Figures 2 and 3 between the guanidyl and phosphate groups within the asymmetric unit resembles very closely the hydrogen bonding interaction between the guanidyl moiety of arginine-35 and the 5′-phosphate group of the deoxythymidine 3′,5′-diphosphate (pdTp) inhibitor observed in the high-resolution structure of staphylococcal nuclease and shown in Figure 1. Additionally, in the enzyme the third guanidyl nitrogen atom of this arginine forms bridging hydrogen bonds to backbone carbonyl oxygen atoms. In methylguanidinium dihydrogenphosphate, the third nitrogen atom, N_2, hydrogen bonds weakly through its two hydrogen atoms (H_{n21} and H_{n22}) to oxygen atoms of phosphate groups in two other asymmetric units. The remaining guanidinium hydrogen atom, H_{n31}, also hydrogen bonds to a phosphate oxygen in another asymmetric unit.

Organometallic Chalcogen Complexes. XXVII. Structure and Bonding of a Metal Carbonyl Tetramer, $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$, Containing a Planar Tetrametal Cluster System. A Direct Stereochemical Appraisement of Strong Metal–Metal Interactions in a Ligand-Bridged Complex[1,2]

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Contribution from the Biology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, the Department of Organic Chemistry of the University of Chemical Engineering, Veszprém, Hungary, Laboratory of the Chemistry and Technology of the Radioelements of the CNR, 35100-Padova, Italy, and the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received January 22, 1973*

Abstract: A structural characterization of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ has not only revealed a new kind of organometallic cluster system of general formula $M_4L_4(\mu_2\text{-}X)_8$ containing a planar array of four metal atoms but also has afforded from the determined molecular parameters a *direct* assessment of the effect of localized metal–metal interactions upon the molecular geometry of a ligand-bridged complex. The four cobalt atoms are situated at the corners of a rectangle with each pair of cobalt atoms connected by two bridging mercapto sulfur atoms. Each chemically equivalent cobalt atom has a distorted (tetragonal-pyramidal)-like environment of four bridging sulfur atoms in the basal plane and the carbonyl ligand at the apex. An electron-pair metal–metal bond may be assumed to complete an octahedral-like coordination about each cobalt atom. The basic $Co_4(CO)_4(\mu_2\text{-}S)_8$ framework of the molecule ideally conforms to D_{2h} symmetry which is lowered by inclusion of the sulfur-attached ethyl groups to the crystallographically required C_i symmetry. The *severe* orthorhombic D_{2h} distortion of the Co_4S_8 core from a tetragonal D_{4h} model is ascribed to the energy stabilization of the tetramer by the formation of two localized electron-pair cobalt–cobalt bonds such that each Co(II) attains a closed-shell electronic configuration. The considerable bond strength of these localized metal–metal bonds is directly gauged in this molecule *per se* through (1) the resulting short Co–Co bonding distance of 2.498 (5) Å for one opposite pair of cobalt atoms in the tetracobalt rectangle *vs.* a normal nonbonding Co···Co distance of 3.312 (9) Å for the other opposite pair, and (2) the sharply acute Co–S–Co bond angles of 67.8° (av) for the two (metal–metal)-bonded Co_2S_2 fragments compared to the normally obtuse Co–S–Co bond angles of 94.0° (av) for the other two Co_2S_2 fragments without the cobalt–cobalt bonds. The architecture of the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule is compared with those of the structurally related $Fe_2(CO)_6(\mu_2\text{-}SC_2H_5)_2$-type dimer and of the structurally analogous $Ru_4(NO)_4(\mu_2\text{-}Cl)_4(\mu_2\text{-}P(C_6H_5)_2)_4$ tetramer, and its metal–metal bonding is discussed relative to that for a hypothetical tetragonal D_{4h} model. One salient feature is that, whereas the two $S\text{-}CH_2$ bonds in each (cobalt–cobalt)-bonded $Co_2(SC_2H_5)_2$ fragment are "equatorial-axial" anti, the two $S\text{-}CH_2$ bonds in each $Co_2(SC_2H_5)_2$ fragment without the Co–Co bond are "bisequatorial" syn (relative to the tetracobalt plane); the fact that this latter arrangement is unprecedented in the dinuclear $Fe_2(CO)_6(\mu_2\text{-}SR)_2$ molecules is rationalized from stereochemical considerations. $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$: triclinic; $P\bar{1}$; $a = 9.22$ (2), $b = 10.55$ (2), $c = 10.84$ (2) Å; $\alpha = 61°\ 21\ (10)'$, $\beta = 79°\ 10\ (10)'$, $\gamma = 66°\ 12\ (10)'$; $\rho_{obsd} = 1.63$ *vs.* $\rho_{calcd} = 1.69$ g cm^{-3} for $Z = 1$. Least-squares refinement gave $R_1(F) = 8.3\%$ and $R_2(F) = 7.4\%$ for 1575 independent photographically collected data.

During the last 10 years considerable effort has been directed toward preparative and structural studies of organometallic sulfur clusters in order to elucidate the detailed nature of metal–metal interactions in these complexes and especially to systematize the influence of

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[2] Previous paper in this series: G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 2164 (1973).

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valence electrons upon molecular geometries. This work was largely catalyzed by an extensive investigation of the reactions of dicobalt octacarbonyl with elemental sulfur and sulfur-containing reagents[4] which have yielded a wide variety of polynuclear cobalt carbonyl sulfur complexes. Crystallographic studies of these complexes, which include $Co_3(CO)_9(\mu_3\text{-}S)$,[5] $FeCo_2(CO)_9(\mu_3\text{-}S)$,[6] $[Co_3(CO)_7(\mu_3\text{-}S)]_2(\mu_4\text{-}S_2)$,[7] $Co_3(CO)_3\{(\mu_2\text{-}SC_2H_5)_5(\mu_2\text{-}CO)\}$,[8] $Co_6(CO)_6(\mu_2\text{-}CO)_5(\mu_2\text{-}SC_2H_5)(\mu_3\text{-}SC_2H_5)_3(\mu_3\text{-}S)$,[9] $Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_4\text{-}S)_2$,[10] $Co_6(CO)_{14}(\mu_2\text{-}CO)(\mu_3\text{-}S)\text{-}CS_2$,[11,12] and $Co_6(CO)_{16}C_2S_3$,[12,13] have revealed highly unusual structures[14] containing new metal–sulfur linkages of biological importance as well as of considerable theoretical interest.

