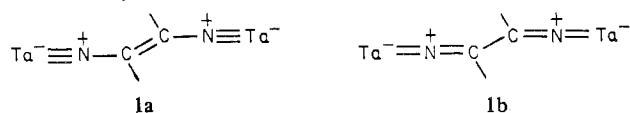have to be multiple bonds in order to complete the octet at each nitrogen atom. Thus, the entire central chain could be described by the formal structure **1a**, where we also take into


account the fact that the Ta–N–C chain is essentially linear. The triple bond shown in **1a** is partly dative: two of the electron pairs result from electrons contributed by both the metal atom and the nitrogen atom while the third pair is donated by the nitrogen atom alone. The only other formal structure that is consistent with the geometry and provides an octet for each C and N atom is **1b** which leaves one unpaired electron formally on each tantalum atom. The central C–C distance observed is 1.35 (1) Å, and the standard C=C distance is 1.335 Å,[5] thus suggesting that **1a** alone may provide a good description of the bonding in this part of the molecule, with **1b** making at most a minor contribution. The C–CH₃ distance, 1.51 (1) Å, is exactly that expected for a single bond between sp² ($r \approx 0.74$ Å) and sp³ ($r \approx 0.77$ Å) hybridized carbon atoms. The C–N distance, 1.41 (1) Å, is also consistent with expectation for a single bond between an sp hybridized nitrogen atom ($r < 0.70$ Å) and an sp² hybridized carbon atom ($r \approx 0.74$ Å).

Structure **1a** also implies that the multiplicity of the Ta–N bond is between double and triple, where the uncertainty arises because one component of the triple bond represented in **1a** is the result of electron donation by N to Ta and this need not be complete. The Ta–N distance, 1.75 (1) Å, while vastly shorter than Ta^V–N single-bond distances (~ 1.97 Å in Ta-(NMe₂)₂(O₂CNMe₂)₃[6] for example), but not so short as some other M–N multiple-bond distances, where bond order should be 3.0 or nearly so, is not inconsistent with assigning a bond order >2.0.[7] In the case of [(Me₃CCH₂)₃Ta≡CCMe₃]⁻ we have a Ta≡C triple bond to tantalum(V) and the distance is 1.76 (2) Å,[8] from which we might estimate that a full Ta^V≡N bond should be ca. 1.70 Å. Thus, it is safe to say that **1a** can account satisfactorily for all the structural features of the tantalum compound, although a slight contribution from **1b** is possible.

One of the fascinating problems raised by this structure (and, of course, those of analogous niobium compounds) is how the metal atoms promote the dimerization of CH₃CN. The formal process is, after all, a highly unusual one and might have synthetic utility if properly controlled, modified, and exploited. McCarley has suggested that the active agent, either arising spontaneously by disproportionation of Ta^{IV} or introduced deliberately by reduction, is the trivalent metal atom. The trivalent species is then oxidized to the pentavalent state as the product is formed.

Another problem, perhaps more tractable, is to decompose the products in such a way as to recover the dimerized entity and regenerate a Nb^{III} or Ta^{III} species capable of reacting with more acetonitrile. Conceivably, a reductive cleavage reagent could be found so that the role of the metal could be made catalytic as shown, for example, in eq 2. Further studies to

$$2CH_3CN + 4[H] \xrightarrow{M^{III}} H_2NC(CH_3)=C(CH_3)NH_2 \rightarrow$$
$$\text{final products (2)}$$
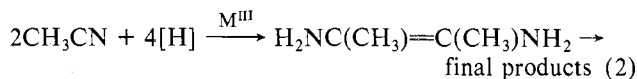
explore both the pre- and postchemistry of these interesting dinuclear complexes are being planned.

Supplementary Material Available: A table of structure factors (9 pages). Ordering information is given on any current masthead page.

References and Notes

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Crystal Structure of Tetrairidium Dodecacarbonyl, Ir₄(CO)₁₂. An Unpleasant Case of Disorder

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Tetrairidium dodecacarbonyl, Ir₄(CO)₁₂, has been investigated via a single-crystal X-ray diffraction study. The structure was solved using the trigonal space group $P3$, with $a = 13.290$ (3) Å, $c = 8.981$ (2) Å, $V = 1373.7$ (5) Å³, and ρ(calcd) = 4.01 g cm⁻³ for mol wt 1105.0 and $Z = 3$. Data were collected with a Syntex $P2_1$ diffractometer and the structure was solved via Patterson, Fourier, and least-squares refinement techniques, yielding $R_F = 5.76\%$ and $R_{wF} = 4.65\%$ for 1172 reflections. The unit cell contains three distinct molecules of Ir₄(CO)₁₂, each of which lies on a threefold axis. There is a severe and complex disorder problem in that there is inversion disorder of Ir₄(CO)₁₂ molecules at two of these sites. There is a 0.833:0.167 disorder at site I (centered at 0, 0, $\sim$0.176) and a 0.555:0.445 disorder at site III (centered at ²/₃, ¹/₃, $\sim$0.496), while site II (centered at ¹/₃, ²/₃, $\sim$−0.183) appears to be ordered. This disorder leads to problems in determining accurate atomic positions; however, the essential T_d symmetry of the Ir₄(CO)₁₂ molecule is confirmed and the average Ir–Ir bond length is found to be 2.693 Å.

Introduction

The trinuclear and tetranuclear "binary" carbonyls of the iron and cobalt subgroups have been subjected to intensive study via the method of single-crystal X-ray diffraction.

Accurate crystal structures have now been reported for Fe₃(CO)₁₂,[1] Ru₃(CO)₁₂,[2] Os₃(CO)₁₂,[3] Co₄(CO)₁₂,[4] and Rh₄(CO)₁₂.[5] There has, however, been no report in the primary literature of the crystal structure of Ir₄(CO)₁₂. This

species was studied by G. R. Wilkes[6] in the laboratories of Professor L. F. Dahl and the resulting structure (I) has been widely quoted as the archetypal example of a $M_4(CO)_{12}$ species with T_d symmetry (as opposed to the C_{3v} symmetry of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$, II).

I

II
M = Co, Rh
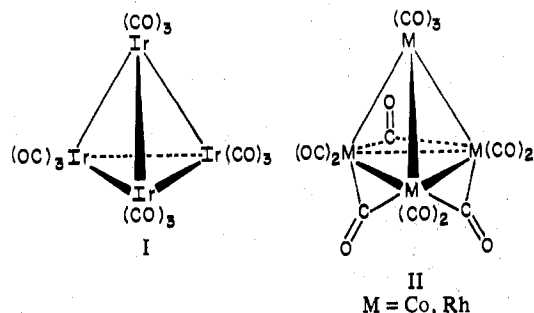
The study of $Ir_4(CO)_{12}$ by Wilkes[6] was based on film data, the final discrepancy indices being R_F = 11.2% and R_{wF} = 15.7%, where R_F and R_{wF} are defined in eq 1 and 2. Although

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100 \ (\%) \qquad (1)$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100 \ (\%) \qquad (2)$$

Cotton et al.[4] have stated that "the crystal structure determination [of $Ir_4(CO)_{12}$] apparently presented no unusual features...", a careful survey of Wilkes' study suggests that there were a significant number of problems in determining the structure. Among these were the following.

