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Crystal Structure of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$. A 4-fold Disordered Structure in a Crystal Isomorphous with $Fe_3(CO)_{12}$

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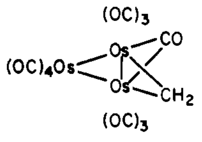
The protonation of $[Os_3(CO)_{11}(CHO)^-]$ has been shown to give rise to a neutral complex of stoichiometry $Os_3(CO)_{11}(CH_2)$. Steinmetz and Geoffroy[1] have proposed a structure for this complex in which a bridging methylene and a bridging carbonyl group span one edge of the triangular Os_3 framework (I). The two bridging groups are each of considerable contemporary interest, for the following reasons: (1) Bridging methylene groups are implicated as intermediates in such processes as the Fischer-Tropsch synthesis.[2] (2) Bridging carbonyl groups are extremely rare in osmium carbonyl chemistry. To the best of our knowledge $Os_3(CO)_{10}(PhC_2Ph)$[3] is the only trinuclear osmium carbonyl derivative shown crystallographically to have a bridging carbonyl ligand and here it is an *asymmetric* bridge.



I

Johnson[4] has commented that the Os_3 triangle cannot be accommodated in the cavity formed by an icosahedral arrangement of CO groups, so that $Os_3(CO)_{12}$ has an (all terminal) anticuboctahedral arrangement of carbonyl ligands in contrast to the icosahedral arrangement (ten terminal, two bridging) in $Fe_3(CO)_{12}$.

We initially began this study in 1979. We outline below the key steps in solving this 4-fold disordered structure and the chemical information obtainable therefrom.

Experimental Section

A. Data Collection. Deep red, well-formed crystals of $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ were provided by Professor G. R. Geoffroy. An irregular fragment, cleaved to an average dimension of ~0.1 mm, was sealed into a glass capillary and was used for all measurements. Description of our operation of the Syntex $P2_1$ diffractometer has been published;[5] details of the present analysis are in Table I.

Table I. X-ray and Crystal Parameters for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$

(A) Crystal Parameters[a] at 23 (1) °C

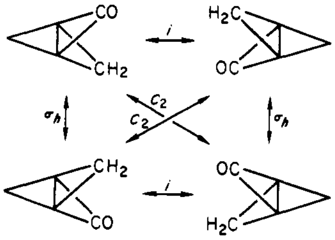
crystal system: monoclinic	$a = 8.5620$ (14) Å
space group: $P2_1/n$	$b = 11.2352$ (22) Å
mol wt = 892.6	$c = 9.1486$ (16) Å
ρ(calcd) = 3.39 g cm^{-3}	$\beta = 96.274$ (13)°
$Z = 2$	$V = 874.8$ (3) Å

(B) Intensity Data

radiation: Mo K$\bar{\alpha}$ [$\bar{\lambda} = 0.710\,730$ Å]
2θ range: 3.0-45.0°
scan type: θ(crystal)-2θ(counter)
scan speed: 2.00° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.0]° - [2\theta(\alpha_2) + 1.0]°$
reflctns measd: $\pm h+k\pm l$ (2 forms)
reflctns collected: 2153 collected yielding 1153 independent data
abs coeff: 258 cm^{-1}

[a] Based on a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ peaks of 24 reflections with 2θ = 20-30°.

Scheme I



Two complete asymmetric units of diffraction data were collected. The intensities were corrected for absorption by an empirical ψ-scan method; six curves were used with $(I_{max})/(I_{min})$ values in the range 1.18-1.40. Data averaging, as well as all subsequent calculations, utilized the Syntex XTL program package as modified at SUNY-Buffalo.