In 1965 Markó and Bor[15] reported the preparation of an additional cobalt carbonyl–sulfur complex, $Co_4(CO)_4(SC_2H_5)_8$, which was obtained by the reaction of hydrated cobalt dichloride with sodium hydroxide, ethyl mercaptan, and carbon monoxide in methanol at room temperature. The formulation of this compound as a tetramer was based on a molecular weight determination in benzene. An infrared examination was also carried out, but no possible structural models were proposed at that time.[15]

Our interest in elucidating the stereochemical nature of this new type of complex resulted in the structural determination of $Co_4(CO)_4(SC_2H_5)_8$ which revealed a new basic polyhedral unit for an organometallic $M_4L_4(\mu_2\text{-}X)_8$ system. This complex also has a unique stereochemical feature in that it affords from the determined architecture of *one* complex a *direct* measurement of the deformation of the molecular geometry of a ligand-bridged complex due to a metal–metal interaction. Previous assessments[16–19] of the influence of metal–metal interactions on the molecular geometries of organometallic ligand-bridged complexes have arisen from comparisons of *two* corresponding complexes differing from each other only by the necessity of an electron-pair interaction in one as opposed to none being required in the other in order for each of the metal atoms to achieve a so-called closed-shell electronic ground-state configuration. This latter kind of systematic analysis which showed the drastic effects of metal–metal interactions on ligand-bridged organometallics was first demonstrated from structural investigations[16] of two dimeric complexes $M_2(h^5\text{-}C_5H_5)_2(\mu_2\text{-}P(C_6H_5)_2)_2$ (where M = Co, Ni) and more recently was obtained by an alteration of valence electrons either through replacement of different metal atoms and/or different ligands[20] or through redox reactions.[21,22] This paper reports the details of the stereochemistry and bonding of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$, which have been briefly communicated earlier.[1b]

Experimental Section

Single-Crystal X-Ray Data. Black air-stable crystals of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ were recrystallized from petroleum ether solution, from which a needle crystal of length 0.38 mm and width 0.12 mm was isolated and used for the collection of intensity data. The crystal, sealed in a thin-walled glass capillary tube, was mounted for rotation about the needle axis which corresponded to the *b* axis of an arbitrarily chosen A-centered triclinic unit cell. The lattice parameters of this A-centered triclinic cell were determined from 0*kl* and *hk*0 precession photographs. Multiple-film equiinclination Weissenberg data were obtained for reciprocal levels *h*0*l* through *h*10*l* with Zr-filtered Mo Kα radiation. In order to eliminate systematic errors due to spot compaction on the lower half of Weissenberg film,[23] the intensities of only the upper half of the Weissenberg film were determined. This required two separate sets of film data for the nonzero reciprocal levels corresponding to a 360° rotation range. In addition, multiple-exposure precession data were collected for the *hk*0, 0*kl*, 1*kl*, and 2*kl* reciprocal levels. The intensities of all films were visually estimated by comparison with calibrated sets of standard spots. Absorption corrections were not made since for Mo Kα radiation the estimated μR_{max} was only 0.37, and hence the maximum variation in intensity due to absorption is estimated to be less than 12%. After correction of the intensities for Lorentz–polarization effects and spot extension,[24] all indices were transformed from the A-centered triclinic unit cell to the reduced primitive triclinic unit cell[25] according to the $a < b < c$ convention.[26] Reflections common to both sets of Weissenberg films and the precession data then were utilized in a least-squares merging program[27] which placed all 1575 independent diffraction maxima on a single common scale. Standard deviations of the observed structure amplitudes were assigned as follows. If $I_o < 4I_o(\min)$, $\sigma(F_o) = [F_o/20][4I_o(\min)/I_o]^2$; if $I_o \geq 4I_o(\min)$, $\sigma(F_o) = F_o/20$. Neither extinction nor dispersion corrections were made.[28,29]

Crystal Data. The reduced primitive triclinic unit cell with lattice parameters $a = 9.22 \pm 0.02$, $b = 10.55 \pm 0.02$, $c = 10.84 \pm$

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[11] J. F. Blount, L. Markó, G. Bor, and L. F. Dahl, to be submitted for publication.

[12] Initially formulated from elemental analyses as $Co_4(CO)_{10}CS_2$.[4d,i]

[13] C. H. Wei and P. A. Agron, to be submitted for publication.

[14] The preparation, structure, and bonding of another stereochemically related mercaptocobalt carbonyl cluster, $Co_5(CO)_7(\mu_2\text{-}CO)_3(\mu_2\text{-}SC_2H_5)_3(\mu_3\text{-}SC_2H_5)_2$, were reported: C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **90**, 3969 (1968).

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[28] For Mo Kα radiation the values of the dispersion corrections to the atomic scattering factors are $\Delta f' = 0.4$ and $\Delta f'' = 1.1$ for cobalt; $\Delta f' = 0.1$ and $\Delta f'' = 0.2$ for sulfur.[29] Since $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ possesses a centrosymmetric space group, these relatively small dispersion corrections do not affect significantly the atomic coordinates.

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Table I. Final Atomic Parameters ($\times 10^4$)[a,b]

