the protons of the benzene ring. It therefore seemed reasonable to correlate σ_p with *ortho* and *meta* proton shieldings in substituted benzene systems.

It should also be noted that the second *para* group, the $(C_5H_5)_2Ti$ group, is also perturbing and interacting with the delocalized phenyl π electron system. It is interesting to consider the influence of this group relative to the other *para* substituent. The fact that all phenyl proton shifts in this study appear at higher field strength compared to benzene suggests that the $(C_5H_5)_2Ti$ system is releasing electron density to the benzene ring. The following comparisons are of value[28]: (a) The phenyl shift in the xylenes is -7.0 to -7.1 p.p.m., whereas in $Cp_2Ti(p\text{-}CH_3C_6H_4)_2$ it is -6.6 p.p.m.; the methyl resonance in the xylenes is at -2.25 to -2.3 p.p.m., while in the titanocene compound the methyl group is found at -2.18 p.p.m.

(28) Chemical shifts of benzene compounds taken from "Varian NMR Spectra Catalog," Varian Associates, 1962.

(b) In $Cp_2Ti(C_6H_5)_2$, $Cp_2Ti(p\text{-}ClC_6H_4)_2$, and $Cp_2Ti(p\text{-}BrC_6H_4)_2$ the phenyl shift is approximately -6.8 p.p.m., whereas in C_6H_6, C_6H_5Cl, and C_6H_5Br it is about -7.2 to -7.3 p.p.m. (c) In $Cp_2Ti(p\text{-}CH_3OC_6H_4)_2$ the phenyl shift is -6.53 p.p.m. and the CH_3O -3.65 p.p.m. In $C_6H_5OCH_3$ and $CH_3C_6H_4OCH_3$ the phenyl proton shift is -6.9 p.p.m. and the methoxy group appears at -3.75 to -3.78 p.p.m. (d) Finally, in $p\text{-}(CH_3)_2NC_6H_4Br$ the *ortho* and *meta* protons (to $(CH_3)_2N$) are shifted to -6.43 and -7.18 p.p.m., respectively, and the CH_3 shift is found at -2.88 p.p.m. In the related $Cp_2Ti(p\text{-}(CH_3)_2NC_6H_4)_2$ compound the corresponding proton shifts are at -6.32 and -6.62 p.p.m., and the methyl shift at -2.82 p.p.m.

The conclusion drawn from these facts is that $(C_5H_5)_2Ti$ as a *para* substituent on the benzene ring is more electron-releasing than the second *para* substituent and may be considered approximately as electron-donating as a dimethylamino substituent.

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The Crystal Structure of Ditechnetium Decacarbonyl[1]

By MARCIA F. BAILEY[2] and LAWRENCE F. DAHL[3]

A three-dimensional single crystal X-ray analysis of $Tc_2(CO)_{10}$ has made possible a detailed comparison of the molecular features of $Tc_2(CO)_{10}$ and $Mn_2(CO)_{10}$. These two compounds and $Re_2(CO)_{10}$ are isomorphous and consist of dimeric molecules of approximately D_{4d} symmetry in which each metal atom is octahedrally coordinated to five carbonyl groups and the other metal atom such that the equatorial carbons are arranged in a staggered configuration. Crystals of $Tc_2(CO)_{10}$ contain four dimeric molecules in a monoclinic unit cell of symmetry I2/a and of dimensions $a = 14.65 \pm 0.03$ Å., $b = 7.18 \pm 0.02$ Å., $c = 14.93 \pm 0.03$ Å., and $\beta = 105.6 \pm 0.1°$. Anisotropic refinement of all atoms has resulted in final discrepancy factors of $R_1 = 6.9\%$ and $R_2 = 7.4\%$ for 1296 observed reflections. The observed Tc–Tc bond distance is 3.036 ± 0.006 Å. compared to a Mn–Mn distance of 2.923 ± 0.003 Å. in $Mn_2(CO)_{10}$ and a Re–Re distance of 3.02 ± 0.01 Å. in $Re_2(CO)_{10}$. All of the carbonyl groups are less strongly bonded to the metal in $Tc_2(CO)_{10}$ than in $Mn_2(CO)_{10}$, as evidenced by longer Tc–C bond distances (Tc–C 1.98 Å. (av.) *vs.* Mn–C 1.83 Å. (av.)). The average Tc–C bond distance of the four equatorial carbonyls is significantly greater (by 0.10 Å.) than the Tc–C_1 bond distance of the apical carbonyl; however, the average equatorial C–O bond distance of 1.12 Å. is significantly less than the apical C_1–O_1 distance of 1.21 Å., so that all nonbonding Tc $\cdots$ O distances are equal within the estimated error. The four equatorial carbonyl groups attached to each technetium are bent away from the apical carbonyl toward the other half of the dimer.

Introduction

Two-dimensional X-ray analyses of the isomorphous compounds $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ first established the molecular configuration of these two metal carbonyls.[4] A subsequent three-dimensional X-ray analysis of $Mn_2(CO)_{10}$,[5] which included anisotropic least-squares refinement, gave additional information concerning the crystallographic and molecular features

(1) Based in part on a dissertation submitted by M. F. Bailey to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
(2) National Science Foundation Predoctoral Fellow, 1962–1964.
(3) Alfred P. Sloan Fellow, 1963–1965.
(4) L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, **26**, 1750 (1957).
(5) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

of this compound. A three-dimensional investigation of $Re_2(CO)_{10}$ was not carried out, however, due to the large scattering power and high linear absorption of the rhenium atoms which would result in relatively inaccurate carbon and oxygen positional parameters. The later synthesis of $Tc_2(CO)_{10}$[6] provided an excellent opportunity for a detailed comparison of its molecular parameters with those of $Mn_2(CO)_{10}$, since the congener element, technetium, provides a relatively small percentage of the scattering power in $Tc_2(CO)_{10}$ and since absorption is much lower in $Tc_2(CO)_{10}$ than in $Re_2(CO)_{10}$. A preliminary X-ray study of $Tc_2(CO)_{10}$[7] indicated that

(6) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *J. Am. Chem. Soc.*, **83**, 2953 (1961).
(7) D. Wallach, *Acta Cryst.*, **15**, 1058 (1962).

it is isomorphous with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Our three-dimensional single crystal analysis of Tc_2-$(CO)_{10}$ has confirmed this basic isomorphism and has shown some significant differences between the manganese and technetium carbonyls.