(i) A problem in obtaining a single crystal.

(ii) Failure to obtain meaningful results upon refining the light atoms (carbon and oxygen).

(iii) A wide range in the final isotropic thermal parameters of the iridium atoms (from 0.10 (29) to 2.08 (58) $Å^2$).

(iv) Unusual features in a "partial difference electron density synthesis" (cf. ref 6, Figure 1, p 19). Here it appears that the positions of carbon atoms are associated with higher and more diffuse electron density contours than are the positions of the oxygen atoms.

We decided to reinvestigate the crystal structure of $Ir_4(CO)_{12}$ for two principal reasons: (1) to obtain an accurate Ir–Ir bond distance against which we could compare Ir–Ir distances in other (substituted) tetranuclear iridium carbonyl cluster complexes which we are currently investigating and (2) to provide accurate molecular dimensions for $Ir_4(CO)_{12}$ and to provide an accurate picture of its overall molecular geometry.

However, as will be seen below, our study of $Ir_4(CO)_{12}$ was beset with the same sort of problems that Wilkes encountered. In fact, this structural study is perhaps the most aggravating that we have yet encountered. Our analysis reveals an extremely unpleasant disorder problem; our progress toward solving this problem is outlined below.

Experimental Section

Tetrairidium dodecacarbonyl, $Ir_4(CO)_{12}$, was obtained from Alfa Inorganics. After many fruitless attempts, crystals of pleasing appearance and appropriate size were obtained by the following method. Powdered $Ir_4(CO)_{12}$ was placed in a Soxhlet extractor and was extracted for ~2 h with dry 1,1,1-trichloroethane, under argon. The resulting saturated solution was cooled slowly to room temperature. The yellow crystals which formed were washed with cyclohexane and pentane. Upon examination under a polarizing microscope many of the hexagonal-shaped crystals were found to be suffering from threefold twinning. An apparently single crystal of dimensions 0.13 mm × 0.10

Table I. Details of Data Collection for $Ir_4(CO)_{12}$

(A) Crystal Parameters at 23 °C
crystal system: trigonal (but see text)
space group: $P\overline{3}$ $[C_3^{-1}$; No. 143]
$a = 13.2902$ (26) Å
$c = 8.9809$ (20) Å
$V = 1373.7$ (5) $Å^3$
$Z = 3$
mol wt = 1105.0
ρ(calcd) = 4.01 g cm^{-3}
ρ(obsd) > 3.8 g cm^{-3}

(B) Measurement of Intensity Data
diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\overline{\lambda}$ 0.710 730 A)
monochromator: highly oriented graphite
reflections measd: entire sphere for $2\theta = 3$–35°
scan-type: coupled θ(crystal)–2θ(counter)
scan speed: 2.0°/min in 2θ
scan width: [2θ(Mo Kα_1) – 0.9]° to [2θ(Mo Kα_2) + 0.9]°
bkgd measurement: stationary crystal and counter; at beginning and end of scan–each for half the time taken for the 2θ scan
standard reflections: 3 measd every 97 reflections; no significant deviations from the mean were observed
absorption coeff: μ = 252.8 cm^{-1}
absorption cor: empirical method (2θ and ϕ interpolation between measd curves–see text)
reflections collected: 3529 total, yielding 1186 point-group independent reflections
data averaging: $R(I)$ = 7.07% for 1172 reflections mostly with three contributors ($P\overline{3}$ averaging–see text)

mm × 0.03 mm was finally selected for the X-ray diffraction experiment. This crystal was glued to the tip of a glass fiber which was then sealed (with beeswax) into an aluminum pin and mounted on a eucentric goniometer. The quality of the crystal was checked by taking a series of precession and cone-axis photographs. These photographs indicated apparent trigonal symmetry, yielded cell dimensions consistent with those obtained previously by Wilkes[6] (viz., $a = b = 13.27$ (2) Å, $c = 8.95$ (2) Å, $\alpha = \beta = 90°$, $\gamma = 120°$), and suggested that the crystal was single. The crystal was transferred to a Syntex $P2_1$ four-circle diffractometer and was centered optically. Crystal alignment, determination of orientation matrix and cell parameters, and data collection were all carried out as described previously.[7] Details are presented in Table I.

The unit cell dimensions reported in Table I are the *idealized trigonal values*. Values obtained from independent refinement of all six lattice parameters were as follows: $a = 13.2876$ (25) Å, $b = 13.2928$ (25) Å, $c = 8.9809$ (20) Å, $\alpha = 90.064$ (17)°, $\beta = 89.982$ (16)°, $\gamma = 119.984$ (13)°.

The value for α is 3.8σ from 90° and deviates from ideality by a greater amount than for any other crystal that we have examined on the current diffractometer. The possibility that the crystal was actually triclinic, approximating very closely to trigonal, was borne in mind.

A complete sphere of data from $2\theta = 3°$ to $2\theta = 35°$ was collected. (This represents the limit to which strong intensities could be measured.) These data were corrected for absorption by the following empirical method. A series of close-to-axial reflections, distributed over the range of 2θ values used in data collection and each of fairly strong intensity (but not so strong as to be affected significantly by any possible secondary extinction) were measured at 10° invervals around their diffraction vectors (from $\psi = 0°$ to $\psi = 350°$). Each reflection was used to define a normalized absorption curve vs. ϕ, corrected for ω and χ. The curves bracketing the 2θ value of the reflection under consideration were interpolated both in 2θ and in ϕ to derive the "pseudo transmission coefficient" for the reflection under consideration. Reflections used for the absorption curves were as follows: $3\overline{3}0$ and $\overline{3}30$ [$2\theta = 10.61°$, (maximum intensity)/(minimum intensity) = 2.214 and 2.124, respectively], $44\overline{1}$ and $\overline{4}41$ (14.88°, 2.251 and 2.197), $56\overline{1}$ and $\overline{5}61$ (20.28°, 2.253 and 2.129), $8\overline{7}0$ and $\overline{8}70$ (26.91°, 1.910 and 1.976), $98\overline{1}$ and $\overline{9}81$ (30.88°, 2.018 and 2.114). The curves of Friedel pairs were averaged to provide a total of five curves for use in the absorption correction process. All five curves were mutually consistent, i.e., had maxima and minima at essentially the same ϕ values and showed similar profiles of intensity vs. ϕ.