B. Solution and Refinement of the Structure. The use of direct methods (MULTAN)[6] followed by an "E map" revealed immediately that the structure was disordered. A "Star-of-David" pattern, characteristic of a triangular cluster disordered about a crystallographic inversion center, was found about the positions (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) in space group $P2_1/n$. From this point, the complete solution of the structure proceeded very slowly since there was no certainty *at this time* of the exact connectivity of ligands in the complex. The completion of the structural study was aided immensely by two occurrences: (1) the proposal, by Steinmetz and Geoffroy, of structure I for the complex and (2) the belated realization that the present structure is not only similar to but actually *isomorphous* with $Fe_3(CO)_{12}$.[7-9]

The computational steps essential to solution of this structural problem were as follows.[10]

(1) The three crystallographically independent osmium atoms were assigned occupancies of $^1/_2$, and their positional and anisotropic thermal parameters were refined.

(2) Six crystallographically independent oxygen atoms were located from a difference-Fourier synthesis, and their positional and anisotropic

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(1) Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278.
(2) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1981**, *103*, 1287.
(3) Pierpont, C. G. *Inorg. Chem.* **1977**, *16*, 636.
(4) (a) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1976**, 211. (b) Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1743.
(5) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.
(6) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.
(7) (a) The entire saga of the solution of this structure is described in the paper: Wei, C. H.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 1351. (b) Further resolution of the structure was carried out later. See: Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4155.
(8) It is interesting to note that the structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$ is disordered and is isomorphous with $Fe_2(CO)_9$.[9] See: Meyer, B. B.; Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1981**, *20*, 3024.
(9) (a) The initial solution of the structure of $Fe_2(CO)_9$ is reported in: Powell, H. M.; Ewens, R. V. G. *J. Chem. Soc.* **1939**, 286. (b) The structure was later redetermined: Cotton, F. A.; Troup, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 800.
(10) The reader will note similarities to the solution of the structure of disordered $Ir_4(CO)_{12}$: Churchill, M. R.; Hutchison, J. P. *Inorg. Chem.* **1978**, *17*, 3528.

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Table II. Final Positional Parameters for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$

atom	occupancy	x	y	z	B_{iso}, Å^2
Os(1)	$^1/_2$	−0.05413 (20)	−0.01578 (14)	−0.17093 (15)	
Os(2)	$^1/_2$	−0.11670 (17)	0.04600 (15)	0.11844 (15)	
Os(3)	$^1/_2$	−0.18497 (19)	−0.01192 (16)	0.06899 (17)	
C(11)	$^1/_2$	−0.022 (3)	0.111 (1)	−0.196 (3)	
O(11)	$^3/_4$	0.003 (3)	0.234 (3)	−0.230 (3)	
C(12)	1	−0.084 (2)	−0.172 (2)	−0.122 (2)	
O(12)	$^3/_4$	−0.101 (3)	−0.275 (3)	−0.096 (3)	
C(21a)[a]	$^1/_2$	−0.228	0.180	0.052	5.1 (9)
C(21b)[a]	$^1/_2$	−0.256	0.170	−0.018	3.9 (7)
O(21)	1	0.295 (2)	−0.262 (1)	−0.012 (2)	
C(22a)[a]	$^1/_2$	−0.132	0.074	0.306	5.4 (9)
C(22b)[a]	$^1/_2$	−0.071	0.064	0.334	5.7 (10)
O(22)	1	−0.144 (2)	0.095 (2)	0.427 (2)	
C(31a)[a]	$^1/_2$	0.308	0.071	−0.043	4.5 (8)
C(31b)[a]	$^1/_2$	0.283	0.060	−0.115	4.5 (8)
O(31)	1	0.385 (2)	0.123 (2)	−0.113 (2)	
C(32a)[a]	$^1/_2$	0.314	0.004	0.226	7.9 (14)
C(32b)[a]	$^1/_2$	0.273	0.015	0.278	6.7 (12)
O(32)	1	0.398 (2)	0.009 (2)	0.343 (2)	

[a] These carbon atoms were included in fixed positions.

