CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Organometallic Sulfur Complexes. VI. The Molecular Structure of a Tricyclic Complex, Tricobalt Enneacarbonyl Sulfide[1]

BY CHIN HSUAN WEI AND LAWRENCE F. DAHL[2]

Received November 11, 1966

A three-dimensional X-ray characterization of $SCo_3(CO)_9$, obtained by the reaction of dicobalt octacarbonyl with phenyl mercaptan, has provided the detailed molecular features of an organometallic complex containing a sulfur atom symmetrically bridging three metal atoms. Tricobalt enneacarbonyl sulfide forms triclinic crystals with four molecules in a centrosymmetric primitive unit cell of lattice parameters a = 9.67 A, b = 13.23 A, c = 13.41 A, α = 110° 00′, β = 108° 23′, and γ = 97° 21′. Structural refinement by a full-matrix, least-squares method yielded an unweighted reliability index of R_1 = 10.9%. The idealized molecular configuration of trigonal C_{3v} symmetry consists of an apical sulfur atom coordinated by three Co–S bonds to a $Co_3(CO)_9$ fragment of three equilaterally arranged $Co(CO)_3$ groups bonded to one another by cobalt–cobalt bonds. The salient stereochemical features of $SCo_3(CO)_9$ are compared with those of $Co_3(CO)_9CCH_3$ and other related molecular complexes.

Introduction

The accidental synthesis in our laboratories of $SCo_3(CO)_9$ and the subsequent structural analysis was a direct consequence of our desire to provide another equally dramatic illustration[3-5] of the importance of metal–metal interactions in determining the molecular configurations of polynuclear metal carbonyl and cyclopentadienyl complexes containing ligand-bridged groups in addition to the metal–metal bonds. X-Ray work[6-9] on several iron carbonyl chalcogenide complexes has shown for the molecular compounds $[C_2H_5SFe(CO)_3]_2$[6] and $[SFe(CO)_3]_2$[8] a nonplanar Fe_2S_2 fragment with similar remarkably acute Fe–S–Fe angles of 68 and 70°, respectively. Since a bent iron–iron bond previously was proposed[10] to be responsible for the molecular geometry of each of these two complexes, it was decided to attempt a synthesis of the presumably corresponding cobalt molecular analogs $[RSCo(CO)_3]_2$ (R = C_2H_5, C_6H_5), reported earlier by Hieber and Spacu,[11] for which no metal–metal interactions are required in order for each of the metal atoms to achieve a closed-shell electronic ground-state configuration. Our attempted preparation of the ethylthiocobalt carbonyl complex resulted in the synthesis of a new pentanuclear metal complex, $Co_5(CO)_{10}(SC_2H_5)_5$, for which a structural analysis revealed the first known example of thioalkyl ligands coordinated to three transition metal atoms through the utilization of five valence electrons (including both normally unshared electron pairs).[12]

The analogous reaction of dicobalt octacarbonyl with phenyl mercaptan carried out in our laboratories yielded the unexpected product $SCo_3(CO)_9$ whose composition as well as atomic arrangement was elucidated from a three-dimensional X-ray diffraction study reported in this paper. This compound was synthesized earlier by Markó, Bor, and co-workers,[13-15] who have prepared under various conditions a large number of cobalt carbonyl sulfide complexes[13-19] of which several have been shown from X-ray work[20] to possess unusual structural features and novel types of bonding.

Experimental Section

Preparation of the Compound.—Freshly prepared dicobalt octacarbonyl (2.4 g)[21] and thiophenol (4.8 ml) were allowed to react by the method of Hieber and Spacu[11] at 0° *without solvent* for 45 hr under a continuous slow stream of carbon monoxide gas in a specially constructed glass vessel equipped with a refluxing condenser. After removal of the liquid portion of the resulting brown reaction product through glass wool from the bottom of the vessel, the remaining residue was dissolved, washed, and filtered through glass wool with successive portions of petroleum ether (bp 60–80°). The collected petroleum ether solution was first concentrated by the blowing of gaseous nitrogen over the liquid surface and then was chilled to −20° whereupon small, black, shining crystals were obtained. The approximate yield of the

---

[1] (a) For previous papers in this series see: I: L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963); II: C. H. Wei and L. F. Dahl, *ibid.*, **4**, 1 (1965); III: C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965); IV: M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1306 (1965); V: C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966); (b) presented in part at the National Meeting of the American Crystallographic Association, Montana State College, Bozeman, Mont., July 26–31, 1964.

[2] Alfred P. Sloan Fellow, 1963–1965.

[3] An X-ray examination[4] of the structures of the molecular compounds $[(C_6H_5)_2PCoC_5H_5]_2$ and $[(C_6H_5)_2PNiC_5H_5]_2$, first synthesized by Hayter,[5] revealed for the cobalt complex a nonplanar Co_2P_2 fragment with a symmetrically bridging Co–P–Co angle of 73° and a bonding Co–Co distance of 2.56 A; in sharp contrast with these structural features the nickel analog contains a planar Ni_2P_2 fragment with a normal symmetrically bridging Ni–P–Ni angle of 103° and a nonbonding Ni · · · Ni distance of 3.36 A.

[4] J. M. Coleman and L. F. Dahl, presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; *J. Am. Chem. Soc.*, **89**, 542 (1967).

[5] R. G. Hayter, *Inorg. Chem.*, **2**, 1031 (1963); R. G. Hayter and L. F. Williams, *J. Inorg. Nucl. Chem.*, **26**, 1977 (1964).

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

[7] L. F. Dahl and P. W. Sutton, *ibid.*, **2**, 1067 (1963).

[8] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 1 (1965).

[9] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965).

[10] L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

[11] W. Hieber and P. Spacu, *Z. Anorg. Allgem. Chem.*, **233**, 353 (1937).

[12] C. H. Wei and L. F. Dahl, submitted for publication.

[13] L. Markó, G. Bor, and E. Klumpp, *Chem. Ind.* (London), 1491 (1961).

[14] L. Markó, G. Bor, E. Klumpp, B. Markó, and G. Almásy, *Chem. Ber.*, **96**, 955 (1963).

[15] S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometal. Chem.* (Amsterdam), **1**, 373 (1964).

[16] L. Markó, G. Bor, and G. Almásy, *Chem. Ber.*, **94**, 847 (1961).

[17] L. Markó, G. Bor, and E. Klumpp, *Angew. Chem.*, **75**, 248 (1963).

[18] E. Klumpp, L. Markó, and G. Bor, *Chem. Ber.*, **97**, 926 (1964).

[19] L. Markó and G. Bor, *J. Organometal. Chem.* (Amsterdam), **3**, 162 (1965).

[20] C. H. Wei and L. F. Dahl, submitted for publication; D. L. Stevenson, V. Magnuson, and L. F. Dahl, submitted for publication.

[21] *Cf.* W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, p 168.

compound was 0.5 g. Because of the sensitivity of the compound to air and its tendency to decompose and separate out as a brown amorphous powder from organic solvents, purification of the compound by means of recrystallization was not successful. Consequently, an elemental analysis[22] only conclusively showed the mole ratio Co:S = 3:1 for the partially decomposed product. The infrared spectrum of the compound in carbon tetrachloride solution, taken on a Perkin-Elmer 421 grating spectrometer with NaCl plates, gave carbonyl absorption bands only in the 2000–2110-cm^{-1} region characteristic of terminal carbonyl stretching modes. Furthermore, the observed spectrum appeared to be similar to that reported for $SCo_3(CO)_9$.[13,14]

X-Ray Data.—A single crystal of dimensions 0.35 × 0.35 × 0.15 mm was used to obtain the X-ray data. The crystal was immersed in grease and then mounted in a thin-walled Lindemann glass capillary such that rotation about the a axis approximately corresponded to a diagonal direction of a rhombohedral-type face of the crystal. The lattice constants for the reduced primitive cell were determined from NaCl-calibrated precession photographs. Multiple-film equiinclination Weissenberg data were taken for ten reciprocal layers, $0kl$–$9kl$, with Zr-filtered Mo Kα radiation. In order to collect the Weissenberg intensity data for a given reciprocal lattice level of this triclinic crystal from only the upper halves of the films and thereby to eliminate spot compaction for the upper layers,[23] two separate sets of multiple-film exposures were made for each reciprocal level (except the zero layer) at angular crystal settings which were approximately 180° apart. In order to record the diffraction maxima over a wide intensity range, a given set contained two (or three) multiple-film packets of nine films each which were exposed for 72, 12, and 2 hr (if necessary). The intensities of all reflections in the linear range were estimated visually for each film by comparison with a calibrated set of standard intensities. For a given reflection the estimated intensities were averaged by use of a statistical weighting scheme to a single value with the INTAV program.[24] Our regular utilization of Mo Kα radiation rather than Cu Kα radiation for obtaining photographic intensity data of organometallic and inorganic complexes arises not only from the usual consideration of absorption effects but also from the distinct advantage of the much lower absorption coefficient per film (*viz.*, ~1.3 for Mo Kα as contrasted to a value of ~3.7 for Cu Kα radiation). Hence, a given reflection with a nonweak intensity is judged at least five or six times in the linear range by a human photometer which thereby leads to more precise film intensity data.[25] After application of the usual Lorentz-polarization (Lp) factors, the corrected intensities of the two different sets of Weissenberg data for each reciprocal level were placed on a single scale by a least-squares program[26] which merged the reflections common to both film sets. Timed-exposure $h0l$ and $hk0$ precession data also were collected with Mo Kα radiation, and the resulting Lp-corrected intensities were used to correlate the Weissenberg data onto a single relative scale. A total of 1602 independent, observed reflections were obtained by this procedure. No absorption correction was applied to the intensities, since the estimated maximum absorption parameter, $\mu R_{\max}$, of the crystal used was less than 0.4. The linear absorption coefficient for Mo Kα radiation is 35 cm^{-1}. Variable weights assigned to the individual reflections for the least-squares refinement are as follows: if $I_o \geqslant 4I_o(\min)$, then $w = 20/F_o$; if $I_o < 4I_o(\min)$, then $w = 1.25I_o^2/F_oI_o(\min)^2$.

Results

Unit Cell and Space Group.—Tricobalt enneacarbonyl sulfide, $SCo_3(CO)_9$ (mol wt, 461.0), forms triclinic crystals with reduced cell constants a = 9.67 ± 0.02 A, b = 13.23 ± 0.03 A, c = 13.41 ± 0.03 A, α = 110° 00′ ± 10′, β = 108° 23′ ± 10′, and γ = 97° 21′ ± 10′. The volume of the unit cell is 1476 A^3, and the density is $\rho_{\text{obsd}} = 2.00$ g cm^{-3} (from flotation) *vs.* $\rho_{\text{calcd}} = 2.08$ g cm^{-3} for four formula species per unit cell. The total number of electrons per unit cell, $F(000)$, is 892. The centrosymmetric space group, $P\bar{1}$ (C_i^1, No. 2), was verified by the satisfactory least-squares refinement of the structure. All atoms occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[27] A Delaunay reduction[28] verified the triclinic symmetry.

TABLE I

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10\sigma_B$)
Co_1	0.3257 (4)	0.0973 (4)	0.2309 (4)	2.10 (1.1)
Co_2	0.4670 (4)	0.3110 (4)	0.3449 (4)	2.30 (1.1)
Co_3	0.6140 (4)	0.1671 (4)	0.2666 (4)	2.16 (1.1)
S	0.4228 (9)	0.2076 (7)	0.1708 (8)	2.83 (2.0)
C_1	0.1368 (29)	0.1167 (25)	0.2006 (25)	2.0 (6)
O_1	0.0169 (23)	0.1237 (19)	0.1812 (19)	3.9 (5)
C_2	0.3580 (37)	0.0664 (31)	0.3421 (36)	4.9 (9)
O_2	0.3694 (30)	0.0432 (24)	0.4194 (27)	6.5 (7)
C_3	0.2814 (47)	−0.0445 (43)	0.1114 (41)	6.2 (11)
O_3	0.2497 (31)	−0.1252 (27)	0.0399 (29)	6.9 (8)
C_4	0.3087 (36)	0.3683 (29)	0.3307 (28)	3.3 (8)
O_4	0.2066 (31)	0.4038 (24)	0.3072 (23)	6.4 (7)
C_5	0.5077 (35)	0.3108 (29)	0.4910 (35)	3.0 (8)
O_5	0.5418 (28)	0.3100 (22)	0.5767 (26)	5.7 (7)
C_6	0.6063 (40)	0.4287 (32)	0.3795 (31)	4.2 (9)
O_6	0.7040 (30)	0.5031 (23)	0.4030 (23)	6.1 (7)
C_7	0.6248 (37)	0.0417 (34)	0.1688 (33)	4.1 (9)
O_7	0.6369 (29)	−0.0410 (25)	0.1033 (24)	6.2 (7)
C_8	0.7665 (37)	0.2641 (31)	0.2729 (31)	3.7 (8)
O_8	0.8573 (29)	0.3263 (23)	0.2693 (24)	6.3 (7)
C_9	0.6936 (38)	0.1578 (31)	0.3961 (34)	4.3 (9)
O_9	0.7471 (30)	0.1336 (23)	0.4780 (26)	6.8 (7)
Co_1'	0.7244 (4)	0.6576 (4)	0.0753 (4)	2.02 (1.1)
Co_2'	0.9329 (4)	0.6133 (4)	0.2209 (4)	2.11 (1.1)
Co_3'	0.7917 (4)	0.7599 (4)	0.2983 (4)	2.02 (1.1)
S'	0.6996 (8)	0.5848 (7)	0.1913 (7)	2.34 (1.9)
C_1'	0.7027 (30)	0.5434 (28)	−0.0534 (28)	2.4 (7)
O_1'	0.6916 (26)	0.4716 (22)	−0.1361 (23)	5.5 (6)
C_2'	0.8271 (41)	0.7660 (33)	0.0668 (32)	4.9 (9)
O_2'	0.9160 (24)	0.8377 (21)	0.0639 (19)	4.6 (6)
C_3'	0.5418 (33)	0.6920 (26)	0.0343 (26)	2.6 (7)
O_3'	0.4223 (26)	0.6943 (19)	−0.0047 (20)	4.5 (5)
C_4'	0.9363 (32)	0.4860 (29)	0.1188 (29)	3.0 (7)
O_4'	0.9461 (27)	0.4042 (23)	0.0573 (23)	5.5 (6)
C_5'	1.0791 (49)	0.7126 (38)	0.2304 (39)	5.9 (11)
O_5'	1.1865 (26)	0.7661 (21)	0.2275 (22)	5.1 (6)
C_6'	1.0126 (40)	0.5981 (33)	0.3618 (37)	4.6 (10)
O_6'	1.0748 (33)	0.5894 (25)	0.4401 (27)	7.7 (8)
C_7'	0.6259 (32)	0.8073 (26)	0.2810 (27)	2.7 (7)
O_7'	0.5263 (29)	0.8458 (22)	0.2828 (22)	6.1 (7)
C_8'	0.8441 (36)	0.7687 (30)	0.4406 (35)	4.3 (8)
O_8'	0.8811 (26)	0.7720 (22)	0.5326 (25)	5.4 (7)
C_9'	0.9213 (38)	0.8816 (32)	0.3269 (31)	3.9 (8)
O_9'	1.0005 (32)	0.9628 (25)	0.3354 (24)	6.8 (7)

[a] The unprimed and primed atoms correspond to molecules A and B, respectively.