Data were next averaged; three tests were made, intensities being averaged according to C_i, C_3, and S_6 symmetry. Results were as

Table II. Statistics for Intensity Distribution for Diffraction Data of $Ir_4(CO)_{12}$

| | | theoretical[a] | |
	obsd	centric	acentric
$\langle |E|^2 \rangle$	1.00	1.00	1.00
$\langle |E| \rangle$	0.766	0.798	0.886
$\langle |E^2 - 1| \rangle$	1.110	0.968	0.736
$|E| > 1.0$ (%)	27.15	31.73	36.79
$|E| > 2.0$ (%)	6.41	4.55	1.89
$|E| > 3.0$ (%)	1.26	0.27	0.01

[a] See I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).

follows: $R(I) = 2.74\%$ for 1764 data, each with two contributors, for C_i symmetry (corresponding to space group $P\bar{1}$); $R(I) = 7.07\%$ for 1172 data, mostly with three contributors, for C_3 symmetry (corresponding to space group $P3$); $R(I) = 7.17\%$ for 593 data, mostly with six contributors, for S_6 symmetry (corresponding to space group $P\bar{3}$).

The "R factor" for averaging intensities, $R(I)$, is defined in eq 3.

$$R(I) = \left[\frac{\sum |I - I_{av}|}{\sum I} \right] \times 100 \ (\%) \qquad (3)$$

Here, I is an individual (absorption-corrected) intensity belonging to a set that is averaged, and I_{av} is the average of this set of group theoretically equivalent intensities.

We elected, at this time, to use the 1172 data resulting from the C_3 averaging (i.e., corresponding to space group $P3$). The considerably better agreement for C_i averaging was carefully noted. However, one expects the empirical absorption correction to be considerably more consistent for C_i-related reflections than for C_3- or S_6-related reflections. Nevertheless, there remains the possibility that the crystal is actually triclinic, approximating very closely to trigonal (see above).

The statistical distribution of $|E|$ values, shown in Table II, suggests that the crystal structure is "supercentric"—i.e., each of the indicators is statistically further removed from the ideal acentric case than is the ideal centric case. However, the implicit assumption of a random distribution of electron density in the unit cell is clearly invalid for a structure containing molecules with Ir_4 cores (4 × 77 electrons) in which the basal Ir_3 planes are all parallel (vide infra).

Following correction for absorption, intensities were next corrected for Lorentz and polarization factors and were converted to $|F_o|$ values. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$. Estimated standard deviations (esd's) of the observed structure factor amplitudes, $\sigma(|F_o|)$, were based upon the larger of (i) counting statistics or (ii) the internally generated esd obtained by averaging symmetry-equivalent reflections (C_3 averaging).

Solution and Refinement of the Structure

All subsequent calculations were performed on the CDC 6600-Cyber 173 computing system at the State University of New York at Buffalo. Programs used during the structural analysis were the following: LSHF (full-matrix least-squares refinement and structure factor calculations, by B. G. DeBoer), JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP by J. A. Ibers), STAN1 (distances and angles, with esd's, by B. G. DeBoer), and ORTEP-II (thermal ellipsoid plotting program, by C. K. Johnson).

The analytical scattering factors of Cromer and Mann[8a] for neutral atoms were corrected for both the real and imaginary components of anomalous dispersion.[8b] The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where the weights were calculated as shown in eq 4. The "goodness of fit" (GOF) is defined

$$w = [\{\sigma(|F_o|)\}^2 + (0.02|F_o|)^2]^{-1} \qquad (4)$$

in eq 5, where NO is the number of observations and NV is the number of variables.

$$\text{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(\text{NO} - \text{NV})} \right]^{1/2} \qquad (5)$$

The structure was solved via a three-dimensional Patterson synthesis. There are three molecules of $Ir_4(CO)_{12}$ in the unit cell, *each one of*

which lies on a crystallographic C_3 axis. The crystallographic asymmetric unit thus consists of one-third of each of three independent $Ir_4(CO)_{12}$ molecules.

Least-squares refinement of the positional parameters of the six independent iridium atoms (three in special positions of C_3 symmetry and three in general positions), along with their isotropic thermal parameters, led to convergence with $R_F = 16.6\%$. Fourier and difference-Fourier syntheses now yielded the positions of several oxygen atoms of the carbonyl groups and also suggested that there was inversion disorder of the Ir_4 tetrahedra.

After many models had been tried (over a period of about 18 months), an overall structure was finally determined by the following essential steps.

(1) Positional and isotropic thermal parameters for the iridium atoms were refined. This led to $R_F = 10.6\%$ after we had allowed the coupled refinement of major and minor components of disordered Ir_4 tetrahedra at each of the three sites. At site I (centered at 0, 0, $\sim$0.176) there is 83.34 (36)%:16.66 (36)% disorder of the major to minor (C_i-related) components. At site II (centered at $^1/_3$, $^2/_3$, $\sim$0.183) there is essentially *no* disorder. (Refinement led to a ratio of 99.5%:0.5% for major to minor components. This site was then defined as containing only the ordered major component.) Finally, at site III (centered at $^2/_3$, $^1/_3$, $\sim$0.496) there is disorder with a 55.52 (80)%:44.48 (80)% ratio of major to minor components.

(2) Oxygen atoms were located from difference-Fourier syntheses and their positional and thermal parameters were refined. There are 12 independent oxygen atoms in the crystal structure; all were reasonably well behaved (see below).

(3) Carbon atoms either were located from difference-Fourier maps or were placed in calculated positions. Attempts to refine their positional and thermal parameters led to unreasonable geometry for some Ir–C–O systems and unreasonable thermal parameters for some carbon atoms.

(4) Carbon atoms were next input with idealized positions (based upon $d(C–O) = 1.14$ Å and Ir–C–O = 180°) and with isotropic thermal parameters set at 3.0 Å^2. Shifts in the positions of carbon atoms of the major components were tied to those of their associated oxygen atoms (i.e., these C–O ligands were treated as rigid, nonrotating groups). If large shifts were observed for the oxygen atoms, then the carbon atom positions were recalculated so as again to yield linear Ir–C–O systems.

(5) Carbon atoms of the minor components were input in calculated positions with $d(C–O) = 1.14$ Å and Ir'–C'–O = 180° but were not refined. Their positions were updated as necessary.

(6) After a total of some 15 cycles of refinement, our final model converged with $R_F = 5.76\%$, $R_{wF} = 4.65\%$, and GOF = 1.508. The largest peak on a final difference-Fourier synthesis was 2.8 e Å^{-3} in height and was between the positions of Ir(9) and Ir(10). There was no evidence of secondary extinction and the usual tests confirmed that the weighting scheme was reasonable. Inversion of the entire structure led to marginally higher residuals, indicating that we have defined the correct enantiomeric structure in the polar space group $P3$.

