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THE TWINNED AND DISORDERED CRYSTAL STRUCTURE OF TETRAHEDRAL TRI-μ-CARBONYLENNEACARBONYLDICOBALTDIIRIDIUM

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Summary

Tetrahedral tri-μ-carbonylenneacarbonyldicobaltdiiridium crystallizes in the monoclinic space group $P2_1/c$ but an incoherent twinning mechanism leads to apparent orthorhombic diffraction symmetry. The cell parameters are a 9.12(1), b 11.62(1), c 17.31(2) Å, β 90°, $Z = 4$. Diffractometer data have been refined by full matrix least squares method to a final R of 0.051 for 570 composite reflections $[F_o(hkl)^2_{ort} = F_o(hkl)^2_{mon} + F_o(\bar{h}kl)^2_{mon}]$. The molecular structure of $Co_2Ir_2(CO)_{12}$ is very similar to that of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. Of the CO ligands, 9 are bonded linearly and 3 are involved in edge bridging about a tetrahedron of metal atoms. Cobalt and iridium are partially disordered at the tetrahedron vertices, but iridium has a pronounced preference for the apical position to which only terminal ligands are coordinated.

Introduction

It is well known that carbonyl cluster compounds are essentially characterized by the type of metal atom polyhedron and by associated typical numbers of valency electrons. These factors determine the number of ligands on the cluster surface, but not their spatial arrangement, and, indeed, different ligand geometries have been found in isoelectronic trinuclear, tetranuclear and hexanuclear complexes. In the family $M_4(CO)_{12}$ (M = Co, Rh, Ir) two kinds of ligand stereochemistry occur around the tetrahedral cluster. The iridium compound posesses terminal ligands only, and T_d symmetry [1], while the cobalt and rhodium analogues have three edge-bridging ligands, with lowering of the molecular symmetry to C_{3v} [2,3]. Bridging CO groups are again present in substituted derivatives of $Ir_4(CO)_{12}$, i.e. $Ir_4(CO)_{10}(PPh_3)_2$ and $Ir_4(CO)_9(PPh_3)_3$ [4].

A major cause for these structural differences is very probably the different basicities of the metal atom clusters. The basicity depends on the nature of the metal atom species and, when other ligands partially replace carbonyl groups, on their σ—π bonding ability. Atomization energies and ionization potentials indicate that the donor properties of the metal atom clusters are lower for iridium than for cobalt and rhodium, while the presence of phosphines, which possess weaker π acidity than CO, increases the back-donation toward the remaining carbonyl groups. The bridging groups are therefore preferred when the cluster basicity is sufficient for their stabilization by metal-to-ligand back-donation, and this back-donation, as indicated by C—O distances and IR stretching frequencies, is greater in this geometry than in the linear ones [5]. Another factor, which is certainly important in determining the ligand arrangement, is the minimization of the intramolecular ligand—ligand interaction, which leads to highly symmetric stereochemistries.

In this paper we report the single crystal X-ray structure of the mixed cluster compound $Co_2Ir_2(CO)_{12}$ [6] which contains two congener elements with a high and low tendency, respectively, to give bridging coordination of the CO groups. The elucidation of the stereochemistry of such a molecule should provide new experimental evidence relevant to the above discussion.

Experimental

Crystal data and space group

The diffraction pattern of $Co_2Ir_2(CO)_{12}$, obtained by precession photographs, displayed orthorhombic D_{2h}-*mmm* Laue symmetry with cell parameters *a* 9.12(1), *b* 11.62(1), *c* 17.31(2) Å, *U* 1834.3 Å^3, D_m 3.01(2) (by flotation), $Z = 4, D_c$ 3.04 g cm^{-3}, $F(000) = 1504$, Mo-K_α radiation λ 0.7107 Å, μ(Mo-K_α) 172.8 cm^{-1}. The systematic absences of reflections *h*0*l* for *l* odd and 0*kl* for *k* odd were not consistent with an orthorhombic space group. Cell dimensions, observed absences of reflections, and general weakness of reflections *hkl* for *l* odd indicated strict similarity of these crystals with those of $Rh_4(CO)_{12}$ [2,3]. For that compound the inconsistency was successfully explained in terms of an incoherent twinning mechanism, involving a monoclinic unit cell with the same dimensions of the observed orthorhombic one (β 90°) and $P2_1/c$ space group. The twinning took place through either a (100) or (001) twin mirror plane causing a mixing of non equivalent octants in the reciprocal space. Our treatment of $Co_2Ir_2(CO)_{12}$, which paralleled that of Wei, Wilkes, and Dahl for $Rh_4(CO)_{12}$ [2,3], led to the correct interpretation of the structure.

