TABLE IV

BOND LENGTHS (Å.)

Atoms	Distances	Atoms	Distances
NiS_1	2.168 (11)	C_3N_1	1.44 (6)
NiS_2	2.146 (11)	C_2N_2	1.51 (4)
NiN_1	1.86 (2)	C_6N_1	1.33 (4)
NiN_2	1.85 (3)	C_5N_2	1.34 (4)
C_1S_1	1.82 (5)	C_6H_8	1.47 (6)
C_4S_2	1.82 (5)	C_5C_7	1.51 (7)
C_1C_2	1.35 (6)	C_5C_6	1.44 (5)
C_3C_4	1.52 (7)		

TABLE V

BOND ANGLES

Atoms	Angle, deg.	Atoms	Angle, deg.
S_1NiS_2	97.3 (4)	$C_2C_1S_1$	119 (3)
		$C_3C_4S_2$	114 (3)
N_1NiN_2	82.9 (11)		
		$N_1C_3C_4$	112 (3)
N_1NiS_1	172.7 (9)	$N_2C_2C_1$	113 (3)
N_2NiS_2	172.6 (9)		
		$C_3N_1C_6$	120 (3)
N_1NiS_2	89.8 (9)	$C_2N_2C_5$	125 (3)
N_2NiS_1	90.0 (9)		
		$N_1C_6H_5$	111 (3)
NiS_1C_1	96 (2)	$N_2C_5C_6$	113 (3)
NiS_2C_4	100 (2)		
		$N_1C_6C_8$	122 (3)
NiN_1C_3	123 (2)	$N_2C_5C_7$	123 (3)
NiN_2C_2	120 (2)		
		$C_5C_6C_8$	126 (3)
NiN_1C_6	117 (2)	$C_6C_5C_7$	123 (3)
NiN_2C_5	115 (2)		

selected portions of the molecule. The only satisfactory plane through a five-membered ring was through the ring containing the two nitrogen atoms. The equation to this plane is

$$-0.0316X + 0.0092Y + 0.9995Z = 1.6954$$

The departures from this plane are Ni, +0.009; N_1, −0.011; N_2, −0.009; C_5, +0.004; C_6, +0.006; C_7, +0.174; C_8, +0.152 Å.

It will be observed that none of the five atoms in the ring departs significantly from the plane, which is evidence for the delocalization of electrons in this chelate ring. The two methyl groups, however, both lie out of this plane and on the same side. No suitable planes can be constructed through the other two five-membered rings without significant departures of the methylene groups. Accordingly, planes through N_1–Ni–S_2 and N_2–Ni–S_1 were constructed. The equations of these planes and the departures of the carbon atoms are

$$N_2NiS_2\text{:}\quad -0.0482X + 0.0129Y + 0.9987Z = 1.6855$$
$$C_3,\ +0.161;\ C_4,\ -0.032\ \text{Å}.$$

$$N_3NiS_1\text{:}\quad -0.0604X - 0.0202Y + 0.9980Z = 1.6509$$
$$C_1,\ +0.348;\ C_2,\ -0.124\ \text{Å}.$$

All van der Waals contacts less than 4 Å. were calculated. There are 28 such distances, the two shortest being 3.48 Å. between N_2 and C_4 and 3.54 Å. between C_4 and C_5. The closest approaches to a nickel atom from a neighboring molecule are 3.65 Å. for C_3 and 3.71 Å. for N_1. It can therefore be concluded that the nickel atom is four-coordinate in this complex in the solid state.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Molecular Structure of the Dimer of Bis(*cis*-1,2-bis(trifluoromethyl)ethylene-1,2-dithiolate)cobalt

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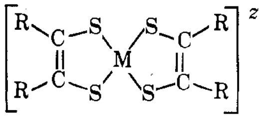
A three-dimensional X-ray diffraction study has verified the dimeric structure of $(CF_3)_2C_2S_2CoS_2C_2(CF_3)_2$, which has previously been shown to be diamagnetic and dimeric in solution. Dimerization occurs through the unusual Co–S linkages of 2.38 Å. in length which require the Co atom to be 0.37 Å. out of the plane of the S_4 group within each monomer unit. One dimeric molecule is present in the unit cell having parameters $a = 7.98$, $b = 9.89$, $c = 10.12$ Å., $\alpha = 103.0$, $\beta = 98.5$, and $\gamma = 100.8°$. The space group is $P\bar{1}$.

The discovery first by Schrauzer and Mayweg[2] and by Gray, *et al.*,[3] of *cis*-1,2-disubstituted ethylene-1,2-dithiolate complexes



(where z is 0, −1, or −2, R is CF_3, CN, or C_6H_5, and M is a transition metal) has been followed by extensive

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[1] National Science Foundation Predoctoral Fellow, 1963–1965.

[2] G. N. Schrauzer and V. Mayweg, *J. Am. Chem. Soc.*, **84**, 3221 (1962).

[3] H. B. Gray, R. Williams, I. Bernal, and E. Billig, *ibid.*, **84**, 3596 (1962).

studies[4] of the chemistry of oxidation–reduction processes and of unusual valence states of the transition metal M. X-Ray crystallographic studies[5–8] have established the nearly square-planar configuration of bonds about the transition metal for the cases M = Co, R = CN, $z = -2$; M = Cu, R = CN, $z = -1$; M = Ni, R = CN, $z = -2$; and M = Ni, R = CN, $z = -1$. The first indication[9,10] of a weak dimerization of these units occurs in the magnetic studies of the crystal of this last case (M = Ni, R = CN, $z = 1$), and the direct structural evidence that weak dimers are formed is the determination of the Ni···S distance of 3.59 Å. within dimer units, as compared with the somewhat longer Ni···S distance of 3.75 Å. between different dimers in the crystal. In acetone solutions, however, this complex is a monomer.