Experimental

Pale yellow crystals of $Tc_2(CO)_{10}$ were generously supplied to us by Professor H. D. Kaesz of the University of California at Los Angeles. Two crystals, each approximately cubic in shape and about 0.024 cm. on a side, were used to obtain intensity data. Each crystal was mounted in a thin-walled glass capillary which was subsequently evacuated, filled with argon, and hermetically sealed; during 6 weeks of exposure to the X-ray beam neither crystal showed any decomposition. The lattice constants a, b, and c were determined from $hk0$ and $0kl$ precession photographs which were calibrated by superimposing a zero-level NaCl exposure on the same film; the β angle was obtained from an $h0l$ Weissenberg photograph.

Multiple-film equi-inclination Weissenberg data about the b and c axes (viz., $h0l$–$h7l$ and $hk0$–$hk10$) were obtained with zirconium-filtered Mo $K\alpha$ radiation. The intensities were estimated by comparison with a calibrated standard set of intensities prepared from the same crystal. After Lorentz-polarization and spot extension[8] corrections, the 1050 and 862 Weissenberg reflections collected about the b and c rotation axes, respectively, were correlated via least squares[9] to give a total of 1296 independent reflections on a common scale; the weighted reliability index for the least-squares merging was 4.1%. Extinction corrections were not made and absorption was neglected due to the low absorption coefficient of $Tc_2(CO)_{10}$ for Mo $K\alpha$ radiation ($\mu = 18.4$ cm.$^{-1}$; $\mu R_{max} < 0.4$). The standard deviations of the structure amplitudes were assigned as[10] $\sigma(F_o(hkl)) = F_o(hkl)/20$ if $I_0(hkl) \geqslant \sqrt{10}I_{min}$, $\sigma(F_o(hkl)) = F_o(hkl)/20[\sqrt{10}I_{min}/I_0(hkl)]^2$ if $I_0(hkl) < \sqrt{10}I_{min}$.

Crystal Data

The unit cell of $Tc_2(CO)_{10}$ is monoclinic with $a = 14.65 \pm 0.03$ Å., $b = 7.18 \pm 0.02$ Å., $c = 14.93 \pm 0.03$ Å., and $\beta = 105.6 \pm 0.1°$. Four dimeric molecules per unit cell give a calculated density of 2.10 g./cc. which compares well with the observed density[7] of 2.11 g./cc. Our lattice parameters are in reasonable agreement with those reported by Wallach[7]: $a = 14.73 \pm 0.05$ Å., $b = 7.22 \pm 0.02$ Å., $c = 14.90 \pm 0.02$ Å., and $\beta = 104.6 \pm 0.1°$. The estimated error in the β angle obtained by Wallach is probably too low,

(8) D. C. Philipps, *Acta Cryst.*, **7**, 746 (1954).

(9) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC 1604," University of Wisconsin, 1963.

(10) D. L. Smith, "DACOR- A Data Reduction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

TABLE I
FINAL POSITIONAL PARAMETERS WITH STANDARD DEVIATIONS FROM ANISOTROPIC LEAST-SQUARES REFINEMENT

Atom	x	10^3 $\sigma(x)$	y	10^3 $\sigma(y)$	z	10^3 $\sigma(z)$
Tc	0.1530	0.04	0.2302	0.09	0.9306	0.05
C_1	0.0339	0.7	0.2375	1.2	0.8399	0.9
O_1	0.9620	0.8	0.2438	1.8	0.7775	1.1
C_2	0.1061	0.6	0.3419	1.4	0.0313	0.8
O_2	0.0784	0.5	0.3989	1.2	0.0904	0.6
C_3	0.2220	0.7	0.1096	1.2	0.8451	0.8
O_3	0.2586	0.6	0.0423	1.1	0.7979	0.7
C_4	0.1273	0.6	−0.0192	1.4	0.9760	0.8
O_4	0.1087	0.5	0.8435	1.1	0.0027	0.7
C_5	0.1894	0.6	0.4834	1.3	0.8949	0.7
O_5	0.2088	0.5	0.6270	0.9	0.8781	0.5

as he did not determine the β angle directly from a $h0l$ Weissenberg or precession photograph.

Systematic absences of $h + k + l = 2n + 1$ for $\{hkl\}$ data and $h = 2n + 1$ for $\{h0l\}$ data indicate the probable space group to be either Ia or I2/a. The centrosymmetric space group, I2/a, which requires the molecule to lie on either a center of symmetry or a twofold rotation axis, was confirmed by the structural refinement.

Solution of Structure

An interpretation of a three-dimensional Patterson function yielded the fractional values of $x = 0.153$, $y = 0.240$, $z = 0.930$ for the one independent technetium atom. The coordinates of the other ten independent atoms (i.e., five carbonyl groups) were ob-

TABLE II
FINAL ANISOTROPIC TEMPERATURE COEFFICIENTS ($\times 10^4$)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tc	35.6 ± 0.3	171 ± 2	38.3 ± 0.5	3.2 ± 0.5	4.2 ± 0.2	-20.7 ± 0.7
C_1	55 ± 5	262 ± 24	76 ± 8	16 ± 8	2 ± 5	-28 ± 11
O_1	85 ± 7	838 ± 62	135 ± 12	21 ± 12	-52 ± 7	-85 ± 16
C_2	52 ± 5	215 ± 19	47 ± 6	-4 ± 8	-1 ± 4	-10 ± 10
O_2	64 ± 4	371 ± 22	71 ± 6	12 ± 7	31 ± 4	-60 ± 9
C_3	67 ± 6	172 ± 18	49 ± 7	4 ± 8	13 ± 5	17 ± 9
O_3	114 ± 6	286 ± 19	62 ± 6	51 ± 8	49 ± 5	-6 ± 9
C_4	49 ± 5	238 ± 21	69 ± 8	-12 ± 8	23 ± 5	-12 ± 11
O_4	82 ± 5	238 ± 16	109 ± 7	-35 ± 7	45 ± 5	10 ± 10
C_5	53 ± 5	206 ± 19	34 ± 6	16 ± 7	6 ± 4	-19 ± 9
O_5	97 ± 5	184 ± 16	52 ± 5	8 ± 7	9 ± 4	9 ± 7

tained from a three-dimensional electron density map phased on the technetium atoms. A three-dimensional isotropic least-squares refinement of these eleven atoms resulted in discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 10.9\%$, and $R_2 = [\Sigma w||F_o| - |F_c||^2/(\Sigma w|F_o|^2)]^{1/2} \times 100 = 13.0\%$.

