$$\boldsymbol{\mu} = \left(\frac{\mathbf{i}}{2} - \frac{\mathbf{j}}{2} - \frac{\mathbf{k}}{\sqrt{2}}\right)\mu \qquad (6)$$

is assumed to be located at the metal atom; it bisects the X–M–X angle and points toward the positive end of the dipole. Consequently, the x, y, and z components of the electric field at the ith proton are given by

$$E_x = -\frac{\partial V}{\partial x} = \mu\left[-\frac{1}{2r_i^3} + \frac{3x_i(x_i - y_i - \sqrt{2}z_i)}{2r_i^5}\right] \qquad (7)$$

$$E_y = -\frac{\partial V}{\partial y} = \mu\left[\frac{1}{2r_i^3} + \frac{3y_i(x_i - y_i - \sqrt{2}z_i)}{2r_i^5}\right] \qquad (8)$$

$$E_z = -\frac{\partial V}{\partial z} = \mu\left[\frac{1}{\sqrt{2}r_i^3} + \frac{3z_i(x_i - y_i - \sqrt{2}x_i)}{2r_i^5}\right] \qquad (9)$$

The component of **E** along the C–H bond, which determines the more important term in eq 4, is $E \cos \gamma$ where γ is the angle between **E** and the C–H bond direction, and E is simply $(E_x^2 + E_y^2 + E_z^2)^{1/2}$. For the ring proton these equations simplify since $x_i = r_i$ and $y_i = z_i = 0$; hence

$$E_{\text{C-H}} = \frac{\mu}{r_i^3} \text{ and } E = \frac{\sqrt{7}\mu}{2r_i^3} \qquad (10)$$

The coordinates used in the calculations are based on bond distances and bond angles given in a previous paper.[42] The geometry assumed for the Ti(acac)$_2$X$_2$ complexes is given in structure V of ref 42; that for the tin, zirconium, and hafnium compounds is shown in structure VI. Assumptions about the M–O bond distances and the orientation and restricted rotation of the methyl group are the same as in ref 42. The calculated $\Delta\sigma$ for the methyl protons was averaged over the six nonequivalent environments.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706,
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Structural Analyses of Tetracobalt Dodecacarbonyl and Tetrarhodium Dodecacarbonyl. Crystallographic Treatments of a Disordered Structure and a Twinned Composite[1]

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A statistically disordered crystal structure and detailed molecular configuration of Co$_4$(CO)$_{12}$ have been unambiguously determined from a three-dimensional single-crystal X-ray photographic analysis. The compound crystallizes with four tetrameric molecules in an orthorhombic unit cell of symmetry Pccn and dimensions a = 8.99 (2) Å, b = 11.70 (2) Å, and c = 17.28 (4) Å. A three-dimensional X-ray photographic investigation of twinned apparent orthorhombic crystals of Rh$_4$(CO)$_{12}$ has also been completed. The successful analysis of the structure of Rh$_4$(CO)$_{12}$ was accomplished by the assumption of a simple twinning mechanism and the application of derived mathematical relations which made possible a breakdown of the observed F^2 data for the twin composite into the appropriate F coefficients for the single-crystal component. The results of the analysis conclusively showed (a) that the individual twin component contains four tetrameric molecular species in a centrosymmetric monoclinic unit cell of dimensions a = 9.24 (2) Å, b = 12.02 (2) Å, c = 17.74 (3) Å, and β = 90°, with symmetry P2$_1$/c, and (b) that the twinning mirror plane parallel to the unique b axis and perpendicular to either the a or c axis results in apparent orthorhombic D$_{2h}$-mmm Laue symmetry. Both structures solved by the heavy-atom technique (complicated in each case by the pseudomirror symmetries imposed by metal atom positions) were refined isotropically by full-matrix least squares to conventional discrepancy factors $R_1(F)$ = 0.126 for Co$_4$(CO)$_{12}$ and $R_1(F)$ = 0.096 for Rh$_4$(CO)$_{12}$, based on 529 and 962 nonzero observed photographic data, respectively. Despite the different ways in which these complexes crystallize, the molecular configurations of the two polynuclear metal carbonyls are strikingly similar and have idealized C$_{3v}$-3m symmetry. Each molecule consists of an apical M(CO)$_3$ group coordinated by the three metal–metal bonds to a basal M$_3$(CO)$_9$ fragment containing three chemically identical M(CO)$_2$ groups linked to each other by metal–metal bonds and bridging carbonyl groups. A detailed structural comparison of Co$_4$(CO)$_{12}$ and Rh$_4$(CO)$_{12}$ is given.

Introduction

During the course of stereochemical investigations of metal carbonyl complexes, the correct detailed molecular architecture of tetracobalt dodecacarbonyl has been the source of much speculation and controversy. The apparent contradictions that have arisen between theoretical considerations and experimental data for this compound are perhaps paralleled only by those surrounding triiron dodecacarbonyl.[3]

First synthesized in 1932 by thermal decomposition of Co$_2$(CO)$_8$, cobalt tricarbonyl was formulated as a tetramer by molecular weight determination in iron pentacarbonyl solution.[4] The infrared spectrum of this black compound, later investigated by Friedel,

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(2) Biology Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

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(4) W. Hieber, F. Mühlbauer, and E. A. Ehman, *Ber.*, **65**, 1090 (1932).

et al.,[5] with rock-salt optics, showed a ratio of 2:1 for terminal-to-bridging carbonyls in the molecule. Although Cable and Sheline[6] at one time favored a dimeric configuration over a tetrameric structure, two-dimensional X-ray work by Corradini[7] revealed that the structure possesses four cobalt atoms of tetrahedral configuration surrounded by the 12 carbonyl groups, of which three bridging carbonyls are most likely located between the basal three cobalt atoms. Because of crystal disorder, however, Corradini was not able to determine unambiguously the positions of the carbonyl groups.

High-resolution infrared spectra, as independently studied by Cotton and Monchamp[8] (with fluorite prism) and by Bor and Markó[9] (with LiF prism), indicated well-defined carbonyl stretching bands, four terminal and one bridging, in sharp contrast with the group theoretical prediction of a more complicated spectrum consisting of six terminal and two bridging infrared-active carbonyl bands derived on the basis of a proposed molecular symmetry of C_{3v}-3m.[7] An explanation was given by Cotton and Monchamp[8] as to why the experimentally observed simpler spectrum of $Co_4(CO)_{12}$ might be caused by accidental effects. On the basis of a different interpretation of the infrared spectrum of $Co_4(CO)_{12}$ and of a similar spectrum of $Rh_4(CO)_{12}$, Beck and Lottes[10] rationalized the discrepancy observed between the experimental and the expected spectra of $Co_4(CO)_{12}$ and thus supported the Corradini model. Reexamination of the infrared spectrum of $Co_4(CO)_{12}$ in *n*-hexane solution and new assignments of the bands were subsequently made by Bor.[11] Five terminal and two bridging carbonyl stretching bands were recognized as being compatible with the rationalization of Cotton and Monchamp.[8]

Meanwhile, on the grounds of geometrical considerations involving the comparison of $Co_2(CO)_8$ and its acetylene derivatives $Co_2(CO)_6(RC_2R')$ with $Co_4(CO)_{12}$ and $Co_4(CO)_{10}(RC_2R')$, Krüerke and Hübel[12] proposed another idealized model of C_s-m symmetry for $Co_4(CO)_{12}$, in which two doubly bridging carbonyl groups were each attached to two cobalt atoms of opposing edges of a tetrahedron. The correctness of the Corradini structure was questioned by Smith,[13] who from an infrared spectrum analysis proposed a third possible alternative molecular model of D_{2d}-$\bar{4}$2m symmetry involving a different arrangement of the four bridging carbonyl groups; his model appears to be consistent with the observed infrared spectrum[8,9] without invoking any accidental carbonyl frequency degeneracies.

The obvious contradictions between the different molecular models of Corradini[7] and Smith[13] were later rationalized by Cotton[14] as being the consequence of possible intramolecular rearrangement of the carbonyl groups *via* facile paths from one configuration to the other in solution. The ^{59}Co nuclear magnetic resonance spectra of $Co_4(CO)_{12}$ in heptane and *n*-hexane solutions, however, have been shown by Lucken, *et al.*,[15] and by Haas and Sheline[16] to possess two closely spaced resonances with the intensity ratio 3:1, thereby indicating that the predominant species in solution possesses Corradini's C_{3v} solid-state model rather than Smith's D_{2d} model.

Although accumulating evidence seems to favor the Corradini model (at least in the solid state), a disquieting uncertainty, reflected in a recent paper,[17] still remains about the structure of $Co_4(CO)_{12}$. Our three-dimensional crystallographic investigation of $Co_4(CO)_{12}$ was undertaken to clarify the nature of its disorder and to establish conclusively the arrangement of the carbonyl groups in the crystalline state. The results that support the Corradini model have been presented briefly in a previous communication.[18]

An X-ray study[19] of the structure of tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$, revealed a molecular configuration of the symmetry T_d-$\bar{4}$3m, without bridging carbonyls, that is distinctively different from that of $Co_4(CO)_{12}$, while another metal carbonyl complex of a congener element rhodium (first reported by Hieber and Lagally[20] as $[Rh(CO)_3]_n$) was suggested by Beck and Lottes[10] to have a structure similar to that of $Co_4(CO)_{12}$. A three-dimensional X-ray analysis of this rhodium complex has been undertaken not only to establish its tetrameric character and to ascertain the relationship of its molecular configuration to that of $Co_4(CO)_{12}$, but also to confirm the general trend of increasing stability of the $M_4(CO)_{12}$-type complexes toward the nonbridged configuration for $Ir_4(CO)_{12}$ as compared to the bridged configuration for $Co_4(CO)_{12}$, as one goes from the first transition series to their analogs in the second and third series. Preliminary accounts of our work on $Rh_4(CO)_{12}$ with a proposed crystallographic treatment of a twin composite applied to the structural determination of this complex have been reported.[21]

Experimental Section

Samples.—No attempt was made to prepare a large quantity of tetracobalt dodecacarbonyl in a pure condition. Black crystals of $Co_4(CO)_{12}$ were obtained from the partially decomposed product of a toluene solution of $Co_2(CO)_8$. Reddish orange tetrarhodium dodecacarbonyl—prepared by the high-pressure

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(20) W. Hieber and H. Lagally, *Z. Anorg. Allgem. Chem.*, **251**, 96 (1943).

(21) (a) C. H. Wei, Abstracts of Papers, National Meeting of the American Crystallographic Association, University of Minnesota, Minneapolis, Minn., Aug 20–25, 1967, p 83; (b) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).

carbonylation of anhydrous $RhCl_3$, with freshly reduced copper as the halogen acceptor[19,20]—was supplied by Dr. G. R. Wilkes at the University of Wisconsin.

Collection of X-Ray Data.—Intensity data were collected with zirconium-filtered Mo $K\alpha$ radiation (λ 0.7107 Å) by the equi-inclination Weissenberg and precession methods. Approximate dimensions of crystals used were $0.15 \times 0.18 \times 0.54$ mm for $Co_4(CO)_{12}$ and $0.10 \times 0.10 \times 0.15$ mm and $0.12 \times 0.11 \times 0.15$ mm for $Rh_4(CO)_{12}$. Crystals were mounted parallel to their longest dimensions in thin-walled glass capillary tubes. For the $Co_4(CO)_{12}$ crystal, $h0l$ through $h12l$ Weissenberg data were recorded, and 494 independent reflections were obtained. An additional 35 independent reflections were obtained by $0kl$, $1kl$, and $hk0$ precession photographs. In the case of $Rh_4(CO)_{12}$, $0kl$ through $8kl$ and $hk0$ through $hk3$ Weissenberg data were collected from the first and second crystals, respectively. From the second crystal another 16 independent reflections were obtained from $0kl$ and $1kl$ precession data. Thus a total of 962 independent intensity maxima corresponding to one octant[22,23] of the reflection sphere were recorded. Cell parameters were determined from precession photographs for both complexes.

Intensities were estimated visually by comparison with corresponding standard strips. In each case, corrections for Lorentz and polarization effects were made; common reflections appearing in both Weissenberg and precession photographs were used to assign initial individual relative scale factors for the 16 reciprocal levels of the cobalt complex and for 15 levels of the rhodium complex. No corrections were made for absorption or extinction. The linear absorption coefficient ($\mu = 38$ cm^{-1}) for the cobalt complex results in a value of 0.34 for $\mu R_{\max}$; for the rhodium complex the μ of 33 cm^{-1} gives $\mu R_{\max}$ values of 0.16 and 0.20 for the first and second crystals, respectively. For these values of $\mu R_{\max}$, the variation of absorption correction factors with θ is not appreciable,[24] and the maximum variation due to absorption of the intensities on a given layer was approximately 10%.

Minimum observed intensities, $I_o(\min)$, were estimated for each reciprocal level, and variable weights for the observed structure amplitudes, F_o, were assigned in the following way: $\sqrt{w(F_o)} = 20/F_o$ if $I_o \geq 4I_o(\min)$; $\sqrt{w(F_o)} = 1.25I_o^2/F_oI_o(\min)^2$ if $I_o < 4I_o(\min)$.

Crystal Data

$Co_4(CO)_{12}$.—The crystals of $Co_4(CO)_{12}$ are orthorhombic with lattice parameters $a = 8.99 \pm 0.02$ Å, $b = 11.70 \pm 0.02$ Å, and $c = 17.28 \pm 0.04$ Å (lattice parameter errors were estimated on the basis of reproducibility of the measurements). These cell parameters are in agreement with the values of $a = 11.66 \pm 0.07$ Å, $b = 8.94 \pm 0.05$ Å, and $c = 17.14 \pm 0.10$ Å, reported by Corradini,[7a,25] within the limits of errors of the determinations. The volume of a unit cell is 1818 Å^3. The calculated density is 2.09 g cm^{-3} based on four formula units of $Co_4(CO)_{12}$ in a unit cell. The total number of electrons per unit cell, $F(000)$, is 1104. Systematic absences of $0kl$ for l odd, $h0l$ for l odd, and $hk0$ for $h + k$ odd are uniquely characteristic of the centrosymmetric space group Pccn (D_{2h}^{10}, no. 56).[26] This choice was confirmed by a satisfactory refinement of the solved structure.