We report here the determination of the first structure of a strong dimer, the case M = Co, R = CF_3, and $z = 0$, which appears to persist in the dimeric state in CCl_4 solution.[4b] Dimerization occurs by the formation of two Co–S bonds 2.38 Å. in length between monomer units, such that each Co atom becomes essentially five-coordinated. The correct formula of this dimer is thus $Co_2S_8C_8(CF_3)_8$.

Structure Determination

Single crystals were obtained as shiny black plates when a CCl_4 solution was slowly evaporated in a nitrogen atmosphere. The preliminary indication from Weissenberg and precession photographs of several crystal orientations was that the crystals were triclinic. The unit cell parameters of $a = 7.98 \pm 0.02$, $b = 9.89 \pm 0.01$, $c = 10.12 \pm 0.02$ Å., $\alpha = 103.0 \pm 0.2$, $\beta = 98.5 \pm 0.2$, and $\gamma = 100.8 \pm 0.2°$ were established from films calibrated with Al powder lines. A careful study of a model of the reciprocal lattice supported the conclusion from the symmetry and unit cell parameters that the crystals are indeed triclinic. The calculated density of 2.28 g./cm.^{3} is in excellent agreement with the experimental value, determined by flotation, of 2.27 g./cm.^{3}. Of the two possible space groups, P1 or $P\bar{1}$, we chose the latter partly on the assumption that all reasonable models of the dimer are centrosymmetric, and partly for the reason that $P\bar{1}$ is considerably more prevalent than P1. This assumption was later verified by the successful refinement of the structure.

For collection of the X-ray data a rod-shaped crystal elongated along a and having approximate dimensions 0.75 × 0.25 × 0.25 mm. was chosen. Equi-inclination Weissenberg photographs of the multiple film type were taken of levels Hkl for $0 \leqslant H \leqslant 7$ with the use of Mo Kα radiation. Thin brass foils were interleaved between the films in order to give suitable intensity reductions. Also, timed exposures using Mo Kα radiation were taken by the precession method of levels $h0l$, $k1l$, $h2l$, $h3l$, $hk0$, $hk1$, $hk2$, and hkk. Visual estimates were made with the aid of a timed scale, Lorentz-polarization corrections were made, and these corrected intensities were correlated to a single scale (Table I). No corrections were made for absorption ($\mu = 18.9$ cm.$^{-1}$ for Mo Kα radiation).

The Co atom and four S atoms of the asymmetric unit were located from a three-dimensional Patterson function, which had been sharpened so that the average intensity was independent of sin θ and which had an origin peak no higher than a single Co···Co interaction. A three-dimensional electron density map computed from phases of these Co and S positions yielded fourteen new peaks, five of which seemed reasonable for C atoms and nine of which seemed to be plausible F atoms. Inclusion of these fourteen new atoms yielded two more possible C atoms and one more possible F atom in the next map, but three of the original fourteen atoms appeared to be incorrect and one CF_3 group was poorly resolved. After refinement of the Co and S atoms by two cycles of least squares, a third electron density map was computed with the additional contributions of five C atoms and nine F atoms which seemed most reliable. All remaining atoms of the structure, and no spurious peaks, appeared in this map. At this stage the value of $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ was 0.38.

Four cycles of three-dimensional least-squares refinement in which individual isotropic temperature factors were assigned then reduced R to 0.20. At this stage, the thermal parameters of Co, S, and F were still changing by amounts as large as five times their standard deviations, and the thermal parameters of F were becoming quite large. Unfortunately, these indications that anisotropic refinement was required meant that 226 parameters (three positional parameters and six thermal parameters for each atom, plus the over-all scale factor) had to be refined. Because of a limitation in the size of the least-squares program, we refined the structure in two sections as suggested by the different behavior of temperature factors. First, the Co, S, and carbon atoms C_1, C_2, C_5, and C_6 were held fixed while the CF_3 groups were refined anisotropically. Then the Co, S, and C atoms were refined anisotropically while the F atoms were held fixed. Each of these anisotropic cycles was then repeated, and finally the positional parameters of all atoms were refined while the anisotropic thermal parameters were held fixed. Weighting factors used in the least-squares treatment were derived from essentially constant percentage errors in the intensities, but with additional allowance for the number of times each reflection was observed. The final value of $R_F = 0.080$ was found for the 2031 observed reflections, omitting those 34 reflections (Table I) which showed a slightly substandard behavior during the correlation. A structure factor calculation for the 847 reflections which were below the observa-

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(4) For example, see A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki: (a) *Inorg. Chem.*, **2**, 1227 (1963); (b) *ibid.*, **3**, 814 (1964); (c) *J. Am. Chem. Soc.*, **86**, 2794 (1964).