To obtain more reliable positional parameters, an anisotropic least-squares refinement then was undertaken. Individual atom temperature factors of the form $\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13} \cdot hl + 2B_{23}kl]\}$ were used. After four cycles all coordinate shifts were less than 10% of their individual standard deviations, and the discrepancy factors were $R_1 = 6.9$ and $R_2 = 7.4\%$. The final positional and temperature parameters obtained in this anisotropic refinement are given in Tables I and II. In Tables III the observed

TABLE III

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS FROM THE FINAL ANISOTROPIC REFINEMENT

H	K	L	FO	FC
0	2	0	260.9	-249.7
0	4	0	149.5	138.2
0	6	0	70.1	-67.0
0	8	0	42.0	43.0
1	3	0	150.3	141.3
1	5	0	127.9	-121.9
1	7	0	38.2	39.4
2	2	0	45.6	-31.3
2	4	0	32.8	-35.8
2	6	0	19.0	21.0
2	8	0	15.0	-15.5
3	1	0	84.8	-73.8
3	3	0	57.7	54.6
3	7	0	20.4	21.3
4	0	0	189.1	-198.8
4	2	0	175.5	173.0
4	4	0	88.8	-96.3
4	6	0	32.2	34.0
4	8	0	16.5	-17.0
5	1	0	218.6	224.4
5	3	0	205.1	-209.4
5	5	0	85.9	85.7
5	7	0	44.5	-43.0
6	0	0	132.9	126.9
6	2	0	199.4	-187.9
6	4	0	132.6	142.2
6	6	0	57.8	-57.6
6	8	0	20.4	22.1
7	1	0	76.1	-75.0
7	3	0	77.6	80.0
7	5	0	39.5	-42.1
7	7	0	20.3	16.6
8	0	0	41.3	38.7
8	2	0	22.2	-21.7
8	4	0	20.3	20.4
9	1	0	107.0	-109.8
9	3	0	93.6	93.8
9	5	0	49.2	-48.9
9	7	0	24.4	26.8
10	0	0	129.3	-130.5
10	2	0	136.5	135.7
10	4	0	107.0	-105.3
10	6	0	52.6	53.7
10	8	0	15.7	-15.4
11	1	0	124.6	127.0
11	3	0	83.3	-79.3
11	5	0	53.2	52.8
11	7	0	22.6	-24.7
12	0	0	39.4	39.5
12	2	0	41.9	-44.5
12	4	0	33.2	31.6
12	6	0	21.0	-22.8
14	0	0	44.1	45.8
14	2	0	37.6	-41.3
14	4	0	25.1	26.4
14	6	0	18.7	-21.2
15	1	0	71.4	-74.3
15	3	0	57.1	53.8
15	5	0	34.2	-33.2
15	7	0	16.8	17.8
16	0	0	63.1	-63.4
16	2	0	59.8	64.8
16	4	0	31.5	-33.5
16	6	0	23.1	25.1
17	1	0	28.4	33.1
17	3	0	23.2	-26.2
17	5	0	16.3	16.5
19	1	0	16.0	21.5
19	3	0	16.5	-18.2
20	0	0	28.6	29.0
20	2	0	25.8	-28.7
21	1	0	20.7	-25.4
21	3	0	18.9	20.9
0	3	1	72.0	-62.0
0	5	1	94.9	92.0
0	7	1	51.6	-58.0
0	9	1	24.5	30.8
1	2	1	25.5	18.7
1	2	-1	126.5	-93.1
1	4	1	32.0	29.8
1	4	-1	86.9	78.7
1	6	1	30.6	-31.3
1	6	-1	50.2	-54.8
1	8	1	26.2	28.9
1	8	-1	47.9	55.3
1	10	-1	21.5	-25.5
2	3	1	21.1	-20.1
2	3	-1	64.8	58.8
2	5	1	10.7	10.0
2	5	-1	43.2	-41.9
2	7	-1	44.4	47.7
3	2	1	74.4	67.4
3	2	-1	201.2	159.5
3	4	1	52.7	50.3
3	4	-1	20.3	-17.9
3	6	1	41.7	-43.4
3	6	-1	14.3	-17.5
3	8	1	30.7	34.4
4	1	-1	90.5	-81.8
4	3	1	67.0	64.3
4	3	-1	33.1	33.9
4	5	1	78.2	-81.1
4	5	-1	42.8	-44.5
4	7	1	43.9	48.7
4	7	-1	12.3	15.4
4	9	1	26.4	-29.6
5	2	1	49.3	44.0
5	2	-1	20.1	20.7
5	4	1	73.7	-74.7
5	4	-1	60.2	-58.3
5	6	1	42.0	45.0
5	6	-1	54.8	60.4
5	8	1	40.0	-45.0
5	8	-1	34.0	-36.9
5	10	1	18.4	20.1
6	1	-1	54.7	49.1
6	3	1	59.9	-52.5
6	3	-1	74.8	-71.1
6	5	1	28.8	30.1
6	5	-1	66.6	64.4
6	7	1	35.2	-35.4
6	7	-1	44.0	-48.4
6	9	1	14.9	16.8
6	9	-1	24.1	26.7
7	2	1	67.8	-63.1
7	2	-1	40.6	-41.5
7	4	1	16.4	15.9
7	4	-1	67.5	66.6
7	6	1	14.1	15.3
7	6	-1	44.8	-47.3
7	8	-1	17.9	22.2
8	1	1	56.3	55.2
8	1	-1	50.2	47.2
8	3	1	19.6	-18.4
8	3	-1	19.5	18.4
8	5	1	46.8	42.0
8	7	1	16.7	-20.5
8	7	-1	17.0	14.7
9	2	1	35.6	-35.3
9	2	-1	35.8	-37.4
9	4	1	47.7	46.1
9	4	-1	20.8	21.1
9	6	1	47.5	-49.0
9	8	1	26.4	28.6
10	1	1	34.5	-31.4
10	1	-1	31.4	-30.3
10	3	1	40.8	40.8
10	3	-1	32.2	31.7
10	5	1	42.4	-43.8
10	5	-1	49.7	-48.0
10	7	1	29.6	32.6
10	7	-1	23.5	28.7
10	9	1	15.9	-19.1
11	2	1	17.4	18.0
11	2	-1	34.7	33.4
11	4	1	31.2	-31.3
11	4	-1	51.0	-52.5
11	6	1	26.1	28.1
11	6	-1	37.8	40.6
