–C(5)	2.101 (6)	C(9)–C(10)	1.389 (11)
Co(2)–C(6)	2.121 (6)	C(10)–C(1)	1.383 (10)
Co(2)–C(7)	2.118 (6)		1.400 (av)
Co(2)–C(8)	2.105 (6)		
Co(2)–C(9)	2.096 (7)		
Co(2)–C(10)	2.126 (7)		
	2.112 (av)		
B. Bond Angles			
S(1)–Co(1)–S(2)	86.18 (6)	Co(1)–S(1)–Co(2)	93.12 (4)
S(1)–Co(1)–S(2′)	82.84 (6)	Co(1)–S(1)–Co(2′)	97.23 (4)
S(2)–Co(1)–S(2′)	83.82 (6)	Co(2)–S(1)–Co(2′)	95.64 (4)
S(1)–Co(2)–S(1′)	84.16 (6)	Co(1)–S(2)–Co(1′)	95.99 (4)
S(1)–Co(2)–S(2)	86.22 (6)	Co(1)–S(2)–Co(2)	92.86 (4)
S(1′)–Co(2)–S(2)	82.84 (6)	Co(1′)–S(2)–Co(2)	97.01 (4)
C(1)–C(2)–C(3)	106.8 (6)	C(6)–C(7)–C(8)	108.4 (7)
C(2)–C(3)–C(4)	107.7 (6)	C(7)–C(8)–C(9)	106.5 (7)
C(3)–C(4)–C(5)	108.2 (6)	C(8)–C(9)–C(10)	108.1 (6)
C(4)–C(5)–C(1)	108.3 (7)	C(9)–C(10)–C(6)	107.8 (7)
C(5)–C(1)–C(2)	109.0 (6)	C(10)–C(6)–C(7)	109.2 (6)
C. Selected Intermolecular Distances[a]			
$C(1)\cdots C(7)^{I}$	3.655 (9)	$H(1)\cdots H(7)^{I}$	2.444
$C(3)\cdots C(3)^{II}$	4.029 (11)	$H(3)\cdots H(3)^{II}$	2.221
$C(4)\cdots C(7)^{III}$	3.668 (9)	$H(4)\cdots H(7)^{III}$	2.471
$C(8)\cdots C(8)^{IV}$	3.907 (15)	$H(8)\cdots H(8)^{IV}$	2.122
$C(10)\cdots C(10)^{V}$	3.577 (15)	$H(10)\cdots H(10)^{V}$	2.384

[a] The superscripts refer to the following symmetry operations: (I) $x, y-1, z$; (II) $\bar{x}, \bar{y}, \bar{z}$; (III) $^1/_2-x, y-{}^1/_2, {}^1/_2-z$; (IV) $^1/_2-x, {}^1/_2-y, 1-z$; (V) $\bar{x}, 1-y, 1-z$.

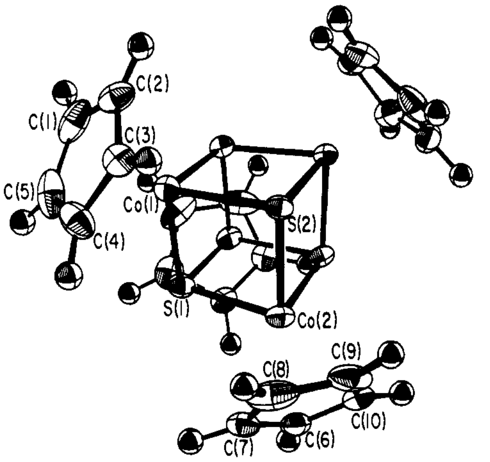

Figure 2. The neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule of crystallographic C_2-2 site symmetry ideally conforms to cubic T_d-$\bar{4}3m$ molecular symmetry. The nonhydrogen atoms are represented by thermal elliposoids of 40% probability.

while the six nonbonding S···S distances vary by 0.098 Å (*vide infra*).