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TABLE I

OBSERVED MAGNITUDES OF STRUCTURE FACTORS FOR THE DIMER OF $(CF_3)_2C_2S_2CoS_2C_2(CF_3)_2$[a,b]

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 H=0 (K)(L)( 0)( 0, 0)2225,(-12)( 2, 2)*,(-11)( -2, 6)37,*,*,45,61,84,59,
46,*,(-10)( -3, 8)196,130,101,43,40,71,114,49,*,*,*,*,( -9)( -5, 9)*,86,84,88,*,
*,*,*,43,*,43,44,*,U,*,( -8)( -6,10)68,70,68,*,39,75,108,73,71,57,38,62,77,
63,44,*,*,( -7)( -7,11)124,193,137,122,*,78,*,82,48,*,*,50,74,74,47,*,*,*,49,
( -6)( -8,11)*,92,111,141,*,*,*,90,190,56,*,97,84,*,38,67,41,46,*,48,
( -5)( -9,12)71,56,*,44,*,*,145,62,111,69,82,198,206,163,80,53,105,*,64,76,*,*,
( -4)(-10,12)72,121,81,*,75,39,*,35,81,273,198,19,165,171,191,47,122,92,138,
114,92,*,*,( -3)(-10,12)62,95,68,*,67,154,50,*,48,172,63,57,277,594,310,337,
100,63,55,147,46,*,*,( -2)(-11,12)*,59,83,118,50,110,161,36,281,220,*,244,328,
894,420,105,101,249,41,*,90,*,*,*,( -1)(-10,12)*,48,61,*,72,126,27,110,92,403,
113,U,U,U,435,142+,118,101,75,*,77,*,38,*,51,( 0)( 2,12)224,122,*,143,156,
49,56,46,36,*,36
 H=1 (K)(L)(-12)( 1, 2)*,37,(-11)( -1, 2)33,40,33,49,(-10)( -2, 2)*,*,*,*,*,
( -9)( -5, 9)*,*,*,*,62,105,132,*,91,97,65,*,*,*,*,( -8)( -8,10)40,U,79,84,
113,62,63,68,100,41,*,98,160,107,69,*,*,*,*,( -7)( -8,10)*,53,73,108,61,*,*,
46,143,66,*,56,*,92,86,90,*,*,*,( -6)( -8,10)*,*,*,*,*,127,128,160,248,288,
242,156,114,104,97,100,*,*,*,( -5)(-10,11)*,103,78,89,*,34,*,55,54,169,363,
369,121,153,126,74,117,63,63,94,79,*,( -4)( -9,11)98,92,*,78,134,47,79,83,219,
39,*,60,43,59,97,102,73,62,126,65,*,( -3)(-10,11)*,48,40,49,40,*,171,317,514,
259,52,35+,123,94,*,54,100,*,*,123,38,*,( -2)(-11,12)61,44,81,137,49,70,215,
245,560+,33,349,301,62,201,78,126,83,34,127,32,33,*,( -1)(-12,13)45,30,58,71,
106,44,53,88,127,232,197,235,529,U,307,63,21,150,182,122,78,77,76+,38,*,*,
( 0)(-12,11)53,31,23,*,52,76,152,157,223,15,201,223,232,49,281,160,72,58,*,
235,62,*,*,53,( 1)(-13,11)24,69,55,57,40,106,59,100,108,92,215,542,208,118,
301,183,154,222,303,214,81,142,54,59,( 2)(-12,11)53,48,*,48,31,87,210,195,
222,526,389,92,357,291,*,48,56,168,237,226,69,*,30,*,( 3)(-11, 9)*,*,29,74,
112,164,125,195,119,313,187,191,121,69,133,84,49,77+,93,*,*,( 4)(-11, 7)*,*,*,
*,90,80,212,107,274,108,175,104,39,277,328,271,139,53,*,( 5)(-11, 7)*,*,104,
82,100,69,69,*,159,129,233,97,208,210,243,139,*,92,*,( 6)(-11, 7)*,*,*,*,81,
77,67,162,210,*,40,56,38,*,109,*,88,67,78,( 7)(-10, 6)*,*,*,*,102,96,*,*,*,
128,129,115,*,*,*,*,78,( 8)( -9, 5)*,*,61,140,67,83,78,101,74,54,62,50,60,*,*,
( 9)( -8, 4)*,*,87,*,*,*,31,56,87,79,89,103,67,( 10)( -6, 2)*,*,*,*,*,35,39,
45,37,( 11)( -2, 1)*,30,36,*
 H=2 (K)(L)(-12)( 1, 2)32,34,(-11)( -3, 4)51,37,*,*,57,61,52,48,(-10)( -3, 5)
*,*,*,*,*,*,*,*,*,( -9)( -4, 6)*,76,82,73,48,32,28,*,42,*,*,( -8)( -6, 9)*,*,
77,*,81,93,127,90,62,*,*,61,77,111,*,*,( -7)( -8,10)50,*,*,*,*,79,33,48,122,
195,191,99,67,123,142,179,63,*,*,( -6)( -7,10)70,36,*,*,*,47,146,149,278,90,
119,*,80,126,73,*,*,*,( -5)(-10,10)*,*,53,60,*,36+,35,91,184,*,179,113,*,216,
203,47,66,93,76,*,*,( -4)( -9,11)*,40,*,90,33,238,98,364,394+,217,167,118,198,
83,80,176,69,84,104,67,*,( -3)(-10,10)*,*,91,54,51,128,215,487,570,34,35,43,
177,111+,34,80,54,47,*,*,( -2)(-11,11)*,*,*,69,89,67,52,44,261,U,340,411,109,U,
153,326,63,90,137,27,*,*,*,( -1)(-12,12)24,38,44,*,*,162,236,271,237,114,64,
48,376,*,281,179,100,201,129,*,*,*,38+,43,( 0)(-12,11)55,57,93,44,146,128,
313,243,*,26,340,*,118,85,46,425,45,67,165,142,78,99,42,58,( 1)(-12,11)52,
57,56,30,*,44,193,120,49,27,64,332,30,*,115,45,161,123,181,186,63,*,*,*,
( 2)(-12,10)*,*,61,68,71,36,132,181,141,117,106,110,125+,447,99,55,141,*,108,
81,52,57,57,( 3)(-10, 9)56,52,72,49,116,47,43,116,243,140,161,*,145,399,242,
231,57,69,*,83,( 4)(-10, 6)40,52,88,*,*,31,*,35,32,62,120,196,270,292,356,*,
38,( 5)(-10, 7)*,59,77,*,65,89,*,148,34,71,101,*,*,102,*,46,*,47,( 6)(-10, 6)