11	8	-1	18.9	-22.1
12	1	1	14.5	-13.0
12	3	-1	26.3	-26.0
12	5	-1	25.4	26.7
12	7	-1	21.3	-20.5
13	2	1	21.9	22.5
13	4	1	15.6	-16.6
14	1	1	15.4	14.4
14	3	1	22.8	-22.4
14	5	1	25.9	27.7
14	7	1	18.0	-19.3
15	2	1	19.4	-20.6
15	2	-1	18.6	-19.0
15	4	1	26.7	27.5
15	4	-1	19.8	22.4
15	6	1	19.5	-23.5
15	6	-1	17.4	-19.8
16	3	-1	19.4	20.7
16	5	-1	17.2	-21.1
0	2	2	159.7	-142.0
0	4	2	65.2	65.9
0	6	2	22.8	-23.0
0	8	2	19.3	17.6
1	3	-2	288.0	277.2
1	5	2	12.5	14.8
1	5	-2	115.5	-114.9
1	7	-2	52.2	50.5
2	2	2	44.4	-45.8
2	2	-2	306.7	286.1
2	4	2	67.5	73.3
2	4	-2	190.0	-181.7
2	6	2	33.4	-35.0
2	6	-2	68.6	70.6
2	8	2	21.8	21.1
2	8	-2	35.2	-35.7
3	1	2	240.2	-231.1
3	1	-2	86.7	83.7
3	3	2	135.1	143.1
3	3	-2	125.8	-124.1
3	5	2	95.7	-107.4
3	5	-2	56.4	58.9
3	7	2	39.9	40.2
3	7	-2	26.0	-25.6
4	0	2	399.1	-526.1
4	0	-2	65.9	-64.2
4	2	2	202.5	180.8
4	2	-2	28.6	26.3
4	4	2	106.3	-109.4
4	4	-2	29.4	-28.6
4	6	2	49.1	52.2
4	6	-2	16.7	-11.9
4	8	2	35.3	-34.0
5	1	2	174.2	164.7
5	1	-2	92.6	95.5
5	3	2	104.1	-105.0
5	3	-2	88.0	-90.6
5	5	2	78.1	79.5
5	5	-2	47.7	49.5
5	7	2	32.3	-29.5
5	7	-2	22.8	-24.0
6	0	2	78.1	75.6
6	0	-2	132.4	135.9
6	2	2	12.8	-11.2
6	2	-2	153.5	-151.5
6	4	2	27.3	25.8
6	4	-2	140.6	151.1
6	6	2	14.1	-12.9
6	6	-2	60.5	-62.6
7	1	2	79.0	76.1
7	1	-2	234.8	-249.3
7	3	2	53.0	-51.7
7	3	-2	121.8	122.7
7	5	2	23.4	25.6
7	5	-2	82.7	-84.1
7	7	2	21.9	-22.0
7	7	-2	35.9	35.5
8	0	2	161.9	171.8
8	0	-2	101.9	-110.7
8	2	2	156.1	-151.6
8	2	-2	100.1	98.1
8	4	2	102.6	100.2
8	4	-2	86.8	-87.9
8	6	2	41.6	-41.6
8	6	-2	51.5	51.5
8	8	2	15.9	15.4
9	1	2	165.1	-163.3
9	1	-2	32.2	30.7
9	3	2	130.9	130.9
9	5	2	65.8	-64.7
9	5	-2	20.5	21.7
9	7	2	32.1	31.4
10	0	2	60.7	-56.8
10	0	-2	62.5	-63.3
10	2	2	82.5	83.9
10	2	-2	62.0	64.1
10	4	2	80.0	-75.1
10	4	-2	33.1	-34.0
10	6	2	32.5	33.5
10	6	-2	30.5	31.0
11	1	2	20.8	20.9
11	1	-2	129.5	136.8
11	3	2	19.9	-21.6
11	3	-2	92.3	-89.6
11	5	2	18.0	16.9
11	5	-2	51.2	49.3
11	7	-2	28.1	-30.8
12	0	2	28.8	-29.5
12	0	-2	106.0	108.2
12	2	2	25.1	25.5
12	2	-2	119.9	-120.6
12	4	2	16.2	-16.5
12	4	-2	58.1	57.8
12	6	-2	42.1	-45.3
13	1	2	64.1	67.0
13	1	-2	65.7	-67.4
13	3	2	59.5	-58.6
13	3	-2	54.5	55.3
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13	5	-2	30.4	-31.5
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14	0	2	76.2	77.3
14	2	2	80.8	-80.0
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14	4	2	55.4	54.1
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15	1	2	59.5	-61.4
15	1	-2	23.2	-25.6
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15	3	-2	20.5	22.1
15	5	2	27.0	-29.8
16	0	-2	52.7	-51.2
16	2	2	16.9	20.4
16	2	-2	49.4	52.3
16	4	-2	30.0	-32.0
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17	3	-2	42.5	-48.0
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18	0	2	31.3	-31.5
18	0	-2	36.1	40.3
18	2	2	24.5	28.5
18	2	-2	35.0	-39.5
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18	4	-2	19.3	22.9
19	1	2	37.0	35.2
19	3	2	26.7	-27.2
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20	2	2	22.8	-25.8
21	1	-2	17.5	-23.3
22	0	-2	21.0	-23.9
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1	4	-3	73.2	75.3
1	6	-3	53.0	-56.2
1	8	-3	33.1	41.0
2	1	3	80.2	73.6
2	3	3	54.2	-54.2
2	3	-3	115.3	107.9
2	5	3	45.5	45.7
2	5	-3	71.4	-81.1
2	7	3	44.4	-47.6
2	7	-3	49.8	57.3
2	9	3	22.0	23.6
2	9	-3	26.8	-31.7
3	2	3	88.9	-82.7
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3	6	3	48.2	-49.6
3	6	-3	45.7	48.6
3	8	3	45.6	49.5
3	8	-3	27.9	-31.0
4	1	3	24.4	-22.4
4	1	-3	144.8	-140.1