Intensity measurements

The crystal used for the collection of the intensity data was a small parallelepiped measuring 0.11 × 0.11 × 0.24 mm. It was mounted on a Pailred linear equi-inclination diffractometer with the maximum elongation axis, *b*, coincident with the ω axis of the instrument. Integrated intensities were collected for two octants with $2\theta \leqslant 50°$, using graphite monochromatized Mo-K_α radiation. Intensities were monitored by ω-scan technique at a rate of 1.0°/min with stationary crystal stationary counter background counts of 40 sec taken on each side of the scan. Increasing scan ranges, from 1.6 to 2.8°, were used with increasing μ. 2100 reflections, in the reciprocal lattice layers *h*0*l*—*h*10*l*, were collected. Three standard reflections, sampled after completion of each layer, revealed no crystal decay. The integrated intensities were corrected for Lorentz and polarization factors; the latter was evaluated taking account of the partial polarization of the incident beam [7]. The transmission coefficients, calculated with the Busing and Levy method [8], were found in the range 0.27—0.34 and the absorption corrections were performed using a 8^3 sampling of the crystal. No extinction corrections were made. A careful examination of couples of reflections hkl—$\bar{h}kl$ showed that they were equal within the limit of experimental error. The resulting orthorhombic symmetry indicated equal contributions of the two component lattices to the twinned crystal and therefore the "equivalent" couples were averaged in a unique set of 570 non zero reflections, all having $\sigma(I)/I \leqslant 0.20$. These pseudo-orthorhombic observations are related to the monoclinic ones by the following relationship: $F_o(hkl)^2_{\text{ort}} = F_o(hkl)^2_{\text{mon}} + F_o(\bar{h}kl)^2_{\text{mon}}$; we have assumed a (100) twinning plane, the two possibilities being equivalent.

Determination and refinement of the structure

The structure resolution was facilitated by use of the metal atom coordinates of the isomorphous $Rh_4(CO)_{12}$ [3] as starting values. Two-dimensional Fourier maps, phased using these coordinates, and mixed (1/2 Co + 1/2 Ir) atomic scattering factors, gave projections of the structure in the (001) and (100) planes, and allowed the most probable positions of the cobalt and iridium atoms to be determined. After modifying our structure factors, Fourier, and least squares refinement computing programmes, the full set of composite observations was used. Monoclinic structure factors were estimated by apportioning the observed orthorhombic ones according to Wei [3], i.e. $F_o(hkl) = [F_o(hkl)^2_{\text{ort}} \times F_c(hkl)^2_{\text{mon}}/F_c(hkl)^2_{\text{ort}}]^{\frac{1}{2}}$ and $F_o(\bar{h}kl) = [F_o(hkl)^2_{\text{ort}} \times F_c(\bar{h}kl)^2_{\text{mon}}/F_c(hkl)^2_{\text{ort}}]^{\frac{1}{2}}$. A three-dimensional Fourier map of electron density revealed the positions of most of the light atoms in positions strictly comparable with those in the corresponding positions of $Rh_4(CO)_{12}$. The oxygen peaks were all well resolved while some of the carbon peaks were broadened. A full matrix least squares refinement of the structure gave unrealistically low isotropic thermal factors for the cobalt atoms (see Table 1); for comparison, the range of values found in $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ was 2.3—3.0 and 2.4—2.5 Å^2, respectively. We attribute this discrepancy to disorder among the cluster atoms. A model of random occupation of the tetrahedron vertices was equally unsatisfactory, and therefore the disorder was treated by introducing mixed metal atom species

TABLE 1

ISOTROPIC THERMAL FACTORS (Å^2) AND DISCREPANCY INDICES OBTAINED FROM REFINEMENT OF VARIOUS MODELS FOR THE CLUSTER ATOMS

	M(1)	M(2)	M(3)	M(4)	R
I[a]	2.3(1)	0.6(2)	3.4(1)	—0.8(1)	0.085
II[b]	1.0(1)	6.6(2)	1.7(1)	5.3(1)	0.079
III[c]	2.3(1)	3.3(1)	2.5(1)	2.7(1)	0.058

[a] Ordered model: M(1) = M(3) = Ir, M(2) = M(4) = Co. [b] Completely disordered model: M(1) = M(2) = M(3) = M(4) = 0.5 Ir + 0.5 Co. [c] Partially disordered model with occupancy factors obtained by least squares refinement: M(1) = 0.89 Ir + 0.11 Co, M(2) = 0.17 Ir + 0.83 Co, M(3) = 0.74 Ir + 0.26 Co, M(4) = 0.30 Ir + 0.70 Co.