*,53,50,*,60,84,45,91,38+,119,274,258,130,95,*,*,*,( 7)( -8, 5)*,42,126,88,
63,99,179,249,122,112,65,*,*,*,( 8)( -8, 4)*,38,101,74,63,39,47,36,94,98,*,*,
*,( 9)( -7, 2)*,*,56,78,61,*,*,62,41,34,( 10)( -2, 1)*,*,53,*,( 11)( -2,-1)
34,*
 H=3 (K)(L)(-12)( 1, 5)56,57,*,*,*,(-11)( -3, 4)*,*,*,34,77,42,*,*,
(-10)( -3, 7)*,47,73,43,*,50,58,77,61,43,*,( -9)( -5, 8)28,34,112,150,158,69,
47,99,96,90,43,*,*,*,( -8)( -7, 9)29,*,*,46,76,164,96,32,*,*,39,30,58,82,77,
44,*,( -7)( -8,10)32,*,58,86,55,43,*,*,69,27,*,38,63,94,74,78,40,*,*,
( -6)( -9,11)*,*,95,134,179,143,60,39,73,125,*,*,*,29,*,68,73,78,*,*,*,
( -5)(-10,11)46,*,27,59,126,146,105,104,40,98,105,41,117,153,72,73,122,84,119,
*,34,*,( -4)(-10,10)*,52,*,*,76,45,104,72,134,171,96,73,32,179,83,*,88,74,80,
49,37,( -3)(-11,11)*,49,80,88,36,34,*,*,46,25,239+,102,67,*,141,216,160,58+,
36,93,89,76,40,( -2)(-11,11)*,54,89,81,86,110,44,123+,50,86,76,117,*,86,492,
343,198,203,33,78,70,62,*,( -1)(-12,11)*,*,49,71,113,60,168,210,117,31,259,
99,25,167,271,214,230,126,50,54,47,34,47,*,( 0)(-12,10)*,*,47,*,54,56,87,56,
73,109+,79,112,57,460,118,138,115,77,34,48,*,23,35,( 1)(-12,10)*,*,31,34,65,
22,62,190,17,61,88,335,712,615,189,108,*,35,102,54,*,*,*,( 2)(-12,10)36,30,
53,55,98,59,83,292,162,215,74,262,226+,237,51,114,119,60,64,41,35,53,37,
( 3)(-12, 9)*,*,33,*,47,28,92,57,43,161,195,134,80+,167,46,105,73,47,62,35,*,
56,( 4)(-12, 6)*,*,*,73,116,54,52,93,179,337,205,63,111+,42,37,55,*,*,35,
( 5)(-11, 6)*,38,100,101,98,74,61,100,97,122,135,104,115,74,25,*,*,37,
( 6)(-11, 7)*,*,64,41,*,39,*,37,123,164,103,67,124,*,*,*,*,*,*,( 7)(-11, 6)
35,*,*,*,*,*,*,40,43,*,*,67,94,*,*,39,43,64,( 8)(-10, 4)*,*,*,*,25,60,64,45,*,
*,67,35,*,*,57,( 9)( -8, 3)35,36,39,45,38,29,43,*,74,68,41,*,( 10)( -6, 1)*,*,
*,*,*,*,*,*
 H=4 (K)(L)(-12)( 1, 3)*,*,*,(-11)( -2, 6)46,45,*,*,35,56,59,63,*,
(-10)( -4, 8)*,33,54,85,55,*,50,84,99,59,*,49,35,( -9)( -6, 9)*,*,*,*,52,74,*,
*,*,*,*,33,*,*,*,*,( -8)( -7, 9)27,*,56,50,44,46,*,128,163,84,39,91,127,48,*,
49,47,( -7)( -8,10)*,40,105,101,129,107,29,131,75,45,*,61,120,122,51,39,34,*,*,
( -6)( -9,10)*,*,45,65,123,160,*,72,83,32,78,44,*,25,*,34,*,*,*,*,( -5)(-10,10)
*,*,67,*,23,28,*,159,90,70,148,194,225,101,62,73,58,39,*,40,*,( -4)(-10,10)
45,82,93,116,77,41,85,*,43,148,165+,161,152,114,150,103,87,*,59,64,83,
( -3)(-11,10)*,34,110,109,45,39,131,67,46,79,29,61,173+,113,73,115,86,108,*,
81+,66,79,( -2)(-11,10)*,*,46,*,52,*,*,123,340,121,20,80,93,*,*,151,76,42,38,*,
*,63,( -1)(-11,10)57,*,43,114,113,81,58,85,168,81,360,88,212,103,142,21,88,
110,106,70,46,60,( 0)(-12,10)32,31,26,45,80,25,*,*,158,187,75,191,389,320,
190,194,40,100,147,48,*,72,68,( 1)(-12, 9)27,37,29,*,*,*,66,48,110,40,112,
111,143,176,297,82,53,38,*,85,61,*,( 2)(-12, 9)42,48,47,24,21,23,49,30,93,
143,214,50,133,*,73,133,80,42,162,130,96,49,( 3)(-12, 8)*,*,28+,39,57,115,
101,88,137,380,256,266,46+,72,95,*,*,80,98,117,68,( 4)(-12, 6)*,*,31,45,56,
98,86,92,129,152,125+,65,153,47,56,51,56,*,*,( 5)(-11, 7)*,*,31,*,*,91,88,*,
84,140,*,*,*,80,136,118,68,39,*,( 6)(-11, 6)28,28,33,42,39,102,43,37,81,111,
96,95,56,92,92,82,59,32,( 7)(-10, 5)36,*,*,35,44,37,*,90,65,*,*,*,26,46,46,*,
( 8)( -9, 3)*,*,*,29,58,*,*,*,*,24,*,*,*,( 9)( -8, 1)*,*,43,56,38,25,34,34,*,
*,( 10)( -6,-2)*,37,28,*,29
 H=5 (K)(L)(-11)( -2, 5)*,34,*,27,40,41,*,*,(-10)( -4, 7)*,48,41,*,*,29,58,
45,46+,47,*,*,( -9)( -5, 8)*,*,*,*,*,*,*,*,*,43,72,*,*,*,( -8)( -7, 8)44,*,*,*,
73,50,58,78,47,*,*,64,79,*,*,*,( -7)( -8, 9)*,26,*,35,49,69,44,37,40+,74,68,*,
31,36,71,61,51,*,( -6)( -9, 9)*,24,*,*,*,31,*,42,39,102,133,157,113,46,68,122,
113,100,*,( -5)( -9, 9)*,*,39,56,40,21,*,69,*,155,231,199,120,*,62,90,53,*,*,
( -4)(-10,10)41,31,57,61,*,78,53,59,19,106+,61,88,47,128,37,*,39,79,47,38,
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44,64,*,*,( 2)( -6, 1)*,39,37,*,44,41,*,55,( 3)( -1,-1)29