The packing of the tetrameric molecules is presum-

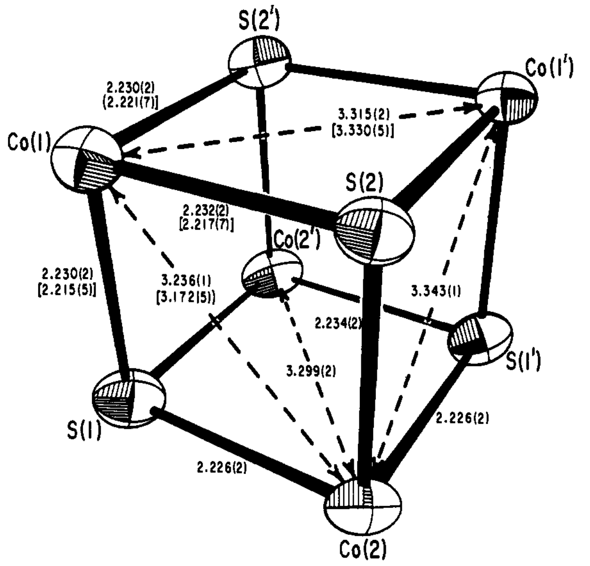

Figure 3. The Co_4S_4 framework of $[Co_4(h^5\text{-}C_5H_5)_4S_4]^n$ (n = 0, +1) with the crystallographically independent interatomic distances of the neutral molecule (of crystallographic site symmetry C_2-2) and the monocation (of crystallographic site symmetry S_4-$\bar{4}$). Those of the monocation are given in brackets.

Table V. Interatomic Distances (Å) and Angles (deg) for $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$

A. The $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ Cation[a]

	Refinement A	Refinement B	Refinement C
Co(1)–Co(1′)	3.314 (6)	3.330 (5)	3.330 (5)
Co(1)–Co(2)	3.165 (5)	3.172 (5)	3.172 (5)
Co(1)–S(1)	2.212 (5)	2.215 (5)	2.214 (5)
Co(1)–S(2)	2.200 (8)	2.217 (7)	2.215 (7)
Co(1)–S(2′)	2.222 (7)	2.221 (7)	2.223 (7)
Co–C(1)	2.073 (24)	2.074 (22)	2.089 (22)
Co–C(2)	2.069 (23)	2.078 (24)	2.065 (22)
Co–C(3)	2.065 (30)	2.062 (24)	2.066 (22)
Co–C(4)	2.128 (22)	2.087 (24)	2.072 (23)
Co–C(5)	1.909 (40)	2.047 (30)	2.082 (28)
	2.049 (av)	2.070 (av)	2.075 (av)
C(1)–C(2)	1.406 (37)	1.391 (34)	1.380 (34)
C(2)–C(3)	1.328 (43)	1.352 (34)	1.326 (35)
C(3)–C(4)	1.310 (44)	1.319 (38)	1.351 (38)
C(4)–C(5)	1.334 (53)	1.457 (43)	1.467 (42)
C(5)–C(1)	1.294 (39)	1.344 (36)	1.356 (35)
	1.334 (av)	1.373 (av)	1.376 (av)
S(1)···S(1′)	2.924 (11)	2.929 (10)	2.930 (10)
S(1)···S(2′)	3.077 (8)	3.085 (8)	3.083 (8)
S(1)–Co(1)–S(2′)	87.7 (3)	88.1 (3)	88.0 (3)
S(1)–Co(1)–S(2)	88.4 (3)	88.2 (2)	88.2 (2)
S(2)–Co(1)–S(2′)	82.8 (2)	82.6 (2)	82.6 (2)
Co(1)–S–Co(2)	91.8 (2)	91.3 (3)	91.3 (3)
Co(1)–S–Co(2′)	91.7 (2)	91.4 (2)	91.5 (2)
Co(1)–S–Co(1′)	97.1 (2)	97.2 (3)	97.2 (2)
C(1)–C(2)–C(3)	110 (3)	109 (3)	111 (3)
C(2)–C(3)–C(4)	110 (3)	112 (3)	110 (3)
C(3)–C(4)–C(5)	103 (3)	104 (3)	104 (3)
C(4)–C(5)–C(1)	117 (4)	109 (3)	108 (3)
C(5)–C(1)–C(2)	99 (3)	106 (3)	105 (3)