$Rh_4(CO)_{12}$.—The diffraction pattern of $Rh_4(CO)_{12}$ shows an orthorhombic D_{2h} Laue symmetry with cell parameters $a = 9.24 \pm 0.02$ Å, $b = 12.02 \pm 0.02$ Å, and $c = 17.74 \pm 0.03$ Å. The volume of a unit cell is 1970 Å^3. The observed density of 2.58 ± 0.02 g cm^{-3} (by flotation) compares satisfactorily with the calculated value of 2.52 g cm^{-3} based on four $Rh_4(CO)_{12}$ formula species per unit cell; $F(000) = 1392$. The systematic absences of $h0l$ for l odd and $0k0$ for k odd indicate probable space groups $Pmc2_1$, P2cm, and Pmcm, provided that the $0k0$ absences are considered to be accidental. However, the correct space group of the single-crystal component having a monoclinic unit cell of the same dimensions ($\beta = 90°$) (*vide infra*) was deduced to be $P2_1/c$ (C_{2h}^5, no. 14),[27] which was subsequently confirmed by the successful refinement of the derived twinned structure.

Determination of Structures

Because the ways of handling the problems caused by the crystal disorder of $Co_4(CO)_{12}$ and the problems involved in the twinning of $Rh_4(CO)_{12}$ may be of interest to others, this section of the paper is given in some detail.

Analysis of $Co_4(CO)_{12}$.—A three-dimensional Patterson function, sharpened by the use of $|F|^2\ [\Sigma Z_j/\Sigma f_j]^2$ as coefficients,[28] was computed from the corrected intensities by the Blount program.[29] A resulting hexagonal-like distribution of 18 large peaks (of which *six* are independent) around the origin of the unit cell in the Harker section at $z = 0$ strongly resembled that obtained from a hexagon (with side lengths 1.4–1.6 Å) of identical atoms[3,30] located on a (001) plane. With the addition of two independent Patterson peaks (both found at the section $z = 10.2/60$), corresponding to presumably cobalt–cobalt intramolecular vectors of length approximately 2.5 Å, it became evident that the two tetrameric molecules are each composed of a tetrahedral array of cobalt atoms randomly oriented in one of two positions so as to yield a crystallographic twofold axis in the c direction for the average structure, thereby conforming to the disordered arrangement of the cobalt atoms in the unit cell as first proposed by Corradini.[7a] Examination of other Patterson peaks (intermolecular vectors), together with these intramolecular vectors between cobalt atoms, established a self-consistent assignment of positional parameters

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[22] Although the true crystal system of $Rh_4(CO)_{12}$ was later confirmed to be monoclinic for the twin component, a large number of crystals examined showed an orthorhombic diffraction symmetry. To obtain untwinned $Rh_4(CO)_{12}$ single crystals, several organic solvents were utilized for recrystallization,[19] which, however, invariably led to the identical diffraction pattern. Attempts to obtain good crystals by sublimation were also unsuccessful.[23]

[23] Private communication from Dr. W. Murayama of the Central Laboratories of Ajinomoto Co., Inc., Kawasaki, Japan, June 1967.

[24] "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

[25] The choice of labeling for the unit cell axes of $Co_4(CO)_{12}$ was made for ease in comparing these values with those of $Rh_4(CO)_{12}$, which has a unique monoclinic axis. Our labeling differs from that of Corradini[7a] in an interchanging of the a and b axes. The observed space group Pccn for $Co_4(CO)_{12}$ is invariant to this axial transformation.

[26] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 144.

[27] Reference 26, p 99.

[28] See, *e.g.*, H. Lipson and W. Cochran, "The Determination of Crystal Structure," B. Bell and Sons Ltd., London, 1957, p 170.

[29] J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

[30] *Cf.* Figure 184(c) of H. Lipson and W. Cochran in ref 28, p 184; Figure 12.4(a) of G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 305.

for four cobalt atoms, one of them (Co_4) being located on the crystallographic twofold axis. Since one atom of the cobalt tetrahedron (Co_3) is located approximately on a c_b glide plane at $y = {}^1/_4$, which in this case also serves as a quasimirror plane for the framework of cobalt atoms, the net contribution of the four heavy atoms to the structure factors on the basis of the space group Pccn is appreciable only for the reflections with l even. The reflections with l odd would then be almost entirely due to the light atoms. Indeed, this model is compatible with the observed intensity data.[31] Consequently, only the reflections with l even should be used for the initial least-squares refinement of the trial parameters of the cobalt atoms. Because of the quasimirror plane that coincides with the c glide plane at $y = {}^1/_4$, however, a least-squares refinement in which all four cobalts are treated as independent atoms is not feasible, owing to a high degree of parameter interaction between the two cobalt atoms (Co_1 and Co_2) related by this quasimirror plane.[32] This difficulty was overcome by taking a unit cell of half the original size with half the original c dimension, so that the original space group Pccn becomes Pmmn ($D_{2h}{}^{13}$, no. 59), with only three cobalt atoms (Co_1, Co_3, and Co_4) considered as crystallographically independent. For this generated unit cell the l indices are half those for the original unit cell.

A full-matrix least-squares refinement[33] was carried out in which an assumed initial isotropic temperature factor of 2.0 $Å^2$ was assigned to each cobalt atom, and all parameters except the y coordinate of Co_3 and the x and y coordinates of Co_4 were allowed to vary for the reflections with new l indices (original reflections with l odd were omitted). From a multiplicity consideration, the Co_3 and Co_4 atoms were each given one-fourth and the Co_1 atom was given half of the full scattering power of a cobalt atom. The function minimized was $\Sigma w(F_o)||F_o| - s|F_c||^2$, where s is the adjusted scale factor. After three cycles the discrepancy factors, $R_1(F) = \Sigma||F_o| - s|F_c||/\Sigma|F_o|$, had decreased to 0.22, with no anomalies present in the temperature factors.[32]

A three-dimensional Fourier synthesis was then calculated[29] in the space group Pmmn phased on only the cobalt atoms. Aside from real peaks for a partially correct structure, there appeared corresponding images, which are related to the true ones by two mirror planes, one perpendicular to the a axis at $x = {}^1/_4$ and the other perpendicular to the b axis at $y = {}^1/_4$. Hence, of the four possible positions for each of the light atoms only one position should be selected. After careful examination of this complicated Fourier map, a choice was made to distinguish the real positions for carbonyl atoms from their mirror-related images, and thus 12 independent peaks were assigned as six carbon and six oxygen atoms. The other six carbonyl groups in the $Co_4(CO)_{12}$ molecule were found to be related to these assigned carbonyl groups by a crystallographic twofold axis located at $({}^1/_4, {}^1/_4, z)$. The light atoms were not well resolved, and it was not possible to obtain their positional parameters with great precision. Presumably, resolution was incomplete partially because each peak representing a light-atom position is the superposition of two light-atom peaks (*vide infra*).

The addition of these light atoms to the heavy-atom framework destroys the mirror symmetries in both the a and b directions. Refinement of parameters for 16 independent atoms in the unit cell of the original space group Pccn with all data (*i.e.*, with l both even and odd) was subsequently carried out with only the x and y coordinates of Co_4 being fixed. Initial isotropic temperature factors of 4.0 $Å^2$ for carbon and 5.0 $Å^2$ for oxygen atoms were arbitrarily assigned. In this structural analysis the Co_4 atom was assumed to occupy the special fourfold set of positions (4d) [*viz.*, $\pm({}^3/_4, {}^1/_4, z; {}^3/_4, {}^1/_4, {}^1/_2 + z)$]; all other atoms were assumed to occupy the general eightfold set of positions (8e) [*viz.*, $\pm(x, y, z; {}^1/_2 - x, {}^1/_2 - y, z; {}^1/_2 + x, -y, {}^1/_2 - z; -x, {}^1/_2 + y, {}^1/_2 - z)$]. On the basis of the disordered structure, an assignment of 50% full atomic scattering factor was made for all four cobalt atoms. After four cycles of isotropic refinement, the $R_1(F)$ value had dropped to 0.126, and $R_2(F) = \{\Sigma w(F_o)[|F_o| - s|F_c|]^2/\Sigma w(F_o)|F_o|^2\}^{1/2}$ also stood at 0.126. The standard deviation of an observation of unit weight, defined as $\{\Sigma w(F_o)||F_o| - s|F_c||^2/(n - p)\}^{1/2}$ where n is the number of observations and p is the number of parameters fitted to the data set, was 1.80. At this stage the shifts of all parameters were less than 32% of the corresponding estimated standard deviations. The values of 16 scale factors ranged from 0.144 to 0.257. As a final check of the correctness of the structure, a three-dimensional difference Fourier was computed. It showed positive peaks of up to 1.5 $e^-/Å^3$ in the neighborhood of the cobalt atoms and no other peaks greater than 0.7 $e^-/Å^3$, which is approximately equivalent to 15% of the average peak height of a carbon atom in this structure. An attempt to carry out anisotropic refinements for all atoms (with a single scale factor obtained by relative scaling of all of the observed structure factors based on the scale factors from the isotropic refinement) was not successful. Although a refinement in which the four cobalt atoms alone were assigned anisotropic thermal parameters yielded slightly lower $R_1(F)$ and $R_2(F)$ values of 0.124 and 0.119, the results of the isotropic refinement with multiple scales are presented in this paper. The atomic scattering factors used were those of Thomas and Umeda[34] for cobalt and rhodium atoms and those of Berghuis, *et al.*,[35] for carbon and

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[31] The reflections with l odd (66 out of a total of 529 measured) are mostly weak and constitute only about 12.5% of the total number of observed diffraction maxima.

[32] When the refinement was actually carried out for the four cobalt atoms in space group Pccn, it resulted in isotropic temperature factors of 29.0 and −23.3 $Å^2$ for the mirror-related Co_1 and Co_2 atoms, respectively. A subsequent Fourier synthesis based on this result would have been physically meaningless.

[33] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, a Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

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

[35] J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *Acta Cryst.*, **8**, 478 (1955).

oxygen. No correction was made for anomalous dispersion.[36,37]

Analysis of $Rh_4(CO)_{12}$.—The three-dimensional Patterson function, sharpened by the use of $|F|^2\ [\Sigma Z_j/\Sigma f_j]^2$ as coefficients,[27] was computed[28] from the intensity data. Attempts to interpret the resulting maps in terms of any orthorhombic space group, however, were fruitless. Instead, the only trial model that conformed to the observed symmetry elements and Patterson vectors was based on the four rhodium atoms in a nearly regular tetrahedral configuration with an edge length of approximately 2.7 Å in a monoclinic unit cell of the same dimensions as the orthorhombic unit cell and of space group $P2_1/c$ (Figure 1). The contradiction between the observed Laue symmetry and the space group of the deduced crystal model based only on the heavy atoms led us to suspect that some sort of twinning was present in this structure.

The assumption was made that the observed intensity distribution is a consequence of the superposition of two monoclinic reciprocal lattices with $\beta^* = 90°$, with the twinning mirror plane normal to the a axis, as shown in Figure 2. The presence of this (100) twinning mirror plane operating on the monoclinic reciprocal lattices would give rise to the same apparent unit cell for the twinned composite and would thereby result in the observed pseudoorthorhombic diffraction pattern without double-lattice character.[38] Based on this simple twinning mechanism involving a monoclinic single crystal with $\beta = 90°$, the observed intensity for every reflection would be actually the sum of the intensities for a pair of hkl and $\bar{h}kl$ reflections, as shown in the relationships[39]

$$|F(hkl)_o|^2 = m|F(hkl)_{o'}|^2 + (1 - m)|F(\bar{h}kl)_{o'}|^2 \quad (1)$$

$$|F(hkl)_c|^2 = m|F(hkl)_{c'}|^2 + (1 - m)|F(\bar{h}kl)_{c'}|^2 \quad (2)$$

where $|F(hkl)_o|^2$ and $|F(hkl)_c|^2$ stand for the observed and calculated intensities for the apparent orthorhombic twinned composite; $|F(hkl)_{o'}|^2$ and $|F(\bar{h}kl)_{o'}|^2$ and $|F(hkl)_{c'}|^2$ and $|F(\bar{h}kl)_{c'}|^2$ are the observed and calculated intensities for the monoclinic twin component; m stands for the fraction of one component lattice. Consequently, the calculated Patterson function based on the observed orthorhombic intensity data would be the superposition of the Patterson function for one monoclinic component and the mirror-related image of that function across the U axis.[40] The two-dimensional data for the $hk0$ reciprocal net would not be subject to the effect of this twinning mechanism, because the relation $|F(hk0)| = |F(\bar{h}k0)|$ is still correct for the twin composite, and the projections on the (001) plane would be identical for both nontwinned and twinned structures. To test the validity of the twinned model, parameters of the three independent rhodium atoms (instead of four, *vide infra*) were refined[33] in the two-dimensional space group p2gm[41] with the $hk0$ data (comprised of 91 reflections) to give an $R_1(F)$ value of 0.19. A two-dimensional Fourier projection was next computed. With the aid of the determined molecular configuration of $Co_4(CO)_{12}$, which was presumably similar to that of $Rh_4(CO)_{12}$, seven peaks were assigned as the probable projected positions for 12 oxygen atoms, some of which were assumed on the basis of the $Co_4(CO)_{12}$ configura-

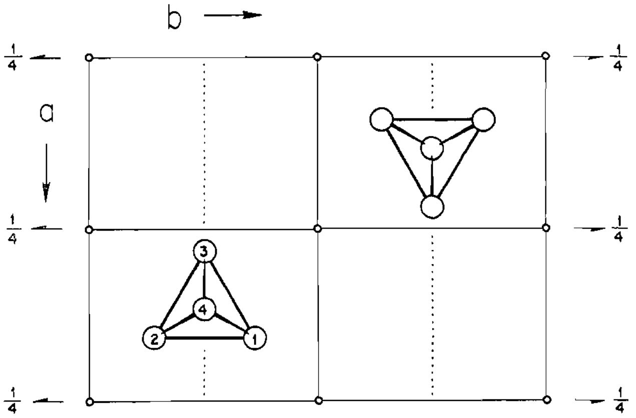

Figure 1.—An arrangement of rhodium tetrahedra as obtained from the interpretation of the Patterson function calculated with the apparent orthorhombic data. Only basic atoms are numbered. This arrangement, based only on a heavy-atom framework, conforms to the symmetry requirements of the monoclinic space group $P2_1/c$.

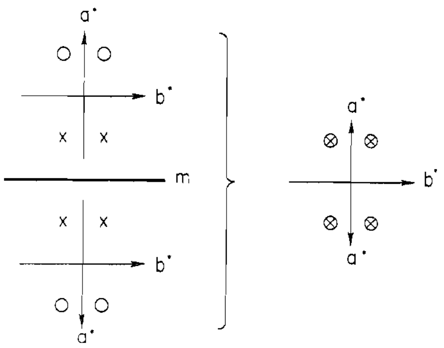

Figure 2.—Twinning mechanism of $Rh_4(CO)_{12}$ involving a (100) twinning mirror plane operating on monoclinic lattices with $\beta^* = 90°$. Each registered point of one monoclinic reciprocal lattice with point group symmetry C_{2h}-2/m coincides precisely with that of the other twin component, thus forming a composite reciprocal lattice of apparent orthorhombic D_{2h}-mmm Laue symmetry.