 H=10 (K)(L)( -2)( -3,-1)*,*,*,( -1)( -3,-1)*,*,*,( 0)( -6,-6)29
```

[a] The value of *k* and the range of *l* are given in parentheses. Unobserved reflections are indicated by an asterisk, experimentally unobservable reflections by U, and reflections not used in the refinement by a plus sign. The summation for F_{000} is over the entire unit cell, and F_{000} is on the arbitrary scale of the observed intensities. [b] The 34 reflections denoted by a plus sign were not used in the refinement because they did not correlate well. A final structure factor calculation yielded $R_F = 0.03$ for these 34 reflections.

TABLE II

VARIATION OF R_F WITH SIN θ[a]

Range of sin θ	R	Range of sin θ	R
0.00–0.40	0.108	0.70–0.75	0.067
0.40–0.50	0.075	0.75–0.80	0.072
0.50–0.60	0.077	0.80–0.85	0.074
0.60–0.65	0.067	0.85–0.90	0.070
0.65–0.70	0.074	0.90 1.00	0.090

[a] $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

tional limit in the regions of observation showed that none was significantly above the minimum observable value. A final difference electron density map from which all atoms were subtracted showed that the highest residual peak was at the Co atom and was less than 7% of the height of a carbon atom. In lieu of calculated structure factors, which will be tabulated in the Ph.D. thesis of J. H. E., the variation of R_F with sin θ is shown in Table II. Final values of the atomic parameters are given in Table III.

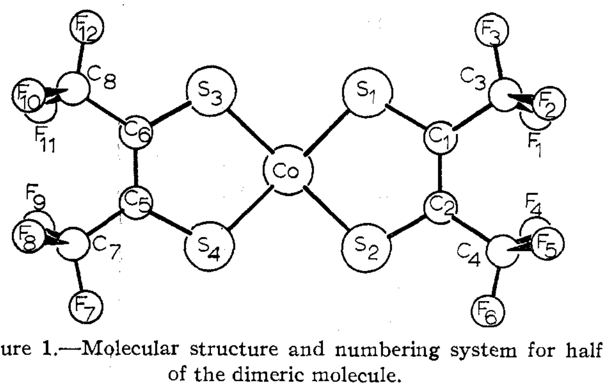

Figure 1.—Molecular structure and numbering system for half of the dimeric molecule.

Results and Discussion

The numbering scheme is shown in Figure 1 for the half-molecule. Projections of the crystal structure along *a* and along [01$\bar{1}$] are shown in Figures 2 and 3, respectively. Bond distances and angles computed from the final parameters of Table III are shown in

TABLE III

FINAL ATOMIC PARAMETERS[a]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Co	0.6313	0.5976	0.4726	88	77	76	11	−8	0
S_1	0.9037	0.6953	0.5344	97	100	110	15	6	4
S_2	0.5738	0.7958	0.5750	107	87	108	21	2	1
S_3	0.3651	0.5402	0.3622	98	95	90	20	−12	11
S_4	0.6994	0.4460	0.3083	120	116	90	23	1	−13
C_1	0.9164	0.8611	0.6325	128	113	89	−5	−5	30
C_2	0.7669	0.9073	0.6514	149	105	78	−11	7	3
C_3	1.0995	0.9486	0.6986	158	120	134	−2	4	14
C_4	0.7606	1.0534	0.7312	187	97	163	11	19	1
C_5	0.3638	0.4308	0.2040	126	121	89	16	−17	19
C_6	0.5173	0.3859	0.1832	142	115	102	−10	1	33
C_7	0.1937	0.3805	0.1040	192	166	89	−20	−39	12
C_8	0.5295	0.2796	0.0539	226	133	110	−2	22	6
F_1	1.1305	0.9761	0.8296	245	383	148	−90	−75	19
F_2	1.1255	1.0737	0.6713	240	212	371	−90	−59	131
F_3	1.2152	0.8855	0.6518	101	248	458	−36	21	−114
F_4	0.8436	1.0875	0.8596	467	244	164	136	−97	−104
F_5	0.8217	1.1541	0.6745	679	106	378	46	235	26
F_6	0.6020	1.0680	0.7398	234	177	347	67	12	−102
F_7	0.0816	0.4487	0.1496	224	649	208	223	−107	−95
F_8	0.2011	0.3994	−0.0149	291	436	129	−24	−87	98
F_9	0.1272	0.2452	0.0835	393	264	337	−147	−245	71
F_{10}	0.4839	0.3157	−0.0577	640	305	66	156	24	9
F_{11}	0.4371	0.1548	0.0388	552	150	251	−97	165	−59
F_{12}	0.6898	0.2623	0.0577	285	365	167	119	17	−122

[a] x, y, and z are in fractional triclinic coordinates. The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

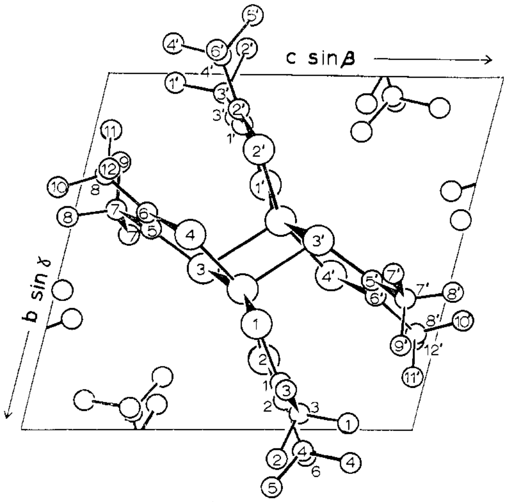

Figure 2.—Projection of the crystal structure along the a axis. Large circles are Co or S; small circles are C or F.

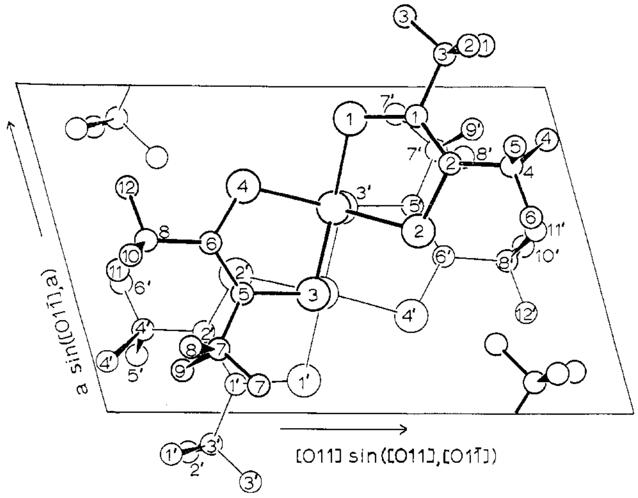

Figure 3.—Projection of the crystal structure along the [011] axis. Large circles are Co or S; small circles are C or F.