TABLE 2

FINAL POSITIONAL AND THERMAL PARAMETERS

Metal atoms[a,b]	m[c]	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
M(1)	0.83(1)	8325(3)	3513(2)	1173(2)	59(3)	−2(6)	8(4)	49(2)	2(3)	16(1)
M(2)	0.16(1)	7995(6)	1276(4)	1152(4)	81(9)	−12(10)	−13(10)	52(5)	−23(7)	30(2)
M(3)	0.70(1)	5648(3)	2535(3)	1178(2)	54(3)	20(7)	1(4)	59(2)	−5(5)	21(1)
M(4)	0.27(1)	7334(5)	2483(6)	2400(3)	82(6)	10(11)	3(6)	55(4)	1(6)	21(2)

Light atoms[d]	x	y	z	B(Å^2)	Light atoms[d]	x	y	z	B(Å^2)
C(1)	862(8)	368(6)	13(4)	4.6(16)	C(7)	667(7)	140(5)	31(3)	2.3(10)
O(1)	881(6)	379(5)	−55(3)	5.4(13)	O(7)	640(6)	134(5)	−32(3)	5.7(12)
C(2)	830(6)	346(5)	301(3)	1.9(10)	C(8)	644(6)	176(5)	309(3)	1.8(11)
O(2)	905(5)	388(4)	350(3)	4.5(12)	O(8)	596(7)	107(6)	362(3)	6.9(16)
C(3)	767(5)	513(4)	140(2)	0.1(9)	C(9)	746(8)	−28(6)	110(4)	4.1(15)
O(3)	730(5)	599(4)	159(2)	3.9(10)	O(9)	736(5)	−116(4)	126(3)	4.5(10)
C(4)	1020(11)	368(10)	166(6)	7.9(27)	C(10)	399(6)	147(6)	134(3)	2.9(13)
O(4)	1145(6)	365(5)	171(3)	5.5(12)	O(10)	320(6)	88(5)	160(3)	5.8(12)
C(5)	891(6)	132(5)	212(3)	2.3(14)	C(11)	564(6)	340(5)	222(3)	1.9(11)
O(5)	982(5)	96(4)	256(3)	4.2(10)	O(11)	473(5)	416(4)	252(3)	3.9(10)
C(6)	974(7)	123(5)	66(4)	2.6(13)	C(12)	450(6)	355(5)	54(3)	1.7(10)
O(6)	1081(6)	124(4)	26(3)	4.9(12)	O(12)	380(5)	410(5)	23(3)	4.4(10)

[a] Positional and thermal parameters × 10^4. [b] The anisotropic temperature factors are given by $\exp-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$. [c] Occupancy factor of iridium species (see text). [d] Positional parameters × 10^3.

with scattering curves $f_{mix} = mf_{Ir} + (1-m)f_{Co}$ with m defining the occupancy factors to be refined; this treatment gave satisfactory results (see Table 1). In the final least squares refinement the structure model was made more flexible by using anisotropic temperature factors for the metal atoms. This treatment partially takes into account the spreading of electron density caused by the non-coincidence of the cobalt and iridium nuclei at the vertices of the average cluster tetrahedron.