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4	3	-3	26.4	-25.2
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4	7	3	45.8	50.3
4	7	-3	25.2	-25.1
4	9	3	25.2	-25.0
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5	2	-3	37.1	35.6
5	4	3	19.4	-19.4
5	6	3	14.8	17.9
5	6	-3	19.6	20.6
6	1	3	12.3	-8.8
6	1	-3	82.3	79.8
6	3	-3	28.0	-26.0
6	5	3	19.6	-16.8
6	5	-3	61.0	60.3
6	7	-3	25.6	-29.9
6	9	-3	18.6	23.0
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7	2	-3	48.3	-46.1
7	4	3	47.0	-46.5
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7	6	-3	58.2	-63.2
7	8	3	28.3	-30.6
7	8	-3	24.0	27.5
7	10	-3	19.3	-18.0
8	1	-3	11.3	-14.6
8	3	3	48.9	-45.5
8	3	-3	43.5	41.7
8	5	3	59.5	58.5
8	5	-3	47.4	-48.5
8	7	3	33.3	-38.4
8	7	-3	29.6	35.0
8	9	3	21.4	23.9
8	9	-3	18.2	-24.8
9	2	3	21.0	-20.3
9	4	3	47.6	45.6
9	6	3	29.8	-32.6
9	6	-3	30.2	31.1
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11	2	-3	40.5	41.1
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11	6	-3	19.1	26.5
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14	7	3	19.6	-18.6
17	4	-3	16.7	-16.3
17	6	-3	18.8	21.0
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0	6	4	35.9	34.3
0	8	4	24.5	-20.4
1	1	4	113.6	122.6
1	1	-4	20.8	-22.0
1	3	4	129.1	-134.6
1	3	-4	64.9	71.3
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1	5	-4	29.8	-27.8
1	7	4	34.1	-31.2
2	0	4	248.3	308.5
2	0	-4	136.6	-143.5
2	2	4	178.1	-203.8
2	2	-4	153.9	174.7
2	4	4	126.1	139.4
2	4	-4	175.4	-170.2
2	6	4	60.0	-58.5
2	6	-4	56.9	60.7
2	8	4	40.9	34.4
2	8	-4	18.7	-13.8
3	1	4	175.2	-176.6
3	3	4	173.6	181.1
3	3	-4	168.0	-181.1
3	5	4	94.2	-98.3
3	5	-4	102.8	110.4
3	7	4	39.8	37.0
3	7	-4	40.5	-45.6
4	0	4	188.5	-211.1
4	0	-4	144.8	164.6
4	2	4	86.3	85.7
4	2	-4	142.4	-141.7
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4	4	-4	119.4	129.9
4	6	4	19.3	18.0
4	6	-4	66.3	-70.9
4	8	4	19.3	-14.2
4	8	-4	20.6	19.4
5	1	4	18.5	13.2
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5	5	-4	41.3	-36.2
6	0	4	123.9	-129.4
6	0	-4	52.0	53.0
6	2	4	97.1	98.6
6	2	-4	60.6	-63.3
6	4	4	83.7	-82.4
6	4	-4	34.8	31.4
6	6	4	39.1	38.1
6	6	-4	29.1	-29.7
6	8	4	19.8	-20.0
7	1	4	181.8	190.8
7	1	-4	154.0	-173.8
7	3	4	128.1	-132.4
7	3	-4	85.3	89.4
7	5	4	78.5	78.1
7	5	-4	48.4	-43.7
7	7	4	43.2	-37.0
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8	0	4	186.5	211.1
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8	2	4	115.8	-115.5
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8	4	-4	91.4	-90.3
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8	6	-4	64.8	63.2
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10	4	-4	27.8	28.8
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12	4	-4	50.3	49.2
12	6	4	32.4	27.8
12	6	-4	32.6	-27.7
13	1	4	87.4	87.9
13	1	-4	93.8	-99.2
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14	4	4	40.7	35.6
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16	2	-4	23.4	10.3
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19	1	4	23.7	22.3
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23	1	-4	27.8	17.8
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12	2	-16	33.1	-33.4
1	1	18	25.8	25.0
1	3	18	30.5	-21.3
2	0	18	32.2	34.7
2	0	-18	42.3	-44.2
2	2	18	31.3	-30.8
2	2	-18	34.1	37.3
3	1	18	33.0	-34.0
3	1	-18	41.6	43.1
3	3	18	36.2	33.0
3	3	-18	35.0	-37.0
4	0	-18	27.2	29.7
4	2	-18	28.7	-30.4
6	0	-18	31.1	30.2
7	1	-18	39.5	-41.1
8	0	-18	37.3	-43.3
8	2	-18	24.3	30.3
9	1	-18	26.0	26.2
13	1	-18	26.8	-27.5
4	0	-20	31.4	36.7