B. The PF_6^- Anion

	Refinement A	Refinement B	Refinement C
P–F(1)	1.569 (62)	1.522 (49)	1.483 (70)
P–F(2)	1.470 (63)	1.610 (36)	1.576 (75)
P–F(3)	1.484 (64)	1.504 (52)	1.445 (40)
F(1)–P–F(1′)	112 (9)	111 (5)	135 (8)
F(1)–P–F(2)	87 (8)	88 (3)	80 (5)
F(1)–P–F(3)	85 (4)	88 (2)	82 (3)
F(1)–P–F(2′)	93 (5)	85 (3)	91 (7)
F(2)–P–F(3)	91 (6)	91 (3)	97 (6)
F(2)–P–F(3′)	90 (6)	99 (3)	103 (7)
F(3)–P–F(3′)	85 (15)	73 (4)	61 (6)
F(1)–P–F(3′)	170 (16)	160 (4)	142 (6)
F(2)–P–F(2′)	179 (11)	167 (4)	157 (9)

[a] Co(1) and Co(2) are crystallographically equivalent and are related by symmetry operation $y, \bar{x}, \bar{z}$; Co(1) and Co(1′) are related by symmetry operation $\bar{x}, \bar{y}, z$ as are Co(2) and Co(2′). The corresponding sulfur atoms are related by similar symmetry relationships.

ably dictated by van der Waals interactions among the cyclopentadienyl rings. The cyclopentadienyl rings act as buffers to the Co_4S_4 core of each molecule such that there are no short intermolecular contacts involving the cobalt or sulfur atoms. The interactions resulting from the H···H separations (Table IV) less than 2.4 Å, twice van der Waals radius for hydrogen, probably represent major contributions to the crystal packing forces. A [010] projection of the monoclinic unit cell of $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ is presented in Figure 4.

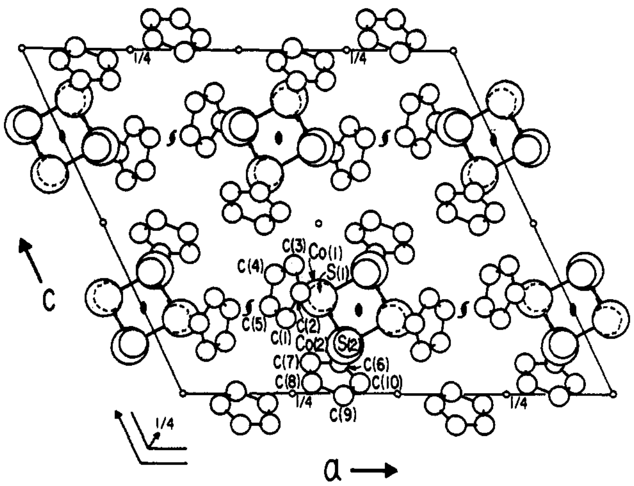

Figure 4. View down the [010] direction showing the orientations of the four neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecules, each lying on a crystallographic twofold axis, in the monoclinic unit cell of symmetry *C*2/*c*.