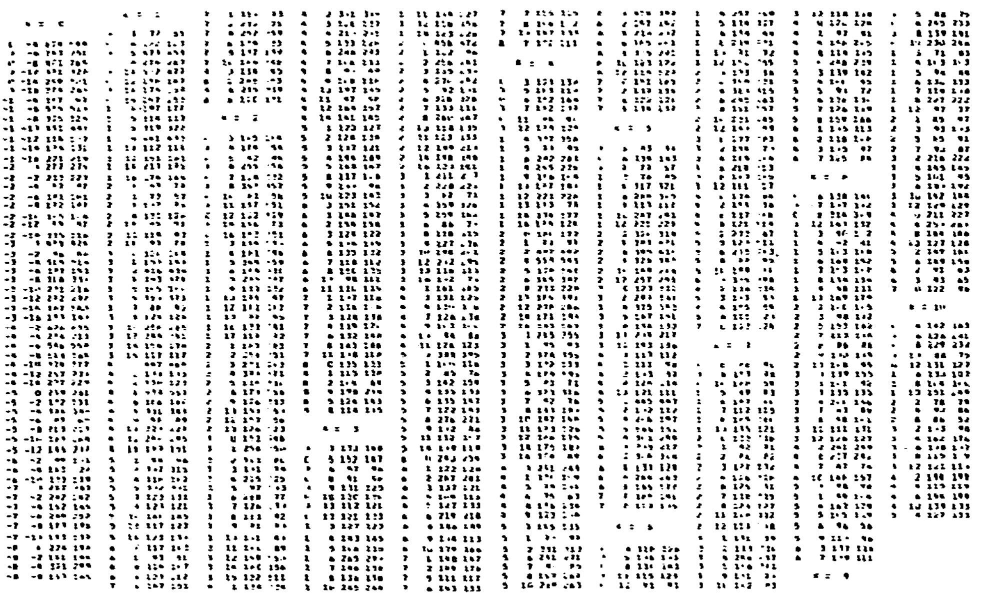
The final R and R' factors were 0.051 and 0.071 with the discrepancy indices defined as follows: $R = \Sigma|k|F_o(hkl)_{ort}| - (F_c(hkl)^2_{mon} + F_c(\bar{h}kl)^2_{mon})^{\frac{1}{2}}|/k|F_o(hkl)_{ort}|$ and $R' = \{\Sigma w[k|F_o(hkl)_{ort}| - (F_c(hkl)^2_{mon} + F_c(\bar{h}kl)^2_{mon})^{\frac{1}{2}}]^2/\Sigma wF_o(hkl)^2_{ort}\}^{\frac{1}{2}}$. The weights were assigned according to the formula $w = 1/(A + BF_o + CF_o^2)$ where the final values $A = 20.0$, $B = 1.0$, and $C = 0.001$ were chosen so that the mean value of $w[kF_o(hkl)_{ort} - |F_c(hkl)_{ort}|]^2$ was practically constant over all ranges of F_o and $\sin\theta/\lambda$. The atomic scattering factors were taken from ref. 9, and the real part of the anomalous scattering was taken into account.

In Table 2 the final parameters of the atoms are reported, together with the occupancy factors of the iridium species. The final list of observed and computed $F(hkl)_{ort}$ composite structure factor moduli is reported in Table 3.

All the computations were performed on a Univac 1106 computer using local programmes.

TABLE 3

OBSERVED AND COMPUTED PSEUDO-ORTHORHOMBIC STRUCTURE FACTOR MODULI OF $Co_2Ir_2(CO)_{12}$



Description of the structure and discussion

The crystal structure of tetrahedral tri-μ-carbonylenneacarbonyldicobaltdiiridium contains discrete molecules as shown in Fig. 1. The carbonyl groups are arranged about the metal atom cluster in almost the same way as in the tetracobalt and tetrarhodium analogs. It consists of an apical $M(CO)_3$ group and of a triangular $M_3(CO)_9$ moiety linked by metal—metal bonds. Of the CO groups in the triangular moiety, 3 are coordinated by edge bridging and 6 terminally. The approximate coordination symmetry of the ligands is C_{3v}, while the proper molecular symmetry is C_s. The ligands are pointing toward the vertices of a distorted icosahedron oriented with one of its faces nearly parallel to the basal triangle of the cluster.

The final values of the occupancy factors give a total of 1.96(2) iridium atoms in the cluster, which is in significant agreement with the expected value of 2. As one can see from the occupancy values, the cobalt—iridium disorder is only partial, both atomic species having the preferred locations reported in Fig. 1. The disorder can be rationalized as follows: the iridium population (0.83) in site M(1) indicates that the crystal contains the two possible structural isomers A and B (see Fig. 2) in the ratio 5/1. From the lower value of iridium population in site M(3) (0.70) a partial rotational disorder of both isomers about the three-fold symmetry axis can be inferred. The metal—metal bond distances reported in Table 4 are only weighted averages of Co—Co, Co—Ir, and Ir—Ir values, and so can not be discussed in detail. As expected, they range between the values found