---

(22) Alfred Bernhardt Mikroanalytisches Laboratorium in Max-Planck Institut für Kohlenforschung, Mulheim, Germany.

(23) *Cf.* M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp 227–229.

(24) J. F. Blount, Ph.D. Thesis, University of Wisconsin, 1965.

(25) Experienced undergraduate spot judgers continually employed on a part-time basis for this tedious and uninspiring work generally provide excellent results, which on comparison of common data have surpassed those obtained by most of the graduate students when the latter happened to estimate some of the intensity data for their own structural problems.

(26) C. H. Wei, "A Crystallographic Intensity Merging Program for the CDC 1604 Computer," University of Wisconsin, 1964.

(27) "International Tables for X-Ray Crystallography," Vol. 1, The Kynoch Press, Birmingham, England, 1952, p 75.

(28) *Cf.* L. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Co., Inc., New York, N. Y., 1958 pp 167–180.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
1	0	0	92.8	-75.2
2	0	0	35.3	-34.7
3	0	0	74.6	77.0
5	0	0	28.5	-32.2
6	0	0	22.4	-17.0
8	0	0	41.4	-34.8
1	1	0	200.3	-182.9
1	-1	0	79.0	67.5
2	1	0	25.7	-32.9
3	1	0	39.6	37.4
4	1	0	71.3	-76.3
4	-1	0	48.1	-55.8
5	-1	0	107.8	113.6
6	1	0	70.9	71.8
7	1	0	69.3	-61.1
7	-1	0	46.6	42.5
8	1	0	60.4	53.7
9	1	0	24.6	37.3
9	1	0	52.4	37.3
0	2	0	134.9	-118.0
1	2	0	110.4	106.1
2	2	0	52.5	-50.1
3	2	0	83.9	83.6
3	-2	0	301.0	255.0
4	-2	0	39.3	-35.1
5	-2	0	118.8	-122.1
6	-2	0	32.2	42.3
7	-2	0	28.1	30.2
8	-2	0	36.4	-28.7
10	2	0	38.9	-50.6
10	-2	0	29.7	45.0
1	3	0	48.8	-47.5
1	-3	0	31.7	25.1
2	3	0	89.3	74.6
3	3	0	50.1	-40.5
3	-3	0	38.6	-38.0
4	3	0	41.8	-37.2
4	-3	0	192.7	192.4
5	3	0	33.0	-28.3
5	-3	0	85.1	-83.9
7	-3	0	29.2	31.8
9	-3	0	38.3	-20.5
0	4	0	93.7	-85.5
1	4	0	57.5	-50.3
2	4	0	64.7	55.4
2	-4	0	108.8	-120.1
3	4	0	96.0	-90.5
3	-4	0	85.3	-94.6
5	4	0	74.6	66.7
5	-4	0	62.0	68.6
9	-4	0	59.9	61.0
1	5	0	54.1	41.5
1	-5	0	118.2	116.4
2	5	0	40.8	29.7
2	-5	0	32.4	-28.6
4	-5	0	102.3	-111.4
5	5	0	96.8	87.2
6	5	0	71.1	-78.2
7	-5	0	41.5	-29.6
9	-5	0	47.5	-44.5
1	6	0	134.7	-133.5
1	-6	0	43.0	-31.0
2	6	0	42.8	34.4
2	-6	0	68.1	65.8
6	6	0	57.0	-48.3
7	6	0	53.5	42.8
8	-6	0	61.3	65.4
9	-6	0	71.1	-65.7
1	7	0	54.8	46.6
1	-7	0	78.3	-83.2
2	7	0	60.5	55.9
2	-7	0	38.5	41.0
3	-7	0	39.3	-35.3
4	-7	0	26.5	-23.7
5	7	0	35.9	-25.9
5	-7	0	38.8	40.0
6	7	0	40.8	45.3
6	-7	0	51.5	-50.5
9	-7	0	50.8	36.8
1	8	0	148.3	159.6
2	8	0	84.6	-87.0
8	-8	0	47.9	-42.0
2	9	0	84.0	-82.7
3	-9	0	50.5	-42.9
9	9	0	37.1	33.3
4	-9	0	32.7	28.8
6	-9	0	62.0	62.7
0	10	0	33.2	18.9
1	10	0	45.9	-43.4
2	10	0	68.5	69.3
2	-10	0	40.3	32.6
4	-10	0	38.2	-38.3
0	11	0	39.0	-33.8
2	-11	0	47.9	-34.4
3	-11	0	96.2	110.0
2	-12	0	55.3	-67.0
3	-13	0	65.2	-59.9
7	-14	0	31.6	53.1
1	0	1	101.2	94.9
1	0	-1	72.1	-58.3
2	0	-1	123.9	-103.7
3	0	1	75.6	71.4
5	0	-1	55.6	57.7
4	0	1	27.4	26.3
5	0	-1	44.5	-46.4
6	0	1	38.7	38.9
6	0	-1	97.9	-110.7
7	0	-1	84.9	88.5
8	0	-1	36.8	-36.3
3	1	1	35.9	-31.2
4	1	1	79.4	-71.7
4	-1	1	94.4	-100.1
5	-1	1	34.3	32.3
6	1	-1	31.7	31.8
6	-1	1	31.9	31.1
7	1	1	49.7	-42.3
7	1	-1	61.2	55.3
7	-1	1	29.9	-15.5
8	1	1	49.7	-44.1
8	-1	1	54.2	48.0
0	2	1	89.3	-92.7
1	2	1	52.7	-42.9
3	2	1	109.1	-112.9
4	2	1	78.2	71.5
4	-2	1	54.8	-58.2
5	2	1	46.2	42.1
5	2	-1	50.6	-54.3
6	2	-1	35.7	33.0
6	-2	1	24.1	-24.5
7	2	-1	44.9	-42.2
8	2	1	48.0	32.8
8	-2	1	39.7	-29.4
0	3	-1	42.7	39.7
1	3	1	30.3	-21.7
1	3	-1	43.8	-38.9
1	-3	-1	52.1	50.6
2	3	1	53.9	49.4
2	3	-1	211.8	-233.4
2	-3	1	88.8	-98.1
2	-3	-1	24.7	-22.2
3	3	-1	56.2	96.8
4	3	1	54.5	50.8
4	3	-1	67.3	-67.7
4	-3	1	35.7	35.0
5	3	1	46.9	-39.6
5	3	-1	30.5	32.9
5	-3	1	44.1	43.4
6	3	1	70.1	-63.6
6	3	-1	47.0	45.2
7	3	1	39.1	29.4
7	-3	-1	34.2	45.1
9	-3	-1	42.5	-37.1
0	4	1	92.6	-83.8
0	4	-1	19.1	10.3
1	4	-1	50.8	-43.9
1	-4	-1	44.6	-44.8
2	-4	1	51.6	47.4
2	-4	-1	55.1	58.9
3	4	-1	91.8	91.8
3	-4	1	131.6	-149.2
3	-4	-1	54.0	51.3
4	4	1	79.7	-76.5
4	4	-1	25.2	23.5
5	-4	1	80.2	-81.9
5	-4	-1	100.2	111.9
6	4	-1	49.9	37.6
6	-4	1	61.1	69.7
6	-4	-1	58.9	-65.0
7	4	1	46.2	36.6
7	4	-1	42.4	-36.6
8	-4	1	49.0	-50.7
8	-4	-1	53.8	69.6
9	-4	1	52.8	37.3
0	5	1	62.8	57.7
0	5	-1	60.5	-57.6
1	5	1	84.2	84.2
1	5	-1	43.2	-60.0
1	-5	1	26.2	-13.6
1	-5	-1	143.9	-158.5
2	5	1	37.6	-22.3
2	5	-1	104.7	102.7
2	-5	-1	40.4	32.8
3	5	-1	68.6	-60.5
3	-5	1	62.5	60.9
3	-5	-1	55.4	-57.3
4	5	1	59.1	55.3
4	-5	1	53.9	52.2
4	-5	-1	73.1	-69.2
5	5	1	33.7	35.4
5	5	-1	46.6	-42.4
5	-5	1	75.5	-80.9
6	-5	-1	35.2	32.8
7	5	-1	44.3	-36.4
7	-5	1	44.7	50.0
7	-5	-1	36.7	-39.8
8	-5	1	50.1	-49.1
0	6	1	91.2	89.5
0	6	-1	65.5	-56.0
1	6	1	74.8	74.8
1	6	-1	37.5	-31.9
1	-6	1	29.1	18.4
1	-6	-1	43.0	31.2
2	6	1	66.1	-41.3
2	6	-1	38.1	27.1
2	-6	1	102.1	-105.2
2	-6	-1	32.5	24.9
3	6	-1	47.2	-31.9
3	-6	1	39.2	32.5
4	6	1	50.3	47.5
4	6	-1	40.6	-37.2
5	6	1	62.0	-61.1
5	6	-1	40.2	39.6
5	-6	-1	48.9	66.1
6	6	-1	30.8	-23.4
6	-6	1	44.4	-46.9
6	-6	-1	29.0	-21.1
7	6	1	47.1	-26.7
7	6	-1	43.0	43.4
8	-6	1	49.7	45.5
8	-6	-1	36.4	-29.4
0	7	1	73.9	-82.7
0	7	-1	49.5	41.0
1	-7	1	41.6	61.0
2	7	1	86.8	-76.2
2	7	-1	75.2	76.1
2	-7	-1	32.2	31.0
3	7	1	61.9	57.0
3	7	-1	47.6	-30.2
3	-7	1	55.5	-56.0
4	7	-1	34.5	-28.4
5	7	1	52.7	-37.3
5	7	-1	53.2	51.5
6	7	1	38.7	28.3
6	-7	1	28.2	-28.9
6	-7	-1	56.9	54.9
7	-7	1	63.3	-64.1
9	-7	-1	51.7	44.6
1	8	1	40.2	27.7
1	8	-1	42.7	-24.1
2	8	1	64.1	55.3
2	8	-1	53.4	-44.2
2	-8	1	63.4	61.6
2	-8	-1	47.7	44.6
3	8	-1	67.4	-59.9
5	-8	1	90.5	90.7
5	-8	-1	128.5	-130.0
6	8	-1	40.1	-24.6
6	-8	-1	40.5	38.6
7	8	-1	48.8	-31.0
0	9	1	60.8	64.1
0	9	-1	51.6	-43.9
1	9	1	55.7	-52.6
1	9	-1	45.9	33.8
2	9	-1	57.5	-47.1
2	-9	-1	65.7	-63.4
3	9	1	56.1	-45.5
3	9	-1	90.8	91.8
3	-9	-1	60.4	55.8
4	-9	1	33.0	-24.1
4	-9	-1	53.0	54.1
6	-9	1	35.8	-31.0
7	-9	1	45.2	36.5
1	10	1	51.7	-48.0
1	10	-1	61.8	61.0
1	-10	-1	47.8	38.8
2	-10	1	75.8	82.0
2	-10	-1	78.7	-81.0
4	10	-1	43.2	-43.2
4	-10	1	34.7	27.0
4	-10	-1	44.2	-45.6
5	-10	-1	41.2	41.2
1	-11	1	63.9	-63.9
2	-11	-1	52.7	40.2
3	11	-1	64.1	-58.4
4	11	-1	53.1	62.9
5	-11	-1	39.5	-30.4
6	-11	1	45.3	44.6
1	-12	1	65.1	71.9
2	-12	1	55.5	-56.3
6	-13	-1	50.8	-47.3
1	-14	1	51.2	-55.1
0	0	2	280.2	-182.6
3	0	-2	99.3	-91.2
4	0	2	75.8	73.8
5	0	-2	92.2	-92.3
6	0	2	47.8	-49.3
7	0	2	68.9	59.6
7	0	-2	25.9	37.5
8	0	-2	34.8	39.3
9	0	-2	37.8	-32.9
2	1	2	63.5	-65.7
3	1	2	36.7	-27.8
3	-1	2	39.3	-46.0
4	1	2	28.9	23.2
4	-1	2	33.1	-28.0
5	1	2	71.7	-66.6
5	-1	2	43.8	-41.6
7	1	2	41.2	25.1
7	1	-2	44.8	45.2
7	-1	2	80.0	-78.1
8	1	2	48.8	-38.7
8	1	-2	51.5	-55.5
0	2	2	58.2	-54.7
1	2	2	61.6	56.1
1	-2	2	56.6	-52.5
3	2	2	93.9	-91.2
3	-2	2	87.7	86.2
4	2	2	42.7	-42.0
4	2	-2	60.1	57.8
5	2	2	50.5	41.4
5	-2	2	32.9	26.5
6	2	-2	111.1	-119.8
6	-2	2	85.5	81.6
7	-2	2	39.3	-35.6
0	3	2	87.8	91.9
1	3	2	49.7	41.4
1	3	-2	100.2	-99.8
1	-3	2	28.3	-21.9
1	-3	-2	277.2	-336.9
2	3	2	106.4	-101.4
2	3	-2	194.9	225.5
2	-3	2	56.1	-56.4
2	-3	-2	31.8	-21.3
3	3	2	64.1	57.7
3	3	-2	44.3	33.7
4	3	2	58.8	51.8
4	3	-2	82.1	84.4
4	-3	2	103.4	-109.6
5	3	2	66.3	61.8
5	3	-2	24.0	-23.0
5	-3	2	72.1	67.9
6	3	2	58.0	-56.3
6	3	-2	31.2	35.5
7	3	2	41.8	33.0
7	3	-2	38.6	25.4
8	3	-2	34.8	29.7
8	-3	2	44.1	35.6
0	4	2	99.2	96.3
1	4	2	95.3	-93.3
1	4	-2	99.2	96.0
2	-4	2	68.1	75.3
2	-4	-2	124.6	134.3
3	4	2	76.9	74.2
3	4	-2	83.5	73.1
3	-4	2	81.4	91.3
3	-4	-2	50.4	-44.0
4	4	2	37.2	-32.5
4	4	-2	94.4	-92.4
4	-4	2	76.0	-91.2
5	4	2	90.2	-83.9
5	4	-2	28.8	-33.2
5	-4	2	26.3	-32.3
6	4	-2	37.6	27.0
6	-4	2	34.2	29.8
9	-4	-2	42.0	-43.7
0	5	2	86.7	-91.9
0	5	-2	21.4	8.8
1	5	2	60.1	52.3
1	5	-2	45.5	40.4
1	-5	2	45.2	41.6
1	-5	-2	47.8	-34.1
2	5	-2	96.9	-98.0
2	-5	2	56.0	49.6
3	-5	-2	58.3	56.7
4	5	-2	64.3	-62.7
4	-5	2	106.4	117.5
4	-5	-2	118.6	-121.8
5	5	2	45.5	-38.3
5	5	-2	26.3	-16.5
5	-5	2	55.8	-58.2
6	5	2	63.1	65.7
6	5	-2	33.2	31.9
6	-5	-2	34.8	36.0
7	-5	2	36.1	26.8
7	-5	-2	30.7	27.0
9	-5	-2	65.9	69.3
0	6	2	43.0	52.0
0	6	-2	76.8	70.1
1	6	2	61.1	61.0
1	6	-2	55.2	-48.6
1	-6	-2	39.7	38.2
2	6	2	54.7	-51.0
2	-6	2	80.8	-81.7
2	-6	-2	120.0	-130.0
3	6	2	52.6	39.3
3	6	-2	34.7	20.1
3	-6	2	52.1	-53.5
3	-6	-2	55.2	43.0
4	6	-2	100.0	93.6
4	-6	-2	60.1	51.6
5	-6	-2	100.0	-112.8
6	6	-2	47.0	44.2
6	-6	2	38.4	-33.5
8	-6	2	48.1	-52.0
8	-6	-2	35.8	-30.0
0	7	2	55.2	53.1
0	7	-2	60.6	-59.6
1	7	2	93.3	-94.3
1	7	-2	44.2	-63.4
1	-7	2	122.7	129.4
1	-7	-2	69.1	71.5
3	7	-2	37.3	-18.1
3	-7	2	35.9	25.1
4	7	2	43.5	-41.8
4	7	-2	44.8	-42.5
4	-7	-2	104.6	100.3
5	-7	2	28.7	24.1
6	7	-2	34.7	-27.4
6	-7	-2	58.8	53.4
7	-7	-2	45.3	-42.7
8	-7	2	54.2	-45.2
0	8	-2	55.7	-53.6
1	8	2	73.3	-68.1
1	-8	2	40.3	-40.9
2	8	2	49.4	46.5
2	8	-2	45.5	37.6
2	-8	2	47.3	-50.5
2	-8	-2	54.4	-46.0
3	-8	2	48.0	45.2
4	-8	-2	80.8	-84.3
5	8	-2	40.1	35.0
5	-8	2	60.8	-61.3
6	8	-2	40.0	-33.0
6	-8	2	52.7	54.5
7	8	-2	60.9	47.0
8	-8	2	58.7	48.4
8	-8	2	42.3	48.4
0	9	-2	49.3	41.3
1	9	-2	37.6	-22.6
1	-9	-2	40.4	33.7
2	9	-2	83.0	83.7
3	-9	2	43.9	-33.0
3	-9	-2	78.6	77.0
6	-9	2	72.1	-80.9
6	-9	-2	50.5	-49.2
9	-9	-2	66.1	-62.0
9	-9	-2	74.7	-62.0
0	10	-2	47.1	-32.4
1	10	-2	48.0	38.0
1	-10	-2	43.1	-30.5
2	-10	2	59.7	63.0
3	10	-2	53.4	-37.0
4	-10	-2	53.7	56.3
5	10	-2	53.4	40.3
5	-10	2	78.1	86.9
8	-10	-2	50.3	45.5
1	11	-2	45.3	44.0
2	11	-2	49.7	-44.9
3	11	-2	60.1	46.3
3	-11	2	58.6	-56.7
3	-11	-2	64.4	-62.3
2	-12	2	60.5	61.5
5	12	-2	52.8	-53.3
3	-13	2	58.1	50.6
2	-14	2	50.0	-43.8
0	0	3	51.5	45.2
1	0	3	38.8	-33.7
1	0	-3	60.1	-60.1
2	0	-3	12.8	12.7
3	0	3	114.8	-117.5
4	0	3	73.2	79.5
5	0	-3	69.5	73.0
6	0	3	50.4	-42.7
6	0	-3	59.6	66.4
7	0	-3	43.7	-49.9
0	1	3	38.5	36.2
0	1	-3	78.0	-71.2
1	-1	3	102.4	107.6
2	1	3	35.8	-23.4
2	-1	3	100.6	87.7
2	-1	-3	41.5	-45.1
3	1	3	107.8	107.7
3	-1	3	55.7	-46.7
4	1	3	55.8	54.4
5	1	3	48.9	-45.0
6	-1	3	31.6	-25.6
7	1	3	41.9	28.4
7	1	-3	108.6	-130.3
8	1	-3	29.5	33.1
8	-1	3	90.1	-81.0
0	2	3	22.9	-4.5
0	2	-3	133.7	-149.8
1	2	3	74.9	69.3
1	-2	3	36.3	34.2
1	-2	-3	24.1	20.8
2	-2	-3	124.8	139.5
3	2	3	75.6	73.8
3	-2	3	32.9	-22.9
3	-2	-3	60.3	62.9
4	2	3	115.9	-118.2
4	2	-3	33.9	38.1
4	-2	3	44.1	42.6
6	2	-3	64.0	-68.9
6	-2	3	48.0	41.0
7	2	-3	78.5	83.4
7	-2	3	49.9	42.9
8	2	-3	51.9	49.5
0	3	3	81.5	78.6
1	-3	3	30.0	-23.5
1	-3	-3	109.4	-102.6
2	3	3	65.8	-61.3
