Synthesis, Structural Characterization, and Molecular Organization in the Solid State of $[H_2Os_{10}C(CO)_{24}]$

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The neutral dihydrido cluster $[H_2Os_{10}C(CO)_{24}]$ has been obtained from the protonation of the dianion $[Os_{10}C(CO)_{24}]^{2-}$ in MeCN with H_2SO_4 and, alternatively, from the thermolysis of $[Os_3(CO)_{12}]$ in cyclohexane. The X-ray diffraction study of the black needles obtained from the latter reaction reveals a structure closely related to that of the carbido clusters $[Os_{10}C(CO)_{24}]^{2-}$ and $[HOs_{10}C(CO)_{24}]^-$ and to that of the tetrahydrido species $[H_4Os_{10}(CO)_{24}]^{2-}$. The X-ray analysis has afforded convincing evidence of the presence of two bridging H ligands on the surface of the Os_{10} metal frame and not, as previously suggested, in tetrahedral interstitial sites. A detailed examination of the molecular organization within the crystal lattice has been carried out by means of computer graphics and potential energy calculations.

Introduction

In 1982 it was reported[1] that protonation of the carbido dianion $[Os_{10}C(CO)_{24}]^{2-}$ (2) with concentrated H_2SO_4 gives first the hydrido monoanion $[HOs_{10}C(CO)_{24}]^-$ (3) and then the neutral dihydrido cluster $[H_2Os_{10}C(CO)_{24}]$ (1). At that time it was further established from X-ray analysis of the $[Ph_4As]^+$ and $[Ph_3MeP]^+$ salts of the hydrido monoanion 3 that the structure contained a close-packed carbonyl distribution very similar to that of the dianion 2,[2] and primarily on this basis, it was concluded that the H ligand occupies a tetrahedral site within the Os_{10} microlattice.

The formation of the monoanion or the neutral dihydrido species was found to be highly dependent on the basicity of the solvent. Thus, whereas acidification in tetrahydrofuran gives an equilibrium mixture of 1-3, acidification in acetonitrile gives initially 3 and finally a precipitate (quantitatively) of the dihydrido 1. In contrast, protonation in nondonor solvents such as chloroform or dichloromethane gives only the monoanion 3. The dihydrido 1 was always obtained as a black, amorphous solid which proved to be insoluble in all nondonor solvents and dissolved in donor solvents such as tetrahydrofuran (thf) and MeCN only on deprotonation. Despite many attempts we were unable to obtain crystals of 1 suitable for single-crystal analysis. However, because of its mode of preparation and reactivity toward donor molecules, we assumed that the fundamental $Os_{10}C(CO)_{24}$ core was similar to that observed for 2 and 3[2] and for the tetrahydride $[H_4Os_{10}(CO)_{24}]^{2-}$ (4).[3]

Very recently, we have observed that crystals of $[H_2Os_{10}C(CO)_{24}]$ may be obtained directly by heating a cyclohexane solution of $[Os_3(CO)_{12}]$ in a sealed tube at 300 °C for 1 h. These black crystals were found to be highly suitable for X-ray analysis (see below). That samples of 1 could be prepared by the two independent routes was confirmed from a comparison of their IR spectroscopic and analytical data (see Experimental Section). The aims of this paper can be summarized as follows: (i) to briefly compare the molecular structure of 1 with that of other related Os_{10} species; (ii) to address the question of the location (whether peripheral or interstitial) of the two H(hydride) atoms required by the electron counting in 1; (iii) to investigate the *crystal structure* of 1 in order to "decode" how the shape of the ligand envelope controls the molecular organization in the lattice of this high-nuclearity neutral cluster. To this latter purpose we have applied methods and procedures previously developed to study the relationship between molecular and crystal structure of mononuclear and polynuclear organometallic complexes.[4]

The location of the H(hydride) atoms appears to be of some importance in the understanding of the physical properties of crystalline 1: recent magnetic susceptibility and electron paramagnetic resonance (EPR) experiments have shown that 1, as well as other high-nuclearity osmium clusters, has unusual "metametallic" properties.[5] In particular, the temperature dependence of the EPR spectral parameters in crystalline 1 has been related to the mobility of the H(hydride) ligands within the cluster above 100 K.