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(36) For Mo Kα radiation, the real and imaginary dispersion corrections, $\Delta f'$ and $\Delta f''$, for atomic scattering factors are 0.4 and 1.1 for cobalt atom and −1.1 and 1.2 for rhodium atom, both at a $(\sin \theta)/\lambda$ value of 0.[37] The effects on the atomic scattering factors caused by these values are considered small enough to be insignificant.

(37) D. H. Templeton, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 215, Table 3.3.2C.

(38) *Cf.* (a) M. J. Buerger, "Crystal-Structure Analysis," John Wiley & Sons, Inc., New York, N. Y., 1960, Chapter 5 and pp 190-193; (b) R. Sadanaga, "X-Ray Crystallography," I. Nitta, Ed., Vol. 1, Maruzen Co., Ltd., Tokyo, 1959, pp 495–504.

(39) Dr. W. Murayama, who also carried out an X-ray study of $Rh_4(CO)_{12}$ crystals, interpreted his observed orthorhombic data on the basis of an identical monoclinic twinning model for the single-crystal component with symmetry $P2_1/c$, although his attempts to determine the carbonyl atom positions were not successful.[23]

(40) Reference 26, p 526.

(41) Reference 26, p 62.

tion to overlap closely in this projection. Inclusion of these positions in the two-dimensional least-squares refinement lowered the $R_1(F)$ value to 0.14. Since the relation $|F(0kl)| = |F(0k\bar{l})|$ also holds for any monoclinic space group, the two-dimensional $0kl$ data phased on the rhodium atoms would also result in the identical Fourier projection for both nontwinned and twinned structures. However, for this projection [the refinement on the $0kl$ data was terminated with $R_1(F) = 0.27$], the data with l odd could not be included (*vide infra*), and as expected the resulting map was less informative than in the former case.

As shown in Figure 1, the initial rhodium atom positions were to a first approximation interrelated by a mirror plane coincident with the c glide plane in the centrosymmetric unit cell of $P2_1/c$. Because of this pseudomirror plane, the rhodium atoms make no contribution to the calculated structure factors for hkl reflections with l odd. This fact is consistent with the observed intensity distribution.[42] As in the case of $Co_4(CO)_{12}$, the generated space group $P2_1/m$, obtained by halving the c-axis length (here the original reflections with l odd were excluded, and the even l indices were halved), was used for the initial refinement of the three independent rhodium atoms together with 15 scale factors. The refinements based on F^2 data were performed with standard errors $\sigma(F_o^2)$ related to the previously defined $\sigma(F_o)$ values by the relation $\sigma(F_o^2) = 2F_o\sigma(F_o)$, where $\sigma(F_o)$ is equal to $1/\sqrt{w(F_o)}$. An isotropic full-matrix least-squares refinement[33] was carried out with the assumption that $|F(hkl)_c|^2 = 0.5[|F(hkl)_{c'}|^2 + |F(\bar{h}kl)_{c'}|^2]$,[43] and $\partial F|(hkl)_c|^2/\partial p = 0.5[(\partial|F(hkl)_{c'}|^2/\partial p) + (\partial|F(\bar{h}kl)_{c'}|^2/\partial p)]$, where the derivative of $|F(hkl)_c|^2$ with respect to an individual atom parameter p (see ref 33, p 6) is taken over the two component quantities. The function minimized was $\Sigma w(F_o^2)\cdot||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|^2$. After three cycles $R_1(F^2)$, defined as $\Sigma||F(hkl)_o|^2 - s^2|F(hkl)_c|^2|/\Sigma|F(hkl)_o|^2$, became 0.17. A Fourier synthesis phased on only the rhodium atoms was next computed, with the estimated monoclinic structure factors, $F(hkl)_{o'}$ and $F(\bar{h}kl)_{o'}$, used as coefficients. These two values were computed from the corresponding observed quantity, $|F(hkl)_o|^2$, for the twin composite as follows[44]

$$|F(hkl)_{o'}| = \left[|F(hkl)_o|^2\frac{|F(hkl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2} \qquad (3)$$

$$|F(\bar{h}kl)_{o'}| = \left[|F(hkl)_o|^2\frac{|F(\bar{h}kl)_{c'}|^2}{|F(hkl)_c|^2}\right]^{1/2} \qquad (4)$$

The signs for $F(hkl)_{o'}$ and $F(\bar{h}kl)_{o'}$ were provided by the corresponding signs of $F(hkl)_{c'}$ and $F(\bar{h}kl)_{c'}$. In this first approximation to an electron density map, each possible atom peak was accompanied by a false image peak related to it by a mirror plane of the generated space group $P2_1/m$. However, 13 light-atom positions were located from stereochemical considerations supplemented by knowledge of the structure of $Co_4(CO)_{12}$. With the addition of these light atoms to the heavy atoms, the quasimirror plane symmetry imposed by the rhodium atoms was destroyed, and the subsequent least-squares refinement for these 17 atoms was carried out in the original space group $P2_1/c$ with all diffraction data included. All atoms occupy the general fourfold set of positions (4e): $\pm(x, y, z; x, {}^1/_2 - y, {}^1/_2 + z)$. After three cycles, the $R_1(F^2)$ value was lowered to 0.29. The second Fourier synthesis, which revealed all the remaining atom positions, was followed by seven cycles of least-squares refinement for all 28 independent atoms. At the end of the refinement, $R_1(F^2)$ stood at 0.175, $R_1(F)$,[45] defined as $\Sigma||F(hkl)_o| - s|F(hkl)_c||/\Sigma|F(hkl)_o|$, stood at 0.96, and $R_2(F^2)$, defined as $\{\Sigma w(F_o^2)[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2/\Sigma w(F_o^2)\cdot[|F(hkl)_o|^2]^2\}^{1/2}$, stood at 0.195. The standard deviation of an observation of unit weight, defined as $\{\Sigma w(F_o^2)\cdot[|F(hkl)_o|^2 - s^2|F(hkl)_c|^2]^2/(n - p)\}^{1/2}$, was 1.46. All parameter shifts became less than 20% of the corresponding standard deviations. The values of 15 scale factors ranged from 0.0533 to 0.0702 for the Weissenberg data. A difference Fourier synthesis at this stage showed positive peaks of up to 2.5 $e^-/Å^3$ in the immediate vicinity of the rhodium atoms. An attempt to carry out the anisotropic refinement for all atoms was not successful. Another refinement for which anisotropic temperature factors were assigned only for the rhodium atoms, with a single scale factor for the whole set of data, resulted in a slightly lower $R_1(F^2)$ value, 0.170, but all positional and thermal parameters remained essentially the same for all of the atoms. This paper, therefore, gives the results of the isotropic refinement with multiple scale factors.

Although a full-matrix least-squares refinement of the twinned $Rh_4(CO)_{12}$ structure was carried out on F^2 data and the subsequent calculations were based on results of this refinement, the refinement was also performed on F with the function minimized being $\Sigma w(F_o)\cdot||F(hkl)_o| - s|F(hkl)_c||^2$ where $|F(hkl)_c|$ is defined in eq 2, and the derivative of $|F(hkl)_c|$ with respect to an individual atom parameter p (see ref 33, p 6) be-

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(42) Among 962 independent reflections observed, 201 reflections have l odd. Most of these are weak and constitute approximately 20% of total diffraction maxima.

(43) In order to test the validity of this assumption, the parameter m in eq 2 was varied in addition to all other parameters in the least-squares program,[33] with the use of the relation $\partial|F(hkl)_c|^2/\partial m = |F(hkl)_{c'}|^2 - |F(\bar{h}kl)_{c'}|^2$ (see ref 33, p 6). A value of $m = 0.504 \pm 0.009$ was obtained with other parameters essentially remaining the same as in the case in which m was held constant at 0.5. Hence, $m = 0.5$ was considered to be valid for the twin model.

(44) In the discussion following the presentation of a part of this work at the National Meeting of the American Crystallographic Association,[21a] Dr. D. Harker of the Roswell Park Memorial Institute, Buffalo, N. Y., pointed out that these relations were also previously assumed for "diffuse" reflections (but not for "sharp" reflections) in their successful structural analysis of decaborane: *cf.* J. S. Kasper, C. M. Lucht, and D. Harker, *Acta Cryst.*, **3**, 436 (1950). In their study of this compound, the intensity of each diffuse reflection hkl was considered to represent the average of the intensities for a pair of the reflections hkl and $h\bar{k}l$.

(45) This quantity is closely related to but not identical with a calculated discrepancy index for a twin composite, $R_1(F)_T$ (=0.095), which has been defined[21] as $\Sigma\{||F(hkl)_{o'}| - s|F(hkl)_{c'}|| + ||F(\bar{h}kl)_{o'}| - s|F(\bar{h}kl)_{o'}||\}/\Sigma\{|F\cdot(hkl)_{o'}| + |F(\bar{h}kl)_{o'}|\}$. Unless the ratio $|F(hkl)_o|/F(hkl)_c|$ is independent of individual reflections, it can be shown that $R_1(F) \neq R_1(F)_T$.

Table I

Atomic Parameters with Standard Deviations for the Averaged Disordered Structure of $Co_4(CO)_{12}$

Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B, Å^2 ($10\sigma_B$)
Co_1	0.8313 (16)	0.3450 (9)	0.1163 (8)	2.98 (2.6)
Co_2	0.8049 (11)	0.1330 (7)	0.1208 (7)	2.37 (2.7)
Co_3	0.5808 (9)	0.2508 (13)	0.1207 (4)	2.16 (1.4)
Co_4	0.7500	0.2500	0.2374 (3)	2.57 (1.2)
C_1	0.8463 (63)	0.3502 (35)	0.0220 (33)	7.8 (13)
O_1	0.8665 (42)	0.3737 (22)	−0.0391 (21)	7.5 (8)
C_2	0.8307 (43)	0.3358 (24)	0.3030 (21)	3.4 (7)
O_2	0.8928 (35)	0.3985 (22)	0.3477 (16)	6.4 (7)
C_3	0.7488 (72)	0.5068 (26)	0.1374 (20)	5.3 (7)
O_3	0.7502 (61)	0.5942 (24)	0.1398 (15)	7.9 (6)
C_4	1.0506 (53)	0.3547 (28)	0.1483 (24)	4.4 (9)
O_4	1.1470 (45)	0.3905 (26)	0.1659 (19)	7.8 (9)
C_5	0.9316 (48)	0.1559 (28)	0.2146 (25)	4.5 (8)
O_5	1.0108 (34)	0.0967 (19)	0.2519 (14)	5.2 (6)
C_6	1.0197 (62)	0.1425 (33)	0.0533 (29)	6.2 (12)
O_6	1.0793 (39)	0.1035 (26)	0.0254 (19)	7.7 (8)

Table II

Atomic Parameters with Standard Deviations for the Twinned Structure of $Rh_4(CO)_{12}$

Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B, Å^2 ($10\sigma_B$)
Rh_1	0.8298 (5)	0.3537 (4)	0.1172 (4)	2.40 (1.4)
Rh_2	0.8030 (6)	0.1296 (4)	0.1170 (4)	2.48 (1.4)
Rh_3	0.5600 (4)	0.2593 (5)	0.1190 (3)	2.44 (0.9)
Rh_4	0.7298 (4)	0.2555 (4)	0.2439 (2)	2.37 (0.9)
C_1	0.8323 (56)	0.3767 (39)	0.0098 (31)	2.0 (11)
O_1	0.8761 (68)	0.3694 (45)	−0.0588 (40)	7.9 (17)
C_2	0.8089 (75)	0.3586 (49)	0.3076 (40)	3.9 (15)
O_2	0.8930 (38)	0.3959 (30)	0.3594 (23)	2.9 (9)
C_3	0.7715 (60)	0.5162 (41)	0.1394 (30)	2.0 (11)
O_3	0.7244 (43)	0.6023 (30)	0.1520 (22)	2.9 (9)
C_4	1.0354 (82)	0.3627 (57)	0.1459 (51)	4.7 (18)
O_4	1.1282 (58)	0.3782 (38)	0.1630 (33)	5.2 (12)
C_5	0.8832 (53)	0.1536 (37)	0.2152 (29)	0.8 (10)
O_5	0.9967 (55)	0.0891 (38)	0.2596 (34)	5.9 (12)
C_6	0.9825 (67)	0.1205 (46)	0.0489 (36)	2.0 (12)
O_6	1.0669 (59)	0.1127 (46)	0.0176 (37)	7.3 (16)
C_1'	0.6474 (123)	0.1652 (88)	0.0439 (64)	10.2 (33)
O_1'	0.6401 (69)	0.1512 (38)	−0.0300 (36)	6.9 (14)
C_2'	0.6439 (102)	0.1553 (61)	0.3192 (55)	7.1 (22)
O_2'	0.5747 (61)	0.1250 (45)	0.3639 (39)	7.2 (16)
C_3'	0.7376 (84)	−0.0368 (61)	0.1115 (51)	6.5 (20)
O_3'	0.7378 (58)	−0.1299 (41)	0.1271 (34)	6.8 (13)
C_4'	0.4057 (57)	0.1501 (46)	0.1342 (40)	2.7 (13)
O_4'	0.3267 (63)	0.0934 (45)	0.1584 (35)	7.7 (17)
C_5'	0.5642 (59)	0.3592 (45)	0.2217 (36)	2.5 (12)
O_5'	0.4753 (50)	0.4269 (38)	0.2452 (31)	5.0 (11)
C_6'	0.4601 (62)	0.3554 (44)	0.0658 (39)	3.1 (13)
O_6'	0.3834 (42)	0.4077 (32)	0.0209 (26)	3.2 (9)

comes $(1/|F(hkl)_c|)\{[m|F(hkl)_{c'}|\partial|F(hkl)_{c'}|/\partial p] + [(1-m)|F(\bar{h}kl)_{c'}|\partial|F(\bar{h}kl)_{c'}|/\partial p]\}$. The validity of this refinement (m was fixed at 0.5 here) is evidenced by the successful convergence which resulted in essentially the same least-squares results as those obtained from the refinement based on F^2 data with $R_1(F) = 0.098$ and $R_2(F) = 0.108$.