(b) $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$. Crystalline $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ is comprised of discrete $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ cations and twofold-disordered PF_6^- anions. The central phosphorus atom of the anion lies on a crystallographic $\bar{4}$ axis with the two disordered sets of fluorine atoms related by this rotary-inversion symmetry axis. The tetrameric cation is arranged about the other crystallographically independent $\bar{4}$ axis with a geometry closely approximating D_{2d}-$\bar{4}2m$ tetragonal symmetry. The gross configuration of the monocation is quite similar to that of the neutral tetramer in that the oxidation does not produce a drastic change in configuration but only a small but yet highly significant tetragonal distortion of the Co_4S_4 core which is evident from comparison of the corresponding distances and bond angles. The crystal packing is undoubtedly dominated by long-range ionic forces as well as van der Waals forces. There is only one distance less than the sum of van der Waals radii—*viz.*, a weak hydrogen bond of 2.18 Å between H(4′) and F(1). The regular tetragonal deformation of the Co_4S_4 framework of the monocation from the *idealized* tetrahedral T_d geometry of the neutral homolog coupled with the long contacts between ionic species is compatible with the premise that crystal-packing interactions do not play a dominant role in accounting for the observed distortion. A [001] projection of the tetragonal unit cell of $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+PF_6^-$ is given in Figure 5.

Within the tetragonal unit cell, the PF_6^- anions are randomly distributed in one of two orientations about a crystallographic S_4-$\bar{4}$ axis. Only the phosphorus atom has unit occupancy, while the three crystallographically independent fluorine atoms are each half-weighted which generates (*via* the $\bar{4}$ site symmetry) 12 half-weighted fluorine atoms. The two orientations of the hexafluorophosphate anions are related to each other by a rotation of 90° around the $\bar{4}$ symmetry axis (Figure 1). The geometry of the octahedral-like anion is *poorly defined* primarily due to the composite effects of excessive thermal motion of the fluorine atoms and the crystallographic disorder. Refinement A, which was based on the initial data set, provided the most octahedral-like geometry with the seven independent cis F–P–F angles varying from 85 (15) to 112 (9)° and with the two independent trans F–P–F angles being 170 (16) and 179 (11)°. The P–F bond distances were 1.47 (6), 1.48 (6), and 1.57 (6) Å. Refinement B, which

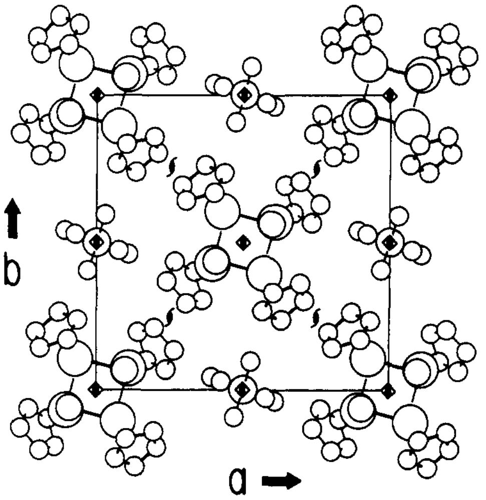

Figure 5. View down the [001] direction depicting the packing the two $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocations and two PF_6^- anions in the tetragonal unit cell of symmetry $I\bar{4}$. Each of the two *ordered* monocations is located about a $S_4\text{-}\bar{4}$ crystallographic axis (corresponding to the one set of twofold special positions 2a), and the composite of the two orientations of each of the two disordered PF_6^- anions lies on a $S_4\text{-}\bar{4}$ axis (corresponding to the one set of twofold special positions 2c). Only one of the two orientations of each crystal disordered PF_6^- anion is shown.

utilized isotropic thermal parameters for the fluorine atoms, resulted in P–F bond distances of 1.50 (5), 1.52 (5), and 1.61 (4) Å; cis F–P–F angles of range 73 (4) to 111 (5)°; and trans F–P–F angles of 160 (4) and 167 (4)°. Refinement C, which utilized anisotropic thermal parameters for the fluorine atoms and which thereby is purportedly a better thermal model, exhibited an even wider range of interatomic parameters. The P–F bond distances are slightly shorter at 1.44 (4), 1.48 (7), and 1.58 (8) Å; there is an even greater angular distortion of the octahedral geometry with the cis F–P–F angles ranging from 61 (6) to 135 (8)° and with the trans F–P–F angles being 142 (6) and 157 (9)°. The chemically unreasonable distortions of the anion and large esd's of the distances and bond angles for the three refinement models are readily attributed to the large anisotropic thermal motion of the fluorine atoms, the crystal disorder of the anion, and the low data-to-parameter ratio. This is reflected in the variance–covariance matrix which reveals strong coupling among the individual positional and thermal parameters of the fluorine atoms. Fortunately, this problem of low resolution for the anion is *not* encountered for the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation (*vide supra*).