2	3	-3	163.1	189.5
2	-3	-3	27.2	22.3
3	3	3	55.1	-46.3
3	-3	3	44.4	-35.9
4	3	3	32.5	23.1
4	3	-3	57.5	52.4
4	-3	-3	44.7	43.0
6	3	3	38.7	40.2
6	-3	3	30.1	-23.1
7	3	-3	101.1	106.0
7	-3	3	46.8	-34.1
8	3	-3	53.1	-55.5
8	-3	3	47.7	34.5
0	4	3	63.1	73.8
0	4	-3	93.7	-59.9
1	4	3	34.9	-21.9
1	4	-3	64.1	59.9
1	-4	-3	75.5	82.1
2	4	-3	59.5	55.7
2	-4	3	26.4	24.0
2	-4	-3	126.2	-140.8
3	4	3	54.0	40.3
3	4	-3	131.6	-149.8
3	-4	3	96.7	104.9
4	4	3	52.6	52.8
4	-4	3	35.8	-30.9
4	-4	-3	57.0	58.1
5	4	3	49.0	-47.5
5	-4	3	86.2	94.2
6	4	3	53.1	47.3
6	-4	-3	32.0	-34.6
7	4	-3	47.1	-36.0
7	-4	3	46.2	-32.2
8	-4	-3	49.7	-52.5
0	5	3	90.1	-98.6
0	5	-3	41.0	39.9
1	5	-3	83.0	76.6
1	-5	-3	119.0	129.4
2	5	-3	129.4	-134.0
2	-5	3	48.1	-43.9
3	5	-3	71.9	74.0
4	5	3	42.1	-42.3
4	5	-3	69.1	70.2
4	-5	3	80.8	-86.5
4	-5	-3	63.5	60.3
5	5	-3	62.0	50.6
5	-5	3	41.7	40.2
6	5	-3	30.3	-22.6
6	-5	3	30.8	30.9
6	-5	-3	112.8	112.9
7	-5	-3	31.9	-22.7
8	5	-3	42.8	34.3
8	-5	3	43.0	31.0
0	6	-3	86.7	87.7
1	6	3	48.3	-38.2
1	6	-3	48.3	-34.6
1	-6	-3	60.3	-61.4
2	6	3	57.6	48.1
2	-6	3	84.1	92.0
3	6	-3	134.2	133.1
3	-6	3	73.4	-80.8
4	6	-3	61.3	-57.1
4	-6	-3	30.8	-25.1
5	6	-3	65.3	-60.2
5	-6	-3	152.0	-147.9
6	-6	-3	54.2	50.3
7	-6	-3	49.7	47.0
0	7	3	80.1	60.4
0	7	-3	42.6	-31.4
1	7	3	49.2	-38.9
1	7	-3	31.7	-16.3
1	-7	3	77.3	-82.9
1	-7	-3	42.4	36.9
2	7	3	73.6	67.0
2	-7	3	69.2	72.3
3	7	-3	65.1	-59.1
3	-7	3	36.6	41.7
4	7	3	41.1	-40.7
4	7	-3	44.9	-37.3
4	-7	-3	38.0	37.0
5	-7	-3	53.3	45.7
6	7	-3	50.2	43.9
6	-7	-3	126.5	-129.7
7	-7	3	47.4	41.4
8	-7	3	43.7	-29.1
9	-7	3	57.2	45.1
0	8	3	40.7	-49.0
2	8	3	44.4	-35.4
2	8	-3	44.5	-41.0
2	-8	3	110.3	-127.2
3	-8	3	57.4	61.4
4	8	-3	40.9	47.5
4	-8	-3	31.5	-30.2
5	-8	3	77.7	-79.6
5	-8	-3	92.9	95.1
6	8	-3	41.7	31.0
1	9	-3	70.1	-67.0
1	-9	3	96.4	107.6
2	9	-3	44.4	36.0
2	-9	3	47.9	-48.6
3	-9	3	37.7	-28.1
3	-9	-3	58.9	-44.8
4	9	-3	34.7	-30.6
4	-9	3	59.7	52.9
7	-9	3	57.6	-52.9
9	-9	-3	56.5	-58.8
1	10	-3	65.9	-55.7
2	-10	-3	56.6	52.5
4	10	-3	37.0	17.8
4	-10	3	35.1	-40.6
6	-10	3	48.0	47.3
3	11	-3	53.8	47.3
6	11	-3	39.1	-29.8
6	-11	3	63.0	-71.8
0	12	3	44.9	48.5
2	-12	3	45.0	39.0
4	12	-3	56.7	-59.0
5	-12	3	52.3	53.0
3	-13	3	57.8	-39.3
4	13	-3	53.4	48.2
1	-14	3	52.3	47.9
0	0	4	78.2	72.4
1	0	4	101.9	100.4
1	0	-4	62.7	-57.2
2	0	-4	38.6	-38.9
3	0	-4	52.7	-52.2
4	0	4	72.2	-68.2
5	0	-4	18.9	22.2
6	0	-4	44.5	-44.6
7	0	4	56.3	-49.7
0	1	4	94.3	88.6
1	1	-4	92.2	-88.2
1	-1	4	42.5	-34.9
1	-1	-4	111.3	-107.9
2	1	4	144.4	-136.2
2	-1	4	59.9	51.7
2	-1	-4	44.1	-44.3
3	1	4	71.2	66.3
3	-1	4	33.7	26.7
3	-1	-4	38.6	-33.0
4	-1	4	44.0	41.8
5	-1	4	68.8	-43.9
6	-1	4	39.8	33.6
7	1	-4	50.5	-54.4
7	-1	4	43.3	33.0
8	1	-4	28.2	31.3
9	1	-4	37.1	29.6
0	2	4	71.6	68.5
0	2	-4	218.7	-272.2
1	2	4	75.8	-68.2
1	2	-4	56.3	52.6
1	-2	4	120.6	-133.5
1	-2	-4	102.6	115.7
2	2	4	68.6	64.0
2	-2	4	51.9	-39.9
2	-2	-4	60.9	56.8
3	2	4	59.8	54.9
3	-2	4	44.8	-35.0
3	-2	-4	75.8	-75.8
4	-2	4	49.1	44.6
5	2	4	67.0	-46.2
5	2	-4	31.2	30.5
5	-2	4	40.0	-33.2
5	-2	-4	66.2	-70.3
6	2	-4	71.5	82.1
6	-2	4	69.0	-85.6
7	-2	4	72.0	71.6
8	2	-4	53.4	52.0
9	2	-4	48.7	-42.2
0	3	4	88.1	-84.3
1	3	-4	58.6	59.4
1	-3	4	132.6	150.6
1	-3	-4	66.0	66.5
2	3	4	51.0	40.4
2	-3	4	40.4	-36.1
3	3	4	84.9	-79.5
3	-3	4	72.8	-74.3
3	-3	-4	108.1	122.4
4	3	-4	63.3	-60.3
4	-3	4	66.7	64.6
5	3	-4	24.2	-21.0
5	-3	-4	24.0	-26.1
6	-3	4	65.4	-64.5
6	-3	-4	33.4	35.7
7	3	-4	36.9	-33.7
7	-3	-4	72.2	72.8
8	3	-4	82.3	-83.7
8	-3	4	47.0	-32.3
0	4	4	33.1	-22.7
0	4	-4	103.8	-113.9
1	4	4	63.2	50.0
1	4	-4	26.3	-20.7
1	-4	4	28.8	11.5
2	4	-4	49.2	49.3
2	-4	4	94.1	91.8
2	-4	-4	119.3	-125.8
3	4	-4	110.1	-111.3
3	-4	4	131.8	-147.5
3	-4	-4	39.6	33.3
4	4	-4	64.2	63.3
4	-4	-4	65.9	70.6
5	4	-4	66.3	69.1
5	-4	4	30.8	25.6
5	-4	-4	49.4	-50.9
6	4	-4	65.1	-60.7
6	-4	4	58.9	57.9
8	-4	-4	50.8	59.2
9	4	-4	74.2	64.8
0	5	4	39.3	22.3
1	5	4	44.7	-39.5
1	-5	-4	59.2	57.9
2	5	4	61.9	53.8
2	5	-4	50.7	49.9
2	-5	4	43.4	-41.2
2	-5	-4	51.0	42.5
3	-5	-4	71.7	-70.5
4	5	4	49.3	-47.4
4	5	-4	117.7	110.9
4	-5	4	28.6	-35.0
4	-5	-4	33.9	26.7
5	5	4	50.8	41.0
5	5	-4	75.5	-49.9
5	-5	4	45.7	-45.2
5	-5	-4	45.3	48.0
6	5	-4	48.1	-44.6
6	-5	-4	29.2	-29.3
7	5	-4	51.2	44.3
7	-5	-4	76.6	-70.5
9	5	-4	73.9	-53.6
0	6	-4	70.3	-66.6
1	6	4	51.0	-40.0
1	6	-4	35.7	28.6
1	-6	4	54.1	52.5
1	-6	-4	63.4	-70.4
2	6	4	41.6	-26.1
2	6	-4	38.2	31.6
2	-6	4	50.7	50.7
2	-6	-4	82.8	79.8
3	-6	4	45.2	39.9
4	6	-4	87.3	-77.9
4	-6	-4	71.0	-70.9
5	6	-4	32.6	-17.4
5	-6	4	72.5	72.4
5	-6	-4	105.7	96.6
7	-6	4	44.2	-36.9
7	-6	-4	52.5	47.8
8	-6	4	54.2	53.3
0	7	-4	32.3	22.3
1	7	-4	68.9	59.8
1	-7	4	126.1	-156.8
2	7	-4	75.3	-70.2
2	-7	4	42.8	41.0
3	7	4	72.6	70.1
3	-7	4	37.8	-31.4
3	-7	-4	40.4	-32.0
5	7	-4	47.8	48.3
6	-7	-4	79.2	-80.1
9	-7	-4	59.0	-53.1
0	8	4	37.6	-35.3
0	8	-4	113.4	122.4
2	8	-4	78.0	-79.1
2	-8	-4	57.2	53.3
3	8	-4	50.1	36.0
3	-8	4	44.8	-38.7
4	8	-4	56.9	58.0
4	-8	-4	33.0	26.1
5	8	-4	48.3	-47.2
6	-8	4	40.5	-40.3
8	-8	4	47.6	-36.0
8	-8	4	46.2	-36.0
0	9	-4	76.1	-78.6
1	9	4	45.2	37.0
1	9	-4	41.8	-35.7
1	-9	4	51.0	44.8
1	-9	-4	43.8	-33.8
2	9	-4	48.6	-43.2
2	-9	-4	46.0	-38.4
3	-9	4	41.9	21.9
4	-9	4	33.7	-34.8
5	9	-4	42.7	-43.5
5	-9	4	37.6	30.3
6	9	-4	44.4	36.8
9	-9	-4	61.6	43.3
1	10	-4	36.2	28.3
1	-10	4	41.7	-45.0
1	-10	-4	46.2	42.5
2	-10	4	39.7	-37.7
3	-10	4	50.3	50.8
5	-10	4	87.3	-97.1
6	-10	4	42.3	42.7
0	11	-4	58.8	57.3
1	11	-4	44.2	-35.3
2	-11	4	42.5	-40.6
4	-11	4	62.6	70.3
8	-11	-4	46.3	48.5
1	12	-4	52.7	-43.4
2	-12	4	44.9	-36.4
3	12	-4	43.5	39.0
5	-12	4	43.8	42.0
2	-14	4	49.4	31.9
1	0	5	54.7	52.3
1	0	-5	51.6	-49.1
2	0	5	41.8	31.6
2	0	-5	84.3	84.0
3	0	5	87.1	86.9
4	0	5	59.9	-56.7
5	0	-5	104.1	-112.2
7	0	-5	22.0	36.6
8	0	-5	52.4	-58.6
0	1	5	46.9	41.9
0	1	-5	93.1	-88.2
1	1	5	36.3	-22.6
1	1	-5	92.5	92.2
1	-1	5	64.2	-58.7
2	1	5	38.6	27.3
2	1	-5	51.5	-48.0
2	-1	5	80.2	-76.1
3	1	5	78.2	-79.0
3	-1	5	101.7	93.7
3	-1	-5	34.3	-29.1
4	1	-5	54.2	-60.9
4	-1	5	28.6	-28.0
4	-1	-5	146.4	149.1
5	1	5	37.6	-18.2
5	1	-5	51.0	59.8
5	-1	-5	33.0	-33.4
6	-1	5	47.8	39.9
7	1	-5	35.4	41.4
7	-1	-5	43.8	51.8
0	2	5	34.0	-26.7
0	2	-5	152.3	166.0
1	2	5	40.2	-31.7
1	2	-5	23.6	-21.6
1	-2	5	63.7	-67.7
1	-2	-5	111.7	116.7
2	2	5	58.9	41.4
2	2	-5	58.0	-56.4
2	-2	5	58.3	-51.3
2	-2	-5	147.1	-159.3
3	2	5	41.9	-28.9
3	2	-5	80.7	83.0
3	-2	5	36.1	-23.0
3	-2	-5	32.8	-26.2
4	2	5	44.1	42.1
4	-2	-5	38.8	-34.0
5	2	5	36.5	25.1
5	-2	5	48.9	-43.3
5	-2	-5	37.3	40.6
7	-2	5	55.8	-42.3
7	-2	-5	24.7	-16.7
0	3	5	42.4	-40.4
0	3	-5	58.4	54.6
1	3	-5	130.3	-139.2
1	-3	5	58.2	58.3
1	-3	-5	82.1	89.4
2	3	5	48.3	36.5
2	-3	5	91.0	89.5
2	-3	-5	47.5	44.8
3	3	-5	45.3	47.4
3	-3	5	50.7	-40.1
4	3	-5	81.0	-85.2
4	-3	-5	35.2	-38.5
5	3	5	52.6	46.0
5	3	-5	22.7	-27.1
5	3	-5	25.6	-27.1
5	-3	5	64.2	58.4
6	3	5	65.7	-66.9
6	3	-5	54.9	59.7
7	3	-5	97.5	-94.9
7	-3	5	44.7	33.8
7	-3	-5	73.3	-68.4
9	-3	-5	54.6	-59.0
0	4	-5	87.7	-95.7
1	4	5	64.3	-67.7
1	4	-5	27.5	34.7
1	-4	5	35.3	-22.5
1	-4	-5	87.7	-92.4
2	-4	-5	70.4	66.5
3	4	-5	55.6	53.0
3	-4	5	47.5	-41.7
4	-4	5	56.7	-54.1
5	4	-5	69.1	64.1
5	-4	5	47.8	-40.1
7	-4	5	51.5	50.3
7	-4	-5	44.2	38.0
8	4	-5	55.2	47.1
8	-4	-5	46.4	43.2
0	5	-5	34.7	32.7
1	5	5	47.9	35.3
1	-5	5	54.7	52.7
1	-5	-5	33.2	-26.0
2	5	5	48.7	37.7
2	5	-5	71.6	65.5
2	-5	5	28.9	-25.7
3	-5	-5	61.0	-57.3
4	-5	5	133.4	144.2
4	-5	-5	43.2	-39.5
5	5	-5	83.3	-84.0
5	-5	5	76.3	-74.7
5	-5	-5	58.1	55.7
6	-5	5	48.3	-42.3
6	-5	-5	125.0	-124.1
8	5	-5	65.9	-54.6
0	6	-5	84.1	-85.0
1	6	5	83.2	79.2
1	6	-5	40.0	-32.1
1	-6	5	56.9	59.5
1	-6	-5	39.2	-40.7
2	6	5	64.0	-68.5
2	6	-5	96.0	98.9
3	6	5	53.2	-33.6
3	6	-5	137.8	-155.3
3	-6	5	37.6	-28.2
4	6	-5	29.6	28.0
4	-6	5	52.7	51.9
5	6	-5	31.4	29.1
5	-6	5	86.2	72.3
5	-6	-5	70.1	69.2
6	6	-5	40.1	40.9
9	6	-5	60.0	37.8
1	7	-5	75.2	76.4
1	-7	5	41.4	34.8
2	7	-5	55.4	-53.3
3	-7	-5	46.8	-30.9
4	7	-5	61.2	60.4
4	-7	5	78.8	-85.0
5	7	-5	51.7	50.1
5	-7	-5	37.7	-44.0
6	7	-5	61.8	-57.4
1	8	-5	36.7	-22.8
1	-8	-5	45.7	48.6
2	8	5	44.2	37.8
2	8	-5	34.8	-18.9
2	-8	5	66.8	66.6
3	8	-5	75.6	67.0
4	8	-5	35.0	-43.9
4	-8	5	33.9	36.0
4	-8	-5	50.8	-38.1
6	8	-5	43.1	-38.3
7	8	-5	52.2	35.4
8	-8	5	54.8	49.8
1	-9	5	104.6	-124.7
2	9	-5	44.0	36.9
2	-9	5	70.8	72.2
3	-9	5	39.1	-23.1
3	-9	-5	70.6	76.2
4	-9	5	44.0	-49.5
5	-9	5	43.3	43.4
6	9	-5	42.1	29.6
6	-9	-5	53.8	52.7
0	10	5	53.0	62.7
0	10	-5	52.6	46.5
1	10	-5	91.7	92.6
2	10	-5	37.7	-30.6
2	-10	-5	45.8	-38.1
3	-10	5	51.1	45.4
4	10	-5	36.0	30.0
5	10	-5	38.3	-27.9
6	-10	5	36.5	-38.1
1	-11	5	44.7	50.0
2	11	-5	54.5	-65.6
4	-11	5	39.7	36.1
6	-11	5	47.6	45.6
1	12	-5	46.6	-38.9
5	-12	5	53.5	-52.8
6	-12	5	40.5	45.8
3	-13	5	68.6	80.8
2	-14	5	45.1	-49.1
0	0	6	52.7	-43.2
1	0	6	59.9	-56.0
2	0	6	84.3	81.2
2	0	-6	39.5	38.4
3	0	6	51.6	-38.8
3	0	-6	85.4	-87.0
4	0	6	74.3	75.8
4	0	-6	32.7	-31.0
5	0	6	44.4	35.3
6	0	-6	51.3	51.3
8	0	-6	35.7	-33.8
9	0	-6	45.6	55.6
1	1	-6	96.3	100.1
1	-1	6	41.6	-30.1
1	-1	-6	149.2	161.5
2	1	6	60.5	50.3
2	-1	-6	32.2	-20.2
3	1	6	43.1	-33.9
3	1	-6	77.2	-72.8
3	-1	-6	95.9	87.3
4	1	-6	155.1	160.6
4	-1	6	51.9	-48.8
6	1	6	59.6	-49.1
6	-1	-6	48.0	-52.8
7	-1	-6	39.4	37.9
9	-1	-6	47.3	-58.6
0	2	6	65.3	-62.0
0	2	-6	40.3	49.9
1	2	6	43.4	33.8
1	-2	6	113.9	120.4
1	-2	-6	37.5	-31.7
2	2	-6	56.1	-54.6
2	-2	6	46.2	-34.3
3	2	-6	63.2	60.8
3	-2	6	47.5	38.5
4	2	6	38.0	-39.3
4	2	-6	33.9	37.9
4	-2	-6	26.6	22.6
5	2	6	35.3	20.9
5	2	-6	67.4	-67.8
5	-2	-6	54.1	54.8
6	2	-6	32.1	-40.3
6	-2	6	49.5	43.4
7	2	-6	50.8	51.0
7	-2	-6	42.6	-45.3
8	2	-6	43.0	-44.9
8	-2	-6	98.1	113.6
0	3	6	45.5	38.5
1	3	6	52.2	38.9
1	3	-6	78.9	-86.2
1	-3	6	70.3	-69.3
1	-3	-6	89.2	-91.3
2	3	-6	47.9	42.3
2	-3	6	62.0	62.5
2	-3	-6	62.1	62.6
3	3	-6	33.1	22.8
3	-3	-6	65.6	-57.1
4	3	-6	76.7	-76.5
4	-3	6	40.8	-35.1
5	3	6	43.5	30.1
6	3	-6	34.8	32.5
6	-3	6	60.9	58.9
7	-3	-6	51.0	-49.4
0	4	-6	83.3	81.5
1	4	-6	57.7	59.7
1	-4	6	108.9	-117.4
2	4	6	78.1	-78.4
2	-4	-6	75.7	83.3
3	4	-6	41.9	36.7
3	-4	6	56.0	51.4
4	-4	6	44.0	-40.4
5	-4	6	35.9	-33.3
5	-4	-6	67.1	62.2
6	4	-6	48.7	48.2
6	-4	6	45.8	-44.3
7	-4	-6	47.8	39.0
8	-4	-6	51.6	-53.1
9	4	-6	56.7	-54.7
0	5	6	31.9	-47.3
0	5	-6	58.5	56.1
1	5	-6	65.4	-62.5
1	-5	6	55.6	55.0
2	5	-6	147.1	-177.0
2	-5	6	49.4	-40.1
3	5	6	63.9	56.7
3	5	-6	76.9	75.9