Final occupancies and positional thermal parameters are listed in Table III.

Results and Discussion

The crystal is composed of discrete molecular units of tetrairidium dodecacarbonyl, which are mutually separated by normal van der Waals distances. Figure 1 shows the packing of molecules in the unit cell, as viewed down the unique axis ("c"). There are three crystallographically independent sites for the $Ir_4(CO)_{12}$ molecules, each of which has crystallographically imposed C_3 symmetry. While sites I and III are each disordered (vide infra), the relative orientations of the *major components* of the structure are such that the Ir_4 tetrahedron at site I has its apex pointing away from the base in the $-c$ direction, whereas the ordered Ir_4 tetrahedron at site II and the major component of the Ir_4 tetrahedron at site III each have their apices pointing in the $+c$ direction relative to their bases.

The labeling of all atoms within the asymmetric unit is shown in Figure 2. Stereoscopic views of the three independent sites are illustrated in Figure 3, while Figure 4 presents a labeled view of the $Ir_4(CO)_{12}$ molecule at site II (i.e., the

Table III. Final Positional and Thermal Parameters for $Ir_4(CO)_{12}$, with Esd's

| atom	occupancy[a]	x	y	z	B, A^2
			Site I		
Ir(1)	0.2778	0	0	0[b]	
Ir(1')	0.0555	0	0	0.3311 (23)	}2.76 (4)
Ir(2)	0.8334 (36)	0.0948 (3)	0.1304 (3)	0.2430 (10)	
Ir(2')	0.1666	0.1327 (9)	0.0354 (9)	0.0832 (14)	}1.96 (6)
Ir(2),[3_1][c]		−0.1304	−0.0356	0.2430	
Ir(2),[3_2][c]		0.0356	−0.0948	0.2430	
Ir(2'),[3_1][c]		−0.0354	0.0974	0.0832	
Ir(2'),[3_2][c]		−0.0974	−0.1327	0.0832	
O(11)	1	0.2237 (25)	0.0400 (23)	−0.1382 (27)	1.6 (6)
O(21)	1	0.1368 (32)	0.1725 (31)	0.5479 (56)	5.0 (13)
O(22)	1	0.0677 (35)	0.3374 (38)	0.1444 (41)	4.0 (12)
O(23)	1	0.3481 (40)	0.2215 (34)	0.1518 (40)	5.9 (12)
C(11)[d]	0.8334	0.1391	0.0249	−0.0859	3.0[e]
C(21)[d]	0.8334	0.1200	0.1554	0.4236	3.0[e]
C(22)[d]	0.8334	0.0777	0.2607	0.1809	3.0[e]
C(23)[d]	0.8334	0.2539	0.1876	0.1857	3.0[e]
C(11')[f]	0.1666	0.0823	0.1038	0.4615	3.0[e]
C(21')[f]	0.1666	0.1789	0.0377	−0.0290	3.0[e]
C(22')[f]	0.1666	0.2144	−0.0261	0.1197	3.0[e]
C(23')[f]	0.1666	0.2591	0.1446	0.1235	3.0[e]
			Site II		
Ir(5)	1/3	1/3	2/3	0.0007 (5)	1.32 (11)
Ir(6)	1	0.2977 (2)	0.7615 (2)	−0.2447 (9)	1.86 (8)
Ir(6),[3_1][c]		0.2385	0.5362	−0.2447	
Ir(6),[3_2][c]		0.4638	0.7023	−0.2447	
O(51)	1	0.1020 (33)	0.5958 (28)	0.2051 (33)	6.4 (10)
O(61)	1	0.2650 (24)	0.7720 (24)	−0.5889 (47)	5.1 (10)
O(62)	1	0.0583 (44)	0.7299 (33)	−0.1581 (38)	6.1 (12)
O(63)	1	0.4398 (32)	1.0140 (37)	−0.1659 (34)	4.4 (10)
C(51)[d]	1	0.1822	0.6204	0.1342	3.0[e]
C(61)[d]	1	0.2768	0.7682	−0.4637	3.0[e]
C(62)[d]	1	0.1465	0.7416	−0.1900	3.0[e]
C(63)[d]	1	0.3858	0.9180	−0.1959	3.0[e]
			Site III		
Ir(9)	0.1854	2/3	1/3	0.6697 (18)	
Ir(9')	0.1482	2/3	1/3	0.3355 (21)	}1.69 (7)
Ir(10)	0.5552 (80)	0.6210 (4)	0.4191 (5)	0.4205 (11)	
Ir(10')	0.4448	0.7592 (5)	0.4685 (6)	0.5717 (12)	}1.77 (5)
Ir(10),[3_1][c]		0.5809	0.2019	0.4205	
Ir(10),[3_2][c]		0.7981	0.3790	0.4205	
Ir(10')[3_1][c]		0.5315	0.2907	0.5717	
Ir(10')[3_2][c]		0.7093	0.2408	0.5717	
O(91)	1	0.4410 (42)	0.2627 (34)	0.8386 (41)	9.5 (12)
O(101)	1	0.6053 (32)	0.4477 (30)	0.0842 (40)	7.3 (12)
O(102)	1	0.3743 (32)	0.3688 (28)	0.5043 (33)	3.3 (7)
O(103)	1	0.7581 (29)	0.6744 (32)	0.5081 (32)	4.9 (8)
C(91)[d]	0.5552	0.5251	0.2890	0.7756	3.0[e]
C(101)[d]	0.5552	0.6112	0.4371	0.2094	3.0[e]
C(102)[d]	0.5552	0.4652	0.3873	0.4734	3.0[e]
C(103)[d]	0.5552	0.7068	0.5788	0.4753	3.0[e]
C(91')[f]	0.4448	0.6283	0.4050	0.1781	3.0[e]
C(101')[f]	0.4448	0.7946	0.5197	0.7226	3.0[e]
C(102')[f]	0.4448	0.8995	0.5622	0.5315	3.0[e]
C(103')[f]	0.4448	0.7586	0.5906	0.5340	3.0[e]

[a] Occupancies of atoms (G) in the disordered sites were coupled (in the least-squares refinement process) to those of the major contributors— i.e., to Ir(2) in site I and Ir(10) in site III. Thus, in site I, $G[Ir(1)] = \frac{1}{3}G[Ir(2)]$, $G[Ir(2')] = 1.0 - G[Ir(2)]$, $G[Ir(1')] = \frac{1}{3}(1.0 - G[Ir(2)])$, $G[C(x)] = G[Ir(2)]$, and $G[C(x')] = 1.0 - G[Ir(2)]$. [b] The origin was defined by setting the z coordinate of Ir(1) to zero. [c] The coordinates of the symmetry-related iridium atoms are provided for the convenience of the reader only. These are not input into the structure factor calculation. [d] C-O groups of the major components were refined as rigid nonrotating groups—i.e., shifts of carbon atoms were "tied" to those of the attached oxygen atoms. The C-O distance was defined as 1.14 Å and the M-C-O angle as 180.0°. [e] All carbon atoms were assigned isotropic thermal parameters of 3.0 Å^2. [f] All carbon atoms of the minor components are in calculated positions, based on $d(C-O) = 1.14$ Å and Ir-C-O = 180°.

only molecule not subject to any appreciable disorder).