Cobalt···Cobalt Distances. The valence electron requirements of each cobalt atom in the neutral tetramer are satisfied by the cyclopentadienyl and bridging sulfur ligands without necessity of any metal–metal interactions. The four independent metal–metal distances of 3.236 (1), 3.299 (2), 3.315 (2), and 3.343 (1) Å are appropriately nonbonding. It is not at all unreasonable to attribute the differences in these extremely long nonbonding metal–metal distances to subtle anisotropic effects in the crystal packing forces which are not obvious from an examination of the interatomic distances. As noted above, the short H···H distances between some of the cyclopentadienyl hydrogen atoms may represent a major portion of these packing forces, although it is not possible to predict the distortions of the Co_4S_4 core resulting from these short contacts. It is noteworthy that similar metal–metal bond-length distortions have been observed in the solid state for other cubane-like tetramers containing a nonbonding tetrahedron of metal atoms—*e.g.*, in the $[Co_4\{(acac)(CH_3OH)\}_4(OCH_3)_4]$ molecule[42] (of crystallographic C_2-2 site symmetry) for which the four independent nonbonding Co···Co distances in the Co_4O_4 core range from 3.10 (1) to 3.17 (1) Å, in $[Os_4(CO)_{12}O_4]$[3,6] (of crystallographic $S_4\text{-}\bar{4}$ site symmetry) for which the two independent nonbonding Os···Os contacts in the Os_4O_4 core are 3.190 (4) and 3.253 (4) Å, and in $[Re_4(CO)_{12}(SCH_3)_4]$[5] (of crystallographic C_2-2 site symmetry) for which the four independent nonbonding Re···Re distances in the Re_4S_4 core vary from 3.854 (3) to 3.957 (3) Å. Although the observed differences in nonbonding metal···metal distances in each of these cubane-like molecules are also statistically significant in the solid state, there is (to our knowledge) *no chemical significance* in the observed variations aside from the presumed anisotropic effects of the crystal packing forces.

The contrasting closeness of all the Co–S distances to one another in both the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule and the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation (*vide infra*) emphasizes that, in general, the metal–ligand bonds are relatively rigid compared to the much weaker metal–metal interactions, and hence any angular deformations of the cubane-like M_4X_4 core due to packing effects will be manifested from potential energy considerations in varying metal–metal distances with a *maximum variation* expected (and found as illustrated above) for metal–metal distances for which the *interactions* are *nonbonding* (or of a repulsive nature). The ability to separate without difficulty the predicted deformation due to electronic effects from the unpredictable, superimposed distortions arising from crystal-packing interactions is made possible by the fact that an alteration of the number of antibonding electrons in a metal cluster system in general causes drastic changes in the metal architecture which (particularly from the resulting directional shifts of the metal atoms) can be easily discerned.[1,15,17,43]

Oxidation of the neutral tetramer produces a tetragonally distorted monocation with two crystallographically independent cobalt–cobalt distances. These two interatomic distances are unequally divided among the six metal–metal distances in the molecule. Four of the distances have been shortened (relative to the average value of 3.295 Å in the neutral tetramer) by 0.12 to 3.172 (5) Å, while the other two distances of 3.330 (5) Å are 0.035 Å longer than the average nonbonding Co···Co distance in the neutral tetramer. The electronic implications of these bond-length changes will be discussed below.

Sulfur···Sulfur Distances. The small distortions in $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ from a regular tetrahedral geometry are also reflected in the nonbonding S···S distances which range from 2.950 (2) to 3.048 (2) Å with a weighted average value of 2.990 Å. Of the six nonbonding S···S distances in the monocation (of which

---

(42) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971).