Atom	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	4540 (2)	3039 (2)	6683 (2)	127 (3)	107 (3)	81 (3)	−49 (3)	−7 (2)	−35 (2)
Co(2)	4731 (2)	5247 (2)	6847 (2)	117 (3)	113 (3)	74 (3)	−39 (2)	−8 (2)	−41 (2)
S(1)	5961 (4)	2839 (4)	8091 (4)	142 (6)	125 (6)	85 (5)	−38 (5)	−27 (5)	−29 (5)
S(2)	2568 (4)	4370 (4)	7897 (4)	129 (5)	150 (6)	89 (5)	−56 (5)	5 (4)	−48 (5)
S(3)	6631 (4)	2848 (4)	4895 (4)	124 (5)	118 (5)	94 (5)	−39 (4)	−10 (4)	−45 (4)
S(4)	3094 (4)	4283 (4)	4877 (4)	130 (5)	119 (5)	91 (5)	−57 (4)	−7 (4)	−38 (4)
C(1T)	4245 (18)	1214 (21)	7468 (19)	184 (28)	218 (34)	175 (32)	−45 (26)	−43 (23)	−101 (27)
O(1T)	4060 (17)	61 (14)	7908 (14)	520 (39)	188 (23)	182 (24)	−214 (25)	−45 (23)	−21 (19)
C(2T)	4578 (16)	6171 (17)	7909 (18)	177 (26)	177 (28)	149 (29)	−63 (22)	−32 (21)	−71 (23)
O(2T)	4463 (14)	6679 (14)	8683 (15)	323 (26)	279 (25)	215 (24)	−85 (19)	−62 (19)	−149 (20)
C(1E)	8097 (15)	2249 (17)	7517 (17)	14 (22)	214 (28)	153 (27)	10 (20)	−66 (20)	−110 (22)
C(2E)	8937 (18)	2083 (20)	8654 (21)	222 (32)	262 (37)	196 (34)	−77 (27)	−31 (26)	−72 (27)
C(3E)	2478 (17)	3470 (17)	9830 (15)	246 (30)	217 (29)	54 (20)	−117 (25)	23 (20)	−42 (19)
C(4E)	1793 (29)	2078 (30)	10505 (22)	559 (66)	532 (63)	139 (33)	−394 (54)	60 (38)	−110 (38)
C(5E)	7049 (16)	1067 (16)	4748 (17)	173 (26)	150 (26)	172 (29)	−64 (21)	31 (21)	−92 (22)
C(6E)	8533 (17)	876 (18)	3555 (18)	207 (30)	200 (31)	152 (27)	3 (24)	8 (23)	−99 (23)
C(7E)	2471 (17)	2859 (15)	4787 (16)	229 (28)	175 (26)	95 (22)	−94 (21)	−51 (20)	−31 (19)
C(8E)	1437 (17)	3596 (19)	3654 (18)	191 (26)	283 (33)	147 (27)	−83 (24)	−58 (22)	−99 (24)

[a] Least-squares derived standard deviations of the least significant figures are given in parentheses in all tables and in the text. Since no absorption corrections were applied, these values represent a lower limit for the true standard deviations. See W. C. Hamilton and S. C. Abrahams, *Acta Crystallogr., Sect. A*, **26**, 18 (1970). [b] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

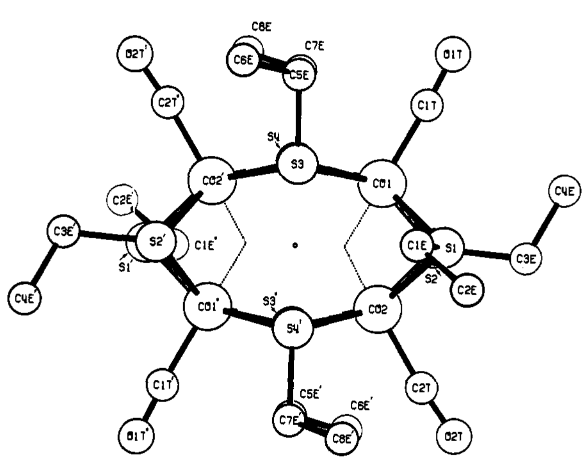

Figure 1. View of the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule approximately perpendicular to the tetracobalt plane. The entire molecule possesses crystallographic site symmetry C_i-$\bar{1}$; the $Co_4(CO)_4(\mu_2\text{-}S)_8$ fragment ideally has D_{2h}-$2/m2/m2/m$ symmetry. The hydrogen atoms are not shown.

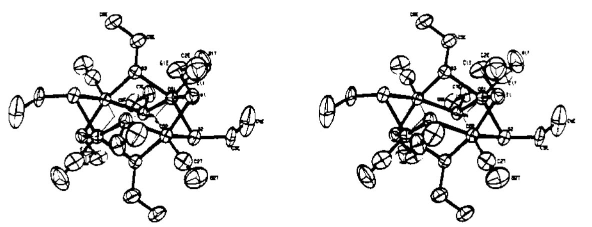

Figure 2. A stereoscopic view of the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule (without the hydrogen atoms) for whicht hermal ellipsoids of 50% probability are shown for each atom

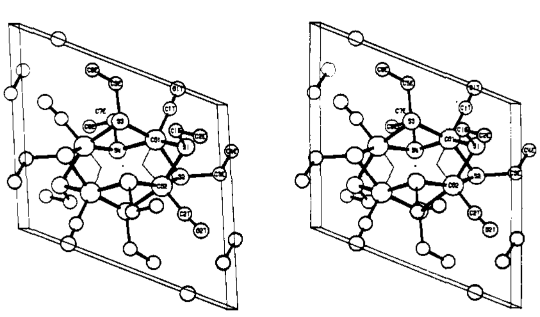

Figure 3. Arrangement of the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule in the triclinic unit cell stereochemically viewed down the center of the cell. The origin of the unit cell is in the upper-left rear corner with the right-handed axial system oriented such that the a axis is up.

0.20 Å, $\alpha = 61° 21 \pm 10'$, $\beta = 79° 10 \pm 10'$, $\gamma = 66° 12 \pm 10'$ contains one formula unit of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$. The volume of the unit cell is 825 Å^3. The total number of nonhydrogen electrons per unit cell equals 388. The observed density of 1.63 g cm^{-3} obtained by flotation agrees reasonably well with the calculated value of 1.69 g cm^{-3} for $Z = 1$. The success of the X-ray analysis confirmed the correctness of our choice of the centrosymmetric space group $P\bar{1}$ (C_i^1, No. 2) which requires the tetrameric molecule to possess a crystallographic center of symmetry. Hence, the structural determination involved the location of two cobalt, four sulfur, ten carbon, two oxygen, and ideally twenty hydrogen atoms.

Determination of the Structure. Initial coordinates for the cobalt and sulfur atoms were obtained from an interpretation of a three-dimensional Patterson function, and the positions of the carbon and oxygen atoms were established from successive Fourier synthesis. Isotropic least-squares refinement of the 18 nonhydrogen atoms yielded an $R_1 = [\Sigma|F_o| - |F_c|/\Sigma|F_o|] \times 100$ of 9.7% and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ of 9.2% after three cycles. In order to obtain a more realistic thermal crystal model, anisotropic least-squares refinement was continued for four additional cycles until all parameter shifts converged within 4% of their corresponding standard deviations at R_1 and R_2 values of 8.3 and 7.4%, respectively. A final difference Fourier map showed no irregularities. Although peaks characteristic of approximately 10 of the 20 independent hydrogen atoms were resolved at the expected positions on this map, no further attempt was made to locate them.