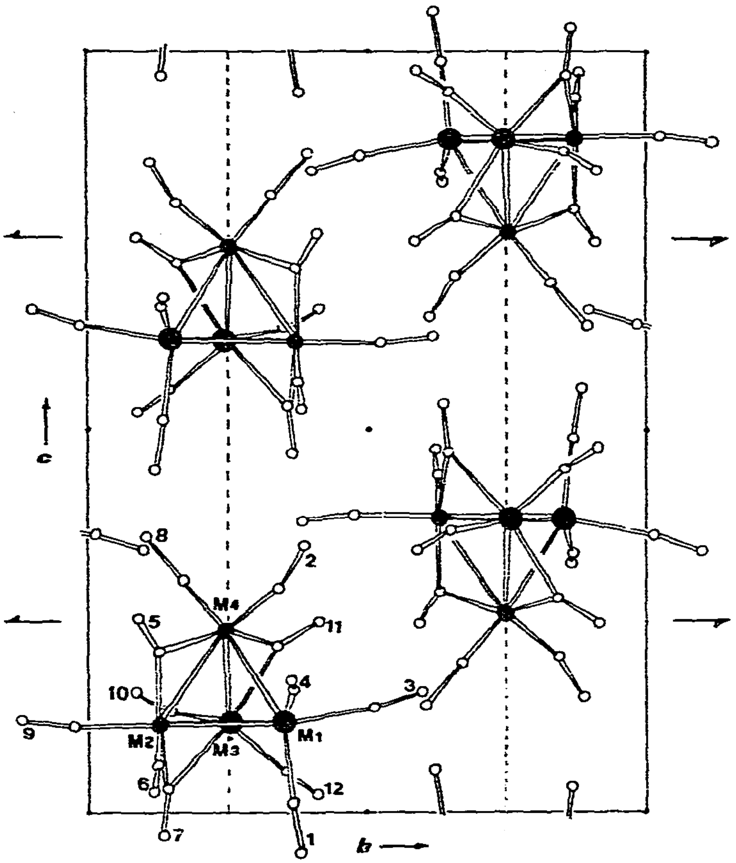


Fig. 1. [100] projection of the unit cell of $Co_2Ir_2(CO)_{12}$. Iridium atoms are essentially located at M(1) and M(3) and cobalt atoms at M(2) and M(4). Only the oxygen atoms of the ligands are labelled, the corresponding carbon atoms having the same numbering.

in $Co_4(CO)_{12}$ (2.44—2.53(1) Å) and in $Ir_4(CO)_{12}$ (2.67—2.69(2) Å). The metal—carbon and carbon—oxygen distances and the metal—carbon—oxygen angles are scattered and subject to high standard deviations because of the molecular disorder. The mean values for the predominantly Ir—C and Co—C interactions in the terminal groups are 1.93 and 1.78 Å, respectively, in good agreement with those found in other cluster carbonyl complexes.

The feature of major interest in this structure is the observed preference of iridium for the apical position, showing that the most stable carbonyl coordination about this metal is the linear one. This result is in agreement with the interpretation of the IR spectrum in solution [6].

It should be noted that the crystal structure of $Co_2Ir_2(CO)_{12}$ is similar to that of $Rh_4(CO)_{12}$, although the cell parameters are closer to those of $Co_4(CO)_{12}$*.

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* $Co_4(CO)_{12}$ crystallizes in the orthorhombic space group *Pccn* and is disordered. The disorder derives from location of the molecules about twofold symmetry axes which are coincident with a threefold axis of the metal atom tetrahedron and with a proper twofold axis of the "idealized" icosahedron defined by the ligands. This causes approximate superimposition of the ligands, but image duplication for three metal atoms. Apart from the twinning, the crystal structure of $Rh_4(CO)_{12}$ closely resembles that of one configuration of $Co_4(CO)_{12}$, with cell constants approximately 3% larger.