Table III. Anisotropic Thermal Parameters (Å^2) for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	4.02 (9)	4.26 (8)	2.24 (6)	0.44 (6)	−0.24 (5)	−0.34 (5)
Os(2)	3.00 (8)	5.39 (9)	3.02 (7)	0.57 (7)	0.28 (5)	−0.92 (6)
Os(3)	3.08 (8)	5.82 (10)	3.54 (7)	0.73 (7)	−0.30 (6)	−0.57 (6)
C(11)	4.3 (13)	16.2 (24)	3.4 (11)	−3.7 (15)	1.9 (9)	−2.6 (14)
O(11)	4.8 (13)	13.8 (20)	8.5 (15)	2.2 (13)	3.3 (10)	6.5 (15)
C(12)	3.6 (11)	4.5 (11)	6.2 (12)	−0.2 (9)	−0.8 (8)	−1.4 (9)
O(12)	7.3 (17)	8.0 (17)	16.3 (24)	−2.3 (14)	2.0 (15)	−5.3 (16)
O(21)	9.3 (12)	5.7 (9)	7.1 (9)	0.9 (8)	0.6 (8)	0.8 (7)
O(22)	9.9 (12)	9.1 (12)	5.9 (9)	2.4 (9)	1.3 (8)	−0.8 (8)
O(31)	7.3 (12)	11.0 (15)	15.2 (17)	−1.9 (10)	2.3 (12)	0.8 (10)
O(32)	8.5 (14)	9.5 (14)	9.6 (13)	0.3 (10)	−4.3 (10)	−2.8 (10)

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor amplitude in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

thermal parameters were refined.[11]

(3) All carbon atoms except those of the bridging (and inversion-related terminal) carbonyl ligands were input in fixed positions (based upon d(C–O) = 1.14 Å and Os–C–O = 180°) and assigned occupancies of $^1/_2$; their isotropic thermal parameters (only) were refined. The bridging methylene group and the carbon atom of the bridging carbonyl group are also mutually disordered and are represented jointly by atoms C(11′) and C(12′), both of which were located from difference-Fourier maps and refined with unit occupancies and anisotropic thermal parameters.

(4) The overall disorder problem was recognized as the inversion disorder of $Fe_3(CO)_{12}$ coupled with a mirror disorder about the Os_3 triangle, which scrambles μ-CH_2 and μ-CO ligands (see Scheme I). Atoms O(11) and O(12) [along with the symmetry-related atoms O(11′) and O(12′)] were now assigned occupancies of $^3/_4$ to achieve the correct molecular formulation (cf. ref 11b).

Refinement of appropriate parameters (108 in all) led to convergence with[12] R_F = 7.9%, and R_{wF} = 8.7% for all 1153 unique reflections. Final positional and thermal parameters are listed in Tables II and III.

Discussion

Figure 1 shows the labeling scheme for atoms in the molecule and indicates the relationship of an individual molecule to the entire disordered ensemble. Relevant distances are collected in Table IV.

Table IV. Important Distances (Å) with Esd's for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH)_2$

(A) Osmium–Osmium Distances			
Os(1)–Os(2)	2.844 (2)	Os(2)–Os(3)	2.749 (2)
Os(1)–Os(3)	2.833 (2)		
(B) Osmium–(Bridging Ligand) Distances			
Os(2)–C(11′)	2.434 (34)	Os(2)–C(12′)	2.228 (22)
Os(3)–C(11′)	2.370 (29)	Os(3)–C(12′)	2.311 (23)
(C) Osmium–(Terminal Carbonyl) Distances			
Os(1)–C(11)	1.750 (37)	Os(1)–C(12)	1.838 (23)
(D) Osmium–Oxygen Distances			
Os(1)...O(11)	2.914 (32)	Os(2)...O(31′)	2.979 (20)
Os(1)...O(12)	3.024 (28)	Os(3)...O(31)	2.936 (20)
Os(1)...O(22′)	3.168 (17)	Os(3)...O(32)	2.943 (21)
Os(1)...O(32′)	3.186 (21)	Os(3)...O(21′)	3.084 (17)
Os(2)...O(21)	2.976 (17)		
Os(2)...O(22)	2.912 (16)		

As a result of the 4-fold disorder of the structure,[13] many interatomic parameters either are restrained or are of limited accuracy. The following points are, however, of chemical interest.