All least-squares refinements[30] were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Scattering factors used for cobalt were those of Thomas and Umeda;[31] for sulfur, those of Dawson;[32] and for carbon and oxygen, those of Berghuis, *et al.*[33] Final positional and thermal parameters with their estimated standard deviations, obtained from the output of

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Table II. Interatomic Distances and Bond Angles

		Interatomic Distances (Å) with Standard Deviations			
Co(1)–Co(2)	2.498 (5)	S(1)–C(1E)	1.79 (1)	S(3)···S(4′)	3.27 (1)
		S(2)–C(3E)	1.83 (2)		
S(1)–Co(1)	2.217 (6)	S(3)–C(5E)	1.83 (1)	S(1)···S(3)	3.30 (1)
S(1)–Co(2)	2.234 (7)	S(4)–C(7E)	1.86 (1)	S(1)···S(4′)	3.35 (1)
S(2)–Co(1)	2.257 (6)		1.83 (av)	S(2)···S(4)	3.18 (1)
S(2)–Co(2)	2.251 (7)			S(2)···S(3′)	3.17 (1)
	2.240 (av)	C(1E)–C(2E)	1.57 (2)		3.25 (av)
		C(3E)–C(4E)	1.58 (3)		
S(3)–Co(1)	2.245 (7)	C(5E)–C(6E)	1.55 (2)	S(1)···C(1T)	3.15 (2)
S(3)–Co(2′)	2.261 (8)	C(7E)–C(8E)	1.52 (2)	S(1)···C(2T)	3.15 (2)
S(4)–Co(1)	2.286 (7)		1.56 (av)	S(2)···C(1T)	3.25 (2)
S(4)–Co(2′)	2.265 (7)			S(2)···C(2T)	3.15 (2)
	2.264 (av)	Co(1)···Co(2′)	3.312 (9)		3.18 (av)
Co(1)–C(1T)	1.79 (2)	Co(1)···Co(1′)	4.173 (12)	S(3)···C(1T)	3.14 (2)
Co(2)–C(2T)	1.78 (2)	Co(2)···Co(2′)	4.123 (8)	S(4′)···C(2T)	3.18 (2)
				S(4)···C(1T)	3.17 (2)
C(1T)–O(1T)	1.14 (2)	S(1)···S(2)	2.91 (1)	S(3′)···C(2T)	3.15 (2)
C(2T)–O(2T)	1.15 (2)	S(3)···S(4)	2.99 (1)		3.16 (av)
		Bond Angles (deg) with Standard Deviations			
Co(1)–Co(2)–Co(1′)	90.7 (2)	S(3)–Co(1)–Co(2)	98.8 (2)	Co(1)–Co(2)–C(2T)	149.4 (5)
Co(2)–Co(1)–Co(2′)	89.3 (2)	S(4′)–Co(2)–Co(1)	100.8 (2)	Co(2)–Co(1)–C(1T)	152.3 (5)
		S(3)–Co(2′)–Co(1′)	99.8 (2)		
Co(1)–S(1)–Co(2)	68.3 (2)	S(4′)–Co(1′)–Co(2′)	99.6 (2)	Co(1)–Co(2′)–C(2T′)	119.8 (5)
Co(1)–S(2)–Co(2)	67.3 (2)		99.8 (av)	Co(2)–Co(1′)–C(1T′)	118.4 (5)
Co(1)–S(3)–Co(2′)	94.6 (3)	S(3)–Co(1)–Co(2′)	42.9 (2)	Co(1)–C(1T)–O(1T)	177.1 (15)
Co(1)–S(4)–Co(2′)	93.4 (2)	S(4′)–Co(2)–Co(1′)	43.6 (2)	Co(2)–C(2T)–O(2T)	175.1 (15)
		S(3)–Co(2′)–Co(1)	42.5 (2)		
S(1)–Co(1)–S(2)	81.2 (2)	S(4′)–Co(1′)–Co(2)	43.1 (2)	Co(1)–S(1)–C(1E)	114.0 (5)
S(1)–Co(2)–S(2)	81.0 (3)		43.0 (av)	Co(2)–S(1)–C(1E)	115.0 (6)
S(3)–Co(1)–S(4)	82.6 (2)	S(1)–Co(1)–Co(2′)	123.8 (2)	Co(1)–S(2)–C(3E)	114.5 (5)
S(3)–Co(2′)–S(4)	82.8 (3)	S(1)–Co(2)–Co(1′)	124.5 (2)	Co(2)–S(2)–C(3E)	108.8 (5)
		S(2)–Co(1)–Co(2′)	117.4 (2)		
S(1)–Co(1)–S(3)	95.5 (2)	S(2)–Co(2)–Co(1′)	118.4 (2)	Co(1)–S(3)–C(5E)	109.0 (5)
S(1)–Co(2)–S(4′)	96.1 (3)		121.0 (av)	Co(2′)–S(3)–C(5E)	108.6 (5)
S(2)–Co(1)–S(4)	88.9 (2)			Co(1)–S(4)–C(7E)	107.3 (5)
S(2)–Co(2)–S(3′)	89.2 (2)	S(1)–Co(1)–C(1T)	103.2 (5)	Co(2′)–S(4)–C(7E)	109.7 (5)
	92.4 (av)	S(1)–Co(2)–C(2T)	102.9 (5)		108.7 (av)
		S(2)–Co(1)–C(1T)	106.1 (5)		
S(1)–Co(1)–S(4)	155.3 (2)	S(2)–Co(2)–C(2T)	102.4 (5)	S(1)–C(1E)–C(2E)	108.2 (10)
S(1)–Co(2)–S(3′)	154.8 (2)		103.7 (av)	S(2)–C(3E)–C(4E)	110.1 (11)
S(2)–Co(1)–S(3)	152.0 (2)			S(3)–C(5E)–C(6E)	110.2 (11)
S(2)–Co(2)–S(4′)	154.3 (2)	S(3)–Co(1)–C(1T)	101.8 (6)	S(4)–C(7E)–C(8E)	111.1 (10)
	154.1 (av)	S(4′)–Co(2)–C(2T)	103.2 (5)		109.9 (av)
		S(4)–Co(1)–C(1T)	101.2 (5)		
S(1)–Co(1)–Co(2)	56.2 (2)	S(3′)–Co(2)–C(2T)	101.8 (5)		
S(1)–Co(2)–Co(1)	55.5 (2)		102.0 (av)		
S(2)–Co(1)–Co(2)	56.2 (2)				
S(2)–Co(2)–Co(1)	56.5 (2)				
	56.1 (av)				

the last cycle, are listed in Table I.[34] Bond lengths and angles, calculated with the Busing–Martin–Levy function and error program[35] modified by Johnson,[36] are summarized in Table II. The "best" least-squares planes formed by specific sets of atoms with perpendicular distances of atoms from these planes[37] are given in Table III. All Patterson and Fourier syntheses were calculated with the Blount program,[38] while all figures were prepared by the use of the Johnson program.[39]