(43) *Cf.* (a) N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970); (b) C. E. Strouse and L. F. Dahl, *ibid.*, **93**, 6032 (1971), and references cited therein.

only two are crystallographically independent), under the idealized D_{2d} geometry two are 2.929 (10) Å and four are 3.085 (8) Å. The shorter S···S distance of 2.929 (10) Å is normal to the two identical longer Co···Co distances of 3.330 (5) Å.

Cobalt–Sulfur Bond Distances. The six crystallographically independent Co–S bonding distances in the neutral tetramer range from 2.226 (2) to 2.234 (2) Å with an average value of 2.230 Å. In the $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]^+$ monocation, the 12 Co–S bonding distances, of which only three are crystallographically independent, are broken down under assumed D_{2d} symmetry into four chemically equivalent bond lengths of identical value 2.215 (5) Å and eight chemically equivalent bond lengths (of 2.217 (7) and 2.221 (7) Å) which average 2.219 Å. The overall bond-length average of 2.218 Å for the 12 Co–S bonds in the monocation being slightly shorter by 0.012 Å than the average Co–S bond length of 2.230 Å in the neutral parent is not unexpected from electronic-charge considerations. The Co–S bonds are sufficiently strong that a removal of one electron, even from an MO containing substantial metal–ligand bonding character between the cobalt atoms and triply bridging sulfur atoms, would not be anticipated to produce any appreciable change in the 12 Co–S bond lengths.

These cobalt–sulfur distances are significantly longer than the average metal to triply bridging sulfur distances found for metal coordinated apical sulfur atoms in triangular metal cluster systems—*e.g.*, $\mathrm{Co_3}(h^5\text{-}\mathrm{C_5H_5})_3\mathrm{S_2}$ (2.157 (3) Å),[1] $\mathrm{Co_3(CO)_9S}$ (2.139 (4) Å),[44] $\mathrm{FeCo_2(CO)_9S}$ (2.158 (4) Å),[45] $[\mathrm{Co_3(CO)_7S}]_2\mathrm{S_2}$ (2.144 (6) Å),[46] and the $\mathrm{SCo_3(CO)_6S_3}$ residue of the $\mathrm{SCo_6(CO)_{11}(SC_2H_5)_4}$ molecule (2.163 (6) Å).[47] However, these distances between the metal and triply bridging sulfur atoms in $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]$ compare favorably with those of average value 2.23 (2) Å in $\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_6}$[23] and of average value 2.217 (3) Å in $[\mathrm{Fe_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]$.[14] These pronounced variations in the average metal to triply bridging sulfur distances in the cubane-like metal clusters from those in triangular metal clusters signify that a meaningful comparison of metal–sulfur distances in these organometallic chalcogen clusters must first take into account the overall geometry of the complex and that one must be exceedingly careful in making correlations of bond length changes with stereochemical or bonding principles in those cases involving metal cluster systems of *different* basic geometry.

The Cyclopentadienyl Ligands. The two independent distances between the cobalt atoms and the centroids of the pentahapto-coordinated cyclopentadienyl rings in the neutral $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]$ tetramer are virtually identical at 1.742 and 1.747 Å. The corresponding ten independent cobalt–carbon distances exhibit a small range of values from 2.096 (7) to 2.126 (7) Å with the average value of 2.112 Å being in relatively good agreement with those in other cobalt–cyclopentadienyl complexes. In the $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]^+$ monocation these values are slightly smaller with the one independent $\mathrm{Co{-}C_5H_5}$ (centroid) distance being 1.701 Å and the five individual cobalt–carbon distances ranging from 2.047 (30) to 2.087 (25) Å with an average value of 2.070 Å. In both complexes the cyclopentadienyl ligands undergo considerable librational motion as evidenced both from the large anisotropic thermal parameters (Tables II and III) and from the elongated ellipsoids shown in Figure 2. The C–C ring distances, which reflect this rotational motion, vary from 1.383 (10) to 1.431 (11) Å in the neutral tetramer and from 1.317 (38) to 1.457 (43) Å in the monocation. The planarity of each of the cyclopentadienyl rings is demonstrated by the fact that no carbon atom in either complex deviates from its mean plane by more than 0.013 Å.