3	-5	-6	49.3	-36.0
4	5	-6	84.6	-84.5
4	-5	6	69.5	65.4
4	-5	-6	39.0	-33.8
5	5	-6	44.5	-45.0
5	-5	6	40.6	55.7
6	5	-6	31.1	25.1
6	-5	6	38.2	-33.8
6	-5	-6	34.0	29.0
9	5	-6	52.7	29.0
0	6	-6	65.6	-64.3
1	6	-6	37.1	-33.0
2	6	6	58.8	54.8
2	6	-6	38.9	30.6
2	-6	-6	42.5	24.6
3	6	-6	45.0	42.3
3	-6	6	105.8	-111.7
4	4	-6	31.7	26.5
5	6	-6	44.6	47.3
5	-6	-6	55.7	-50.0
6	-6	-6	35.5	30.4
9	6	-6	71.3	58.8
2	7	-6	34.4	28.9
2	-7	6	36.0	-25.8
2	-7	-6	56.7	-57.6
3	-7	6	46.4	48.5
3	-7	-6	59.6	48.4
4	7	-6	62.7	44.5
4	-7	6	42.6	32.4
5	7	-6	48.5	-50.4
5	-7	6	73.5	-74.0
7	-7	6	53.9	40.5
0	8	-6	77.5	-77.3
1	-8	6	52.2	55.7
1	-8	-6	51.8	54.3
2	8	-6	36.1	37.2
2	-8	6	49.3	-58.0
2	-8	-6	52.2	-49.8
4	8	-6	65.8	-62.9
4	-8	6	50.3	49.4
5	8	-6	31.1	19.6
6	-8	6	39.0	-29.0
1	9	-6	53.1	50.2
1	-9	6	46.1	-38.0
2	9	-6	40.2	40.9
2	-9	-6	60.3	73.5
3	-9	6	44.6	-33.7
5	9	-6	68.5	73.7
6	9	-6	46.9	-36.9
9	-9	-6	51.2	-31.7
0	10	-6	59.4	63.7
1	10	-6	42.0	-32.7
2	-10	6	63.8	73.3
5	-10	6	46.6	50.4
6	10	-6	47.7	-42.3
7	-10	-6	44.9	67.9
0	11	-6	50.2	-50.5
2	11	-6	50.0	-40.8
2	11	-6	55.4	-40.8
4	-11	6	47.6	-56.2
5	11	-6	43.4	-35.5
6	-11	-6	49.6	-46.6
1	12	-6	61.8	65.6
1	-13	6	49.5	-38.8
2	13	-6	56.2	-39.5
3	13	-6	58.4	-42.2
2	-14	6	50.0	-54.3
0	0	7	57.5	-57.6
1	0	7	38.4	-25.7
1	0	-7	33.4	-20.2
2	0	-7	42.7	-37.1
3	0	7	75.8	-71.1
4	0	-7	68.3	-67.5
5	0	7	52.2	52.2
5	0	-7	123.3	126.8
7	0	-7	49.6	-48.0
8	0	-7	45.7	49.4
9	0	-7	40.7	35.3
0	1	7	44.9	41.0
0	1	-7	37.4	32.0
1	1	7	50.6	42.1
1	-1	7	41.1	-28.9
1	-1	-7	56.6	-60.0
2	1	7	45.0	-42.0
2	-1	7	95.5	93.9
3	1	7	46.2	37.4
3	-1	7	54.1	-45.7
4	1	7	42.5	43.9
4	1	-7	65.1	68.9
4	-1	-7	77.0	-74.3
6	1	-7	82.8	-86.7
6	-1	-7	34.7	35.1
7	-1	-7	46.0	-42.3
8	1	-7	31.7	29.2
9	-1	-7	41.3	-41.4
0	2	7	29.5	15.6
0	2	-7	71.9	-71.8
1	2	7	45.6	-31.6
1	2	-7	32.0	-28.4
1	-2	7	52.1	41.7
2	2	7	46.5	-28.7
2	2	-7	40.7	46.4
2	-2	-7	72.0	71.0
3	2	-7	47.2	-48.7
4	-2	7	36.6	31.0
5	2	7	67.5	-67.2
5	2	-7	104.8	-113.2
6	2	-7	64.2	65.4
6	-2	7	39.5	-34.6
7	2	-7	39.2	39.2
0	3	7	59.6	-55.1
0	3	-7	96.1	-99.8
1	3	7	62.4	54.0
1	3	-7	117.5	129.9
1	-3	-7	62.5	-65.0
2	-3	7	60.6	-57.1
3	3	-7	78.9	-74.5
4	3	-7	39.1	42.0
4	-3	7	53.7	-49.7
4	-3	-7	69.9	-74.0
5	3	-7	48.0	50.3
7	3	-7	35.1	25.0
7	-3	-7	44.2	29.8
8	3	-7	32.0	-28.1
8	-3	-7	36.6	-28.9
9	-3	-7	75.7	75.4
0	4	7	43.5	50.5
0	4	-7	118.8	131.8
1	4	7	64.1	62.6
1	4	-7	31.8	22.9
2	4	-7	90.2	-90.3
2	-4	-7	40.7	-28.0
3	4	-7	37.0	30.1
3	-4	7	55.2	36.5
3	-4	-7	49.7	37.2
4	-4	-7	74.4	70.8
5	-4	-7	53.7	-51.8
6	4	-7	83.5	-88.1
8	4	-7	35.3	-28.8
8	-4	-7	41.9	-35.8
0	5	-7	39.9	29.6
1	5	7	71.0	-72.8
1	5	-7	130.4	-140.5
1	-5	7	46.7	-38.1
2	5	-7	38.9	-50.5
2	-5	-7	44.5	-36.4
3	5	-7	46.6	31.4
4	-5	7	43.7	-45.8
4	-5	-7	36.7	29.3
5	5	-7	32.5	-29.9
5	-5	7	40.3	37.2
6	-5	-7	62.5	59.6
0	6	-7	38.6	38.7
1	6	7	49.4	-39.7
1	-6	7	56.8	-58.2
1	-6	-7	43.8	49.2
2	6	7	53.3	49.3
3	6	-7	64.9	66.8
3	-6	7	75.1	49.6
4	6	-7	38.4	-35.0
4	-6	7	103.7	-113.2
4	-6	-7	48.0	-54.4
5	6	-7	30.0	1.3
0	7	-7	40.0	32.9
1	-7	7	49.3	-63.4
2	7	-7	67.6	-66.4
3	-7	7	51.2	43.5
4	7	-7	54.5	-54.4
4	-7	7	73.1	81.3
5	7	-7	32.0	-25.3
6	7	-7	35.5	22.6
1	8	-7	37.5	-30.9
2	8	-7	36.0	16.8
2	-8	7	51.3	-51.8
3	-8	7	64.4	-65.8
3	-8	-7	54.7	-49.9
4	8	-7	49.4	48.3
4	-8	7	36.1	40.4
4	-8	-7	68.4	66.5
6	8	-7	56.9	58.3
7	8	-7	46.9	-33.7
1	-9	7	82.2	93.0
2	9	-7	41.8	31.0
3	-9	-7	52.2	-40.4
6	-9	-7	44.9	-41.3
7	9	-7	53.7	-38.5
0	10	-7	40.4	-29.1
1	10	-7	41.3	-41.8
6	10	-7	52.9	-47.1
0	11	-7	40.4	37.8
2	11	-7	59.3	61.3
1	12	-7	45.6	33.7
3	12	-7	62.7	-51.3
2	13	-7	59.4	-61.1
2	-14	7	50.5	49.2
0	0	8	41.0	-37.7
1	0	-8	65.3	-66.1
2	0	-8	76.1	77.7
4	0	8	51.4	-59.4
5	0	-8	51.9	48.8
7	0	-8	51.0	-51.1
8	0	-8	55.8	56.9
0	1	8	33.7	22.1
0	1	-8	40.5	27.0
1	1	8	57.1	41.8
1	1	-8	54.9	51.8
1	-1	-8	136.1	-152.7
2	1	8	48.1	-41.4
2	1	-8	44.9	-43.5
2	-1	8	39.8	-34.5
3	1	-8	66.8	59.8
3	-1	8	78.6	68.1
4	1	8	41.5	35.2
4	1	-8	95.7	-99.1
5	-1	-8	48.2	-48.7
6	1	-8	45.2	-43.5
6	-1	-8	33.2	31.6
8	-1	-8	36.5	-36.8
9	1	-8	47.6	-49.1
9	-1	-8	63.7	85.7
0	2	8	48.4	45.3
1	2	-8	54.5	-47.1
1	-2	8	47.9	-38.9
1	-2	-8	95.3	99.3
2	2	8	44.0	-32.3
2	2	-8	68.4	61.7
2	-2	-8	69.4	-87.3
3	2	8	51.0	36.7
3	2	-8	36.9	30.7
3	-2	8	93.9	-90.0
3	-2	-8	43.3	-22.0
4	2	-8	58.1	-59.0
4	-2	8	46.9	51.5
4	-2	-8	32.0	21.3
5	2	-8	64.9	65.5
6	2	-8	62.0	64.5
6	-2	-8	35.6	-32.0
8	2	-8	32.4	-27.4
8	-2	-8	62.3	-58.8
0	3	8	41.1	-41.9
1	3	8	53.1	-40.2
1	3	-8	88.5	70.6
1	-3	8	44.0	33.8
1	-3	-8	40.6	33.7
2	3	-8	35.6	39.4
2	-3	8	73.7	69.5
3	3	-8	75.4	-73.2
3	-3	8	44.9	-36.1
4	3	-8	87.8	86.0
4	-3	8	34.4	-32.1
6	-3	-8	88.8	83.5
7	3	-8	65.1	-68.5
0	4	8	37.9	30.7
0	4	-8	59.1	-53.4
1	4	8	43.3	-26.5
1	-4	8	106.6	116.5
2	4	8	73.5	75.1
2	4	-8	71.7	-68.0
2	-4	-8	43.3	-32.3
3	-4	-8	47.4	34.9
5	4	-8	70.3	-67.3
5	-4	-8	90.4	-99.1
6	4	-8	53.8	-53.9
7	4	-8	39.4	30.5
0	5	-8	66.3	-69.1
1	-5	8	44.3	-31.2
2	5	-8	55.5	56.6
2	-5	8	35.2	24.9
2	-5	-8	45.4	-29.2
3	-5	8	50.2	-35.7
3	-5	-8	55.7	46.9
5	-5	-8	41.5	42.1
6	-5	-8	61.3	-60.2
7	5	-8	74.2	76.3
0	6	-8	96.1	106.9
1	-6	8	64.5	-58.3
2	6	-8	42.5	34.1
2	-6	8	39.3	28.3
3	6	-8	86.3	-93.8
3	-6	8	50.6	51.1
8	6	-8	43.8	-24.1
0	7	-8	41.9	33.9
1	-7	8	51.0	-49.7
2	7	-8	97.7	-108.0
2	-7	8	51.2	-49.8
2	-7	-8	62.7	67.4
3	-7	8	45.7	76.6
3	-7	-8	68.1	-60.0
4	-7	8	56.7	-55.9
5	7	-8	37.6	23.1
5	-7	8	59.3	62.2
8	7	-8	45.2	28.4
2	8	-8	37.1	-31.0
2	-8	8	40.8	33.8
3	8	-8	107.4	116.8
4	-8	8	37.9	-42.0
8	8	-8	49.6	-31.3
1	-9	8	52.7	-49.0
2	-9	8	56.5	52.0
5	9	-8	41.7	-38.1
6	9	-8	44.0	35.6
1	10	-8	41.5	21.6
2	-10	8	60.7	-78.3
6	10	-8	44.8	41.5
0	11	-8	34.7	24.5
1	-11	8	64.5	75.9
2	11	-8	42.5	33.1
1	12	-8	47.4	-69.5
1	0	9	44.0	-27.6
1	0	-9	90.3	83.7
2	0	-9	44.9	35.1
3	0	9	51.0	37.6
3	0	-9	51.8	-49.0
4	0	-9	36.7	29.3
5	0	9	48.0	-43.4
5	0	-9	40.7	-32.8
8	0	-9	55.6	-54.6
0	1	9	75.4	-76.6
0	1	-9	68.5	67.8
1	1	-9	70.6	-65.6
2	1	-9	51.5	-48.1
2	-1	9	80.5	-78.6
3	-1	-9	74.0	64.3
4	-1	9	41.8	38.7
5	-1	-9	35.8	-30.6
6	1	-9	43.7	44.9
6	-1	-9	64.0	58.0
7	-1	-9	54.8	49.4
8	-1	-9	40.7	-33.9
9	-1	-9	46.9	37.8
0	2	9	42.1	42.1
1	2	-9	50.3	-39.8
1	-2	9	54.7	44.5
2	-2	-9	84.3	-89.1
3	2	-9	81.6	82.8
3	-2	9	48.7	-20.1
4	2	-9	39.7	-35.0
4	-2	9	44.8	-39.7
4	-2	-9	70.8	59.1
5	2	-9	84.3	85.3
5	-2	-9	71.8	-71.0
6	2	9	58.4	-2.9
6	-2	-9	37.8	-34.4
0	3	9	52.1	46.6
0	3	-9	53.6	49.2
1	3	9	56.3	-49.5
1	3	-9	73.5	-77.9
1	-3	9	41.6	-21.6
2	3	9	68.0	39.9
2	3	-9	38.2	25.9
2	-3	9	47.0	44.5
3	-3	9	57.9	52.5
4	3	-9	46.9	-47.4
5	-3	9	37.2	-26.0
5	-3	-9	61.0	65.1
6	3	-9	57.9	-57.8
0	4	9	40.1	-26.4
1	4	-9	41.8	-31.4
1	-4	9	41.4	-20.0
2	4	-9	47.8	48.4
4	-4	9	49.6	48.4
4	-4	-9	66.6	-64.0
6	4	-9	69.6	69.9
7	-4	-9	49.9	40.3
8	4	-9	45.9	45.1
0	5	-9	50.3	-52.8
1	5	-9	105.7	108.6
1	-5	9	73.3	70.2
2	-5	9	41.3	-38.7
0	6	-9	48.5	-44.3
2	6	-9	44.8	-33.0
2	-6	-9	50.1	44.1
3	6	-9	71.1	-69.4
4	-6	9	37.4	44.9
4	-6	-9	53.7	51.6
5	6	-9	37.2	40.1
6	6	-9	39.7	-60.2
6	-6	9	42.9	34.0
1	7	-9	49.0	-41.7
2	7	-9	59.1	55.3
3	-7	9	43.6	-36.1
4	7	-9	76.1	82.2
6	7	-9	51.2	-42.3
7	7	-9	59.1	57.2
8	7	-9	58.6	-38.0
2	8	-9	52.7	44.4
3	-8	9	48.9	44.6
4	8	-9	50.8	-56.2
4	-8	9	48.9	-43.1
1	9	-9	47.2	43.0
1	-9	9	54.7	-59.9
2	9	-9	44.0	-44.8
3	9	-9	49.3	-38.6
5	9	-9	39.8	38.7
0	10	-9	67.0	74.2
2	10	-9	45.8	-53.2
4	10	-9	47.8	52.0
5	10	-9	42.9	-45.2
0	11	-9	39.4	-42.0
5	11	-9	44.2	-39.8
0	12	-9	40.5	-33.2
0	13	-9	42.5	55.9
1	0	10	46.8	-27.5
1	0	-10	83.9	90.2
2	0	-10	95.5	-99.8
3	0	-10	46.9	-46.8
0	1	-10	36.2	-21.3
1	-1	-10	42.8	41.0
2	1	-10	52.8	-54.0
2	-1	-10	61.8	80.7
3	1	-10	55.5	45.7
4	1	-10	43.6	60.4
5	1	-10	39.8	-39.6
6	-1	-10	50.4	50.3
7	1	-10	43.0	44.6
1	-2	-10	54.7	-50.4
2	2	-10	80.7	53.5
2	-2	10	50.8	40.9
4	-2	10	40.8	-42.4
4	-2	-10	39.2	-26.1
5	2	-10	66.6	-68.3
7	-2	-10	60.3	55.7
8	-2	-10	41.7	32.2
1	-3	10	50.3	-38.6
2	3	-10	41.0	-37.7
2	-3	10	43.9	-41.5
3	3	-10	45.0	-25.7
3	-3	10	70.9	72.2
4	3	-10	49.3	-49.2
5	-3	-10	50.0	49.5
6	-3	-10	90.6	-94.5
0	4	-10	61.4	67.2
1	4	10	53.3	45.3
1	4	-10	39.7	-38.1
2	-4	10	49.7	-44.3
2	-4	-10	48.8	45.1
3	4	-10	67.1	62.0
5	4	-10	53.9	59.9
6	-4	-10	45.5	43.4
7	-4	-10	58.9	-40.3
8	4	-10	42.1	-35.5
1	5	-10	55.9	-54.5
5	-5	-10	42.2	-35.4
2	5	-10	75.3	-75.8
0	6	-10	54.0	-56.1
8	6	-10	73.1	65.0
1	7	-10	59.8	57.0
3	7	-10	47.8	28.8
3	-7	10	45.9	-29.5
3	-7	-10	54.8	44.6
1	8	-10	41.3	-27.3
2	8	-10	50.9	45.2
3	8	-10	100.6	-114.7
3	9	-10	51.2	-49.6
4	9	-10	60.3	66.8
4	-9	10	57.7	-57.9
6	9	-10	50.1	-43.1
3	10	-10	48.2	43.6
2	-11	10	54.6	54.6
0	12	-10	37.8	35.6
1	0	-11	50.0	-47.8
8	0	-11	78.4	83.7
0	1	-11	38.6	-31.3
1	1	-11	49.0	46.3
2	-1	-11	51.6	46.1
3	1	-11	49.2	49.3
5	-1	-11	59.9	58.5
6	-1	-11	56.4	-49.2
0	2	-11	43.2	-31.2
1	2	-11	61.0	59.6
2	-2	11	47.2	51.0
3	2	-11	54.4	-51.5
4	-2	-11	41.8	-40.3
5	-2	-11	58.0	58.1
8	2	-11	46.6	-44.1
1	-3	11	47.1	-27.1
3	3	-11	48.2	-47.7
4	3	-11	85.2	85.2
5	-3	-11	44.2	-43.3
1	-4	11	47.1	35.2
6	4	-11	51.7	-55.1
1	5	-11	53.3	-52.0
2	-5	-11	53.4	-52.8
3	-5	11	52.7	34.6
3	-5	-11	58.8	48.8
4	5	-11	58.2	-58.8
1	-6	11	53.1	-56.2
4	4	-11	37.2	28.9
6	6	-11	43.8	43.9
1	-7	11	52.3	44.5
2	7	-11	50.6	-37.4
3	7	-11	50.2	49.5
6	7	-11	42.3	42.5
7	7	-11	53.2	-48.3
0	8	-11	52.3	-56.8
3	-8	11	60.4	-56.8
2	9	-11	47.2	47.7
1	-10	11	49.7	42.9
3	10	-11	49.6	-35.4
1	11	-11	47.6	32.1
5	11	-11	54.2	70.6
0	12	-11	38.8	46.0
1	0	-12	47.4	-44.2
2	0	-12	53.0	49.1
5	0	-12	43.3	43.3
0	1	-12	37.3	41.6
2	1	-12	52.5	55.8
0	2	-12	36.7	-25.4
6	-2	-12	46.8	40.0
7	2	-12	57.3	-44.3
7	-2	-12	53.3	-41.8
8	2	-12	46.7	43.5
4	3	-12	35.6	30.1
6	3	-12	41.4	-32.7
6	-3	-12	40.1	37.7
5	4	-12	56.3	-64.1
0	5	-12	44.8	-54.2
3	5	-12	51.3	-48.5
0	6	-12	54.3	59.3
4	6	-12	48.2	48.4
6	6	-12	46.0	-51.9
8	6	-12	51.5	-40.7
1	7	-12	58.3	-64.7
0	8	-12	56.7	-29.8
3	8	-12	53.3	45.8
0	9	-12	41.3	57.0
1	10	-12	47.9	-38.6
3	10	-12	56.1	-23.6
0	12	-12	40.0	-24.1
1	1	-13	49.1	-46.9
6	-1	-13	49.8	50.2
1	2	-13	61.0	-63.2
2	2	-13	60.8	58.6
4	4	-13	55.5	-65.7
1	5	-13	53.1	44.2
3	5	-13	49.2	-41.3
4	5	-13	40.8	45.5
5	6	-13	54.3	-53.6
0	7	-13	51.3	-54.7
0	8	-13	42.5	39.2
0	9	-13	38.9	33.9
2	9	-13	62.4	-60.4
3	10	-13	58.1	59.9
0	3	-14	44.8	67.4
1	3	-14	49.1	-34.9
6	5	-14	40.5	-41.1
1	2	-15	53.6	52.3