Results and Discussion

Description of the Crystal and Molecular Structure. The crystal structure of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ is comprised of discrete identically oriented molecules, each of which has crystallographic site symmetry C_i-$\bar{1}$ in the triclinic lattice. The packing of the molecules is assumed to be mainly dictated by van der Waals forces in that the closest intermolecular contacts (*viz.*, CO···OC, 3.14 Å; CO···C(ethyl), 3.6 Å; and C(ethyl)···C(ethyl), 3.7 Å) do not indicate any abnormal intermolecular interactions.

The configuration of the $Co_4(CO)_4(\mu\text{-}SC_2H_5)_8$ molecule is depicted in Figures 1 and 2, and the arrangement of the molecule in the unit cell is shown in Figure 3.

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(34) Observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4840. Remit check or money order $3.00 for photocopy or $2.00 for microfiche.

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

(36) C. K. Johnson, "OR FFE-II, A Modified Version of OR FFE," Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

(37) D. L. Smith, "A Least-Squares Plane Program," Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

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

(39) C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

Table III

A. Equations of "Best" Least-Squares Planes and Distances (Å) of Atoms from These Planes[a]

(a) Plane through Co_1, Co_2, Co_1', and Co_2'

$0.997X - 0.076Y - 0.006Z - 4.285 = 0$

S_1	1.34	O_{1T}	0.01
S_2	−1.55	O_{2T}	−0.10
S_3	1.48	C_{1E}	3.04
S_4	−1.50	C_{3E}	−1.32
C_{1T}	−0.01	C_{5E}	1.93
C_{2T}	−0.06	C_{7E}	−1.92

(b) Plane through S_1, S_2, S_1', and S_2'

$-0.016X - 0.997Y - 0.082Z + 10.432 = 0$

Co_1	1.26	C_{1T}	2.79
Co_2	−1.24	C_{2T}	−2.77
S_3	1.61	O_{1T}	3.84
S_4	1.66	O_{2T}	−3.72
		C_{1E}	0.02
		C_{3E}	−0.18

(c) Plane through S_3, S_4, S_3', and S_4'

$0.004X + 0.065Y - 0.998Z + 4.003 = 0$

Co_1	−1.66	C_{1T}	−2.49
Co_2	−1.65	C_{2T}	−2.52
S_1	−2.89	O_{1T}	−2.96
S_2	−2.72	O_{2T}	−3.22
		C_{5E}	0.03
		C_{7E}	−0.05

(d) Plane through S_1, S_2, S_3, and S_4

$0.022X + 0.900Y - 0.435Z - 5.663 = 0$

S_1	−0.03	Co_1	−0.51
S_2	0.03	C_{1T}	−2.27
S_3	0.03	O_{1T}	−3.42
S_4	−0.03		

(e) Plane through S_1, S_2, S_3', and S_4'

$0.011X - 0.823Y - 0.568Z + 12.238 = 0$

S_1	−0.01	Co_2	−0.49
S_2	0.01	C_{2T}	−2.23
S_3	−0.01	O_{2T}	−3.39
S_4	0.01		

B. Torsional Angles[b]

Co_1, Co_2, Co_1' *vs.* Co_1, Co_2, S_1	132.7 (2)
Co_1, Co_2, Co_1' *vs.* Co_1, Co_2, S_2	124.2 (2)
Co_1, Co_2, Co_1' *vs.* Co_1, S_3, Co_2'	103.8 (2)
Co_1, Co_2, Co_1' *vs.* Co_1, S_4, Co_2'	105.0 (2)
Co_1, Co_2, Co_1' *vs.* S_3, S_4, S_3'	90.5 (3)
Co_1, Co_2, S_1 *vs.* Co_1, Co_2, S_2	103.1 (3)
Co_1, Co_2', S_3 *vs.* Co_1, Co_2', S_4	151.2 (2)
Co_1, S_1, S_2 *vs.* Co_2, S_1, S_2	94.5 (2)
Co_1, S_3, S_4 *vs.* Co_2', S_3, S_4	153.9 (2)

[a] X, Y, and Z are orthogonal coordinates expressed in Å and are related to the triclinic cell coordinates by the following transformations: $X = x \sin\gamma + z \cos\phi$, $Y = y + z\cos\alpha + x\cos\gamma$, and $Z = z\cos\rho$ where $\cos\phi = (\cos\beta - \cos\gamma\cos\alpha)/\sin\gamma$ and $\cos\rho = (1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}/\sin\gamma$.

[b] Defined from the Busing–Martin–Levy Program[35] as the dihedral angle between the two planes.

Four cobalt atoms are situated at the vertices of a rectangle with each pair of cobalt atoms linked by two bridging mercapto sulfur atoms. The localized environment about each chemically equivalent cobalt atom may be approximately described (with the neglect of metal–metal bonding) as a distorted tetragonal pyramid with the four bridging sulfur atoms at the corners in the basal plane and the carbonyl ligand at the apex. The cobalt atom is displaced perpendicularly by 0.50 Å (av) (Table III, (d) and (e)) out of the "mean" basal sulfur plane toward the axial carbonyl ligand. The reasonably close conformity of the basic $Co_4(CO)_4(\mu_2\text{-}S)_8$ framework of the molecule to D_{2h}-$2/m2/m2/m$ symmetry is indicated not only from a comparison of the chemically equivalent bond lengths and angles (Table II) but also from the perpendicular displacements of the corresponding atoms to the three "mean" molecular mirror planes (Table III, (a)–(c)) varying at most by 0.3 Å from each other. The observed distortions of the $Co_4(CO)_8(\mu_2\text{-}S)_8$ framework from this orthorhombic point group are attributed to steric effects involving primarily the sulfur-attached ethyl groups (*vide infra*) which lower the symmetry by their inclusion to C_i-$\bar{1}$ for the molecule.