The final parameters with estimated standard deviations, obtained from the last cycle of isotropic least-squares refinement, are given in Table I for $Co_4(CO)_{12}$ and in Table II for $Rh_4(CO)_{12}$. Observed structure amplitudes and calculated structure factors are listed for $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ in Tables III and IV, respectively. Bond lengths and angles were calculated with the Busing–Martin–Levy function and error program,[46] and some selected values are summarized in Tables V and VI. The "best" molecular planes formed by sets of specified atoms and the distances of other atoms from these planes, as calculated by the Smith program with a weighted least-squares method,[47] are given in Table VII. The computers used for the calculations in this paper were the CDC 1604 and CDC 3600 computers at the University of Wisconsin and the CDC 1604 and IBM 360 computers at the Oak Ridge National Laboratory.

Discussion

General Description of Structures.—The crystal structures of tetracobalt and tetrarhodium dodecacarbonyls are both composed of discrete molecules with an idealized configuration (depicted in Figure 3) of C_{3v} symmetry. Both molecules consist of four tetrahedrally arranged metal atoms in which an apical $M(CO)_3$ group is symmetrically coordinated to a basal $M_3(CO)_9$ fragment by only metal–metal bonds. The $M_3(CO)_9$ fragment contains three equivalent $M(CO)_2$ groups, each located at a vertex of a nearly equilateral triangle. Each pair of $M(CO)_2$ groups is linked by both a metal–metal bond and a bridging carbonyl group. The 12 carbonyl groups are disposed at corners of a distorted icosahedron which surround the tetrahedron of metal atoms.

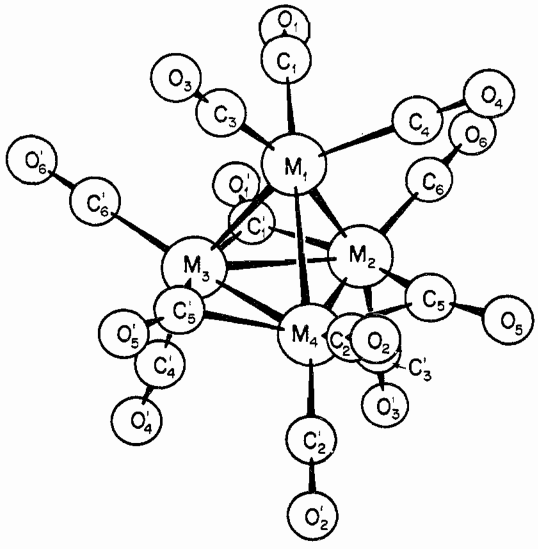

Figure 3.—Molecular configurations of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. In $Co_4(CO)_{12}$ the carbon and oxygen atoms with primed symbols are related to the corresponding atoms with nonprimed symbols (for basic atoms) by a twofold crystallographic axis passing through Co_4 and the center of the equilateral triangle of Co_1, Co_2, and Co_3. In $Rh_4(CO)_{12}$ all primed and nonprimed atoms are crystallographically independent.

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

(47) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, Wis., 1962.

TABLE III

OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS FOR THE AVERAGED DISORDERED STRUCTURE OF $Co_4(CO)_{12}$

H	L	FO	FC
*** K = 0 ***			
0	2	149	-109
0	4	167	-174
0	8	213	282
0	10	83	-70
0	12	111	-115
0	14	61	-64
0	16	82	78
1	4	21	18
1	6	186	-216
1	8	132	-115
1	10	166	190
1	14	55	-44
1	16	66	-60
1	18	70	73
2	0	136	-124
2	2	80	72
2	4	100	94
2	8	86	-93
2	14	52	22
3	2	132	-121
3	4	45	26
3	6	41	-19
3	8	71	-69
3	10	39	-28
3	12	47	58
3	14	56	-52
4	2	122	-115
4	4	87	87
4	6	106	-95
4	8	49	46
4	10	60	-64
4	12	61	46
5	2	51	36
5	4	77	-69
5	6	47	38
5	12	46	-42
6	0	29	-32
6	2	45	42
6	4	40	-27
7	2	42	23
7	4	43	31
7	6	52	-51
8	2	48	-34
8	4	84	91
8	12	54	57
9	2	59	-54
9	6	61	57
*** K = 1 ***			
0	2	247	-286
0	4	31	-30
0	6	105	123
0	8	85	75
0	10	151	-183
0	14	42	38
0	16	64	73
0	18	70	-75
1	0	265	325
1	4	30	-20
1	5	33	22
1	6	107	-108
1	7	32	-14
1	8	126	150
1	12	66	-66
1	14	52	-53
1	16	55	56
2	4	28	-11
2	8	60	-59
2	10	44	45
2	16	47	-43
3	1	57	47
3	2	63	56
3	3	54	46
3	4	134	-126
3	6	59	53
3	10	42	43
3	12	61	-59
4	2	40	28
4	3	28	-26
4	4	31	11
4	6	82	-81
4	9	34	-27
4	12	48	46
4	14	45	-37
5	2	83	-84
5	4	53	57
5	6	47	-51
6	4	39	-27
6	6	48	41
6	8	39	-30
7	1	41	-32
7	2	53	40
7	4	59	-63
8	2	58	61
8	6	60	-67
9	4	62	75
*** K = 2 ***			
0	0	181	-187
0	2	100	72
0	6	102	105
0	8	92	-103
0	12	44	44
0	14	40	42
0	16	47	-46
1	2	76	-53
1	3	34	31
1	5	165	-188
1	8	62	57
1	10	73	-76
1	16	48	49
2	0	45	29
2	1	56	-53
2	2	82	-85
2	3	169	-205
2	4	139	153
2	6	83	-81
2	10	30	-26
2	12	52	49
2	13	31	27
2	14	33	-27
3	1	103	-98
3	2	105	-108
3	3	43	35
3	6	107	101
3	8	40	-36
3	10	35	-26
3	12	39	-38
3	14	60	61
4	2	57	52
4	4	98	-99
4	6	40	40
4	10	41	34
4	12	45	-46
5	1	35	-39
5	4	30	15
5	5	30	27
5	6	31	-29
5	7	42	37
5	8	42	42
5	10	39	-35
6	0	61	61
6	1	39	33
6	2	58	-52
6	5	37	-22
6	6	43	-51
6	8	52	54
8	4	54	-62
9	2	41	33
9	6	42	-41
*** K = 3 ***			
0	2	87	62
0	4	42	-42
0	6	37	-35
0	8	39	-34
0	10	53	58
0	12	58	-55
1	0	137	-112
1	2	99	108
1	4	55	-58
1	5	28	-33
1	6	50	34
1	7	50	47
1	8	48	-50
1	10	53	49
1	12	36	-37
2	2	38	28
2	6	98	-97
2	12	63	55
2	14	63	-61
3	1	56	-58
3	2	84	-97
3	3	44	-46
3	4	101	100
3	6	40	-28
3	10	62	-60
3	12	64	67
4	1	22	-34
4	2	22	-10
4	4	30	-38
4	6	40	38
4	8	27	-25
4	10	29	13
4	14	42	43
5	0	107	-141
5	2	36	32
5	6	43	46
5	8	85	-82
6	2	89	-94
6	6	65	58
6	10	65	-64
7	0	62	69
7	1	37	32
7	6	39	-35
7	8	50	56
8	1	32	25
9	2	32	32
*** K = 4 ***			
0	0	214	-257
0	2	94	-88
0	4	75	73
0	6	95	-96
0	12	48	45
1	1	22	-22
1	4	47	-51
1	6	99	106
1	8	31	24
1	12	69	-55
1	14	60	56
1	20	44	-32
2	2	78	91
2	4	162	-198
2	5	41	-42
2	6	66	53
2	7	30	32
2	8	27	26
2	10	89	83
2	12	80	-84
3	2	133	139
3	3	30	36
3	4	28	39
3	6	105	-110
3	8	65	59
3	10	37	35
3	11	35	40
3	12	53	45
3	14	62	-65
4	0	74	78
4	1	33	-30
4	2	31	-35
4	4	66	58
4	8	30	11
4	9	28	-21
4	10	32	-26
5	1	25	-32
5	2	65	67
5	6	62	-49
5	8	36	-30
5	10	82	72
5	16	41	-31
6	0	137	-150
6	2	43	41
6	4	59	43
6	6	52	57
6	8	94	-97
6	12	38	36
6	14	37	37
6	16	39	-46
7	2	67	-68
7	6	49	44
7	10	59	-65
8	0	41	49
*** K = 5 ***			
0	2	99	86
0	4	31	28
0	6	71	-78
0	8	27	27
0	12	51	31
0	14	49	-33
0	20	36	30
1	0	80	-63
1	1	30	-29
1	2	70	-81
1	4	100	110
1	6	50	-41
1	10	73	-63
1	12	76	71
2	2	81	-75
2	4	30	-40
2	6	120	141
2	10	42	-38
2	12	76	-61
2	14	71	67
3	0	43	32
3	2	61	66
3	3	25	-21
3	4	133	-165
3	5	29	-40
3	6	46	44
3	8	41	37
3	10	46	32
3	12	58	-63
3	16	38	29
4	1	49	51
4	2	34	20
4	6	33	-24
4	8	35	32
4	9	34	20
4	10	42	-16
4	14	44	-38
5	0	122	139
5	2	34	-23
5	5	32	28
5	6	44	-40
5	8	90	75
5	14	42	-30
5	16	41	29
6	2	96	91
6	6	85	-70
6	10	76	79
6	16	46	-43
6	18	49	42
7	0	82	-94
7	4	41	22
7	6	38	39
7	8	65	-66
7	12	40	25
*** K = 6 ***			
0	0	62	-60
0	2	75	72
0	4	49	-59
0	6	45	40
0	8	62	-63
0	10	67	64
0	12	45	-43
1	2	19	31
1	4	32	32
1	5	63	58
1	6	49	-51
1	8	30	30
1	12	48	37
1	14	32	-24
2	0	25	-25
2	2	52	-52
2	3	75	74
2	4	84	91
2	6	28	-21
2	8	27	-29
2	10	50	-45
2	12	51	50
2	14	29	13
3	2	50	-40
3	3	25	-26
3	4	32	-33
3	6	85	91
3	12	44	-36
3	14	60	58
4	0	43	-43
4	1	20	22
4	2	60	61
4	4	70	-73
4	6	49	56
4	8	35	-30
5	1	28	31
5	2	67	-67
5	6	53	45
5	7	34	-28
5	10	55	-53
5	16	34	34
6	0	101	115
6	1	30	-25
6	4	46	-38
6	6	34	-31
6	8	63	70
6	12	36	-32
6	16	35	32
7	2	39	35
7	8	30	-29
7	10	45	44
8	0	37	-39
8	2	33	36
*** K = 7 ***			
0	2	53	51
0	8	36	-33
0	10	58	56
0	16	34	-26
0	18	45	40
1	0	59	-53
1	2	36	39
1	4	21	-20
1	6	49	53
1	7	32	-28
1	8	57	-59
1	10	39	33
1	16	31	-18
2	2	20	14
2	4	32	35
2	6	48	-46
2	8	28	26
2	12	39	32
2	14	35	-31
3	1	21	18
3	2	46	-45
3	3	25	24
3	4	98	104
3	6	39	-37
3	12	40	39
4	6	23	23
4	8	22	-17
4	10	24	17
4	12	33	-24
4	14	31	25
5	0	68	-68
5	2	39	41
5	6	30	30
5	8	38	-43
6	2	37	-37
6	6	25	25
6	8	31	23
6	10	50	-49
7	0	48	52
7	2	36	-33
7	6	27	-24
7	8	30	27
8	6	31	25
9	4	45	-46
*** K = 8 ***			
0	0	173	198
0	4	58	-55
0	6	37	-36
0	8	109	111
0	10	26	-25
0	12	44	-42
0	14	31	-29
0	16	43	41
1	2	68	72
1	6	49	-48
1	8	42	-42
1	10	69	72
1	16	37	-27
1	18	40	38
2	0	49	-50
2	1	18	-22
2	2	42	45
2	4	23	-23
2	5	33	32
2	6	34	33
2	7	28	-22
2	8	42	-41
3	3	29	-27
3	4	27	15
3	6	31	-36
3	11	32	-32
3	12	27	30
3	14	33	-32
4	0	30	24
4	1	25	20
4	2	48	-44
4	4	37	40
4	6	35	-32
4	10	29	-22
4	12	29	19
5	2	29	23
5	10	31	29
6	0	45	-50
6	2	31	31
6	8	36	-35
8	4	46	50
9	6	41	38
*** K = 9 ***			
0	2	125	-130
0	6	74	80
0	8	42	37
0	10	86	-94
0	14	32	29
0	16	46	38
0	18	45	-44
1	0	127	130
1	2	29	-29
1	4	35	-28
1	5	23	-23
1	6	41	-45
1	7	29	24
1	8	77	86
1	12	39	-32
1	14	36	-29
1	16	39	34
2	2	27	16
2	3	22	27
2	8	31	-24
2	10	38	31
2	16	36	-21
3	0	24	-18
3	1	24	-23
3	2	43	39
3	4	42	-37
3	5	33	36
3	6	26	19
3	7	25	-17
3	9	28	-29
3	12	35	-28
4	1	37	-40
4	6	39	-33
5	2	39	-36
5	4	33	29
6	4	33	-15
7	4	43	-34
8	2	41	34
8	6	43	-40
9	4	45	47
*** K = 10 ***			
0	0	107	-113
0	4	39	42
0	6	50	46
0	8	71	-74
0	12	53	44
0	14	42	26
0	16	41	-34
1	2	52	-60
1	6	34	31
1	8	39	30
1	10	60	-57
1	16	45	32
2	0	35	35
2	2	34	-34
2	4	44	40
2	5	29	-29
2	6	39	-37
2	8	29	29
3	1	26	29
3	2	35	-32
3	6	43	34
4	2	33	23
4	4	49	-42
5	4	32	10
5	6	41	-23
6	2	41	-30
6	4	38	24
8	4	51	-42
*** K = 11 ***			
0	2	54	61
0	6	37	-35
0	8	32	-24
0	10	60	55
0	16	34	-26
1	0	67	-73
1	6	30	27
1	8	39	-40
2	6	19	-15
2	8	24	11
3	2	27	-26
3	4	40	46
3	10	30	-25
3	12	30	31
4	2	23	-16
4	4	24	-14
4	6	36	30
5	0	23	-20
5	2	30	21
5	4	28	-22
*** K = 12 ***			
0	0	48	58
0	2	29	-35

Consequence of Crystal Disorder for $Co_4(CO)_{12}$.—The crystal disorder of $Co_4(CO)_{12}$ necessarily requires the cobalt atoms of each molecule to appear as two sets of chemically equivalent tetrahedral arrays of cobalt half-atoms related by a crystallographic twofold axis, located at ($^1/_4$, $^1/_4$, z). Since in our calculations this twofold axis in the c direction is assumed to pass through one of the three basal cobalt atoms of each cobalt tetrahedron (Co_4) and since the other three cobalt atoms (the apical and two basal ones) lie on a plane approximately perpendicular to this twofold axis, this model gives rise to a formation of a hexagonal pyramidal framework of disordered cobalt half-atoms around the twofold axis. The 12 half-carbonyl sites associated with one set of half-weighted cobalt sites overlap the other 12 half-weighted carbonyl sites associated with the other set of half-weighted cobalt sites closely enough so that the two sets of carbonyl sites are not well resolved. Hence, each of the six independent whole-weighted carbonyl groups in this structure represents the *average* of two nearly coincident, alternatively occupied carbonyl positions. The light-atom positions are nearly invariant to the disordered crystal structure, since they are responsible for the molecular packing in the crystal.