Bonding Description. In order to rationalize the observed deformation in the architecture of the central $\mathrm{Co_4S_4}$ core from an idealized cubic T_d geometry in the neutral $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]$ molecule to an idealized tetragonal D_{2d} geometry in the monocation, a delocalized molecular orbital model needs to be employed. Although a simple metal cluster model has been outlined elsewhere in qualitative descriptions of the bonding of other cubane-like molecules,[7,13a,15] a brief résumé is presented here in connection with its particular application to the $[\mathrm{Co_4}(h^5\text{-}\mathrm{C_5H_5})_4\mathrm{S_4}]^n$ ($n = 0,+1$) complexes.

Each cobalt atom has nine valence orbitals (*viz.*, the five 3d, one 4s, and three 4p ao's) which transform under T_d molecular symmetry (with the assumption of cylindrical symmetry for each cyclopentadienyl ring) to yield 36 metal orbital combinations of symmetry $3a_1 + 3e + 3t_1 + 6t_2$. The three valence orbitals per sulfur atom involved in the cobalt–sulfur bonding (*i.e.*, the fourth tetrahedral-like sulfur orbital containing the unshared electron pair may be excluded as nonbonding in this treatment) combine under T_d molecular symmetry to give symmetry orbitals of $a_1 + e + t_1 + 2t_2$ representations. Likewise, the three filled π-orbitals of the cyclopentadienyl rings of $a_1 + e$ localized symmetry transform to give symmetry orbitals of $a_1 + e + t_1 + 2t_2$ representations. The symmetry orbitals of the sulfur and cyclopentadienyl ligands are assumed to interact with the corresponding symmetry orbitals of the tetracobalt fragment to give bonding and antibonding molecular orbitals of which the bonding ones are completely occupied and the antibonding ones are empty.

For simplicity, a perfect-pairing approximation is then utilized in which the metal–ligand interactions are separated from the metal–metal interactions. This leaves a set of orbitals of $a_1 + e + t_1 + 2t_2$ representations which are considered to be essentially tetrametal in character. The qualitative nature of these symmetry arguments is immediately obvious, since the considerable mixing which may occur between the metal–metal and metal–ligand orbitals belonging to the same representation is not taken into account in this metal cluster model.[48,49]

---

(44) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

(45) D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6027 (1971).

(46) D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *ibid.*, **89**, 3727 (1967).

(47) C. H. Wei and L. F. Dahl, *ibid.*, **90**, 3977 (1968).

(48) Recent LCAO–MO–SCF calculations[49] on $\mathrm{Co_3(CO)_9S}$ and other metal cluster systems have demonstrated that the energy levels of the molecular orbitals are strongly dependent upon both the metal–metal and metal–ligand interactions. Nevertheless, with recognition of its inherent limits, this metal cluster model has been found to provide much useful qualitative bonding information concerning the predictions of molecular geometries and of relative variations in metal–metal distances in metal cluster systems.[1,7,13a,15,17]

(49) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, to be submitted for publication.

From the use of symmetry-adapted wave functions (previously derived and available elsewhere) involving a basis set of directed hybrid metal orbitals which are primarily involved in the tetracobalt interactions, it can be readily seen from overlap considerations that three sets of orbitals of $a_1 + e + t_2$ representations are bonding while two sets, $t_1 + t_2$, are antibonding.

For the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule, all of the tetracobalt bonding and antibonding energy levels are fully occupied by the 24 valence electrons available from the four d^6 Co(III) (*i.e.*, this formal oxidation state results from each cobalt providing one electron to complete the Co–C_5H_5 bonding and two electrons to complete the electron pair σ bonds with the sulfur atoms) such that the cobalt–cobalt bond order (in the valence bond formalism) is zero. Furthermore, the separations among the tetracobalt levels are small due to the long metal–metal distances and resulting small overlap integrals. In valence bond terms, this MO picture corresponds to a closed-shell configuration for each cobalt atom without the necessity of any *net* cobalt–cobalt bonding interactions.