and calculated structure factors are listed from the last least-squares cycle.

The Sly–Shoemaker Fourier program[11] was used for the Patterson and Fourier syntheses, and the Busing–Martin–Levy full-matrix least-squares program[12] was employed for the least-squares refinements. Intramolecular bond lengths and angles were calculated from the positional parameters of the last anisotropic least-squares cycle with the Busing–Martin–Levy ORFFE program[13] for which errors are obtained from the full inverse matrix. The bond lengths and angles obtained for $Tc_2(CO)_{10}$ are compared with those found for $Mn_2(CO)_{10}$[5] in Tables IV and V, respectively.

TABLE IV
COMPARISON OF BOND DISTANCES[a] IN $Tc_2(CO)_{10}$ AND $Mn_2(CO)_{10}$[5]

| | $Tc_2(CO)_{10}$ | | $Mn_2(CO)_{10}$[5] | |
| | Distance, | | Distance, | |
Atoms	Å.	σ, Å.	Å.	σ, Å.
M–M	3.036	0.006	2.923	0.003
M–C$_1$	1.899	0.011	1.792	0.014
M–C$_2$	1.983	0.013	1.855	0.015
M–C$_3$	2.023	0.012	1.830	0.016
M–C$_4$	1.986	0.011	1.811	0.016
M–C$_5$	2.006	0.011	1.826	0.014
C$_1$–O$_1$	1.205	0.013	1.151	0.016
C$_2$–O$_2$	1.141	0.011	1.147	0.015
C$_3$–O$_3$	1.104	0.012	1.160	0.017
C$_4$–O$_4$	1.124	0.012	1.156	0.016
C$_5$–O$_5$	1.116	0.011	1.166	0.016

[a] The distances in both compounds are based on the final positional parameters from anisotropic refinements and are uncorrected for thermal motion.

TABLE V
COMPARISON OF BOND ANGLES IN $Tc_2(CO)_{10}$ AND $Mn_2(CO)_{10}$[5]

| | $Tc_2(CO)_{10}$ | | $Mn_2(CO)_{10}$[5] | |
Atoms	Angle, deg.	σ, deg.	Angle, deg.	σ, deg.
M–C$_1$–O$_1$	175.1	1.4	177.0	1.6
M–C$_2$–O$_2$	177.1	1.0	178.2	1.1
M–C$_3$–O$_3$	179.0	0.9	177.8	1.3
M–C$_4$–O$_4$	176.4	0.9	175.5	1.2
M–C$_5$–O$_5$	177.3	0.9	177.8	1.3
C$_1$–M–C$_2$	95.2	0.5	96.1	0.6
C$_1$–M–C$_3$	94.7	0.5	93.8	0.6
C$_1$–M–C$_4$	92.7	0.4	93.0	0.7
C$_1$–M–C$_5$	92.6	0.4	92.3	0.7
C$_2$–M–C$_3$	170.1	0.4	170.1	0.5
C$_2$–M–C$_4$	88.3	0.5	88.9	0.6
C$_2$–M–C$_5$	90.3	0.4	88.9	0.6
C$_3$–M–C$_4$	90.1	0.4	89.7	0.6
C$_3$–M–C$_5$	90.4	0.4	91.6	0.6
C$_4$–M–C$_5$	174.7	0.3	174.5	0.6
C$_1$–M–M'	177.3	0.4	177.3	0.5
C$_2$–M–M'	86.2	0.3	85.5	0.4
C$_3$–M–M'	84.0	0.3	84.6	0.4
C$_4$–M–M'	89.7	0.3	89.2	0.4
C$_5$–M–M'	85.1	0.3	85.7	0.4

Analysis of Anisotropic Thermal Motion

The thermal anisotropy of the atoms in crystalline

(11) W. G. Sly and D. P. Shoemaker, "Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer," MIFR1 (1960).

(12) W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program," ORNL-TM-305, Oak Ridge National Laboratory (1963).

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

$Tc_2(CO)_{10}$ may be indicated qualitatively by analysis of the B_{ij} coefficients. The anisotropic character observed in all of the atoms of $Tc_2(CO)_{10}$ is a maximum for the oxygen atoms, with an average thermal displacement of 0.34 ± 0.03 Å. for the oxygen atoms in directions perpendicular to the corresponding Tc–C bonds compared to an average thermal displacement of 0.21 ± 0.01 Å. along the Tc–C bonds. Two models (A and B) were applied in order to calculate bond distances averaged over thermal motion. In model A the carbon atoms are assumed to ride on the technetium atom and the oxygen atoms to ride on the corresponding carbon atoms, whereas in model B all atoms are assumed to move independently. On comparison with the uncorrected intramolecular distances given in Table IV, model A leads to an increase of 2σ in the Tc–C$_1$ distance and an average increase of $\sigma/2$ in the other four Tc–C distances, while the apical C$_1$–O$_1$ distance increases by 9σ and the four equatorial C–O distances increase by 3–4σ. For model B the increases in the Tc–C$_1$ distance and the four equatorial Tc–C distances are 6σ and 3–4σ, respectively, and the increases in the C$_1$–O$_1$ and the equatorial C–O distances are 17σ and 10–12σ, respectively. The above standard deviations vary from 0.011 to 0.014 Å., as given in Table IV. As in $Mn_2(CO)_{10}$,[5] it is felt that neither of these thermal models (A or B) adequately represents the physical situation in $Tc_2(CO)_{10}$, and the preferred distances are those with no thermal correction (Table IV).

Discussion

In the solid state $Tc_2(CO)_{10}$ is essentially isomorphous with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The dimeric molecules, located on a crystallographic twofold axis perpendicular to the Tc–Tc bond, ideally possess D_{4d} symmetry with octahedral coordination about each technetium atom such that the two sets of four equatorial carbonyls are in a staggered configuration (Figure 1).