The two arrangements of the $Co_4(CO)_{12}$ molecules in the unit cell are shown in the [001] projections of the molecules given in Figures 4a and 4b.[48] Figure 4a shows the cobalt atoms in positions related by symmetry to those in the "basic" molecule in Figure 4b. To aid in the comparison, the bonds of each of the 12 carbonyl carbons to the cobalt atoms in both configurations are tabulated in Table VIII. The atoms composing the asymmetric unit listed in Table I for $Co_4(CO)_{12}$ are labeled with unprimed symbols, whereas those related by the twofold symmetry are marked with the corresponding primed symbols. In the arrangement of Figure 4b, a terminal carbonyl group C_1–O_1 coordinated to the apical Co_1 atom is related by the twofold symmetry to the bridging carbonyl group $C_{1'}$–$O_{1'}$, which is coordinated to two basal cobalt atoms, Co_2 and Co_3. Furthermore, comparison of Figures 4a and 4b reveals that with the exception of C_2–O_2 each of the six independent carbonyls is coordinated to different cobalt atoms in the two alternative configurations. The resulting consequence of this crystal disorder is that either of the two possible orientations of the cobalt framework, together with the 12 whole carbonyls (of which only *six* are crystallographically independent in our calculations), uniquely results in the identical molecular configuration.

The effect of the averaging of the pairs of the symmetry-related carbonyl sites has been discussed in full detail for another averaged disordered structure, $Fe_3(CO)_{12}$.[3] In that structure as well as in this one, each determined atomic position for the carbon and oxygen atom is the spatial average of two atomic sites, and their actual separation affects the determined averaged structure as well as individual temperature factors. Hence, the atomic parameters obtained from the least-squares refinement should be regarded as less certain than normal, and the precision implied by the reasonably good final discrepancy factors mentioned previously

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[48] The drawings shown in Figures 4 and 5 were prepared by the use of the Johnson program: C. K. Johnson, "A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustration," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

TABLE IV

OBSERVED STRUCTURE AMPLITUDES (×10) AND CALCULATED STRUCTURE FACTORS (×10) FOR THE DERIVED TWIN COMPONENT OF $Rh_4(CO)_{12}$

H	L	10FO	10FC
*** K= 0 ***			
0	2	1277	-1310
0	4	3095	-3333
0	6	1543	-1591
0	8	5940	5261
0	12	1612	-1587
0	14	1767	-1690
0	16	1921	1839
0	18	551	633
0	22	831	-976
1	4	622	602
-1	4	468	-453
1	6	2873	-2735
-1	6	3495	3326
1	8	2247	-2214
-1	8	1391	1371
1	10	2697	2759
-1	10	2415	-2470
1	12	554	569
-1	12	452	-464
1	14	785	-773
-1	14	1031	1015
1	16	1321	-1469
-1	16	947	1054
1	18	1205	1074
-1	18	929	-828
2	0	2131	-2239
2	4	810	801
-2	4	75	74
2	6	67	-52
-2	6	2223	1728
2	8	1981	-1857
-2	8	1405	-1317
2	10	1109	1091
-2	10	535	-526
2	12	330	384
-2	12	891	-1036
2	14	529	480
-2	14	1462	1325
2	16	785	-618
-2	16	389	-405
3	0	2780	-2423
3	2	1814	-1673
-3	2	783	722
3	6	695	634
-3	6	550	502
3	8	2339	-2311
-3	8	1280	-1265
3	10	1641	-1763
-3	10	1074	-1154
3	12	2173	2220
-3	12	1163	1188
3	14	18	-18
-3	14	1086	1090
3	16	835	-753
-3	16	983	-887
3	18	1069	-1122
-3	18	692	-726
3	20	1030	957
-3	20	256	238
3	22	118	106
-3	22	985	883
4	0	585	636
4	2	4943	-4855
-4	2	1807	1775
4	6	1640	1609
-4	6	4470	-4384
4	8	1907	1635
-4	8	167	143
4	10	3222	-3023
-4	10	1283	1204
4	12	605	-566
-4	12	2124	1984
4	14	906	904
-4	14	1893	-1888
4	16	1178	1222
-4	16	346	-359
4	18	1009	-1034
-4	18	345	353
4	20	455	-560
-4	20	1004	1236
5	0	1649	1412
5	2	1655	1542
-5	2	488	454
5	4	1765	-2574
-5	4	1290	-1881
5	8	1180	1097
-5	8	1124	1065
5	10	1414	1461
-5	10	815	841
5	12	1735	-1768
-5	12	1131	-1152
5	16	318	261
-5	16	871	716
5	18	947	873
-5	18	499	460
5	20	996	-736
-5	20	297	-220
6	2	924	949
-6	2	548	563
6	4	414	-509
-6	4	997	-1227
6	6	191	-189
-6	6	730	724
6	10	471	503
-6	10	925	988
6	12	468	-385
-6	12	900	-741
6	14	666	-463
-6	14	295	205
7	0	1264	1212
7	2	857	783
-7	2	2436	-2227
7	4	472	601
-7	4	337	-428
7	6	2019	-2116
-7	6	782	820
7	8	605	621
-7	8	1002	1028
7	10	583	578
-7	10	1418	-1407
7	12	861	844
-7	12	692	-678
7	14	1275	-1118
-7	14	607	533
7	16	6	-5
-7	16	934	741
8	0	1151	-1063
8	2	242	-255
-8	2	692	-729
8	4	1561	1832
-8	4	1561	1831
8	8	1346	-1067
-8	8	1028	-814
8	10	822	-696
-8	10	1236	-1047
8	12	1157	943
-8	12	1446	1179
8	16	1281	-729
-8	16	447	-254
9	2	461	-347
-9	2	1323	997
11	0	840	1015
*** K= 1 ***			
0	2	5193	-4306
0	4	710	-663
0	5	271	-286
0	6	2613	2522
0	8	1477	1414
0	10	2934	-2829
0	12	548	-697
0	14	880	955
0	16	1227	1345
0	18	1123	-1177
0	20	514	-619
0	24	674	669
1	3	519	529
-1	3	189	-193
1	4	347	-268
-1	4	849	656
1	5	593	564
-1	5	102	-97
1	6	2367	-2475
-1	6	1756	1837
1	8	2319	2418
-1	8	2986	-3112
1	10	449	400
-1	10	357	318
1	12	776	-763
-1	12	502	493
1	14	1498	-1604
-1	14	1104	1182
1	16	1152	1199
-1	16	1303	-1356
1	22	633	-705
-1	22	525	585
2	0	609	528
2	1	299	-281
-2	1	435	-409
2	2	413	358
-2	2	633	-549
2	3	359	362
-2	3	777	784
2	4	1043	-1134
-2	4	865	940
2	5	318	425
-2	5	342	458
2	8	410	-391
-2	8	887	-846
2	9	666	-639
-2	9	259	-248
2	10	1101	991
-2	10	24	-22
2	12	516	-577
-2	12	387	433
2	16	467	-447
-2	16	607	-581
2	18	750	627
-2	18	84	70
3	1	597	575
-3	1	548	528
3	2	3454	3463
-3	2	1294	1297
3	3	253	-274
-3	3	649	705
3	4	1401	-1700
-3	4	1959	2377
3	5	189	174
-3	5	450	-416
3	6	1146	-1179
-3	6	2910	-2993
3	8	1198	-1153
-3	8	336	-323
3	10	2289	2201
-3	10	616	592
3	12	290	-269
-3	12	2227	2063
3	14	482	-439
-3	14	1613	-1468
3	16	863	-836
-3	16	312	-302
3	18	989	954
-3	18	8	-8
3	20	290	308
-3	20	1023	1087
4	0	2563	-2627
4	1	336	364
-4	1	560	606
4	2	640	-584
-4	2	955	872
4	4	2745	3227
-4	4	2939	-3456
4	5	338	-363
-4	5	416	-447
4	6	514	-502
-4	6	349	-340
4	8	1495	-1645
-4	8	1825	2010
4	9	151	159
-4	9	450	475
4	10	1348	-1404
-4	10	1233	1285
4	12	2201	2118
-4	12	1460	-1405
4	14	326	340
-4	14	739	-769
4	16	464	-406
-4	16	1076	942
4	18	982	-1116
-4	18	604	686
4	20	960	917
-4	20	331	-316
5	0	814	677
5	2	2709	-2676
-5	2	610	-603
5	3	286	292
-5	3	552	-564
5	4	30	-31
-5	4	1029	-1085
5	6	966	823
-5	6	2819	2402
5	8	1205	971
-5	8	843	-679
5	10	1577	-1434
-5	10	421	-383
5	12	376	-317
-5	12	1115	-941
5	14	415	380
-5	14	1409	1289
5	16	917	662
-5	16	156	-113
5	20	624	-392
-5	20	878	-552
6	0	545	-601
6	1	103	89
-6	1	554	-479
6	2	170	155
-6	2	1242	-1134
6	4	838	-872
-6	4	358	372
6	6	1261	1146
-6	6	132	120
6	8	882	-765
-6	8	588	510
6	10	472	371
-6	10	565	-444
6	12	805	-556
-6	12	141	-97
7	0	884	864
7	1	501	-510
-7	1	487	-495
7	2	172	143
-7	2	1487	-1238
7	4	1267	-1597
-7	4	1399	1763
7	6	668	400
-7	6	29	-17
7	8	1010	968
-7	8	393	-377
7	10	316	297
-7	10	1418	-1331
7	12	985	-947
-7	12	1093	1051
8	0	535	566
8	2	952	896
-8	2	1936	1823
8	4	833	875
-8	4	218	-229
8	6	2211	-1920
-8	6	821	-713
8	8	249	171
-8	8	1093	-753
8	10	632	523
-8	10	1401	1158
8	12	1257	841
-8	12	304	204
8	14	1605	-1051
-8	14	555	-364
10	0	493	-463
12	0	705	862
*** K= 2 ***			
0	0	4576	-3340
0	2	1024	1218
0	4	560	309
0	6	1841	1745
0	7	262	-286
0	8	2096	-2159
0	14	1115	1111
0	16	1174	-1096
1	0	3987	1593
1	2	1405	-804
-1	2	1463	837
1	3	408	374
-1	3	536	491
1	4	1061	-1014
-1	4	1093	-1045
1	5	1804	-1665
-1	5	2415	-2228
1	6	66	-64
-1	6	663	-646
1	8	1537	1593
-1	8	333	345
1	10	887	-826
-1	10	1143	1064
1	12	553	-462
-1	12	755	-631
1	16	1098	1069
-1	16	143	-140
1	18	326	-359
-1	18	639	703
2	0	540	502
2	1	155	-138
-2	1	903	803
2	2	979	-1020
-2	2	2117	-2208
2	3	1413	-1607
-2	3	1950	2218
2	4	2217	2686
-2	4	2073	2511
2	5	597	-560
-2	5	559	-524
2	6	1883	-1627
-2	6	976	-844
2	8	299	285
-2	8	622	595
2	10	612	-562
-2	10	1628	-1496
2	12	1284	1248
-2	12	1162	1129
2	14	810	-660
-2	14	453	-370
2	16	39	22
-2	16	772	432
2	18	250	-236
-2	18	795	-752
3	0	513	500
3	1	1631	-1341
-3	1	611	-502
3	2	830	-756
-3	2	2045	1862
3	3	555	553
-3	3	473	-471
3	4	1517	-1653
-3	4	1033	-1099
3	5	681	734
-3	5	330	-356
3	6	1490	1469
-3	6	1073	-1058
3	8	332	227
-3	8	539	368
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8	5	88	-66
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9	2	576	-481
-9	2	483	-403
*** K= 7 ***			
0	2	1311	1325
0	6	868	-703
0	8	572	-456
0	10	994	1114
0	16	497	-649
0	18	775	628
1	0	1593	-1533
1	1	134	-139
-1	1	857	-886
1	2	113	127
-1	2	1388	-1554
1	5	493	569
-1	5	369	427
1	6	1731	1756
-1	6	558	-567
1	7	692	-784
-1	7	236	-268
1	8	1060	-1072
-1	8	1632	1651
1	10	206	-211
-1	10	908	-931
1	14	740	895
-1	14	289	-350
1	16	510	-508
-1	16	864	860
2	0	387	385
2	1	270	-238
-2	1	402	355
2	2	130	-156
-2	2	511	611
2	3	375	-368
-2	3	452	444
2	7	684	645
-2	7	309	-291
2	8	854	708
-2	8	206	-171
3	2	1361	-1240
-3	2	215	196
3	3	569	415
-3	3	86	-63
3	4	1367	1397
-3	4	1505	-1538
3	6	76	65
-3	6	1525	1299
3	10	940	-790
-3	10	237	199
3	12	502	478
-3	12	1095	-1042
3	14	28	-21
-3	14	844	631
4	0	898	899
4	1	482	532
-4	1	162	178
4	2	836	795
-4	2	204	-194
4	3	829	-764
-4	3	1	1
4	4	1362	-1376
-4	4	1378	1394
4	5	264	-264
-4	5	564	-563
4	8	277	270
-4	8	926	-903
4	10	974	936
-4	10	211	-202
4	12	1143	-1006
-4	12	631	556
5	0	1176	-1339
5	1	762	857
-5	1	276	-311
5	2	1117	1173
-5	2	72	75
5	3	577	584
-5	3	743	-753
5	6	174	152
-5	6	1367	-1192
5	7	506	-535
-5	7	746	788
5	8	815	-884
-5	8	907	985
5	14	171	147
-5	14	1003	-865
6	0	476	567
6	1	479	-528
-6	1	351	-387
6	2	730	-551
-6	2	100	75
6	3	682	511
-6	3	235	176
6	4	426	307
-6	4	472	-339
6	5	305	274
-6	5	677	607
6	6	293	-232
-6	6	700	554
6	8	769	780
-6	8	225	-228
6	9	636	-513
-6	9	522	-422
6	10	989	-587
-6	10	182	-108
7	2	294	-276
-7	2	619	581
7	4	617	546
-7	4	599	-530
8	2	212	-220
-8	2	909	-947
8	4	920	-773
-8	4	707	594
8	6	1293	924
-8	6	356	254
*** K= 8 ***			
0	0	3294	3699
0	2	598	-519
0	3	607	397
0	4	1300	-1362
0	6	1055	-961
0	8	2172	2273
0	12	672	-716
0	14	896	-905
0	16	1066	1032
1	1	172	168
-1	1	810	794
1	2	1779	1663
-1	2	1387	-1297
1	3	768	689
-1	3	200	180
1	5	187	170
-1	5	719	-652
1	6	986	-937
-1	6	1402	1334
1	7	815	-870
-1	7	215	-229
1	8	946	-944
-1	8	381	380
1	10	1150	1219
-1	10	1226	-1300
1	14	388	-296
-1	14	530	404
1	16	642	-794
-1	16	409	506
1	18	651	575
-1	18	653	-578
2	0	1231	-1144
2	1	674	-706
-2	1	332	347
2	2	1125	1099
-2	2	682	667
2	3	264	-260
-2	3	1080	-1064
2	4	203	-244
-2	4	562	-677
2	5	1600	1415
-2	5	145	-128
2	6	470	435
-2	6	1198	1108
2	7	151	-126
-2	7	615	517
2	8	1098	-1073
-2	8	864	-844
2	9	483	-408
-2	9	457	386
2	10	649	536
-2	10	214	177
2	11	359	-350
-2	11	679	-661
2	12	142	-129
-2	12	707	-643
2	13	733	586
-2	13	352	-282
2	14	354	340
-2	14	757	727
3	0	1125	-1143
3	1	14	-9
-3	1	537	-331
3	2	515	-556
-3	2	278	-300
3	3	519	-381
-3	3	247	-182
3	4	1603	1646
-3	4	1353	1390
3	8	800	-800
-3	8	751	-752
3	10	734	-794
-3	10	605	-655
3	12	1248	1142
-3	12	587	537
4	0	727	627
4	2	1981	-2110
-4	2	966	1028
4	4	102	121
-4	4	647	773
4	6	985	910
-4	6	2197	-2028
4	8	803	874
-4	8	85	93
4	10	1560	-1520
-4	10	655	638
4	12	441	-401
-4	12	1008	917
4	14	461	449
-4	14	1103	-1072
5	0	673	685
5	1	624	809
-5	1	225	-292
5	2	768	827
-5	2	105	113
5	4	1396	-1340
-5	4	1175	-1128
5	5	360	-438
-5	5	611	744
5	8	404	324
-5	8	801	643
5	9	693	548
-5	9	606	-479
5	10	985	930
-5	10	292	276
5	12	908	-968
-5	12	593	-632
6	1	463	503
-6	1	644	699
6	2	673	702
-6	2	367	383
6	4	381	-291
-6	4	841	-641
6	6	151	106
-6	6	747	524
6	7	504	-495
-6	7	653	-641
7	0	589	619
7	2	364	369
-7	2	1099	-1113
7	6	1259	-1049
-7	6	436	363
7	10	232	170
-7	10	1022	-748
8	0	942	-656
8	4	1259	954
-8	4	1297	982
9	2	134	-122
-9	2	781	711
*** K= 9 ***			
0	2	1974	-2113
0	6	1526	1575
0	8	803	865
0	10	1428	-1577
0	14	574	662
0	16	745	848
0	18	723	-698
1	0	2269	2385
1	1	531	579
-1	1	581	633
1	2	566	-577
-1	2	557	569
1	3	309	318
-1	3	912	-938
1	4	443	-446
-1	4	485	488
1	5	879	-904
-1	5	188	-193
1	6	1060	-1010
-1	6	940	895
1	7	167	176
-1	7	554	583
1	8	1443	1508
-1	8	1666	-1741
1	9	305	312
-1	9	521	533
1	11	251	285
-1	11	645	-732
1	14	965	-962
-1	14	783	780
1	16	811	737
-1	16	828	-752
2	0	351	249
2	1	135	133
-2	1	893	-884
2	2	610	495
-2	2	28	-22
2	3	864	920
-2	3	60	-64
2	4	714	-634
-2	4	750	667
2	5	299	329
-2	5	874	961
2	7	794	-870
-2	7	276	302
2	8	213	-145
-2	8	717	-489
2	9	391	-389
-2	9	659	-654
2	10	895	808
-2	10	45	-40
2	16	376	-228
-2	16	831	-503
3	2	1936	2009
-3	2	731	756
3	3	249	-258
-3	3	746	772
3	4	366	-320
-3	4	1089	954
3	6	849	-738
-3	6	1938	-1684
3	8	709	-636
-3	8	84	-75
3	10	1522	1387
-3	10	417	380
3	11	464	-413
-3	11	700	622
3	12	46	48
-3	12	1116	1170
3	14	370	-351
-3	14	968	-919
4	0	1264	-1401
4	1	366	-288
-4	1	465	366
4	2	401	-299
-4	2	613	457
4	4	1523	1696
-4	4	1576	-1756
4	6	224	-185
-4	6	522	-431
4	8	965	-1048
-4	8	1027	1115
4	10	719	-855
-4	10	655	779
4	12	1111	1246
-4	12	822	-922
5	1	237	-290
-5	1	568	696
5	2	1469	-1462
-5	2	331	-330
5	4	237	178
-5	4	987	-743
5	6	618	511
-5	6	1648	1363
5	10	997	-926
-5	10	194	-180
5	12	223	-158
-5	12	971	-689
6	1	639	878
-6	1	96	-132
6	2	189	164
-6	2	955	-827
6	3	180	-114
-6	3	990	-629
6	4	764	-637
-6	4	248	207
6	6	947	694
-6	6	187	137
6	9	786	600
-6	9	105	80
7	0	544	608
7	2	6	-5
-7	2	739	-641
7	4	1045	-1021
-7	4	1206	1178
8	2	566	588
-8	2	1020	1060
8	6	1360	-1071
-8	6	650	-512
*** K=10 ***			
0	0	2091	-2118
0	2	595	602
0	4	607	666
0	6	1123	1066
0	8	1381	-1492
0	12	497	521
0	14	707	754
0	16	626	-782
1	1	138	-83
-1	1	704	-427
1	2	986	-1030
-1	2	852	890
1	3	299	-752
-1	3	51	-128
1	6	516	529
-1	6	767	-785
1	8	727	755
-1	8	292	-305
1	10	949	-1027
-1	10	698	755
1	16	724	668
-1	16	369	-340
2	0	598	616
2	1	571	610
-2	1	170	-182
2	2	881	-916
-2	2	160	-167
2	3	242	266
-2	3	1011	1111
2	4	600	549
-2	4	675	618
2	5	960	-1005
-2	5	192	-201
2	6	300	-295
-2	6	947	-934
2	8	572	597
-2	8	436	455
2	11	349	370
-2	11	682	723
2	14	322	-271
-2	14	754	-636
3	0	942	867
3	1	214	-235
-3	1	647	712
3	2	113	-106
-3	2	655	612
3	4	981	-1012
-3	4	992	-1023
3	6	393	249
-3	6	694	-440
3	8	486	442
-3	8	665	605
3	10	339	316
-3	10	706	658
3	12	912	-876
-3	12	488	-469
4	2	1330	1427
-4	2	614	-659
4	4	395	-359
-4	4	875	-797
4	6	709	-665
-4	6	1461	1370
4	10	1129	1080
-4	10	339	-325
4	12	38	37
-4	12	906	-685
4	14	315	-343
-4	14	707	770
5	0	409	-321
5	4	1047	1037
-5	4	907	898
6	0	532	62
6	1	183	178
-6	1	738	-717
6	4	483	431
-6	4	806	720
7	0	636	-674
7	2	262	-255
-7	2	831	809
7	6	1066	1019
-7	6	306	-293
8	4	1143	-783
-8	4	1011	-692
*** K=11 ***			
0	2	726	780
0	10	570	656
1	0	951	-922
1	2	213	214
-1	2	983	-991
1	6	759	762
-1	6	227	-228
1	8	535	-563
-1	8	618	651
2	0	497	281
2	1	119	115
-2	1	613	595
3	2	691	-846
-3	2	116	143
3	3	546	579
-3	3	545	-577
3	4	639	635
-3	4	853	-849
3	10	735	-795
-3	10	362	392
4	4	721	-792
-4	4	537	590
4	12	629	-601
-4	12	316	302
5	0	429	-462
6	0	504	658
*** K=12 ***			
0	1	663	-733
0	2	550	-581
0	4	551	555
0	7	569	672
0	12	539	298
1	0	662	-667
1	4	120	218
-1	4	315	572
1	6	300	442
-1	6	164	-241
1	8	264	-472
-1	8	226	-404
2	2	5	-5
-2	2	961	913
2	4	1103	-1087
-2	4	851	-838
2	10	228	207
-2	10	1004	929
2	12	807	-739
-2	12	462	-423
3	0	480	404
3	2	412	432
-3	2	613	-642
3	6	751	-720
-3	6	472	452
4	4	454	392
-4	4	472	408
5	0	449	-512
5	2	751	515
-5	2	176	-120
6	0	464	-572
6	2	390	-385
-6	2	697	687
7	0	545	588
*** K=13 ***			
0	1	485	-628
0	2	457	409
0	3	504	461
0	5	586	691
0	6	516	-419
0	9	535	-612
1	1	476	-555
-1	1	497	580
1	2	103	123
-1	2	846	1018
1	4	865	885
-1	4	696	-712
1	6	740	-767
-1	6	209	-217
1	7	506	584
-1	7	591	-683
1	10	46	-43
-1	10	923	874
1	12	401	671
-1	12	189	-316
2	0	705	-703
2	2	634	-598
-2	2	658	-621
2	4	410	349
-2	4	774	-657
2	6	934	981
-2	6	410	430
2	14	904	684
-2	14	150	114
3	2	83	-82
-3	2	773	-772
3	4	912	-955
-3	4	759	794
4	0	516	474
5	0	595	664
6	0	484	-678
6	2	845	514
-6	2	468	285
*** K=14 ***			
0	1	448	555
0	4	532	-494
0	7	546	-675
0	10	518	382
1	4	349	-272
-1	4	635	-495
1	6	657	-475
-1	6	333	241
2	2	207	215
-2	2	941	-976
2	4	812	799
-2	4	672	661
2	6	774	-665
-2	6	359	309
3	0	531	-513
6	0	504	570