The Cobalt–Cobalt Interaction and Its Stereochemical Consequences. The *severe* orthorhombic D_{2h} distortion of the entire Co_4S_8 core from an idealized tetragonal D_{4h}-$4/m2/m2/m$ model must be attributed to the energy stabilization of the complex by the formation of two localized electron-pair cobalt–cobalt bonds such that each Co(II) attains a closed-shell electronic configuration. The considerable bond strength of these localized metal–metal bonds is directly gauged in this molecule *per se* through (1) the resulting short Co–Co bonding distance of 2.498 (5) Å for one opposite pair of cobalt atoms in the tetracobalt rectangle *vs.* a normal nonbonding Co···Co distance of 3.312 (9) Å for the other opposite pair and (2) the sharply acute Co–S–Co bond angles of 67.8° (av) for the two Co_2S_2 fragments containing the cobalt–cobalt bonds compared to the normally obtuse Co–S–Co bond angles of 94.0° (av) for the two Co_2S_2 fragments without the cobalt–cobalt bonds.

This large orthorhombic deformation of the Co_4S_8 core is not apparent from the 16 Co–S bond lengths (of which eight are crystallographically independent) which divide under assumed D_{2h} symmetry into two distinct sets. One set of eight Co–S bonds (*i.e.*, four independent ones) for the two (metal–metal)-bonded Co_2S_2 fragments has a mean length of 2.24 Å, while the other set of eight Co–S bonds (*i.e.*, four independent ones), which link these two fragments to each other, has a mean length of 2.26 Å. It is significant that a larger analogous trend to this indicated small difference in M–X bonds occurs in each of the isoelectronic cubane-like metal clusters $Fe_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}S)_4$[40] and $Co_4(h^5\text{-}C_5H_5)_4(\mu_3\text{-}P)_4$[22] for which the M–X bonds in the two M_2X_2 fragments containing localized electron-pair M–M bonds are 0.04–0.05 Å shorter than the M–X bonds which connect the other four (metal–metal)-nonbonded M_2X_2 fragments. However, unlike the large variation of X···X distances in the above cubane-like M_4X_4 clusters, the S···S nonbonding distance of 2.91 (1) Å for the two (metal–metal)-bonded Co_2S_2 fragments in the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule is not appreciably larger but is smaller than the S···S nonbonding distance of 2.99 (1) Å for the two (metal–metal)-nonbonded Co_2S_2 fragments. This relatively small change in the S···S distances as the two pairs of cobalt atoms are drawn together by 0.8 Å (from the nonbonding Co···Co value) due to electron-pair bond formation is achieved by a bending deformation of the Co_2S_2 framework along the S···S line such that the torsional angle between the two CoS_2 moieties of the (metal–metal)-bonded Co_2S_2 system is 94.5 (2)° *vs.* a torsional angle of 153.9 (2)° between the analogous two CoS_2 moieties of the (metal–metal)-nonbonded Co_2S_2 system.

Stereochemical Relationship of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$

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

with the $Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2$-Type Structure and with $Ru_4(NO)_4(\mu_2\text{-}Cl)_4(\mu_2\text{-}P(C_6H_5)_2)_4$. The $Co_4(CO)_4(\mu_2\text{-}S)_8$ fragment may be envisioned as being constructed of two identical $Co_2(CO)_2S_6$ moieties, each comprised of a (cobalt–cobalt)-bonded Co_2S_2 fragment, by a fusion at the four sulfur atoms which bridge the nonbonding metal atoms. The geometry of each of these two $Co_2(CO)_2S_6$ moieties is remarkably similar to that adopted by a number of diiron hexacarbonyl complexes of general type $Fe_2(CO)_6(\mu_2\text{-}X)_2$ (where X represents a bridging three-electron donor such as SC_2H_5,[41] $P(CH_3)(C_6H_5)$,[42] and NH_2[43]). A detailed structural comparison[43] shows that in these homologous complexes an over-all uniformity of the bonding electron-pair Fe–Fe distances and Fe–X–Fe angles exists for a given X bridging atom. For $Fe_2(CO)_6(\mu_2\text{-}SC_2H_5)_2$[41] the Fe–Fe bond length of 2.54 (1) Å, the Fe–S–Fe bond angles of 68.3° (av), and the nonbonding S···S distance of 2.93 (1) Å compare very favorably with those previously given for the structurally equivalent $Co_2(CO)_2S_6$ moieties in $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$. These structural resemblances emphasize that the dimeric framework of $Fe_2(CO)_6(\mu_2\text{-}SC_2H_5)_2$ may be considered as a building block for the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule.

The $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ molecule is structurally analogous and electronically equivalent with the ruthenium nitrosyl cluster, $Ru_4(NO)_4(\mu_2\text{-}Cl)_4(\mu_2\text{-}P(C_6H_5)_2)_4$, for which the synthesis and structure were recently communicated by Eisenberg and coworkers.[44] In this complex of crystallographic site symmetry D_{2h}-mmm, the (metal–metal)-bonded ruthenium atoms are bridged by diphenylphosphido groups, while the nonbonding ruthenium atoms are bridged by chlorine ligands. The two bonding pairs of the four planar ruthenium atoms are separated by 2.787 (2) Å and the two nonbonding pairs by 3.672 (1) Å. The fact that this basic geometrical $M_4L_4(\mu_2\text{-}X)_8$ unit is adopted by both of these metal carbonyl and nitrosyl complexes underscores a similarity in their bonding.

Stereochemistry of the Methylene Carbon Atoms in $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ and Resulting Implications. The orientations of the ethyl groups attached to the sulfur atoms in $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ (apparent in Figures 1–3) are of interest with regard to the perceptible deformations of the $Co_4(CO)_4(\mu_2\text{-}S)_8$ fragment from its pseudo-D_{2h} geometry and to the possible existence of stereoisomers.