(1) The doubly bridged Os(2)–Os(3) bond is 2.749 (2) Å in length and is significantly shorter than the nonbridged osmium–osmium bond lengths both in this molecule [Os(1)–Os(2) = 2.844 (2) Å and Os(1)–Os(3) = 2.833 (2) Å] and in the parent molecule $Os_3(CO)_{12}$ [Os–Os = 2.877 [3] Å].[14] A similar feature is observed in $Fe_3(CO)_{12}$, where[7b] Fe–Fe (bridged) = 2.558 (1) Å vis-à-vis Fe–Fe (nonbridged)

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(11) (a) It is probable that each of these "oxygen" atoms actually represents two "half-oxygen" atoms very close together—i.e., there is not precise overlap between the individual images in the disordered structure. (For details, see the Experimental Section of ref 7b.) (b) At this stage we had an overall partial formulation of Os_3O_{12}; the total number of oxygen atoms was later adjusted (see text).

(12) $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$ (%); $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} \times 100$ (%).

(13) A similar 4-fold disorder is found in $HOs_3Re(CO)_{15}$. Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1977**, *16*, 2493 (see Scheme II on p 2496).

(14) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

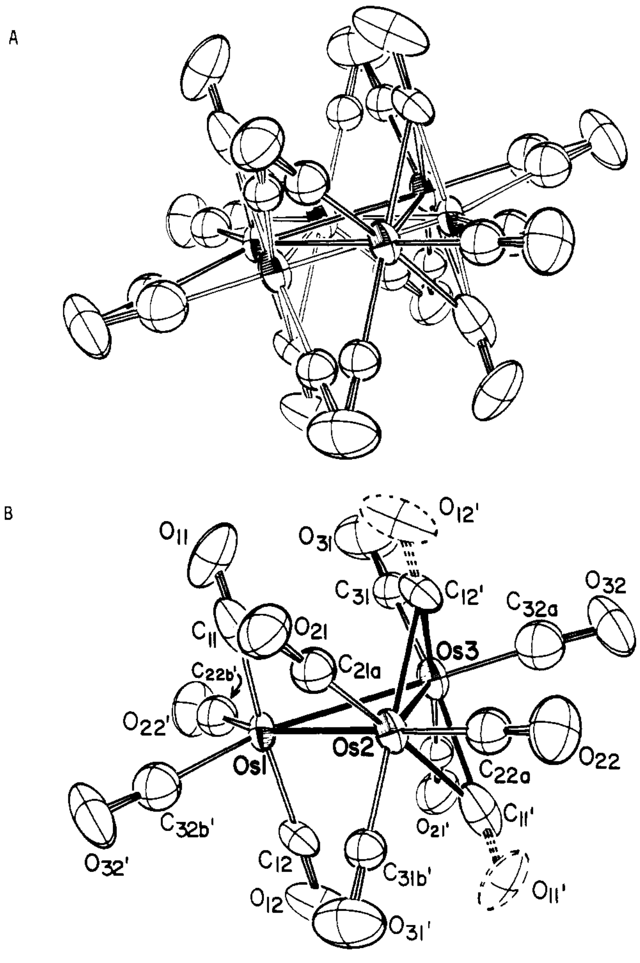

Figure 1. (A) Complete disordered structure. (B) Labeling of atoms in the composite image of two mirror-related $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ molecules showing disorder of the bridging carbonyl and methylene groups. The philosophy behind the labeling is as follows: (a) one Os_3 triangle is chosen; (b) the six unique oxygen atoms are labeled with the first digit identical with the nonprimed osmium atom to which they are joined; (c) the two $^1/_2$-carbon atoms associated with a given oxygen atom are labeled a and b; (d) all atoms related to the basic set by inversion about (0, 0, 0) are labeled with a prime. Note that C(11′) and C(12′) are the composite of disordered methylene and carbonyl carbon atoms (see text).