applies only to the averaged structure, not to the individual molecular components. It is not unexpected, therefore, that while the six bridging Co–C distances remain in a reasonable range (1.96–2.19 Å), the nine terminal Co–C distances vary within an exceptionally wide range of 1.64–2.26 Å. Considerable deviations of terminal Co–C–O angles (143–177°) from linearity are also a consequence of the disorder. A similar nonconformity of the determined molecular parameters to normal values, for disordered structures, is also ob-

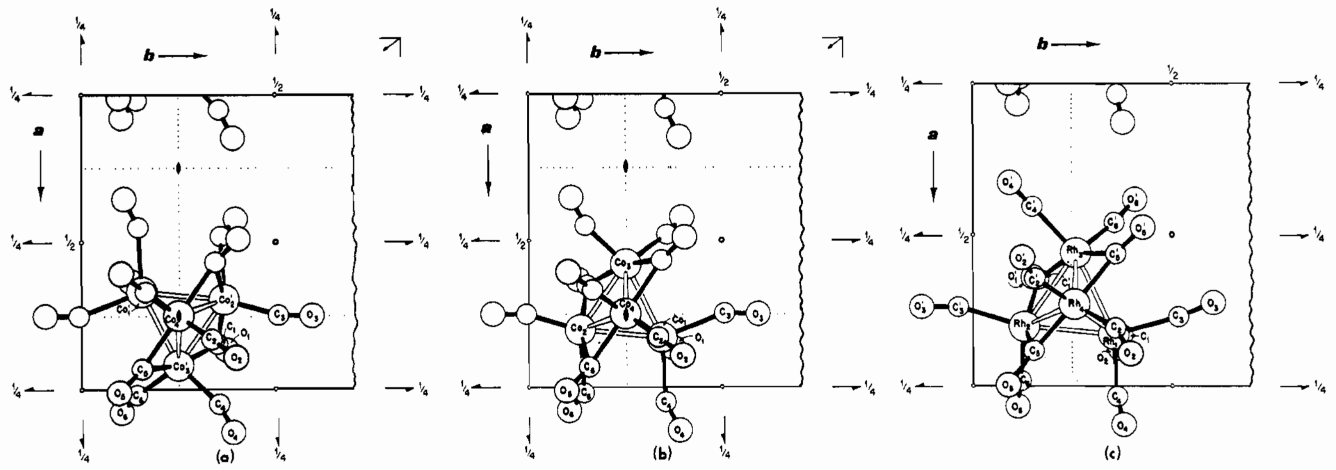

Figure 4.—[001] projections of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ molecules in their unit cells. The crystallographic twofold axis relating the two statistical orientations of the "basic" configuration [shown in (b)] and the alternative configuration [shown in (a)] to each other is shown to be coincident with the localized threefold axis of the tetrahedron of cobalt atoms (this axis passes through a basal cobalt atom, Co_4). The determined carbonyl positions represent the *average* of the nearly coincident positions of the corresponding half-weighted carbonyl groups for these two possible orientations of (a) and (b). Shown in (c) is the projection of the rhodium complex closely resembling that in (b) for the cobalt complex. Primed and nonprimed symbols are assigned to the atoms of the $Rh_4(CO)_{12}$ molecule in corresponding positions as in the $Co_4(CO)_{12}$ molecule.