An anti configuration of the ethyl groups, found[41] crystallographically in the (iron–iron)-bonded $Fe_2(SC_2H_5)_2$ part of the structurally analogous $Fe_2(CO)_6(\mu_2\text{-}SC_2H_5)_2$ dimer, is also observed in each of the two centrosymmetrically related (cobalt–cobalt)-bonded $Co_2(SC_2H_5)_2$ parts of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$. On the other hand, the two S–CH_2 bonds in each of the two centrosymmetrically related (cobalt–cobalt)-nonbonded $Co_2(SC_2H_5)_2$ fragments are both equatorially oriented (relative to the tetracobalt plane), thereby corresponding to the particular syn configuration which in the $Fe_2(CO)_6(\mu_2\text{-}SC_2H_5)_2$ dimer has been precluded[41] from steric considerations as being energetically unfavorable (relative to the anti isomer and to the other syn isomer[45] containing two axially oriented S–CH_2 bonds). This apparent incongruity in the methylene arrangement is rationalized from a close examination of the dimensions of a constructed molecular model of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ as being due (at least partly) to the *absence* of the metal–metal bond in the (cobalt–cobalt)-nonbonded $Co_2(SC_2H_5)_2$ fragment in *not* greatly deforming the Co–S–Co bond angle (*viz.* 94.0° (av) *vs.* 67.8° (av)) such to allow a significant change in the direction of the S–CH_2 bond relative to that in the (cobalt–cobalt)-bonded $Co_2(SC_2H_5)_2$ fragment. This directional dissimilarity, no doubt greatly accented by steric crowding, is manifested in the two equatorial S–CH_2 bonds in the (cobalt–cobalt)-nonbonded $Co_2(SC_2H_5)_2$ fragment being differently displaced to give not only a somewhat larger S···S separation (*viz.*, 2.99 (1) Å *vs.* 2.91 (1) Å) but also (most importantly) a reasonably large C(methylene)···C(methylene) distance of 3.86 (3) Å which is not appreciably shorter than twice the van der Waals radius of 2.0 Å for a methylene group. These different orientations of the equatorial S–CH_2 bonds in the two types of $Co_2(SC_2H_5)_2$ fragments are especially well emphasized by the effect of the great difference between the torsional angle of the two Co_2S planes for the (cobalt–cobalt)-bonded fragment (103.1 (3)°) and that for the (cobalt–cobalt)-nonbonded fragment (151.2 (2)°). If *both* S–CH_2 groups in the (cobalt–cobalt)-bonded fragment are assumed to be equatorial and analogously positioned as found for the one S(2)–C(3E) group, the smaller torsional angle on the cobalt–cobalt bonded edge would lead to an estimated value of only 2.6–2.7 Å for the resulting H_2C(equatorial)···CH_2(equatorial) contact, *i.e.*, 1.2 Å less than the H_2C(equatorial)···CH_2(equatorial) separation of 3.86 (3) Å observed in the (cobalt–cobalt)-nonbonded $Co_2(SC_2H_5)_2$ fragment (due primarily to this latter fragment's having a much larger torsional angle).

It is also presumed that nonbonding interactions involving the axially oriented methylene carbon atom attached to one sulfur atom, S(1), in each (cobalt–cobalt)-bonded $Co_2(SC_2H_5)_2$ fragment may account for this sulfur atom being 0.15 Å further apart from the two vicinal sulfur atoms on its side of the tetracobalt plane compared to the corresponding two distances for the other sulfur atom, S(2), with the equatorially directed methylene carbon atom—*viz.*, 3.30 (1) and 3.35 (1) Å *vs.* 3.17 (1) and 3.18 (1) Å. Hence, this observed breakdown of the idealized D_{2h} geometry in the octasulfur part of the $Co_4(CO)_4(\mu_2\text{-}S)_8$ framework may be ascribed primarily to nonbonding intramolecular interactions involving the sulfur-linked ethyl groups.

The resulting sequence of the S–C(methylene) positions for the four sulfur atoms on a given side of the tetracobalt plane is that there are no *axial* CH_2 groups on *adjacent* sulfur atoms. Other possible stereoisomers, which from intramolecular steric considerations would appear to be favorable, include (1) one of approximately C_2-2 symmetry with the opposite bridge pairs on a given side of the tetracobalt plane having identical directions thereby resulting in an axial–equatorial–axial–equatorial cycle on one side and an all-equatorial cycle

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[41] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963).

[42] J. R. Huntsman, W. M. Douglas, P. M. Treichel, and L. F. Dahl, to be submitted for publication.

[43] L. F. Dahl, W. R. Costello, and R. B. King, *J. Amer. Chem. Soc.*, 90, 5422 (1968).

[44] R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpont, J. Reed, and A. J. Schultz, *J. Amer. Chem. Soc.*, 94, 6240 (1972).

[45] Both the syn and anti isomers of $Fe_2(CO)_6(\mu\text{-}SC_2H_5)_2$ (and of other alkyl-substituted homologs) have been isolated and identified from their solution infrared spectra: G. Bor, *J. Organometal. Chem.*, 11, 195 (1968).

on the other side and (2) two with an axial–equatorial–axial–equatorial cycle on each side of the tetracobalt plane such that one configuration (with axial S–CH_2 bonds on both sulfur atoms of the (cobalt–cobalt)-bonded $Co_2(SC_2H_5)_2$ fragment) can ideally conform to D_{2h} symmetry and the other (with four anti bridged $Co_2(SC_2H_5)_2$ fragments) to C_1 symmetry.

In connection with the contemplated synthesis of structurally analogous complexes with different ligand bridges, it is noteworthy that the ethyl groups in other ethylthio-bridged cobalt carbonyl clusters have been shown to exert a controlling steric influence in accounting for the stoichiometry of these complexes.[8,9,14]

Hypothetical Tetragonal D_{4h} Structure *vs.* Observed Orthorhombic D_{2h} Structure for $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$. In an attempt to rationalize from qualitative MO symmetry arguments the observed D_{2h} shape of the $Co_4(CO)_4(\mu_2\text{-}S)_8$ fragment with the presence of a closed-shell electronic configuration for each metal atom, a hypothetical tetragonal D_{4h} geometry is assumed for the four metal atoms.[46] For simplicity (without detraction from the qualitative conclusions), the metal–ligand interactions are separated under the perfect-pairing approximation from the direct metal–metal interactions, and each metal is presumed[46] to furnish two in plane atomic valence orbitals, $3d_{z^2}$ and $3d_{xz}$, in order to allow for only in-plane metal–metal interactions (which under a valence bond representation would correspond to σ- and σ^*-like interactions).[47–49] These eight atomic metal orbitals are combined under D_{4h} symmetry to give (in accord with orbital overlap considerations) four bonding tetrametal symmetry combinations of representations $a_{1g}(d_{z^2}) + b_{2g}(d_{xz}) + e_u(d_{xz})$ and four antibonding ones, $a^*_{2g}(d_{xz}) + b^*_{1g}(d_{z^2}) + e^*_u(d_{xz})$.