Removal of one electron from either the antibonding t_1 or antibonding t_2 level by oxidation of the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule would produce an orbital degeneracy of the ground state for the monocation (under T_d symmetry) for which a deformation from T_d to D_{2d} geometry is permissible *via* a Jahn–Teller-active vibration.[50] From Jahn–Teller considerations,[51] the triply degenerate levels t_1 and t_2 each split under D_{2d} symmetry such that the doubly degenerate level e is of lower energy than that of the nondegenerate level. If (under T_d symmetry) the antibonding level t_1 lies above the antibonding t_2 one, then the unpaired electron in the monocation would probably occupy (under D_{2d} symmetry) an a_2 level, but if the antibonding level t_2 is higher in energy than the antibonding t_1 one (under T_d symmetry), then the unpaired electron in the monocation would probably reside in a nondegenerate antibonding level of b_2 representation. Examination of the symmetry-adapted orbitals reveals that under D_{2d} symmetry the a_2 and b_2 molecular orbitals are each primarily of importance to four of the six *antibonding* cobalt–cobalt interactions. Hence, if an electron is removed from either of these nondegenerate orbitals, a shortening of four of the six metal–metal distances would be predicted for the monocation compared to the average metal–metal distance in the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule. These predictions are in complete accord with the observed geometrical deformation which occurs upon oxidation of the neutral tetramer to the monocation in that four of the six metal–metal distances (*viz.*, Co(1)–Co(2), Co(1)–Co(2′), Co(1′)–Co(2), and Co(1′)–Co(2′)) in the Co_4S_4 core are shorter by 0.12 Å relative to the average cobalt–cobalt nonbonding distance in the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$. This bond length shortening represents under this metal cluster model an increase in the individual valence bond order from 0 to 0.125 for each of the four equivalent cobalt–cobalt bonds for a total limiting metal–metal bond order of 0.5.[52]

Acknowledgments. This work was made possible through the financial support of the National Science Foundation (No. GP-19175X). One of us (G. L. S.) is indebted to Abbott Laboratories (North Chicago, Ill.) for a research fellowship (Sept 1971–Aug 1972). The use of the UNIVAC 1108 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee. The authors express their gratitude to Mr. Boon Keng Teo at the University of Wisconsin (Madison) for helpful bonding discussions.

---

(50) *Cf.* (a) R. W. Jotham and S. F. A. Kettle, submitted for publication; (b) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 340.

(51) This argument is based on the premise that if the highest antibonding triply degenerate level splits under D_{2d} symmetry to give a doubly degenerate level higher in energy than the nondegenerate one, then there would be three unpaired electrons in the doubly degenerate level which should lead to a further lowering of the symmetry *via* a Jahn–Teller mechanism to the D_2 point group. It is thus assumed that the crystallographically determined $S_4\text{-}\bar{4}$ site symmetry (and idealized $D_{2d}\text{-}\bar{4}2m$ geometry) for the monocation provides experimental evidence for the nondegenerate level lying higher than the doubly degenerate one under D_{2d} symmetry.

(52) Since in a metal cluster system the electrons are delocalized over the entire metal orbital framework, the total metal–metal bond order in the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation may not necessarily be distributed to give zero bond order for each of two pairs of metal atoms and 0.125 bond order for each of four pairs of metal atoms. However, this limiting situation is presumed in the $[Co_4(h^5\text{-}C_5H_5)_4S_4]^+$ monocation on the basis of bond length comparisons which show the two longer identical Co–Co distances in the monocation to be analogous to the average nonbonding Co···Co distance in the neutral $[Co_4(h^5\text{-}C_5H_5)_4S_4]$ molecule.