Determination of the Structure.—At the beginning of the structural determination the actual molecular formula was unknown. Hence, the structural analysis of this compound consisted of initially determining from the Patterson map the positional parameters of as many independent cobalt and sulfur atoms as possible in the unit cell from which the entire structure could be elucidated by the application of successive Fourier syntheses. A three-dimensional Patterson function was computed from the corrected $|F_o|^2$ data with the Blount program.[29] The interpretation of two particularly large Patterson peaks resulted in two sets of two cobalt atoms (Co$_2$ and Co$_3$, Co$_2'$ and Co$_3'$) which are approximately related to each other by a noncrystallographic center of symmetry placed arbitrarily at the midpoint of the unit cell. A further detailed examination of primarily the intramolecular Patterson vectors enabled an assignment of the coordinates of two additional cobalt atoms (Co$_1$ and Co$_1'$), which are not related to each other by the above-mentioned center of symmetry. These stereochemical considerations were compatible with six independent cobalt atoms oriented in the unit cell as two similar equilateral triangles. Attempts to locate sulfur atoms were not successful at this stage. Two cycles of block-diagonal, least-squares refinement,[30] carried out on the basis of the positional parameters for the above noncentrosymmetric model together with 12 scale factors and an initially estimated isotropic cobalt temperature factor of 2.0 A^2 yielded for the usual unweighted reliability index (defined as $[\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$) an $R_1 = 30.5\%$. A three-dimensional Fourier synthesis[29] phased on these six partially refined cobalt atoms was computed next based on the acentric space group P1. The resulting first approximation to the electron density map clearly revealed the positions of two sulfur atoms (S and S′), each coordinated to all three cobalt atoms of one of the two crystallographically independent tricobalt fragments. In addition to these two sulfur–tricobalt groups, *four* other similar sets of peaks observed on the Fourier synthesis were recognized as due to possible positions for *two other* sulfur–tricobalt groups in the unit cell. The occurrence of these *four* sets of peaks is a consequence of the accidental centrosymmetry of four of the six cobalt atoms, related in pairs by the *pseudo*-center of symmetry located at the midpoint of the unit cell, which thereby produces a superposition of peaks for a partially correct structure and its centrosymmetrically related image. From an analysis of the Fourier peak heights coupled with stereochemical knowledge, not only were two of these four peak sets assigned to the two new sulfur–tricobalt groups but also a shift of the origin of the unit cell was made to give a centrosymmetric structure conforming to the space group P$\bar{1}$ whereby these two additional sulfur–tricobalt fragments were symmetry related to the two independent original ones. Least-squares refinement lowered R_1 after two cycles to 22.3% thereby indicating the correctness of the new model. A three-dimensional centrosymmetric Fourier synthesis was computed phased on the six cobalt and two sulfur atoms. From this map an interpretation of additional peaks enabled the location of nine carbonyl ligands per sulfur–tricobalt moiety by which the existence of two independent molecules of formula SCo$_3$(CO)$_9$ was ascertained.[31a] A refinement of the positional and thermal parameters of all 44 atoms, again performed with the block-diagonal, least-squares program,[30] resulted in a decrease of R_1 to 12.4%. Two further cycles of refinement with the Busing–Levy full-matrix, least-squares program[31b] resulted in R_1 =