A list of the independent iridium–iridium and iridium··· oxygen distances is given in Table IV; corresponding angles may be found in Table V. No distances or angles involving carbon atoms are given because these atoms were included with fixed or restrained positions such that $d(C-O) = 1.14$ Å and Ir–C–O = 180°. Each final Ir–C bond length is thus precisely 1.14 Å shorter than its corresponding Ir···O distance.

The pattern of disorder found in the present structure derives from the fact that the 12 peripheral oxygen atoms of the

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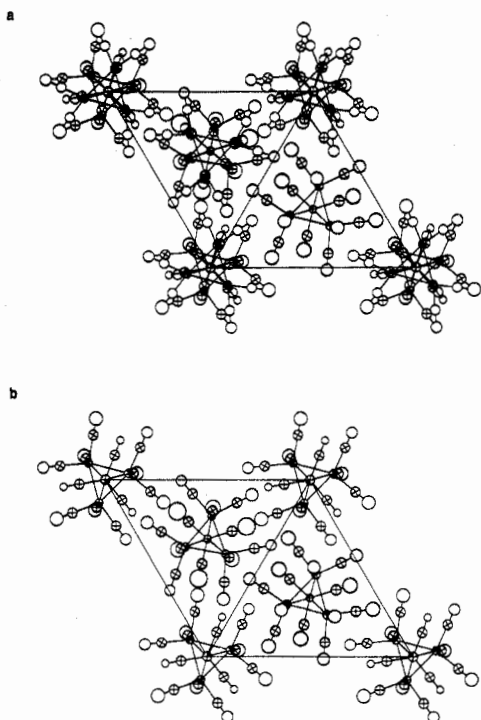
Figure 1. Packing of $Ir_4(CO)_{12}$ molecules within the unit cell, as viewed down the unique axis c: (a) the complete disordered *ensemble*, (b) the "major components" only.

Table IV. Interatomic Distances (Å) with Esd's for $Ir_4(CO)_{12}$

major components		minor components	
(A) Metal–Metal Distances			
Ir(1)–Ir(2)	2.678 (7)	Ir(1')–Ir(2')	2.732 (19)
Ir(2)–Ir(2),[3_1]	2.688 (6)	Ir(2')–Ir(2'),[3_1]	2.741 (19)
Ir(5)–Ir(6)	2.695 (5)		
Ir(6)–Ir(6),[3_1]	2.688 (5)		
Ir(9)–Ir(10)	2.714 (11)	Ir(9')–Ir(10')	2.651 (13)
Ir(10)–Ir(10),[3_1]	2.660 (10)	Ir(10')–Ir(10'),[3_1]	2.755 (12)
	average value = 2.693 Å[a]		
(B) Metal···Oxygen Distances			
Ir(1)···O(11)	3.014 (29)	Ir(1')···O(21)	2.861 (48)
Ir(2)···O(21)	2.795 (51)	Ir(2')···O(11)	2.312 (27)
Ir(2)···O(22)	3.077 (50)	Ir(2')···O(22),[3_2]	2.826 (44)
Ir(2)···O(23)	3.065 (46)	Ir(2')···O(23)	2.758 (43)
Ir(5)···O(51)	3.289 (39)		
Ir(6)···O(61)	3.135 (42)		
Ir(6)···O(62)	3.094 (49)		
Ir(6)···O(63)	2.998 (42)		
Ir(9)···O(91)	3.060 (49)	Ir(9')···O(101)	3.051 (39)
Ir(10)···O(101)	3.064 (36)	Ir(10')···O(91),[3_2]	2.623 (32)
Ir(10)···O(102)	3.094 (37)	Ir(10')···O(102),[3_2]	2.824 (32)
Ir(10)···O(103)	3.044 (38)	Ir(10')···O(103)	2.802 (32)
	average value = 3.009 Å[a]		
(C) Metal–Carbon Distances			
average value = 1.87 Å[b]			

[a] See footnote 10.   [b] Calculated as (average Ir···O distance) − 1.14 Å.

$Ir_4(CO)_{12}$ molecule define a cuboctahedron—a geometric solid which, in the idealized case, has full O_h ($m3m$) symmetry. A *regular* cuboctahedron is thus invariant with respect to inversion. Since the packing of units within a molecular crystal is clearly dictated by the external atoms of the molecule (12 oxygen atoms in the case of $Ir_4(CO)_{12}$), it follows that "inversion disorder" of $Ir_4(CO)_{12}$ is a probable phenomenon—the composite molecular image (as obtained from an X-ray diffraction study) thereby consisting of 12 oxygen atoms, 24 partial carbon atoms, and 8 partial iridium
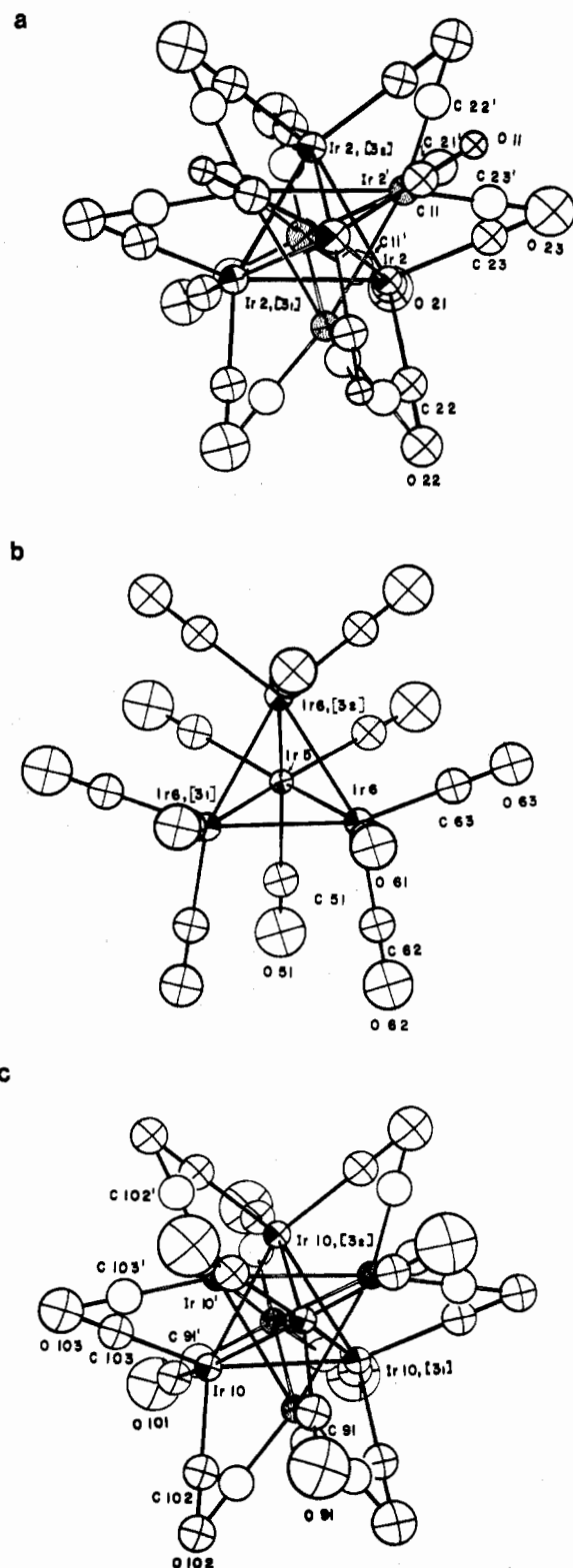
Figure 2. Labeling of atoms: (a) site I, (b) site II, (c) site III. The view for (b) is down c; the other two views are displaced laterally by 10° from the c axis for clarity's sake. Atoms of the major components are shown shaded (Ir) or are shown with full three-dimensional envelopes of the spheres drawn in (O, C). Atoms associated only with the minor components are stippled (Ir) or are shown as hollow circles (C).