= 2.677 (2) and 2.683 (1) Å.

(2) The overall molecular skeleton is very similar to that found in a variety of $Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}L)$ complexes.[15]

(3) The outer oxygen atoms define a geometric figure that is a distorted icosahedron (Figure 2). A similar figure is defined by the oxygen atoms of $Fe_3(CO)_{12}$, whereas the oxygen atoms of both $Os_3(CO)_{12}$[14] and $Ru_3(CO)_{12}$[16] define an alternative symmetrical geometric figure—the anticuboctahedron, which does not possess an inversion center.

(4) The osmium–(bridging ligand) distances range from 2.311 (23) to 2.434 (34) Å; one suspects that the esd's associated with the distances are far too small. Atoms C(11), C(12), C(11′), C(12′) are, in any case, the composites of disordered bridging ligands across Os(2)–Os(3) and Os(2′)–Os(3′) and terminal carbonyl carbon atoms on Os(1) and Os(1′). In known ordered structures, the Os–C (carbene) distances in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$ are 2.148 (9) and 2.173 (8) Å,[17] while those in $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHCH{=}NEt_2)$ are 2.15 (3) and 2.16 (3) Å.[18] One would expect Os–(μ-CO) distances of ~2.1 Å.[19,20]

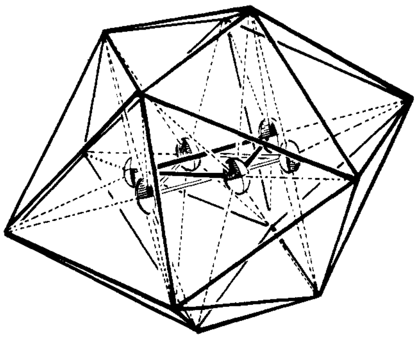

Figure 2. The polyhedron defined by the peripheral oxygen atoms of the $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ structure. Note that any one molecule can only be associated with 11 carbonyl groups and therefore contains only 11 oxygen atoms.

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Registry No. $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$, 77208-32-3.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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(15) (a) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580 (see Table VII on p 1584). (b) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2905–2909.

(16) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

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(19) The crystal structure of the related ordered species $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CHSiMe_3)$ has now been completed (see ref 20). All aspects of this structure are in keeping with our proposals for $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$.

(20) Shapley, J. R.; Sievert, A. C.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 6975–6977.

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Roussin's Red Salt Revisited: Reactivity of $Fe_2(\mu\text{-}E)_2(NO)_4^{2-}$ (E = S, Se, Te) and Related Compounds

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Salts of $Fe_2(\mu\text{-}S)_2(NO)_4^{2-}$ were first synthesized in 1858 by Roussin in an attempt to prepare analogues of the nitroprusside ion.[1] It was not until much later[2] that the structure of "Roussin's red salt" was deduced by analogy to its esters, $Fe_2(\mu\text{-}SR)_2(NO)_4$,[3] and the thiosulfate $Fe_2(\mu\text{-}S_2O_3)_2(NO)_4^{2-}$.[4] In 1958, the X-ray structures of both the ethyl ester[5] and the "black salt" $Cs[Fe_4(\mu_3\text{-}S)_3(NO)_7]H_2O$[6] were published. Since that time these compounds have elicited little interest from the inorganic community despite intense activity in the areas

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(1) Roussin, J. *Ann. Chim. Phys.* **1858**, *52*, 285.

(2) Reihlen, H.; von Friedolsheim, A. *Justus Liebigs Ann. Chem.* **1927**, *457*, 71.

(3) Hoffmann, K. A.; Wiede, O. F. *Z. Anorg. Chem.* **1895**, *9*, 295.

(4) Hoffmann, K. A.; Wiede, O. F. *Z. Anorg. Chem.* **1895**, *8*, 318.

(5) Thomas, J. T.; Robertson, J. H.; Cox, E. G. *Acta Crystallogr.* **1958**, *11*, 599.

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