TABLE 4

INTERATOMIC DISTANCES (Å) AND SELECTED ANGLES (°) IN THE MOLECULE $Co_2Ir_2(CO)_{12}$

M(1)—M(2)	2.617(6)	M(1)—C(1)—O(1)	180(6)
M(1)—M(3)	2.693(4)	M(1)—C(3)—O(3)	173(4)
M(1)—M(4)	2.600(6)	M(1)—C(4)—O(4)	157(9)
M(2)—M(3)	2.594(6)	M(2)—C(5)—O(5)	149(5)
M(2)—M(4)	2.644(9)	M(2)—C(6)—O(6)	172(5)
M(3)—M(4)	2.615(6)	M(2)—C(7)—O(7)	152(6)
M(1)—C(1)	1.84(7)	M(2)—C(9)—O(9)	161(7)
M(1)—C(3)	2.01(5)	M(3)—C(7)—O(7)	128(5)
M(1)—C(4)	1.92(10)	M(3)—C(10)—O(10)	164(5)
M(2)—C(5)	1.88(6)	M(3)—C(11)—O(11)	132(4)
M(2)—C(6)	1.80(6)	M(3)—C(12)—O(12)	169(5)
M(2)—C(7)	1.91(6)	M(4)—C(2)—O(2)	164(5)
M(2)—C(9)	1.87(7)	M(4)—C(5)—O(5)	125(5)
M(3)—C(7)	2.21(6)	M(4)—C(8)—O(8)	169(5)
M(3)—C(10)	1.98(6)	M(4)—C(11)—O(11)	145(4)
M(3)—C(11)	2.06(6)	C(1)—M(1)—C(3)	98(3)
M(3)—C(12)	1.88(6)	C(1)—M(1)—C(4)	107(4)
M(4)—C(2)	1.78(6)	C(3)—M(1)—C(4)	95(4)
M(4)—C(5)	2.03(6)	C(6)—M(2)—C(9)	100(3)
M(4)—C(8)	1.68(5)	C(10)—M(3)—C(12)	95(3)
M(4)—C(11)	1.91(6)	C(2)—M(4)—C(8)	98(3)
C(1)—O(1)	1.19(9)	M(2)—C(7)—M(3)	78(2)
C(2)—O(2)	1.20(7)	M(2)—C(5)—M(4)	85(2)
C(3)—O(3)	1.12(7)	M(3)—C(11)—M(4)	82(2)
C(4)—O(4)	1.15(12)		
C(5)—O(5)	1.19(8)		
C(6)—O(6)	1.20(8)		
C(7)—O(7)	1.11(7)		
C(8)—O(8)	1.29(8)		
C(9)—O(9)	1.07(8)		
C(10)—O(10)	1.09(9)		
C(11)—O(11)	1.31(8)		
C(12)—O(12)	1.11(7)		

A rationalization of this fact is possible only if some plausible explanation of the different structures of the cobalt and rhodium complexes is available. We suggest that these structures depend on the different sizes of the molecules, so that shorter ligand—ligand intramolecular contacts are involved in the cobalt

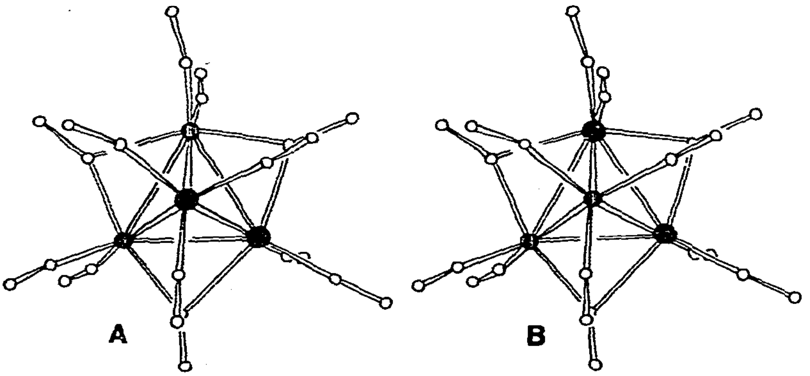

Fig. 2. Schematic drawing of the two possible structure isomers of $Co_2Ir_2(CO)_{12}$. Isomer A is about five times more abundant than B in the crystal, indicating that iridium prefers terminally bonded ligands.

complex. If one considers that in this species the π back-bonding is stronger [10], with consequent greater bulkiness of the ligands [11], it can be inferred that this molecule is more overcrowded than $Rh_4(CO)_{12}$ and, at the same time, the icosahedron defined by the ligands is more rigid and less irregular. In fact the C···C contacts in $Co_4(CO)_{12}$ range from 2.48 to 3.57 Å, while in $Rh_4(CO)_{12}$ range from 2.80 to 4.43 Å [3]. This situation facilitates the disorder of $Co_4(CO)_{12}$, because the more the ligand polyhedron is regular the more the twofold axis relating the two statistical orientations of the molecules becomes effective in superimposing "symmetry equivalent" ligands. Now the ligand polyhedron in $Co_2Ir_2(CO)_{12}$ surely departs from the icosahedral geometry more than in $Co_4(CO)_{12}$; consequently the twofold symmetry does not operate and the resulting crystal structure is that of $Rh_4(CO)_{12}$. The strong dependence of the crystal structure from the polyhedron defined by the outer atoms is demonstrated by the fact that $Ir_4(CO)_{12}$, whose ligands are directed toward the vertices of a cuboctahedron, posesses very different packing in the *P*3 space group [1].

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