TABLE V

BOND DISTANCES (Å) WITH STANDARD DEVIATIONS[a,b]

Bond	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
M_1–M_2	2.494 (12)	2.706 (8)
M_1–M_3	2.508 (16)	2.739 (7)
M_1–M_4	2.480 (14)	2.701 (8)
M_2–M_3	2.441 (14)	2.734 (7)
M_3–M_4	2.527 (10)	2.716 (6)
M_4–M_2	2.486 (13)	2.796 (8)
M_1–C_1	1.64 (6)	1.93 (5)
M_1–C_3	2.06 (4)	2.06 (5)
M_1–C_4	2.05 (5)	1.97 (8)
M_2–C_6	2.26 (6)	2.05 (7)
M_2–C_3'	1.73 (4)	2.09 (7)
M_3–C_6'	1.93 (5)	1.75 (6)
M_3–C_4'	1.77 (4)	1.96 (6)
M_4–C_2	1.68 (4)	1.83 (6)
M_4–C_2'	[1.68 (4)]	1.97 (9)
M_2–C_1'	2.19 (6)	1.98 (11)
M_3–C_1'	2.18 (5)	1.93 (11)
M_3–C_5'	1.96 (4)	2.18 (6)
M_4–C_5'	2.01 (4)	2.01 (6)
M_4–C_5	[2.01 (4)]	1.94 (5)
M_2–C_5	2.00 (5)	1.92 (5)
C_1–O_1	1.11 (6)	1.29 (8)
C_2–O_2	1.20 (4)	1.28 (7)
C_3–O_3	1.02 (3)	1.14 (5)
C_4–O_4	1.01 (5)	0.93 (8)
C_5–O_5	1.18 (4)	1.52 (7)
C_6–O_6	0.85 (5)	0.96 (7)
C_1'–O_1'	[1.11 (6)]	1.32 (12)
C_2'–O_2'	[1.20 (4)]	1.08 (10)
C_3'–O_3'	[1.02 (3)]	1.15 (7)
C_4'–O_4'	[1.01 (5)]	1.09 (7)
C_5'–O_5'	[1.18 (4)]	1.23 (6)
C_6'–O_6'	[0.85 (5)]	1.24 (6)

[a] Standard deviations of the last significant figure(s) are given in parentheses. [b] For $Co_4(CO)_{12}$ there is a pair of symmetry-equivalent values for each bond length owing to the presence of a crystallographic twofold axis. Values with brackets have been duplicated to aid in comparison with the corresponding values for $Rh_4(CO)_{12}$.

served for $Fe_3(CO)_{12}$ (disordered by a center of symmetry)[3] and $Co_6(CO)_{16}C_2S_3$ (disordered by a mirror plane).[49]

Structural Relationship between $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. (a) Crystallographic Aspects.—The cell parameters of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ differ only in that the length of each of the three axes for the cobalt complex is approximately 3% shorter than the corresponding value for the rhodium complex. In spite of the similarity of the unit cell constants and of the molecular structures, the cobalt complex crystallizes in a disordered structure for which coherent diffraction occurs, whereas the rhodium complex forms crystals for which the assumption of an incoherent twinning model was found to be successful in the unraveling of the nature of the crystal twinning.

It is provocative to consider the space group of a possible ordered $Co_4(CO)_{12}$ crystal (*i.e.*, one with a structure containing only one of the two sets of cobalt atom positions). Since the symmetry operations of the orthorhombic space group Pccn can be formally considered to be obtained by the combination of either a twofold axis or an *n* glide plane operation in the *c* direction with those of the monoclinic space group $P2_1/c$ with $\beta = 90°$ (*e.g.*, $P2_1/c$ is a proper subgroup of Pccn), one way to look at the disordered structure of $Co_4(CO)_{12}$ is that the apparent orthorhombic unit cell is the composite of the two monoclinic unit cells of the same dimensions with symmetry $P2_1/c$, in a way that gives rise to superposed atomic positions for the two statistically oriented molecules around the twofold axis in the *c* direction. Indeterminancy of these twofold-related molecular configurations formed during the course of crystal growth, which takes place on a microscopic

(49) C. H. Wei and P. A. Agron, to be submitted for publication.

TABLE VI

SELECTED BOND ANGLES (DEG) WITH STANDARD DEVIATIONS[a,b]

Angle	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
	M–M–M	
M_2–M_3–M_4	60.0 (4)	61.7 (2)
M_3–M_4–M_2	58.3 (4)	59.5 (2)
M_4–M_2–M_3	61.7 (3)	58.8 (2)
M_2–M_1–M_3	58.4 (5)	60.3 (2)
M_1–M_3–M_2	60.5 (4)	59.2 (2)
M_3–M_2–M_1	61.1 (5)	60.5 (2)
M_3–M_1–M_4	60.9 (3)	59.9 (2)
M_1–M_4–M_2	60.1 (4)	60.8 (2)
M_4–M_3–M_1	59.0 (4)	59.3 (2)
M_4–M_1–M_2	60.0 (5)	62.3 (2)
M_1–M_2–M_4	59.7 (5)	58.8 (2)
M_2–M_4–M_1	60.3 (4)	58.9 (2)
	M–M–CO	
M_1–M_2–C_6	81.6 (11)	88.9 (16)
M_1–M_3–C_6'	96.8 (16)	101.5 (18)
M_1–M_4–C_2	100.0 (12)	94.7 (21)
M_1–M_2–C_3'	166.6 (20)	168.2 (22)
M_1–M_3–C_4'	155.8 (16)	160.5 (15)
M_1–M_4–C_2'	164.8 (12)	166.2 (25)
M_1–M_2–C_1'	86.9 (12)	81.5 (31)
M_1–M_2–C_5	80.7 (11)	79.2 (14)
M_1–M_3–C_1'	86.8 (15)	81.6 (33)
M_1–M_3–C_5'	80.3 (13)	76.4 (15)
M_1–M_4–C_5'	80.1 (13)	80.0 (17)
M_1–M_4–C_5	80.8 (12)	78.9 (15)
M_2–M_3–C_1'	56.3 (16)	44.5 (34)
M_3–M_2–C_1'	55.7 (14)	44.8 (33)
M_3–M_4–C_5'	49.6 (12)	52.4 (17)
M_4–M_3–C_5'	51.3 (12)	47.0 (15)
M_4–M_2–C_5	51.8 (13)	43.9 (14)
M_2–M_4–C_5	51.5 (12)	43.2 (15)
M_2–M_3–C_6'	138.7 (16)	143.2 (21)
M_3–M_2–C_6	132.6 (11)	134.5 (16)
M_2–M_3–C_4'	99.0 (14)	102.6 (15)
M_3–M_2–C_3'	107.7 (21)	108.0 (21)
M_3–M_4–C_2	142.8 (11)	136.4 (20)
M_4–M_3–C_6'	140.0 (15)	138.9 (20)
M_3–M_4–C_2'	106.3 (13)	109.3 (27)
M_4–M_3–C_4'	100.6 (14)	107.3 (19)
M_4–M_2–C_6	124.1 (12)	134.2 (16)
M_2–M_4–C_2	142.3 (13)	140.1 (22)
M_4–M_2–C_3'	109.4 (14)	119.0 (24)
M_2–M_4–C_2'	107.7 (11)	108.2 (25)
M_2–M_3–C_5'	111.2 (12)	108.1 (15)
M_2–M_4–C_5'	107.7 (12)	111.2 (18)
M_3–M_4–C_5	109.5 (13)	102.6 (15)
M_3–M_2–C_5	113.3 (13)	102.7 (14)
M_4–M_2–C_1'	117.3 (14)	103.6 (33)
M_4–M_3–C_1'	116.3 (16)	108.2 (35)
	M–M–CO (Continued)	
M_2–M_1–C_1	94.3 (15)	98.2 (15)
M_2–M_1–C_3	150.7 (18)	156.8 (15)
M_2–M_1–C_4	97.9 (11)	98.2 (20)
M_3–M_1–C_1	96.9 (20)	94.7 (15)
M_3–M_1–C_3	94.3 (19)	98.8 (15)
M_3–M_1–C_4	151.5 (12)	153.8 (22)
M_4–M_1–C_1	151.8 (17)	152.9 (15)
M_4–M_1–C_3	99.0 (13)	99.6 (15)
M_4–M_1–C_4	94.6 (12)	98.0 (25)
	M–C–O	
M_1–C_1–O_1	166.8 (43)	158.6 (50)
M_1–C_3–O_3	156.7 (65)	172.7 (46)
M_1–C_4–O_4	158.3 (37)	170.4 (80)
M_2–C_6–O_6	143.4 (51)	177.4 (68)
M_2–C_3'–O_3'	162.8 (66)	156.5 (78)
M_3–C_6'–O_6'	168.6 (60)	169.1 (52)
M_3–C_4'–O_4'	160.3 (40)	164.8 (70)
M_4–C_2–O_2	177.3 (34)	157.0 (52)
M_4–C_2'–O_2'	[177.3 (34)]	160.6 (78)
M_2–C_1'–O_1'	145.4 (49)	131.1 (88)
M_3–C_1'–O_1'	146.5 (49)	137.6 (87)
M_3–C_5'–O_5'	144.2 (35)	129.5 (46)
M_4–C_5'–O_5'	134.6 (35)	148.3 (53)
M_4–C_5–O_5	[134.6 (35)]	133.5 (40)
M_2–C_5–O_5	134.9 (30)	131.3 (38)
	C–M–C	
C_1–M_1–C_3	99.9 (20)	93.2 (21)
C_3–M_1–C_4	104.3 (20)	98.7 (27)
C_4–M_1–C_1	100.8 (23)	103.6 (30)
C_6–M_2–C_3'	111.8 (22)	98.9 (27)
C_6'–M_3–C_4'	107.5 (21)	97.7 (25)
C_2–M_4–C_2'	95.1 (24)	99.0 (33)
C_6–M_2–C_1'	97.1 (21)	102.2 (36)
C_6–M_2–C_5	85.7 (18)	103.3 (22)
C_3'–M_2–C_1'	92.3 (20)	88.1 (38)
C_3'–M_2–C_5	98.7 (18)	107.3 (28)
C_6'–M_3–C_5'	96.5 (19)	95.5 (26)
C_6'–M_3–C_1'	91.1 (20)	103.6 (41)
C_4'–M_3–C_5'	97.3 (17)	105.5 (26)
C_4'–M_3–C_1'	91.9 (18)	90.4 (36)
C_2–M_4–C_5	96.3 (17)	107.3 (27)
C_2–M_4–C_5'	99.0 (16)	90.3 (26)
C_2'–M_4–C_5	[99.0 (16)]	94.9 (28)
C_2'–M_4–C_5'	[96.3 (17)]	101.8 (33)
	M–CO–M	
M_2–C_1'–M_3	68.0 (17)	88.8 (48)
M_3–C_5'–M_4	79.1 (15)	80.6 (21)
M_4–C_5–M_2	76.7 (16)	92.9 (21)

[a] Standard deviations of the last significant figure(s) are given in parentheses. [b] For $Co_4(CO)_{12}$ there is a pair of symmetry-related values for each bond angle owing to the presence of a crystallographic twofold axis. Values with brackets have been duplicated to aid in comparison with the corresponding values for $Rh_4(CO)_{12}$.

scale, leads to the disordered structure obtained for $Co_4(CO)_{12}$.

The presence of a (100) twinning mirror plane, assumed in the twin model for $Rh_4(CO)_{12}$, implies that the unit cells of two types of domains in the crystal are arranged in such a way that they are parallel in the *a* direction and are related by a mirror plane across boundaries of the regions where unit cells for both twin components are formed alternatively with a repeated period on such a fine scale that a pseudomicroscopic polysynthetic twinning on (100) results. Since the twinning operation at a boundary does not involve a gliding, the presence of characteristic symmetry operations involving the screw axis in the *b* direction for the individual twin components is retained, and the twin composite has the common symmetry of the individual twin components, augmented by the operation of the twin law.

On the basis of study of growth habits for 118 species of monoclinic crystals reported in the literature, Wolten

TABLE VII

EQUATIONS OF BEST MOLECULAR PLANES AND DISTANCES (Å) OF ATOMS FROM THESE PLANES[a]

(a) Pseudomirror Plane through M_1, M_2, and Midpoint of M_3–M_4

$-5.426x + 0.384y - 13.765z + 5.980 = 0$ for $Co_4(CO)_{12}$

$-5.352x + 0.657y - 14.430z + 5.900 = 0$ for $Rh_4(CO)_{12}$

	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$		$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
C_3	−0.22	0.10	C_1'	2.19	1.91
O_3	0.21	0.23	C_5	−1.97	−1.83
C_6	−0.23	0.02	O_1'	3.13	3.01
O_6	−0.19	0.01	O_5	−2.94	−3.12
C_3'	0.01	0.32	C_6'	2.78	2.72
O_3'	−0.05	0.03	C_2	−2.57	−2.63
C_5'	0.07	−0.08	O_6'	3.50	3.82
O_5'	0.01	0.10	O_2	−3.50	−3.81
C_1	1.22	1.55	C_4'	1.56	1.89
C_4	−1.63	−1.51	C_2'	−1.76	−2.05
O_1	1.96	2.30	O_4'	1.82	1.93
O_4	−2.38	−2.24	O_2'	−2.06	−2.34

(b) Pseudomirror Plane through M_1, M_3, and Midpoint of M_2–M_4

$2.173x - 6.417y - 13.831z + 2.017 = 0$ for $Co_4(CO)_{12}$

$2.176x - 6.479y - 14.346z + 2.168 = 0$ for $Rh_4(CO)_{12}$

	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$		$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
C_4	−0.03	−0.02	C_5'	−1.92	−2.11
O_4	−0.29	−0.17	C_1'	2.17	1.88
C_6'	0.03	−0.08	O_5'	−2.99	−3.08
O_6'	0.04	0.06	O_1'	3.12	3.01
C_4'	0.10	0.15	C_2	−2.52	−2.81
O_4'	−0.21	0.00	C_6	2.58	2.82
C_5	0.07	0.01	O_2	−3.41	−3.61
O_5	0.11	0.04	O_6	3.35	3.51
C_3	−1.51	−1.50	C_2'	−1.77	−2.02
C_1	1.30	1.40	C_3'	1.79	2.41
O_3	−2.10	−2.34	O_2'	−2.12	−2.61
O_1	2.04	2.52	O_3'	2.32	2.79

(c) Pseudomirror Plane through M_1, M_4, and Midpoint of M_2–M_3

$7.381x - 6.677y - 0.289z - 3.797 = 0$ for $Co_4(CO)_{12}$

$7.512x - 6.991y + 0.506z - 3.820 = 0$ for $Rh_4(CO)_{12}$

	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$		$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
C_1	0.10	−0.20	C_5	1.98	1.85
O_1	0.11	0.15	C_5'	−1.96	−1.98
C_2	0.00	−0.09	O_5	2.94	3.18
O_2	0.03	0.30	O_5'	−2.95	−3.11
C_2'	−0.04	0.09	C_6	2.76	2.74
O_2'	−0.09	−0.19	C_6'	−2.66	−2.81
C_1'	0.02	−0.09	O_6	3.47	3.42
O_1'	0.05	−0.08	O_6'	−3.35	−3.78
C_4	1.55	1.50	C_3'	1.75	2.03
C_3	−1.69	−1.56	C_4'	−1.49	−1.75
O_4	2.01	2.09	O_3'	2.33	2.69
O_3	−2.27	−2.51	O_4'	−1.97	−1.94

(d) Plane through M_2, M_3, and M_4

$4.680x + 8.893y - 6.722z - 4.137 = 0$ for $Co_4(CO)_{12}$

$4.884x + 9.248y - 6.362z - 4.376 = 0$ for $Rh_4(CO)_{12}$

	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$		$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$
C_1'	0.11	0.04	C_6	1.54	1.23
C_5'	0.14	0.29	C_6'	0.93	0.74
C_5	0.17	−0.01	C_2	0.70	0.93
O_1'	0.21	0.34	O_6	1.66	1.76
O_5'	0.05	0.33	O_6'	1.19	1.13
O_5	−0.24	−0.34	O_2	1.25	1.36
C_1	2.79	3.11	C_3'	−1.61	−1.82
C_3	2.95	3.28	C_4'	−1.74	−1.86
C_4	2.94	3.11	C_2'	−1.58	−1.83
O_1	3.50	3.69	O_3'	−2.41	−2.78
O_3	3.72	3.77	O_4'	−2.63	−2.92
O_4	3.59	3.60	O_2'	−2.73	−2.73

[a] *x*, *y*, and *z* represent atomic fractional coordinates in terms of the respective crystal axial systems.