TABLE III

INTRAMOLECULAR BOND DISTANCES (A) WITH STANDARD DEVIATIONS[a]

Bond	Molecule A	Molecule B
Co$_1$–Co$_2$	2.633 (7)	2.612 (6)
Co$_2$–Co$_3$	2.649 (7)	2.627 (7)
Co$_3$–Co$_1$	2.655 (5)	2.641 (6)
	2.648 (4)	2.626 (4)
	Av 2.637 (3)	
Co$_1$–S	2.143 (10)	2.147 (10)
Co$_2$–S	2.131 (10)	2.122 (9)
Co$_3$–S	2.141 (10)	2.148 (10)
	2.138 (6)	2.138 (6)
	Av 2.139 (4)	
Co$_1$–C$_1$	1.81 (3)	1.79 (3)
Co$_1$–C$_3$	1.89 (5)	1.84 (3)
Co$_2$–C$_4$	1.78 (4)	1.78 (4)
Co$_2$–C$_6$	1.74 (4)	1.89 (4)
Co$_3$–C$_7$	1.77 (4)	1.77 (3)
Co$_3$–C$_8$	1.79 (4)	1.77 (4)
	1.79 (2)	1.80 (1)
	Av 1.80 (1)	
Co$_1$–C$_2$	1.63 (5)	1.70 (4)
Co$_2$–C$_5$	1.87 (4)	1.74 (4)
Co$_3$–C$_9$	1.72 (4)	1.75 (4)
	1.76 (2)	1.73 (2)
	Av 1.75 (1)	
C$_1$–O$_1$	1.13 (3)	1.15 (3)
C$_3$–O$_3$	1.09 (5)	1.12 (3)
C$_4$–O$_4$	1.15 (4)	1.15 (3)
C$_6$–O$_6$	1.15 (4)	1.09 (4)
C$_7$–O$_7$	1.19 (4)	1.15 (4)
C$_8$–O$_8$	1.15 (4)	1.15 (4)
	1.14 (2)	1.14 (1)
	Av 1.14 (1)	
C$_2$–O$_2$	1.15 (4)	1.22 (4)
C$_5$–O$_5$	1.10 (4)	1.20 (4)
C$_9$–O$_9$	1.23 (4)	1.18 (4)
	1.16 (2)	1.20 (2)
	Av 1.18 (1)	

[a] Estimated standard deviations of the last significant figures are given in parentheses. The bond lengths are arranged into chemically equivalent sets according to C_{3v} molecular symmetry with the weighted average values (and with estimated standard deviations of the average values in parentheses) given for each of the two independent molecules A and B as well as for both molecules.