The anisotropically refined Tc–Tc bond distance, 3.036 ± 0.006 Å., is 0.11 Å. greater than the Mn–Mn distance of 2.923 ± 0.003 Å. obtained in a similar refinement of $Mn_2(CO)_{10}$,[5] and is 0.02 Å. greater than the Re–Re distance of 3.02 ± 0.01 Å. obtained in a two-dimensional X-ray analysis of $Re_2(CO)_{10}$.[4] Thus, in $Tc_2(CO)_{10}$ the effective single bond radius of the technetium atom is 0.06 Å. greater than that of the manganese atom in $Mn_2(CO)_{10}$ and within the estimated error is equal to the single bond radius of rhenium in $Re_2(CO)_{10}$. Noteworthy is that a much shorter Tc–Tc distance of 2.13 ± 0.01 Å. has been reported for the $Tc_2Cl_8^{-3}$ ion which no doubt arises from a multiple bond between the two metal atoms.[14]

A comparison of the metal–carbon distances in $Tc_2(CO)_{10}$ with those in $Mn_2(CO)_{10}$ (Table IV) shows that the apical Tc–C$_1$ distance (1.90 Å.) is 0.11 Å. longer than the apical Mn–C$_1$ distance (1.79 Å.), and the average equatorial Tc–C distance (2.00 Å.) is 0.17 Å. greater than the average equatorial Mn–C distance

(14) F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).
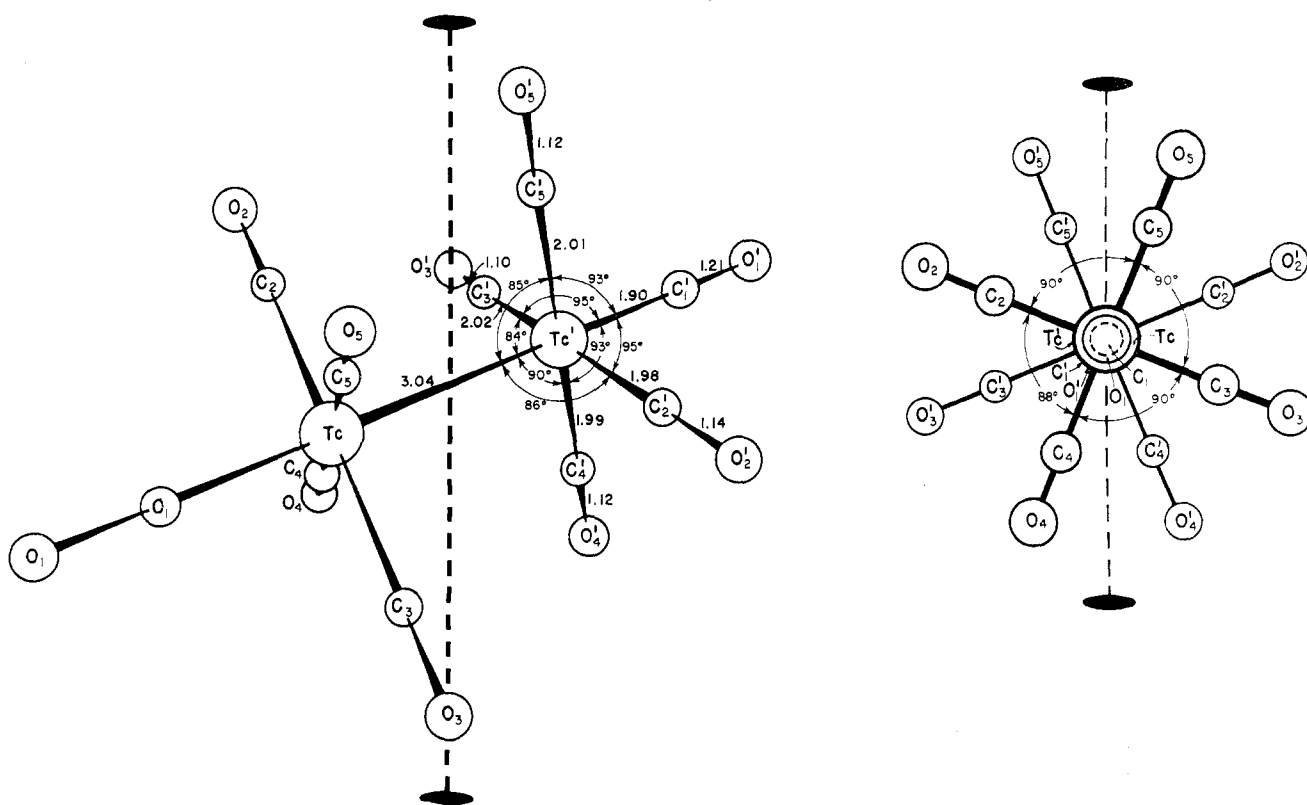
Figure 1.—Two views of the molecular configuration of $Tc_2(CO)_{10}$. Bond distances and angles are uncorrected for thermal motion.

(1.83 Å.). Since only 0.06 Å. of this increase in metal–carbon bond length can be attributed to the larger covalent radius of technetium (see above), it is concluded that the metal to carbonyl bonds are weaker in $Tc_2(CO)_{10}$ than in $Mn_2(CO)_{10}$. This result is consistent with the observed relative ease of cleavage of carbonyl groups in $M_2(CO)_{10}$ in the order $M = Tc > (Re >) Mn$.[15]

A further examination of the metal–carbon and carbon–oxygen bond distances in $Tc_2(CO)_{10}$ reveals a distinct difference between the apical and equatorial carbonyls. For the equatorial carbonyls the average Tc–C distance is 2.00 Å. (individual e.s.d., 0.012 Å.) and the average C–O distance is 1.12 Å. (individual e.s.d., 0.012 Å.); for the apical carbonyl, however, the Tc–C_1 distance is 1.90 ± 0.011 Å. and the C_1–O_1 distance is 1.20_5 ± 0.013 Å. Hence, the equatorial Tc–C distances are 0.10 Å. (av.) longer than the apical Tc–C_1 distance, whereas the equatorial C–O bonds are 0.08_5 Å. (av.) shorter than the apical C_1–O_1 bond. A similar but less marked difference was observed in the metal–carbon distances in $Mn_2(CO)_{10}$ with an average equatorial Mn–C distance of 1.84 Å. (individual e.s.d., 0.016 Å.) and an apical Mn–C_1 distance of 1.79_2 ± 0.014 Å.[5] However, no difference in the carbon–oxygen distances was indicated for $Mn_2(CO)_{10}$ where the average equatorial C–O distance was 1.15_4 Å. (individual e.s.d., 0.017 Å.) and the apical C_1–O_1 distance was 1.15_1 ± 0.016 Å.[5] In the mononuclear manganese carbonyl hydride, $HMn(CO)_5$, the apical Mn–C

bond (1.821 ± 0.009 Å.) is slightly shorter than the average equatorial Mn–C distance of 1.840 Å. (individual e.s.d., 0.010 Å.).[16] The differences between apical and equatorial carbonyls indicated in these three metal carbonyl complexes are consistent with the fact that, for compounds of the form $XM(CO)_5$ where M is octahedrally coordinated and X (here $Tc(CO)_5$, $Mn(CO)_5$, and H, respectively) is a poorer charge acceptor than CO, more of the charge donated by X (to a directionally oriented bonding orbital) accumulates on the CO *trans* to X than on the four CO groups which are *cis* to X. The resulting increased back bonding from the metal to the *trans* carbonyl then gives a stronger (and therefore shorter) metal–carbon bond and a weaker (and therefore longer) carbon–oxygen bond. Both of these effects appear in $Tc_2(CO)_{10}$, whereas in the two manganese carbonyl complexes only a tendency toward a shorter metal–apical carbon distance was indicated and lengthening of the apical C_1–O_1 distances, if it occurs, was not detected.