From orbital-electron bookkeeping which shows that the four metal atoms in $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ contribute a total of 12 electrons to these inplane tetrametal symmetry levels, it follows *via* the *Aufbau* principle that the four bonding combinations will be completely occupied with the remaining four electrons to be allotted to the antibonding levels. Although the order of the antibonding levels will depend upon the nature of the molecules (with mixing occurring among symmetry orbitals belonging to the same representation), if the antibonding $e^*_u(d_{xz})$ level is intermediate between the two antibonding nondegenerate ones, a triplet ground state will result which is incompatible with the diamagnetic character of this complex. Application of the closed-shell criteria then allows the prediction from MO symmetry considerations[50] that $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ should distort to the observed rectangular D_{2h} geometry (corresponding to a singlet state for which the degenerate levels are split) with the six filled, nondegenerate levels equivalent in orbital character to four electrons distributed into σ-like orbital combinations between two opposite pairs of cobalt atoms and eight electrons distributed into both the two bonding and corresponding two antibonding σ-like orbitals involving the other two opposite pairs of cobalt atoms. Occupation of both the bonding and antibonding σ-orbital combinations between two atoms energetically corresponds to two nonbonding electron pairs which give rise to nonbonding metal–metal distances. On this basis, the resulting metal–metal bond order is equal to unity for each of the two bonding metal–metal interactions, while that for the two nonbonding metal–metal interactions is zero. Of obvious interest is that this bonding model, which focuses primary attention on the metal cluster bonding, predicts a change toward a delocalized tetrametal system with a concomitant structural modification toward a square-planar configuration upon successive oxidation.[51]

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(46) A localized cartesian coordinate system is chosen at each metal atom with the z axis directed toward the center of the square and with the x and y axes located in the plane and perpendicular to the plane of the four metal atoms, respectively. With this orientation of axes the main coordinate axes of the complex are chosen with the Z axis perpendicular to the tetrametal plane along the C_4 rotation axis in the D_{4h} point group and with the X and Y axes coincident with the diagonal directions of the square along the two perpendicular C_2' rotation axes. Since the local site symmetry about each cobalt atom may be approximated as a distorted square pyramid, as in the case of $Co_3(CO)_3\{(\mu_2\text{-}SC_2H_5)_5(\mu_2\text{-}CO)\}$,[8] each cobalt is assumed to use its $3d_{xy}$, 4s, and three 4p orbitals for metal–ligand bonding; of the other four d orbitals available for cobalt–cobalt interactions, it is arbitrarily assumed from tetrametal overlap considerations that the $3d_{x^2-y^2}$ and $3d_{yz}$ orbitals are not important in determining the molecular deformation of $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ and can thus be considered as localized electron pairs (*i.e.*, the occupation of both the bonding and antibonding levels nullifies their bonding stabilization). Hence, the in-plane $3d_{z^2}$ and $3d_{xz}$ orbitals, which interact strongly with the neighboring cobalt atoms, are the only ones considered here.

(47) Despite these inherent drastic assumptions, the simplified bonding model given here has also been extensively utilized on other metal cluster systems to provide a reasonable qualitative basis in the prediction of experimental variations in the geometries of the metal clusters.[48] Its success is presumed to be mainly a consequence of the fact that in these organometallic complexes (at least for those of the first-row transition metals) the *metal–ligand interactions* are sufficiently *stronger* than the *metal–metal interactions*. This results in the completely filled *metal–ligand bonding orbitals* being much *lower* in energy than the *metal–metal bonding* and *antibonding orbitals*, which in turn are appreciably lower than the *virtual metal–ligand antibonding orbitals*. Hence, any variation of valence electrons in these complexes either by replacement of the metals and/or ligands or by redox reactions involves primarily the metal–metal orbitals and thereby mainly influences the metal cluster fragment.

(48) (a) C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6032 (1971), and references cited therein; (b) B. K. Teo and L. F. Dahl, to be submitted for publication.

(49) This MO scheme is readily converted from a conceptual viewpoint to a localized valence bond representation of σ- and σ^*-like two-center metal–metal orbitals in that directed hybrid orbitals formed from the d_{z^2} and d_{xz} atomic orbitals on each metal atom give rise to two equivalent metal orbitals which can form localized metal–metal σ- and σ^*-combinations by overlap with the corresponding identical hybrid orbitals of its neighboring metal atoms.

(50) *Cf.* M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 3255 (1965).

(51) A more general qualitative MO model of planar tetrametal systems with proposed geometrical variations based on various orbital-electron schemes has been formulated: B. K. Teo and L. F. Dahl, to be submitted for publication. This model considers not only the *eight* tetrametal symmetry orbitals which are formally responsible for the four edges of a metal square but also *four* other tetrametal symmetry orbitals which are formally involved in metal–metal interactions across the two diagonals of a metal square. This representation, based on the metal–metal interactions of three (rather than two) valence orbitals per metal, allows a possible D_{2h}-type distortion of a metal square not only into a rectangle (due to edge-type metal–metal interactions) *via* a Jahn–Teller active b_{2g} vibrational mode but also into a rhombus (due to a net diagonal-type metal–metal bonding interaction) *via* a vibrational b_{1g} mode. In the case of the $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ and $Ru_4(NO)_4(\mu_2\text{-}Cl)_4(\mu_2\text{-}P(C_6H_5)_2)_4$ molecules which each are treated under this model as a 20-electron system (*i.e.*, 12 bonding and eight antibonding electrons), it is reasonably assumed from orbital overlap considerations that the edge metal–metal interactions are considerably stronger than the diagonal metal–metal interactions such that all *antibonding* edge-type tetrametal orbitals are higher in energy than the diagonal-type tetrametal ones. The removal of four electrons from the 24-electron *nonbonding* metal square (*e.g.*, in the hypothetical $Ni_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$) to give the 20-electron diamagnetic configuration then leads to the metal rectangle found in $Co_4(CO)_4(\mu_2\text{-}SC_2H_5)_8$ and $Ru_4(NO)_4(\mu_2\text{-}Cl)_4(\mu_2\text{-}P(C_6H_5)_2)_4$. It is noteworthy that the geometry of the $[Re_4(CO)_{16}]^{2-}$ anion (R. Bau, B. Fontal, H. D. Kaesz, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 6374 (1967); M. R. Churchill and R. Bau, *Inorg. Chem.*, **7**, 2606 (1968)), a diamagnetic 14-electron tetrarhenium cluster which has a rhombic framework with four electron-pair Re–Re bonding edges and one electron-pair Re–Re bonding diagonal, may be rationalized from this MO model.