---

(29) J. F. Blount, Ph.D. Thesis, Appendix, University of Wisconsin, 1965.

(30) P. W. Sutton, "A Crystallographic Block-Diagonal Least-Squares Program for the CDC 1604 Computer," University of Wisconsin, 1962.

(31) (a) The correctness of our characterization of this compound was substantiated later by comparison of its X-ray data with corresponding Weissenberg and precession data obtained from crystals of SCo$_3$(CO)$_9$, generously supplied to us by Drs. G. Bor and L. Markó of the Hungarian Oil and Gas Research Institute, Veszprém, Hungary; (b) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

Table IV

Bond Angles (Degrees) with Standard Deviations[a]

M–M–M	Molecule A	Molecule B
$\mathrm{Co_1{-}Co_2{-}Co_3}$	60.4 (2)	60.6 (2)
$\mathrm{Co_2{-}Co_3{-}Co_1}$	59.5 (2)	59.4 (2)
$\mathrm{Co_3{-}Co_1{-}Co_2}$	60.1 (2)	60.0 (2)
	60.0 (1)	60.0 (1)
Av	60.0 (1)	
M–S–M		
$\mathrm{Co_1{-}S{-}Co_2}$	76.1 (3)	75.4 (3)
$\mathrm{Co_2{-}S{-}Co_3}$	76.6 (3)	75.9 (3)
$\mathrm{Co_3{-}S{-}Co_1}$	76.6 (3)	75.9 (3)
	76.4 (2)	75.7 (2)
Av	76.1 (1)	
S–M–M		
$\mathrm{S{-}Co_1{-}Co_2}$	51.8 (3)	51.9 (2)
$\mathrm{S{-}Co_2{-}Co_1}$	52.2 (3)	52.7 (3)
$\mathrm{S{-}Co_2{-}Co_3}$	51.8 (3)	52.5 (3)
$\mathrm{S{-}Co_3{-}Co_2}$	51.5 (3)	51.6 (2)
$\mathrm{S{-}Co_3{-}Co_1}$	51.7 (3)	52.0 (3)
$\mathrm{S{-}Co_1{-}Co_3}$	51.7 (3)	52.1 (3)
	51.8 (1)	52.0 (1)
Av	51.9 (1)	
S–M–C		
$\mathrm{S{-}Co_1{-}C_1}$	101.5 (10)	105.7 (11)
$\mathrm{S{-}Co_2{-}C_6}$	104.9 (13)	101.1 (11)
$\mathrm{S{-}Co_3{-}C_7}$	105.5 (12)	101.6 (10)
$\mathrm{S{-}Co_1{-}C_3}$	102.7 (14)	99.8 (10)
$\mathrm{S{-}Co_2{-}C_4}$	102.2 (11)	101.5 (10)
$\mathrm{S{-}Co_3{-}C_8}$	101.3 (12)	104.6 (12)
	103.0 (5)	102.3 (4)
Av	102.6 (3)	
$\mathrm{S{-}Co_1{-}C_2}$	141.7 (13)	143.6 (13)
$\mathrm{S{-}Co_2{-}C_5}$	143.3 (11)	139.9 (15)
$\mathrm{S{-}Co_3{-}C_9}$	140.8 (13)	144.8 (12)
	142.1 (7)	143.2 (8)
Av	142.6 (5)	
C–M–C		
$\mathrm{C_1{-}Co_1{-}C_2}$	103.3 (15)	101.9 (16)
$\mathrm{C_3{-}Co_1{-}C_2}$	101.5 (19)	96.9 (16)
$\mathrm{C_4{-}Co_2{-}C_5}$	99.6 (15)	103.9 (18)
$\mathrm{C_6{-}Co_2{-}C_5}$	100.2 (16)	103.0 (19)
$\mathrm{C_8{-}Co_3{-}C_9}$	100.6 (16)	98.4 (17)
$\mathrm{C_7{-}Co_3{-}C_9}$	102.1 (17)	99.8 (16)
	101.2 (7)	100.4 (7)
Av	100.8 (5)	
C–M–C	Molecule A	Molecule B
$\mathrm{C_3{-}Co_1{-}C_1}$	99.6 (16)	102.4 (13)
$\mathrm{C_4{-}Co_2{-}C_6}$	99.5 (17)	102.8 (16)
$\mathrm{C_8{-}Co_3{-}C_7}$	100.2 (16)	101.0 (15)
	99.8 (9)	102.1 (8)
Av	101.1 (6)	
M–C–O		
$\mathrm{Co_1{-}C_1{-}O_1}$	176.7 (28)	178.3 (27)
$\mathrm{Co_1{-}C_3{-}O_3}$	176.6 (42)	167.8 (29)
$\mathrm{Co_2{-}C_4{-}O_4}$	170.7 (33)	176.2 (30)
$\mathrm{Co_2{-}C_6{-}O_6}$	176.3 (35)	170.8 (37)
$\mathrm{Co_3{-}C_7{-}O_7}$	177.7 (32)	172.3 (30)
$\mathrm{Co_3{-}C_8{-}O_8}$	174.9 (33)	177.8 (33)
	175.5 (14)	174.1 (12)
Av	174.7 (9)	
$\mathrm{Co_1{-}C_2{-}O_2}$	174.8 (32)	171.6 (33)
$\mathrm{Co_2{-}C_5{-}O_5}$	174.8 (29)	169.2 (40)
$\mathrm{Co_3{-}C_9{-}O_9}$	169.7 (34)	173.4 (35)
	172.8 (18)	170.8 (21)
Av	171.8 (14)	
M–M–CO		
$\mathrm{Co_1{-}Co_2{-}C_6}$	152.9 (12)	150.5 (11)
$\mathrm{Co_2{-}Co_3{-}C_7}$	153.3 (11)	149.9 (11)
$\mathrm{Co_3{-}Co_1{-}C_1}$	150.8 (10)	154.8 (11)
$\mathrm{Co_1{-}Co_3{-}C_8}$	151.5 (11)	154.6 (12)
$\mathrm{Co_3{-}Co_2{-}C_4}$	153.1 (11)	151.9 (10)
$\mathrm{Co_2{-}Co_1{-}C_3}$	152.8 (13)	149.1 (10)
	152.3 (5)	151.7 (4)
Av	151.9 (3)	
$\mathrm{Co_1{-}Co_2{-}C_4}$	99.7 (11)	96.4 (10)
$\mathrm{Co_2{-}Co_3{-}C_8}$	98.0 (12)	99.4 (12)
$\mathrm{Co_3{-}Co_1{-}C_3}$	97.8 (13)	94.1 (10)
$\mathrm{Co_1{-}Co_3{-}C_7}$	96.5 (11)	94.4 (11)
$\mathrm{Co_3{-}Co_2{-}C_6}$	94.9 (12)	93.8 (12)
$\mathrm{Co_2{-}Co_1{-}C_1}$	95.5 (9)	97.9 (10)
	96.9 (5)	96.0 (4)
Av	96.4 (3)	
$\mathrm{Co_1{-}Co_2{-}C_5}$	95.3 (11)	93.7 (15)
$\mathrm{Co_2{-}Co_3{-}C_9}$	93.5 (13)	98.8 (12)
$\mathrm{Co_3{-}Co_1{-}C_2}$	95.9 (12)	94.8 (13)
$\mathrm{Co_1{-}Co_3{-}C_9}$	98.2 (11)	98.8 (12)
$\mathrm{Co_3{-}Co_2{-}C_5}$	100.1 (11)	94.1 (15)
$\mathrm{Co_2{-}Co_1{-}C_2}$	96.9 (13)	101.4 (13)
	96.8 (5)	97.3 (5)
Av	97.1 (3)	

[a] Standard deviations of the last significant figures are given in parentheses. The bond angles are arranged into chemically equivalent sets according to C_{3v} molecular symmetry with the weighted average values (and with standard deviations of the average values in parentheses) given for each of the two independent molecules A and B as well as for both molecules.

10.9% and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100)$ = 9.2% for the observed 1602 reflections. The final value of the error of fit function, $[\Sigma w||F_o|-|F_c||^2/(m-n)]^{1/2}$, was 1.280, and all parameter shifts were less than 0.5 of the corresponding standard deviations. A final total difference Fourier synthesis based on the refined parameters showed no residual peak greater than 1.5 electrons/A^3 or less than −2.0 electrons/A^3 and thereby verified the correctness of the refined structure. In the structure factor calculations, scattering factors of Thomas and Umeda[32] were used for cobalt, those of Dawson[33] were used for sulfur, and those of Berghuis, *et al.*,[34] were used for carbon and oxygen. Anomalous dispersion corrections of the scattering factors were neglected, since they are relatively small for Mo Kα radiation.

Table I gives the final positional and thermal parameters with their standard deviations from the last cycle of isotropic least-squares refinement. The observed and calculated structure factors based on these atomic parameters are listed in Table II. Tables III and IV show the interatomic distances and bond angles, respectively, with their estimated standard deviations obtained by the Busing–Levy program[35] from the full

---

(32) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(33) B. Dawson, *Acta Cryst.*, **13**, 403 (1960).

(34) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(35) W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," Oak Ridge National Laboratory Report 59-12-3 (1959).

inverse matrix (which includes the lattice constant uncertainties). Table V furnishes the nonbonding intramolecular C···C and C···S distances. The "best" weighted least-squares molecular planes formed by certain atoms and the distances of these and other atoms from the planes were calculated with the Smith program.[36]

Table V

Nonbonding Intramolecular Carbon–Carbon and Sulfur–Carbon Distances (A) Corresponding to Edges of Polyhedral Fragment in $SCo_3(CO)_9$

	Molecule A	Molecule B
$C_2 \cdots C_5$	3.02	3.06
$C_5 \cdots C_9$	3.09	3.02
$C_9 \cdots C_2$	3.07	3.05
	Av 3.06	Av 3.04
$C_2 \cdots C_1$	2.70	2.71
$C_2 \cdots C_3$	2.73	2.65
$C_5 \cdots C_6$	2.77	2.85
$C_5 \cdots C_4$	2.79	2.78
$C_9 \cdots C_7$	2.71	2.70
$C_9 \cdots C_8$	2.70	2.66
	Av 2.73	Av 2.73
$C_3 \cdots C_1$	2.83	2.83
$C_4 \cdots C_6$	2.69	2.87
$C_8 \cdots C_7$	2.73	2.73
	Av 2.75	Av 2.81
$C_1 \cdots C_4$	3.11	3.06
$C_6 \cdots C_8$	3.05	3.04
$C_7 \cdots C_3$	3.12	2.91
	Av 3.09	Av 3.00
$S \cdots C_3$	3.16	3.06
$S \cdots C_1$	3.07	3.15
$S \cdots C_4$	3.05	3.03
$S \cdots C_6$	3.08	3.11
$S \cdots C_8$	3.05	3.11
$S \cdots C_7$	3.12	3.05
	Av 3.09	Av 3.09
$C_2 \cdots C_7$	3.95	3.88
$C_2 \cdots C_4$	4.13	4.20
$C_5 \cdots C_1$	4.08	4.01
$C_5 \cdots C_8$	4.36	4.09
$C_9 \cdots C_6$	3.85	4.11
$C_9 \cdots C_3$	4.28	4.12
	Av 4.11	Av 4.07

Discussion

The crystal structure of $SCo_3(CO)_9$ consists of discrete molecules with an *idealized* configuration (shown in Figure 1) of C_{3v}-3m symmetry. This trigonal molecular geometry is in agreement with that proposed by Markó, Bor, and co-workers[13–15] from their infrared carbonyl spectral data. The arrangement of the four molecules in the triclinic unit cell viewed down [100] is shown in Figure 2. Minimum intermolecular distances of 3.1 A for O···O contacts, 3.25 A for C··O contacts, 3.4 A for S···O contacts, and 3.5 A for S···C contacts suggest no abnormal interactions among molecules. The degree of distortion of the two crystallographically independent molecules (A and B) from C_{3v} symmetry is indicated by variations up to 0.3 A in the perpendicular distances of mirror-related carbon and oxygen atoms from the three molecular *vertical* mirror planes, each defined by the sulfur atom, one cobalt atom, and the midpoint of the line joining the other two cobalt atoms. It is presumed that the intermolecular repulsions of neighboring molecules are mainly responsible for the deviations of the atoms from their *idealized* positions. Average values for the bond lengths and angles utilized in this discussion are based on C_{3v} symmetry.