Tables IV and V, respectively. Averages of chemically equivalent bonds and angles are shown in Tables VI and VII, along with standard deviations which are to be regarded as upper limits for the appropriate distances. These standard deviations are from two to five times the standard deviations computed from the variance–covariance matrix of the final refinement of position parameters only, and hence are probably a somewhat better measure of the correct standard deviations which would have been obtained if the refinement program could have accommodated all thermal parameters as well as distance parameters for all atoms. Thus in any discussion of bond distances and angles we urge that the standard deviations in Tables VI and VII be employed.

The clearest result is the existence of discrete dimers, $Co_2S_8C_8(CF_3)_8$, which are centrosymmetric with the center of symmetry midway between the Co atoms. However, the two units are not stacked directly above one another, but are staggered so that the Co atom of one unit is directly opposite an S atom of the other $CoS_4C_4(CF_3)_4$ unit of the dimer.

The coordination of the Co is best described as square-pyramidal, in which the four (basal) S atoms of each unit are in a plane from which the Co atom is displaced about 0.37 Å. toward one (apical) S atom of the other unit. Comparison of the average basal Co–S distance of 2.16 ± 0.02 Å. and the apical Co–S distance of 2.38 Å. with the sum of single bond radii[11] (2.20 Å.) suggests

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(11) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 255, 256.

TABLE IV

BOND DISTANCES (Å.)[a]

Bond	Distance	Bond	Distance
Co–Co′	2.781 (6)	C_5–C_7	1.493 (4)
Co–S_3′	2.382 (4)	C_6–C_8	1.510 (4)
C–S_1	2.143 (6)	C_3–F_1	1.267 (2)
Co–S_2	2.165 (4)	C_3–F_2	1.313 (2)
Co–S_3	1.156 (6)	C_3–F_3	1.296 (3)
Co–S_4	2.181 (4)	C_4–F_4	1.305 (3)
S_1–C_1	1.690 (4)	C_4–F_5	1.310 (2)
S_2–C_2	1.678 (5)	C_4–F_6	1.315 (3)
S_3–C_5	1.716 (4)	C_7–C_7	1.295 (3)
S_4–C_6	1.692 (4)	C_7–F_8	1.267 (2)
C_1–C_2	1.379 (3)	C_7–F_9	1.300 (2)
C_5–C_6	1.407 (3)	C_8–F_{10}	1.282 (2)
C_1–C_3	1.520 (4)	C_9–F_{11}	1.277 (3)
C_2–C_4	1.502 (3)	C_9–F_{12}	1.319 (3)

[a] Standard deviation of last significant figure is given in parentheses.

TABLE V

BOND ANGLES (DEG.)

Atoms	Angle	Atoms	Angle
S_1–Co–S_2	89.6 (2)	C_1–C_3–F_1	113.2 (2)
S_2–Co–S_3	86.2 (2)	C_1–C_3–F_2	111.2 (2)
S_3–Co–S_4	90.1 (2)	C_1–C_3–F_3	111.2 (2)
S_4–Co–S_1	86.7 (2)	C_2–C_4–F_4	113.2 (2)
Co–S_1–C_1	105.4 (2)	C_2–C_4–F_5	113.0 (1)
Co–S_2–C_2	106.0 (2)	C_2–C_4–F_6	113.4 (2)
Co–S_3–C_5	105.9 (2)	C_5–C_7–F_7	110.2 (2)
Co–S_4–C_6	104.9 (2)	C_5–C_7–F_8	114.1 (1)
S_1–C_1–C_2	120.3 (2)	C_5–C_7–F_9	113.0 (2)
S_2–C_2–C_1	118.6 (2)	C_6–C_8–F_{10}	113.5 (1)
S_3–C_5–C_6	117.9 (1)	C_6–C_8–F_{11}	113.3 (2)
S_4–C_6–C_5	120.4 (2)	C_6–C_8–F_{12}	111.1 (2)
S_1–C_1–C_3	115.3 (2)	F_1–C_3–F_2	105.0 (2)
S_2–C_2–C_4	115.9 (2)	F_1–C_3–F_3	109.0 (2)
S_3–C_5–C_7	116.6 (2)	F_2–C_3–F_3	106.9 (1)
S_4–C_6–C_8	116.1 (2)	F_4–C_4–F_5	107.9 (2)
C_3–C_1–C_2	124.3 (2)	F_4–C_4–F_6	104.5 (2)
C_4–C_2–C_1	125.4 (2)	F_5–C_4–F_6	103.9 (1)
C_7–C_5–C_6	125.3 (2)	F_7–C_7–F_8	106.2 (1)
C_8–C_6–C_5	123.4 (1)	F_7–C_7–F_9	107.3 (2)
		F_8–C_7–F_9	105.7 (2)
		F_{10}–C_8–F_{11}	106.6 (2)
		F_{10}–C_8–F_{12}	107.1 (1)
		F_{11}–C_8–F_{12}	104.7 (2)

TABLE VI

AVERAGE BOND DISTANCES (Å.)

No. of meas.	Bond	Longest	Average	Shortest	Std. dev.
4	Co–S	2.181	2.161	2.143	0.016
4	S–C	1.716	1.694	1.678	0.016
4	C–CF_3	1.520	1.506	1.493	0.012
2	C–C	1.379	1.393	1.407	0.020
12	C–F	1.319	1.296	1.267	0.018

TABLE VII

AVERAGE BOND ANGLES (DEG.)

No. of meas.	Atoms	Largest	Average	Smallest	Std. dev.
2	S–Co–S (ring)	90.1	89.8	89.6	0.4
2	S–Co–S	86.7	86.4	86.2	0.4
4	Co–S–C	106.0	105.5	104.9	0.5
4	S–C–C	120.4	119.3	117.9	1.2
4	S–C–CF_3	116.6	116.0	115.3	0.5
4	C–C–C	125.4	124.6	123.4	0.9
12	C–C–F	114.1	112.5	110.2	1.0
12	F–C–F	109.0	106.2	103.9	1.5

that the bonding in the dimer is somewhat weaker than that of a single Co–S bond. The Co···Co distance of 2.78 Å. is, on the other hand, 0.46 Å. longer than the Co–Co single bond distance, and while an appreciable interaction between Co atoms might take place, it is probably considerably weaker than the two Co–S interactions which appear to form the strong interactions which form this dimer.[12]