atoms (cf. Figures 2a,c and 3a,c).

We note here that precisely this form of disorder was found by us previously[9] in a structural study of $[AsPh_4^+]_2[(\mu-H)_6Re_4(CO)_{12}^{2-}]$; here, however, the cuboctahedral anion was centered on a crystallographic inversion center and there was

**Table V.** Selected Intramolecular Angles (deg) for $Ir_4(CO)_{12}$

major components		minor components	
(A) Angles between Metal Atoms			
Ir(2)-Ir(1)-Ir(2),[3₁]	60.25 (21)	Ir(2')-Ir(1')-Ir(2'),[3₁]	60.21 (52)
Ir(1)-Ir(2)-Ir(2),[3₁]	59.87 (10)	Ir(1')-Ir(2')-Ir(2'),[3₁]	59.89 (26)
Ir(2),[3₁]-Ir(2)-Ir(2),[3₂]	60.00 (–)	Ir(2'),[3₁]-Ir(2')-Ir(2'),[3₂]	60.00 (–)
Ir(6)-Ir(5)-Ir(6),[3₁]	59.83 (15)		
Ir(5)-Ir(6)-Ir(6),[3₁]	60.08 (8)		
Ir(6),[3₁]-Ir(6)-Ir(6),[3₂]	60.00 (–)		
Ir(10)-Ir(9)-Ir(10),[3₁]	58.69 (3)	Ir(10')-Ir(9')-Ir(10'),[3₁]	62.60 (39)
Ir(9)-Ir(10)-Ir(10),[3₁]	60.66 (15)	Ir(9')-Ir(10')-Ir(10'),[3₁]	58.70 (19)
Ir(10),[3₁]-Ir(10)-Ir(10),[3₂]	60.00 (–)	Ir(10'),[3₁]-Ir(10')-Ir(10'),[3₂]	60.00 (–)
(B) Iridium-Iridium· · ·Oxygen Angles			
Ir(2)-Ir(1)-O(11)	96.8 (5)	Ir(2')-Ir(1')-O(21)	108.6 (8)
Ir(2)-Ir(1)-O(11),[3₁]	91.6 (5)	Ir(2')-Ir(1')-O(21),[3₁]	168.0 (11)
Ir(2)-Ir(1)-O(11),[3₂]	149.4 (5)	Ir(2')-Ir(1')-O(21),[3₂]	111.5 (8)
Ir(1)-Ir(2)-O(21)	155.6 (8)	Ir(1')-Ir(2')-O(11)	171.8 (9)
Ir(1)-Ir(2)-O(22)	96.7 (7)	Ir(1')-Ir(2')-O(22)	106.0 (9)
Ir(1)-Ir(2)-O(23)	96.1 (7)	Ir(1')-Ir(2')-O(23)	105.3 (8)
Ir(2),[3₁]-Ir(2)-O(21)	101.2 (8)	Ir(2'),[3₁]-Ir(2')-O(11)	119.1 (7)
Ir(2),[3₁]-Ir(2)-O(22)	98.9 (8)	Ir(2'),[3₁]-Ir(2')-O(22)	164.9 (10)
Ir(2),[3₁]-Ir(2)-O(23)	151.2 (7)	Ir(2'),[3₁]-Ir(2')-O(23)	111.5 (10)
Ir(6)-Ir(5)-O(51)	103.5 (5)		
Ir(6)-Ir(5)-O(51),[3₁]	159.1 (5)		
Ir(6)-Ir(5)-O(51),[3₂]	101.7 (5)		
Ir(5)-Ir(6)-O(61)	152.6 (6)		
Ir(5)-Ir(6)-O(62)	98.1 (6)		
Ir(5)-Ir(6)-O(63)	99.8 (6)		
Ir(6),[3₁]-Ir(6)-O(61)	94.6 (5)		
Ir(6),[3₁]-Ir(6)-O(62)	98.1 (7)		
Ir(6),[3₁]-Ir(6)-O(63)	156.4 (6)		
Ir(10)-Ir(9)-O(91)	98.4 (7)	Ir(10')-Ir(9')-O(101)	113.8 (7)
Ir(10)-Ir(9)-O(91),[3₁]	154.1 (8)	Ir(10')-Ir(9')-O(101),[3₁]	174.4 (9)
Ir(10)-Ir(9)-O(91),[3₂]	100.4 (7)	Ir(10')-Ir(9')-O(101),[3₁]	112.1 (7)
Ir(9)-Ir(10)-O(101)	155.3 (8)	Ir(9')-Ir(10')-O(91)	167.1 (11)
Ir(9)-Ir(10)-O(102)	98.3 (6)	Ir(9')-Ir(10')-O(102)	107.3 (7)
Ir(9)-Ir(10)-O(103)	96.9 (5)	Ir(9')-Ir(10')-O(103)	105.7 (7)
Ir(10),[3₁]-Ir(10)-O(101)	98.4 (7)	Ir(10'),[3₁]-Ir(10')-O(91)	110.7 (10)
Ir(10),[3₁]-Ir(10)-O(102)	98.6 (7)	Ir(10'),[3₁]-Ir(10')-O(102)	165.8 (7)
Ir(10),[3₁]-Ir(10)-O(103)	153.2 (6)	Ir(10'),[3₁]-Ir(10')-O(103)	107.3 (7)
(C) OC-Ir-CO Angles			
O(11)-Ir(1)-O(11),[3₁]	104.2 (5)	O(21)-Ir(1')-O(21),[3₁]	78.8 (14)
O(21)-Ir(2)-O(22)	101.8 (10)	O(11)-Ir(2')-O(22)	74.0 (11)
O(21)-Ir(2)-O(23)	96.5 (10)	O(11)-Ir(2')-O(23)	82.8 (12)
O(22)-Ir(2)-O(23)	99.6 (10)	O(22)-Ir(2')-O(23)	76.1 (12)
O(51)-Ir(5)-O(51),[3₁]	91.9 (7)		
O(61)-Ir(6)-O(62)	95.6 (8)		
O(61)-Ir(6)-O(63)	101.9 (8)		
O(62)-Ir(6)-O(63)	97.0 (8)		
O(91)-Ir(9)-O(91),[3₁]	97.6 (9)	O(101)-Ir(9')-O(101),[3₁]	71.3 (11)
O(101)-Ir(10)-O(102)	97.8 (9)	O(91)-Ir(10')-O(102)	82.9 (12)
O(101)-Ir(10)-O(103)	99.0 (8)	O(91)-Ir(10')-O(103)	83.9 (11)
O(102)-Ir(10)-O(103)	99.1 (8)	O(102)-Ir(10')-O(103)	77.2 (9)