TABLE VIII

COORDINATION OF CARBONYL CARBONS TO COBALT ATOMS

	Type[a]	Metal atom(s) coordinated in basic confign (Figure 4b)	Type	Metal atom(s) coordinated in alternative confign (Figure 4a)
C_1	T	Co_1	B	Co_2' and Co_3'
C_2	T	Co_4	T	Co_4
C_3	T	Co_1	T	Co_2'
C_4	T	Co_1	T	Co_3'
C_5	B	Co_2 and Co_4	B	Co_3' and Co_4
C_6	T	Co_2	T	Co_3'
C_1'	B	Co_2 and Co_3	T	Co_1'
C_2'	T	Co_4	T	Co_4
C_3'	T	Co_2	T	Co_1'
C_4'	T	Co_3	T	Co_1'
C_5'	B	Co_3 and Co_4	B	Co_2' and Co_4
C_6'	T	Co_3	T	Co_2'

[a] T and B stand for terminal and bridging carbonyl carbons, respectively.

and Chase[50] have proposed a RL (right-handed or left-handed) twinning mechanism for a group of compounds. For the twin composite involving a twinning mirror plane operating on the (100) or (001) plane, the inherent indeterminancy of "β-handedness" was suggested by them to be responsible for twin formation in these classes of compounds. Formation of the $Rh_4(CO)_{12}$ may be attributable to this RL twinning mechanism. That no study was made to identify the twinned $Rh_4(CO)_{12}$ crystals as type A [twinned on (100)][50] or type B [twinned on (001)][50] is immaterial in the treatments of the twin composite of $Rh_4(CO)_{12}$.

Thus, the structural differences between $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ can be attributed to the different modes of growth of single crystals of $P2_1/c$ symmetry. We can offer no explanation at this time for the formation of a disordered structure in one case and a twinned structure in the other from these two chemically analogous compounds.[51]

(b) Interatomic Distances and Molecular Symmetry.—The metal–metal bonding distances vary from 2.44 to 2.53 Å (individual esd, 0.02 Å) for $Co_4(CO)_{12}$, and from 2.70 to 2.80 Å (individual esd, 0.01 Å) for $Rh_4(CO)_{12}$, with no apparent differences in length between the carbonyl-bridged basal–basal M–M bonds and the apical–basal M–M bonds. The weighted average Co–Co value of 2.49 Å agrees with the value of 2.50 Å reported by Corradini,[7a] and it falls within the *normal* range of 2.4–2.7 Å obtained from a large number of organocobalt carbonyl complexes including $Co_2(CO)_8$,[52] $SCo_3(CO)_9$,[53] $Co_3(CO)_9CCH_3$,[54] $Co_3\{(SC_2H_5)_5(CO)\}(CO)_3$,[55] $Co_4(CO)_{10}S_2$,[56] $Co_4(CO)_4(SC_2$-

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[50] G. M. Wolten and A. B. Chase, *J. Chem. Phys.*, **41**, 2966 (1964).

[51] The two models are experimentally distinguishable, however. A distinct difference is the presence of Patterson peaks attributable to interatomic vectors that correspond to the disordered cobalt positions for $Co_4(CO)_{12}$; no such peaks were found for $Rh_4(CO)_{12}$.

[52] G. G. Summer, H. P. Klug, and L. E. Alexander, *Acta Cryst.*, **17**, 732 (1964).

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

[54] P. W. Sutton and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 261 (1967).

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[56] C. H. Wei and L. F. Dahl, presented in part (Paper 15) at the National Meeting of the American Crystallographic Association, Georgia Institute of Technology, Atlanta, Ga., Jan 25–28, 1967.

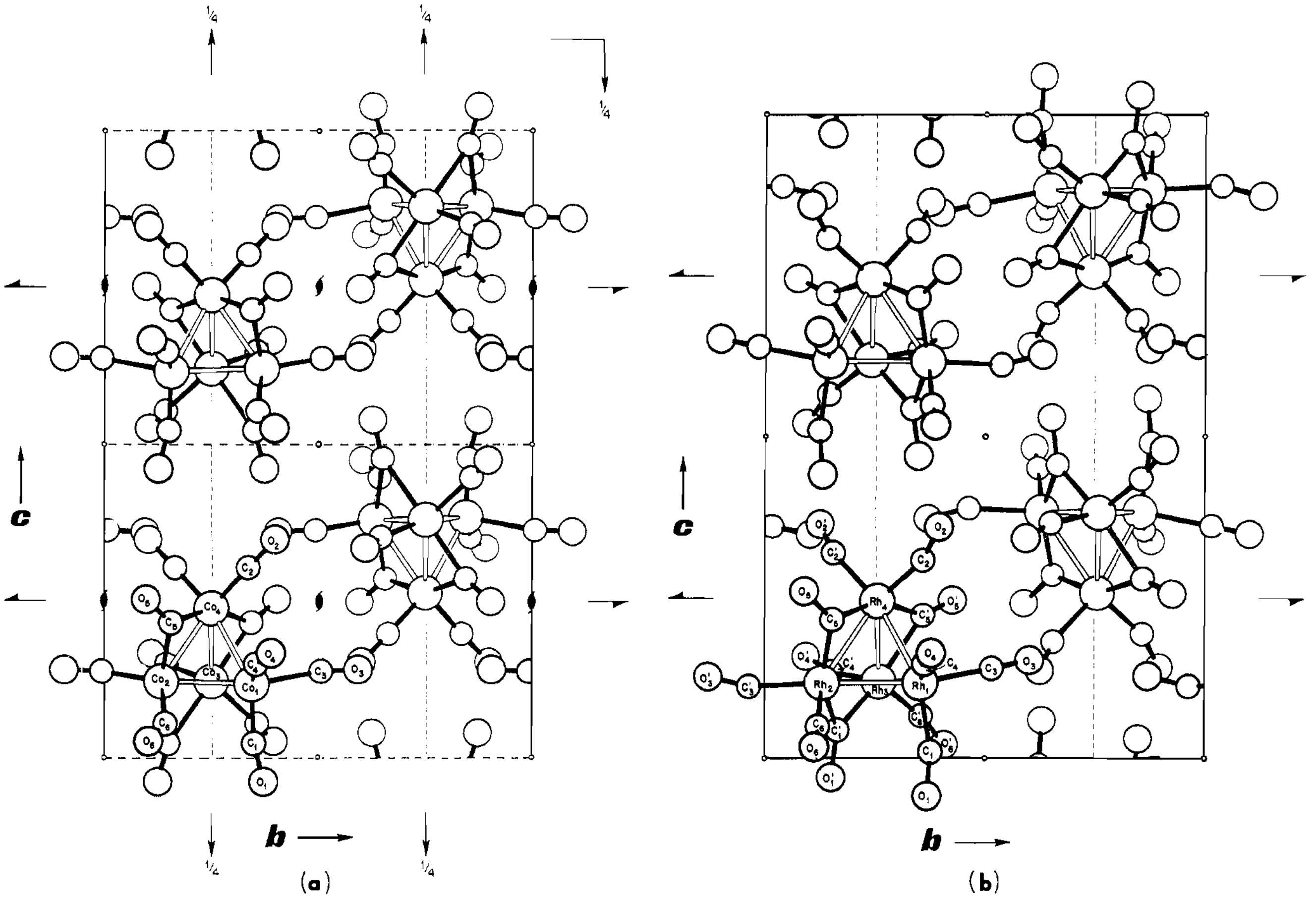

Figure 5.—[100] projections of the unit cells of (a) $Co_4(CO)_{12}$ and (b) $Rh_4(CO)_{12}$. In (a) only one orientation of the cobalt atoms is shown.

$H_5)_8$,[56] $Co_5(CO)_{10}(SC_2H_5)_5$,[57] $SCo_6(CO)_{11}(SC_2H_5)_4$,[58] $[SCo_3(CO)_7]_2S_2$,[59] and $Co_6(CO)_{16}C_2S_3$.[49] The weighted average Rh–Rh value of 2.73 Å—which is 0.24 Å longer than the averaged Co–Co distance, in rough accordance with the smaller metallic radius of 1.162 Å for the cobalt atom as compared to that of 1.252 Å for the rhodium atom[60]—is not much different from values found for other organorhodium carbonyl complexes cited elsewhere.[21b]

The M–C distances (including both terminal and bridging) range from 1.64 to 2.26 Å for $Co_4(CO)_{12}$ (the maximum difference being equivalent to 10–15 individual esd's) and from 1.75 to 2.18 Å for $Rh_4(CO)_{12}$ (maximum difference equivalent to 4–8 individual esd's). C–O bond distances, including both terminal and bridging carbonyls, range from 0.85 to 1.20 Å for $Co_4(CO)_{12}$ (difference of 6–12 esd's) and from 0.93 to 1.32 Å for $Rh_4(CO)_{12}$ (difference of 3–7 esd's), excluding C_5–O_5 (1.52 Å), which is exceptionally long. Although the apparent wide variations in M–C and C–O distances for $Co_4(CO)_{12}$ can be attributed to the crystal disorder, those obtained for $Rh_4(CO)_{12}$ cannot be readily explained, except as the result of errors involved in data collection and in treatment of the data. It is our belief, however, that these anomalies in molecular parameters are not likely to conform to the physical reality of the actual molecular geometry in either case.

The distortion of the carbonyl icosahedron, which surrounds the metal atom framework, from regularity for each of the complexes is shown by the variation in $Co_4(CO)_{12}$ of 16 independent carbon–carbon edge distances ranging from 2.48 to 3.57 Å, and by the variation in $Rh_4(CO)_{12}$ of 30 independent carbon–carbon edge distances ranging from 2.80 to 4.43 Å. Nevertheless, the carbonyl icosahedron for either $Co_4(CO)_{12}$ or $Rh_4(CO)_{12}$ is much closer to regularity than that of $Fe_3(CO)_{12}$,[3] in which the molecule involves the carbonyl icosahedron surrounding an isosceles array of iron atoms. (For a detailed stereochemical relationship between $M_4(CO)_{12}$ and $Fe_3(CO)_{12}$, see ref 3.)

Despite the vexing complexities involved in the structures of disordered $Co_4(CO)_{12}$ and twinned $Rh_4(CO)_{12}$ and despite the large variation of bond distances and angles, the two molecules as a whole are strikingly similar and remarkably close to an idealized C_{3v} symmetry. The pseudo-C_{3v} symmetry of the molecule in both complexes is shown by calculations involving three pseudomirror planes [Tables VIIa, VIIb, and VIIc], each passing through the apical metal atom (M_1), one basal metal atom, and the midpoint of the remaining

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

(60) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 256 or 403.

two metal atoms. In each case the pairs of corresponding atoms related by each of these molecular pseudomirror planes are approximately equidistant from the molecular planes. The bond distances (Table V), bond angles (Table VI), and the calculations of a plane passing through the three basal metal atoms [Table VIId] also corroborate the over-all C_{3v} pseudosymmetry of each of the molecules.

The close resemblance of the arrangement of the individual carbonyl groups as well as of the metal atoms in the two structures is clearly illustrated in the [001] projections of the "basic" molecules in the unit cells represented in Figures 4b and 4c for the cobalt and rhodium complexes, respectively. For convenient comparison, the nonprimed and primed symbols are assigned to atoms in corresponding positions for the two complexes (also see Figure 3). The observed similarity in molecular configurations for both complexes is certainly more than a coincidence and supports the correctness of the determined structures obtained from different approaches. To illustrate this structural similarity further, the [100] projections of the unit cells are shown in Figures 5a and 5b for the cobalt and the rhodium complexes, respectively. To aid in comparison, only one of the two cobalt frameworks is shown in Figure 5a, as for the equivalent space group $P2_1/c$. The inclusion of the other orientation of the cobalt atom framework would result in the disordered structure with the observed space group Pccn. The minimum intermolecular separation is 2.86 Å for $Co_4(CO)_{12}$ and 2.79 Å for $Rh_4(CO)_{12}$, both for O · · · O contacts.

Further Application of the Proposed Treatment for a Twin Composite and Its Crystallographic Implication.—In principle, the simple twinning mechanism and the derived structure factor relations for a twin composite (explained in detail in the section Determination of the Structures) can be applied to other similar twin composites in which the apparent reciprocal lattices are exact superposition of two component reciprocal lattices. The treatment should be valid provided that a proper indexing of individual reflections can be made.

Successful applications have already been made in the structural determinations of an organometallic chalcogen complex $S_2Ni_3(C_5H_5)_3$[61] and a metal derivative of an α-amino acid $Ni(C_6H_5N_2O) \cdot 2H_2O$.[62] Twinning mechanisms similar to that of $Rh_4(CO)_{12}$ were assumed to operate on the centrosymmetric reciprocal lattices of a single-crystal component of hexagonal symmetry $P6_3/m$ for $S_2Ni_3(C_5H_5)_3$ and of monoclinic symmetry $P2_1/c$ (with $\beta^* = 90°$) for $Ni(C_6H_5N_2O)_2 \cdot 2H_2O$ to give rise to an apparent space group of $P6_322$ for the former and to a pseudoorthorhombic symmetry for the latter. Although the detailed treatment of the diffraction data varies from case to case, the fundamental principle of the treatment remains valid and is of general applicability. It will be interesting to see how well this treatment succeeds in further examples.

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