The remainder of the distorted structural features of the dimer appear to be associated with normal van der Waals radii of the S, C, and, especially, the bulky CF_3 groups. Although Co, S_1, S_2, C_1, and C_2 form an essentially planar five-membered ring, the ring composed of Co, S_3, S_4, C_5, and C_6 is somewhat distorted with C_5 and C_6 being folded out of the Co, S_3, S_4 plane about 8°. This is most probably due to repulsions exerted by the S atoms (S_1' and S_2') on C_5, C_6, and, especially, the CF_3 groups bonded to C_5 and C_6. By contrast, the C_1 and C_2 atoms are well separated from S_3' and S_4'. In addition, the folding back of C_5 and C_6 also relieves some crowding between CF_3 groups.

Magnetic susceptibility studies[4b] of the solid $Co_2S_8C_8(CF_3)_8$ structure indicate that all electron spins are paired. Magnetic moments less than the spin-only value for monomeric $NiS_4C_4(CN)_4^-$ ion have shown a temperature dependence[9] indicating a low-lying singlet state, above which is a thermally accessible triplet electronic state. In addition, an X-ray diffraction study[8,9] has shown that these anions are stacked in a staggered arrangement in the crystal, somewhat similar to the mode of dimerization found here by us for $CoS_4C_4(CF_3)_4$ units of the dimer. However, the distances between interacting groups in the anions of $[(C_6H_5)_3PCH_3]^+[NiS_4C_4(CN)_4]^-$ are considerably greater than those in $CoS_4C_4(CF_3)_4$ dimer. For example, Ni···S distances are 3.41 and 3.56 between anions, and Ni···Ni distances are 4.40 and 4.45 Å., where the shorter of each pair is to be associated with the weak dimerization. Thus, these distances are considerably greater than the Co–S distance of 2.38 Å. and the Co···Co distance of 2.78 Å. in $Co_2S_8C_8(CF_3)_8$. Hence, we are not inclined to describe the pairing of electrons to the same kind of weak exchange interactions involving d_{z^2} and d_{xy} orbitals on Ni and S which were employed in the description of magnetic properties of $NiS_4C_4(CN)_4^-$ ions.

The only other possibly significant comparison between the structure of $Co_2S_8C_8(CF_3)_8$ and the anions[5-7] $CoS_4C_4(CN)_4^{-2}$, $CuS_4C_4(CN)_4^-$, and $NiS_4C_4(CN)_4^-$ involves the C=C distance, which is 1.39 ± 0.02 Å for the neutral $Co_2S_8C_8(CF_3)_8$ and is, respectively, 1.32, 1.34, and 1.33 Å in the anions. Although this comparison is only within 2 to 3 times the standard deviations it may be of some importance when the nature of molecular orbitals in this interesting series of compounds is on a more secure basis than it is at present. Also, a somewhat longer C=C bond for the neutral compound agrees with the C=C stretching frequency,[4b] which is

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(12) For a Co atom coordinated to four S atoms and one NO see P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 668 (1962).

only 1466 cm.$^{-1}$ in $Co_2S_8C_8(CF_3)_8$ as compared to 1515 cm.$^{-1}$ in $CoS_4C_4(CF_3)_4^{-2}$. On the subject of other distances we note that the average Co–S distance of 1.69 ± 0.02 Å. compares on the lower side with the average M–S distances of 1.72, 1.72, and 1.75 Å., respectively, in the anions. Other distances and angles agree within experimental error where they can be compared among these four structures.

Finally, the packing of dimers in the crystal is largely determined by the bulky CF_3 groups, but there are no abnormally short intermolecular contacts between dimer units. The F atoms are 3.5 Å. or greater from Co and S atoms.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Crystal and Molecular Structure of Racemic Iodocarbonyl-π-cyclopentadienyl-pentafluoroethylrhodium