thus a 50%:50% ratio of the two inversion-related components to the structure.

Disorder of the $Ir_4(CO)_{12}$ molecules in the present structure is not random (i.e., is not 50%:50% at each site). Rather, it varies from site to site, viz., 83.3%:16.7% at site I, ~100%:0% at site II, and 55.5%:44.5% at site III.

It is probable that these variations in the degree of disorder from site to site result from deviations of the external oxygen atoms from a figure of perfect O_h symmetry. (There are also unrelated deviations of the $Ir_4(CO)_{12}$ molecule from perfect T_d symmetry.) Figure 5 shows the precise nature of the cuboctahedron formed by the oxygen atoms at site I, as viewed down the crystallographic C_3 axis; this figure is also applicable to sites II and III. The 24 edges of the cuboctahedron are defined by eight crystallographically independent distances for each site (see Table VI). There are 14 faces to the cuboctahedron—six rectangular and eight triangular. The "upper equilateral triangle" (Figure 5) defined by the three oxygen atoms associated with the unique iridium (i.e., the *major* component on the C_3 axis) is defined by the edges *aaa*, of length 4.76 (5) Å at site I, 4.73 (7) Å at site II, and 4.60 (8) Å at site III; the "lower equilateral triangle", *hhh*, is defined by O···O contacts of 3.63 (6), 3.49 (5), and 3.56 (7) Å (respectively) at the three sites. There is thus not *precise* C_i (Ī) symmetry to the cuboctahedron defined by the external oxygen atoms of the $Ir_4(CO)_{12}$ molecule—the potential correspondence is avoided by relative atomic displacements of about 0.5 Å. [This inexact correspondence is the cause of the apparent variation in iridium···oxygen distances in the minor components—from 2.312 (27) to 2.861 (48) Å at site I and from 2.623 (32) to 3.051 (39) Å at site III. In contrast to this, the iridium···oxygen distances for the major components

a

b

c
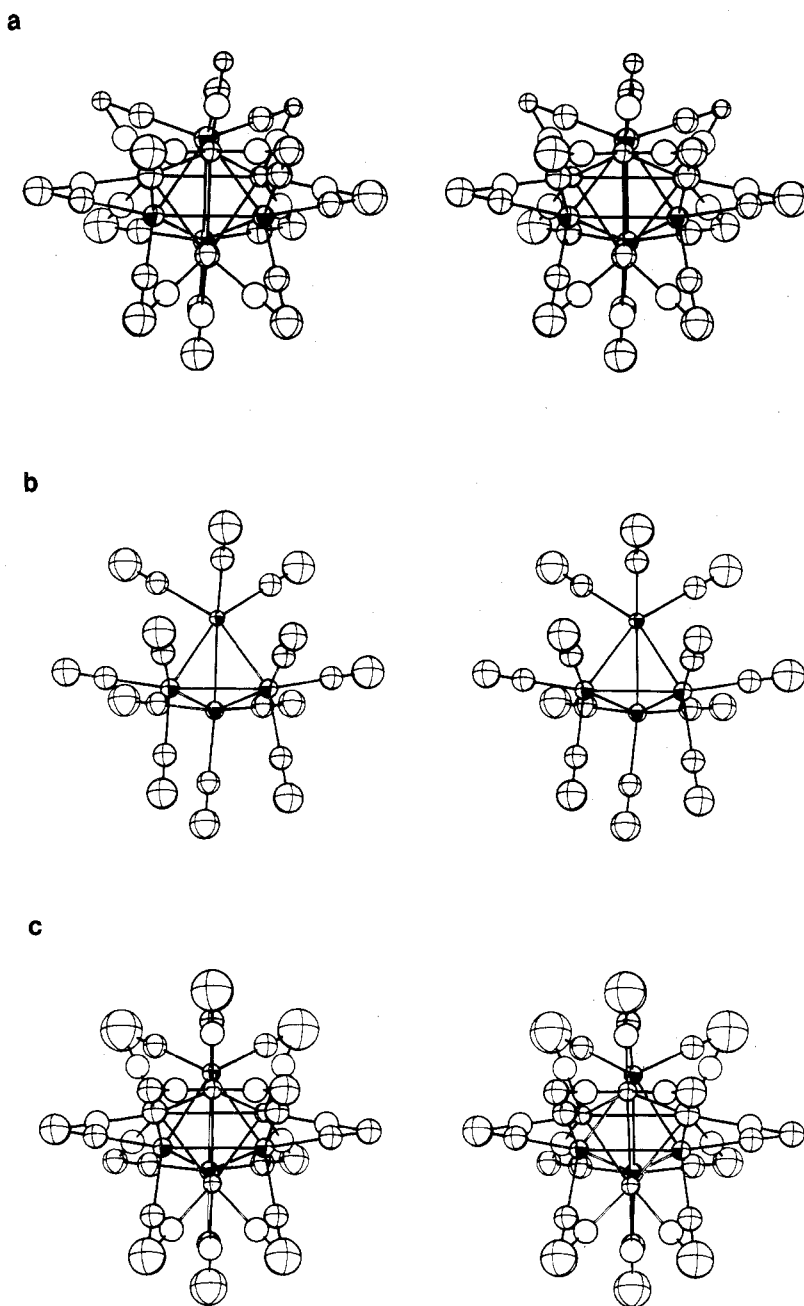
Figure 3. Stereoscopic diagrams of the three independent sites: (a) the disordered molecule at site I, (b) the ordered molecule at site II, (c) the disordered molecule at site III.