The structure can be considered to arise from the coordination of a $Co_3(CO)_9$ fragment with a sulfur atom in which an octahedral-like orbital of each cobalt atom interacts with a tetrahedral-like sulfur orbital. The fourth localized sulfur orbital located on the threefold axis thereby contains an unshared pair of electrons. The resulting conformation of the triply bridging metal-coordinated sulfur atom is not unlike that of a triply bridging metal-coordinated carbonyl group found by X-ray investigations in $(C_5H_5)_3Ni_3(CO)_2$,[37] $Rh_6(CO)_{16}$,[38] $[C_5H_5FeCO]_4$,[39] and $[Fe_4(CO)_{13}]^{2-}$.[40]

The geometry of $SCo_3(CO)_9$ with the sulfur symmetrically linked to the $Co_3(CO)_9$ moiety is analogous to those of $CH_3CCo_3(CO)_9$[41] and $Ir_4(CO)_{12}$[42] in which an apical CH_3C and $(OC)_3Ir$ group, respectively, is bonded to a basal $M_3(CO)_9$ fragment (where M represents the congener elements Co and Ir).[43] In these three molecular compounds the three carbonyl groups attached to each metal atom are all similarly positioned to allow (in a valence-bond representation) the appropriate localized σ-like orbital of each metal atom to point more nearly at the coordinating apical atom (*viz.*, the S, CCH_3, or $Ir(CO)_3$). In $SCo_3(CO)_9$ the three pairs of equatorial carbonyl groups are each tipped upward from the plane of the three cobalt atoms as shown by an averaged calculated value of 25° (individual esd, 1.2°) for the dihedral angle between the plane defined by a given cobalt atom and its two equatorial carbon atoms and the plane of three cobalt atoms; the corresponding average dihedral angle in $Co_3(CO)_9CCH_3$ is 29°. The average equatorial–equatorial and average axial–equatorial OC–Co–CO angles in $SCo_3(CO)_9$ are both 101° which compare favorably with the corresponding average angles of 97 and 102° in $Co_3(CO)_9CCH_3$. A molecular bonding rationale of these bond angle increases over 90°, as well as a comparison of these angles with those of $M(CO)_3$ groups contained in several other re-

---

[36] D. L. Smith, Ph.D. Thesis, Appendix IV, University of Wisconsin, 1962.

[37] A. A. Hock and O. S. Mills in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 640–648.

[38] E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

[39] M. A. Neuman, L. F. Dahl, and R. B. King, submitted for publication; R. B. King, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, p 22-O.

[40] R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

[41] P. W. Sutton and L. F. Dahl, Abstracts of Papers, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p N-128; *J. Am. Chem. Soc.*, **89**, 261 (1967).

[42] G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, 1965; G. R. Wilkes and L. F. Dahl, submitted for publication.

[43] Since the four $Ir(CO)_3$ groups in $Ir_4(CO)_{12}$ are equivalent, the idealized molecular configuration is cubic T_d rather than trigonal C_{3v} symmetry.

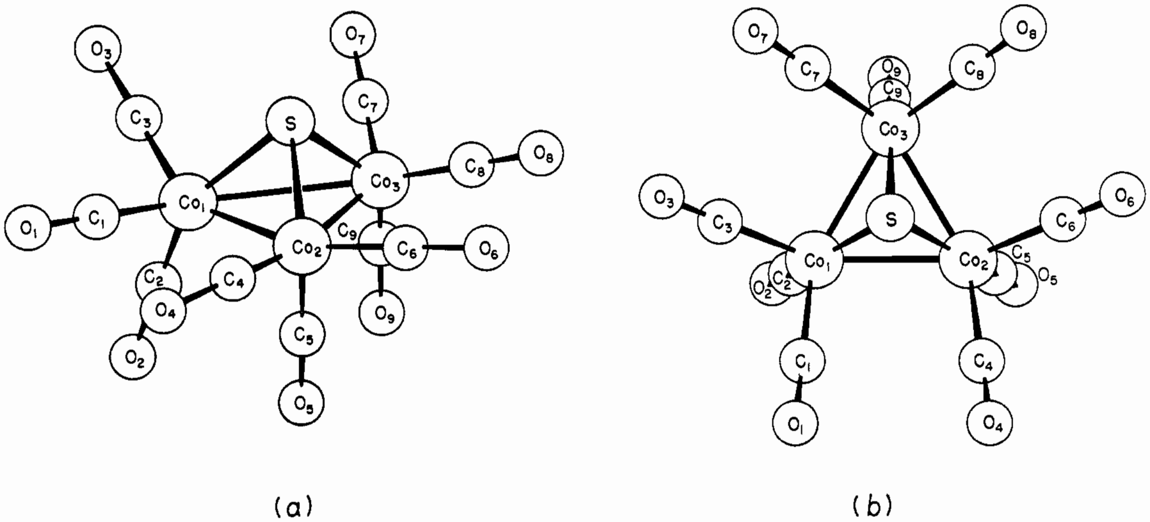

Figure 1.—Idealized molecular configuration of $SCo_3(CO)_9$ corresponding to the trigonal point group C_{3v}-3m. A projection down the principal molecular threefold axis, passing through the sulfur atom and the centroid of the equilateral triangle of basal cobalt atoms, is given in view b which also clearly shows the three equally spaced *vertical* mirror planes.

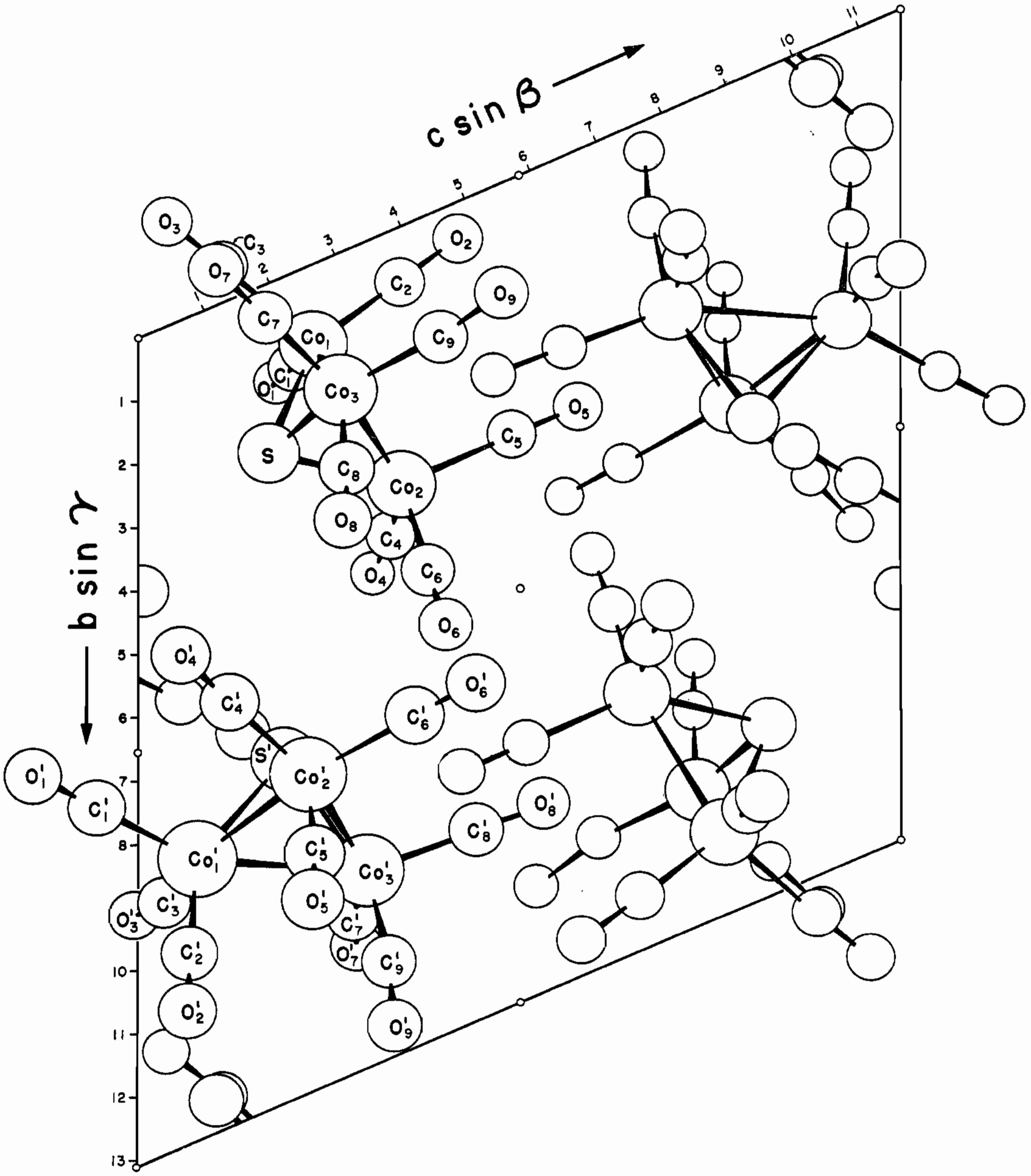

Figure 2.—The packing of the four molecules of $SCo_3(CO)_9$ in the centrosymmetric triclinic unit cell.

lated trinuclear metal carbonyl complexes, is given elsewhere.[41]

The apical group in each of the diamagnetic complexes $Co_3(CO)_9CCH_3$ and $Ir_4(CO)_{12}$ is formally a three-electron donor such that each metal of the $M_3(CO)_9$ fragment achieves a closed-shell electronic configuration, whereas in the paramagnetic complex $SCo_3(CO)_9$ the sulfur effectively contributes *four* electrons to the $Co_3(CO)_9$ fragment such that the entire molecule contains one electron in excess of the "krypton" configuration for each cobalt atom.

A salient structural feature of the SCO_3 fragment of $SCo_3(CO)_9$ is that the average distance of 2.64 A for the Co–Co bonds is longer by 0.1–0.2 A than the Co–Co distances found in $Co_3(CO)_9CCH_3$ (2.46 A) and in other polynuclear cobalt carbonyl complexes.[41] The average Co–S length of 2.14 A is at least 0.1 A shorter than other Co–SR bond lengths in complexes containing triply bridging and/or doubly bridging metal-coordinated mercapto groups[12,20] but agrees closely with Co–S bond lengths in other complexes in which the sulfur is symmetrically coordinated to cobalt atoms.[20]

A preliminary X-ray investigation of the diamagnetic complex $SCo_2Fe(CO)_9$, recently prepared by Khattab, Markó, Bor, and Markó,[15] showed that the crystals of this cobalt–iron complex (in which an iron atom is substituted for one cobalt atom) are isomorphous with those of $SCo_3(CO)_9$. A complete structural determination of this diamagnetic complex is in progress in order to determine the effect of the one unpaired electron on the metal–metal bonds in $SCo_3(CO)_9$. Also, a single-crystal esr study of the paramagnetic $SCo_3(CO)_9$ diluted in the diamagnetic host $SCo_2Fe(CO)_9$ is being carried out in collaboration with Professor John E. Harriman at the University of Wisconsin for the purpose of unraveling the electron density distribution of the unpaired electron. Details of these investigations will be reported in later papers.

Acknowledgments.—This work was made possible through the financial support of the Air Force Office of Air Research and Development Command (518-66). We are especially indebted to Drs. L. Markó and G. Bor for furnishing us with a sample of $SCo_3(CO)_9$ and for their interest in our work. We also are pleased to acknowledge the partial support of NSF and WARF made by the University Research Committee for the use of the CDC 1604 and 3600 computers at the University of Wisconsin Computing Center. Part of the calculations were performed on the IBM 704 computer at the Midwestern Universities Research Association (MURA).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210,
AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Preparation and Structure of $[CH_3SFe_2(CO)_6]_2S$: an Organometallic Complex Containing a Tetrahedral-like Sulfur Atom Coordinated to Four Metal Atoms[1]

BY JUDITH M. COLEMAN,[2a,b] ANDREW WOJCICKI,[2c] PHILIP J. POLLICK,[2c] AND LAWRENCE F. DAHL[2a]

Received October 3, 1966

The reaction of $Fe_3(CO)_{12}$ with methyl thiocyanate has yielded as a condensation by-product the diamagnetic tetramer $[CH_3SFe_2(CO)_6]_2S$. This complex has been characterized by chemical and physical means including a three-dimensional single-crystal X-ray study which not only unambiguously established the actual composition but also revealed the first known example of an organometallic complex containing a tetrahedral-like sulfur atom bridging four metal atoms. The compound crystallizes with two molecules in a triclinic unit cell of symmetry $P\bar{1}$ and of reduced cell parameters $a = 8.93$ A, $b = 9.28$ A, $c = 16.04$ A, $\alpha = 81° 40'$, $\beta = 80° 05'$, and $\gamma = 66° 35'$. A full-matrix, anisotropic–isotropic, least-squares refinement has resulted in discrepancy factors of $R_1 = 9.1\%$ and $R_2 = 9.3\%$. The molecular configuration of approximate C_2-2 symmetry consists of two essentially identical $[CH_3SFe_2(CO)_6]$ fragments bridged by a metal-coordinated tetrahedral-like sulfur atom which donates its *six* valence electrons to the four iron atoms. The properties and structural features are discussed and compared with those of $[C_2H_5SFe(CO)_3]_2$ and other related complexes.

Introduction

The reactions of sulfur and sulfur-containing compounds with metal carbonyls and derivatives have produced a wide variety of unusual organometallic sulfur complexes.[3-11] To date, structural investigations of a number of these compounds have shown sulfur to utilize from one to five of its six valence electrons

---

[1] The structural characterization of this compound represents the VIIth paper concerning systematic structural investigations of organometallic sulfur complexes. For paper VI see: C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

[2] (a) University of Wisconsin; (b) the X-ray work is abstracted in part from the Ph.D. thesis of J. M. Coleman, University of Wisconsin, 1966; (c) The Ohio State University.

[3] S. E. Livingstone, *Quart. Rev.* (London), **19**, 386 (1965), and references contained therein.

[4] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 1663 (1965), and earlier references cited therein.

[5] L. Markó and G. Bor, *J. Organometal. Chem.* (Amsterdam), **3**, 162 (1965), and earlier references cited therein.

[6] F. A. Hartman and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 844 (1966).

[7] M. F. Farona and A. Wojcicki, *Inorg. Chem.*, **4**, 1402 (1965).

[8] M. F. Farona and A. Wojcicki, *ibid.*, **4**, 857 (1965).

[9] P. M. Treichel and G. R. Wilkes, *ibid.*, **5**, 1182 (1966), and references contained therein.

[10] R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *ibid.*, **5**, 892 (1966), and references cited therein.

[11] C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966), and references cited therein.