BY MELVYN R. CHURCHILL

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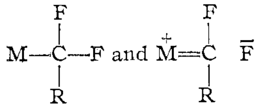
Iodocarbonyl-π-cyclopentadienyl-pentafluoroethylrhodium, $\pi\text{-}C_5H_5Rh(CO)(C_2F_5)I$, crystallizes as an ordered racemate in space group $P2_1/c$, with $a = 12.410 \pm 0.010$, $b = 7.823 \pm 0.008$, $c = 12.632 \pm 0.010$ Å.; $\beta = 109.86 \pm 0.05°$. A three-dimensional single-crystal X-ray analysis, based on 960 independent reflections, using conventional Patterson, Fourier, and least-squares refinement techniques has led to the location of all atoms except hydrogens, with estimated standard deviations ranging from 0.003 Å. for the rhodium–iodine vector to 0.04 Å. for carbon–carbon distances. The final value for the discrepancy index, R_1, is 6.98%. An interesting result of the analysis is that the rhodium–carbon bond distance for the perfluoroethyl group is only 0.11 Å. longer than the rhodium–carbonyl bond length. On allowing for the 0.07 Å. difference in the radii of sp^3 and sp hybridized carbon atoms, the effective difference in rhodium–carbon bond lengths decreases to only 0.04 Å. ($\sim 1.3\ \sigma$). This, coupled with the distortion of the α carbon atom of the perfluoroethyl group from a regular tetrahedral environment, gives some weight to the proposal that the perfluoroethyl group participates in metal–ligand ($d_\pi - \sigma^*$) back donation. A comparison with known metal–carbon bond lengths suggests that for certain transition metal complexes, the metal–perfluoroalkyl linkage may be some 0.2–0.3 Å. shorter than the metal–carbon bond in an analogous nonfluorinated metal–alkyl.

Introduction

One of the remarkable features of transition metal perfluoroalkyl complexes (as compared to the corresponding alkyl derivatives) is their great thermal and aerobic stability. Although it is possible that this may, in part, be a result of the slightly greater size, and concomitantly greater mechanical shielding effect, of the perfluoroalkyl group, Jaffé and Doak's calculations^1 on simple σ-bonded first-row transition metal alkyls indicated that the metal–carbon bonds were inherently unstable. Chatt and Shaw,^{2} likewise, conclude that transition metal alkyls will not exist for metals with filled (or partially filled) d orbitals, unless there is considerable ligand-field stabilization. It seems likely, therefore, that the intrinsically greater stability of perfluoroalkyl compounds owes its origin to an electronic, rather than to a steric, effect. From an electrostatic viewpoint, the stabilization of the metal–perfluoroalkyl bond may be considered the result of metal orbital contraction (due to the high electronegativity of the perfluoroalkyl group); alternatively, in valence bond terms, one can consider stabilization of the perfluoroethyl group as a result of the contribution of such canonical structures^3 as



$$\mathrm{M{-}\overset{F}{\underset{R}{C}}{-}F \quad and \quad \overset{+}{M}{=}\overset{F}{\underset{R}{C}}\ \bar{F}}$$

A more detailed theory of the metal–perfluoroalkyl bonding has recently been proposed^4 in order to explain anomalies in the infrared spectra of some perfluoromethyl compounds. The carbon–fluorine stretching modes of $CF_3Mn(CO)_5$ occur some 100 cm.$^{-1}$ lower than those in simple perfluoromethyl compounds such as CF_3Cl. This is interpreted^4 as a result of electrons drifting from the d_π orbitals of the manganese into some carbon–fluorine antibonding orbitals of appropriate (*i.e.*, "quasi-E") symmetry.

For each description, the net result is that the metal–carbon bond of a transition metal perfluoroalkyl is predicted to be stronger (and, presumably, shorter) than that of an analogous alkyl complex. The present investigation was undertaken to determine whether the

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