Table VI. Intramolecular Oxygen· · ·Oxygen Contacts (Å)

label (see Figure 5)	site I		site II		site III	
a	O(11)· · ·O(11),[3₁]	4.76 (5)	O(51)· · ·O(51),[3₂]	4.73 (7)	O(91)· · ·O(91),[3₂]	4.60 (8)
b	O(11)· · ·O(23)	3.37 (4)	O(51)· · ·O(62)	3.90 (4)	O(91)· · ·O(102)	3.61 (5)
c	O(11)· · ·O(22),[3₂]	3.12 (4)	O(51)· · ·O(63),[3₁]	3.89 (4)	O(91)· · ·O(103),[3₁]	3.63 (5)
d	O(22)· · ·O(23)	4.69 (7)	O(62)· · ·O(63)	4.56 (6)	O(102)· · ·O(103)	4.67 (5)
e	O(22)· · ·O(23),[3₁]	3.44 (5)	O(63)· · ·O(62),[3₂]	3.66 (4)	O(103)· · ·O(102),[3₂]	3.51 (4)
f	O(21)· · ·O(23)	4.37 (6)	O(61)· · ·O(62)	4.61 (6)	O(101)· · ·O(102)	4.64 (5)
g	O(21)· · ·O(22)	4.56 (7)	O(61)· · ·O(63)	4.76 (5)	O(101)· · ·O(103)	4.64 (5)
h	O(21)· · ·O(21),[3₁]	3.63 (6)	O(61)· · ·O(61),[3₂]	3.49 (5)	O(101)· · ·O(101),[3₂]	3.56 (7)

range from 2.795 (51) to 3.077 (50) Å at site I, from 2.998 (42) to 3.289 (39) Å at site II, and from 3.044 from (38) to 3.094 (37) Å at site III. This lack of exact correspondence of oxygen atoms atoms with inversion also explains the immense difficulty we had in refining this structure.]

Further discussion below is limited to the intramolecular oxygen···oxygen distances found at site I; the arguments

presented also apply, mutatis mutandis, to sites II and III. All appropriate distances appear in Table VI and the scheme for labeling cuboctahedral edges is presented in Figure 5.

The set of upper rectangular faces are defined by edges *abdc* in which there are two long and two short edges [*a* = 4.76 (5) Å, *b* = 3.37 (4) Å, *d* = 4.69 (7) Å, *c* = 3.12 (4) Å]; the lower rectangular faces, defined by the edges *fhge*, are fairly similar
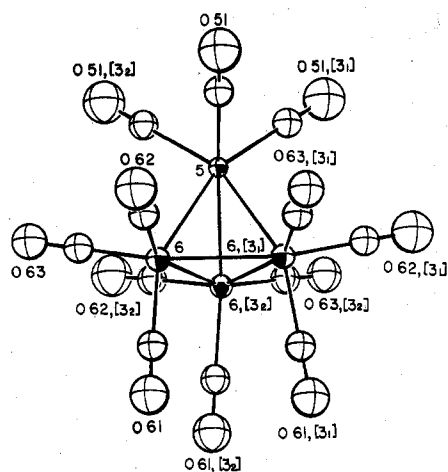
Figure 4. Labeling of atoms in the ordered molecule at site II. Iridium atoms are identified with numbers and transformations only. Carbon atoms, not labeled, are numbered as their attached oxygen atoms.
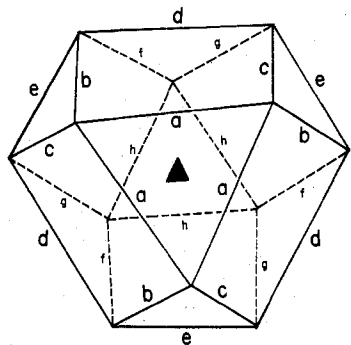

Figure 5. The cuboctahedron defined by the oxygen atoms of the $Ir_4(CO)_{12}$ molecules. This figure is a faithful representation of the geometric arrangement of oxygen atoms at site I and is viewed precisely down c, the crystallographic C_3 axis. Atom designations can be determined by comparison with Figure 2a. This figure is also relevant to oxygen atoms at site II and site III (see Table VI). Note the different sizes of the basal and apical triangular faces.

for which f = 4.37 (6) Å, h = 3.63 (6) Å, g = 4.56 (7) Å, and e = 3.44 (5) Å. The "upper equatorial" triangular faces *bce* each approximate to the lower small equilateral triangular face *hhh*, the individual edge lengths being b = 3.37 (4) Å, c = 3.12 (4) Å, and e = 3.44 (5) Å. The "lower equatorial" triangular faces *gfd* in turn approximate to the upper large equilateral triangular face *aaa*, with distances of g = 4.56 (7)

Å, f = 4.37 (6) Å, and d = 4.69 (7) Å.

It seems probable that the isolated $Ir_4(CO)_{12}$ molecule has T_d symmetry; however, in the crystal the symmetry is reduced to C_3 (*not* C_{3v}—see Figure 2b).

It is possible also that the degree of disorder in a crystal of $Ir_4(CO)_{12}$ may vary from crystal to crystal, depending upon the method and conditions of crystallization. Indeed, it may even be possible to isolate ordered crystals; we saw no evidence for this, however.

Within the $Ir_4(CO)_{12}$ molecule, the four iridium atoms define a regular tetrahedron. The average[10] iridium–iridium bond length is 2.693 Å, indicating a covalent radius of 1.346 Å for iridium(0) in a tetrahedral cluster in the appropriate stereochemistry.

Each iridium atom, in addition to being σ bonded to three other iridium atoms, attains the appropriate noble gas configuration by linking to three terminal carbonyl ligands. The average[10] iridium···oxygen distance of approximately 3.01 Å yields a predicted Ir–CO distance of 1.87 Å.

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(10) The average value for the Ir–Ir distance is calculated as the "weighted mean" via the formula $d(av) = [\sum_{i=1}^{i=N} G_i d(Ir-Ir)_i / \sum_{i=1}^{i=N} G_i]$, where G_i is the fractional occupancy of a given $Ir_4(CO)_{12}$ molecule, $d(Ir-Ir)_i$ is a bond length in that molecule, and the sum is over all independent Ir–Ir bond lengths in the structure.