The Tc′–Tc–(equatorial carbon) and the (apical carbon)–Tc–(equatorial carbon) angles show that the equatorial carbonyls are bent away from the apical carbonyl by an average value of 3.8° (Figure 1). The technetium atom is displaced by 0.13 Å. from the mean plane of the four equatorial carbon atoms and by 0.19 Å. from the mean plane of the four equatorial oxygen atoms. This displacement of the metal in the direction of the apical π bonding carbonyl ligand also occurs in $Mn_2(CO)_{10}$[5] and $HMn(CO)_5$.[16]

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Crystal Structure of Tetrameric Cobalt(II) Acetylacetonate[1a]

BY F. A. COTTON AND R. C. ELDER[1b]

As indicated previously,[2] a structural analysis of $Co^{II}(AA)_2$ has been performed by X-ray crystal techniques. The triclinic unit cell contains one centrosymmetric tetramer. Octahedral coordination is achieved by sharing of oxygen atoms between cobalt atoms. The terminal cobalt atom is joined to the center pair by sharing a common octahedral face with three bridging oxygen atoms. The central two cobalt atoms are joined by sharing an edge with only two bridging oxygen atoms. The bond lengths and angles found are those expected for such a structure.

Introduction

Since the original suggestion that bis(acetylacetonato)cobalt(II) was not tetrahedral but rather square-planar,[3] several problems have remained to the present. The finding that $Ni(AA)_2$ is trimeric[4a,b] and that the nickel atoms are octahedrally coordinated led to the suggestion that perhaps $Co(AA)_2$ was also an octahedrally complexed polymer. The spectral measurements as well as magnetic data all led to this conclusion[5]; however, it was not possible to postulate the actual structure of the solid compound. In order to determine the structure, a single crystal X-ray analysis was undertaken. We report here the results of that determination.

Experimental

Preparation of Crystals.—Crystals of bis(acetylacetonato)cobalt(II) are quite difficult to produce in the laboratory. The compound is extremely soluble in nonpolar, noncoordinating solvents such as benzene and toluene; the hydrated forms are rather insoluble in these same solvents. This makes the crystallization of the anhydrous substance from solution a difficult task. In general, material deposited from solution is of several types: two crystalline modifications of $Co(AA)_2 \cdot 2H_2O$, $[Co(AA)_2 \cdot H_2O]_2$, the structure of which has been determined by single crystal X-ray methods,[6] $[Co(AA)_2]_{2-3} \cdot H_2O$, which is currently under study, and $[Co(AA)_2]_4$. The anhydrous compound can be obtained in crystalline form by extended heating *in vacuo* of the dihydrate according to Cotton and Holm.[3] However, the crystalline material thus obtained is unsuitable for single crystal X-ray work. Soderberg[7] suggests that the material may be sublimed at 120° under vacuum. Attempts were made in the course of a year to grow single crystals by sublimation. The substance sublimes readily to give a material which, in general, appears crystalline. Appreciable decomposition accompanies the sublimation process, and a light violet residue remains. The extent of decomposition seems to increase with increasing temperature, and therefore sublimations were run at approximately 100°.

The crystals obtained by sublimation are exceedingly fragile and many were fractured as they were removed from the cold probe. Several of the crystals which appeared single when viewed through a microscope were mounted in capillaries and studied with the precession camera. After more than 50 crystals had been so examined, no single crystal was obtained; however, one crystal which was twinned, but not seriously cracked, was reserved. All of the next 15 crystals examined were fractured and twinned. Since in the course of the investigation all of the crystals had appeared twinned, we decided to collect intensity data on the previously reserved crystal.

Preliminary Investigation: Unit Cell and Space Group.—All cell constants and intensity data were obtained from this crystal. The similarity of the photographs of the numerous cracked crystals to the photographs used guarantees that the twinned crystal was of the form generally present.

The unit cell is triclinic, which makes it difficult to align and more difficult to index the twinned lattices. The reduced primitive cell dimensions[8] are $a = 8.516 \pm 0.012$, $b = 10.243 \pm 0.017$, $c = 13.781 \pm 0.020$ Å., $\alpha = 93.5 \pm 0.3°$, $\beta = 90.4 \pm 0.3°$, $\gamma = 98.7 \pm 0.3°$, where the standard deviations are determined from the variation within the measurements. The volume of the cell is 1186 Å.[3]. This, together with the measured density of 1.45 g. cm.$^{-3}$, gives a calculated value of 4.1 $Co(AA)_2$ units per cell. Although this calculation is somewhat inexact, there can be no doubt that the final structure accounts for all the atoms in the cell.

Data Measurement: Consideration of Twinning.—The measurement of intensities proved a large problem since the triclinic cell and the twinned lattices gave an extremely complex set of spots on the film. The twinning, which was through the (1,0,0) plane with a twinning angle of 17° 10′, was such that the series $h,0,l$; $h,1,l$; $h,2,l$; $h,3,l$ could be recorded for each lattice separately with these exceptions: The set in the principal zone of twinning $(0,k,l)$ was the superposed image of the two lattices, and thus the lines $0,0,l$; $0,1,l$; $0,2,l$; $0,3,l$ were placed on a separate scale. Also, the layer screen, which is used to remove other levels and was here used to blank out the second lattice, passed

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