Results and Discussion

The molecule lies around a 2-fold symmetry axis in the space group *C*2/*c*. It possesses the metal framework common to most Os_{10} clusters, i.e. a tetracapped octahedron which corresponds to the 1:3:6 close-packed ar-

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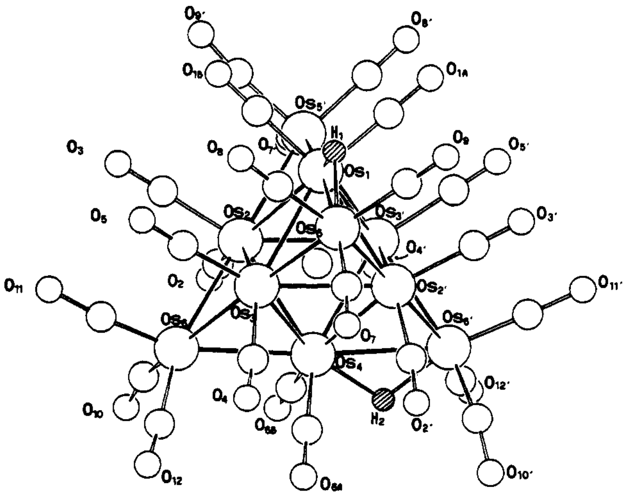

Figure 1. Molecular structure of [$H_2Os_{10}C(CO)_{24}$], showing the atomic labeling scheme (C atoms bear the same numbering as the corresponding O atoms). The crystallographic 2-fold axis passes through Os(1) and Os(4). Only one of the two possible orientations of the disordered CO groups bound to Os(1) and Os(4) is shown (the C atom positions were calculated by assuming linear Os–C–O axes). The H(hydride) positions are those afforded by XHYDEX (see text).

Table I. Relevant Structural Parameters (Å) for $H_2Os_{10}C(CO)_{24}$ and Comparison with Other Related Os_{10} Clusters

outer edges		inner edges	
Os(1)–Os(5)	2.912 (2)	Os(1)–Os(2)	2.891 (3)
Os(2)–Os(6)	2.786 (3)	Os(1)–Os(3)	2.883 (3)
Os(3)–Os(5)	2.768 (3)	Os(2)–Os(3)	2.845 (2)
Os(3)–Os(6)	2.767 (3)	Os(2)–Os(4)	2.881 (3)
Os(4)–Os(6)	2.870 (2)	Os(3)–Os(4)	2.884 (3)
Os(2)–Os(5′)	2.774 (2)	Os(2)–Os(3′)	2.868 (3)
mean "short"	2.774 (2)	mean	2.875 (3)
mean "long"	2.891 (2)		
mean Os–C(CO)	1.87 (4)	mean Os–C_{carb}	2.04 (4)
mean C–O	1.14 (4)		
	[$Os_{10}C(CO)_{24}$]$^{2-}$ (2)[1]		
mean	2.786 (1)	mean	2.883 (1)
		mean Os–C_{carb}	2.03 (2)
	[$HOs_{10}C(CO)_{24}$]$^{-}$ (3)[2]		
mean	2.807 (1)	mean	2.887 (1)
		mean Os–C_{carb}	2.04 (1)
	[$H_4Os_{10}(CO)_{24}$]$^{2-}$ (4)[3a]		
mean "short"	2.750 (1)	mean	2.857 (1)
mean "long"	2.852 (1)		

rangement of metal atoms (see Figure 1). The central octahedral cavity accommodates the interstitial C(carbide) atom. The crystallographic 2-fold axis passes through the midpoint of two noncontiguous edges of the outer tetrahedron, comprising atoms Os(1) and Os(4). The 24 carbonyl ligands are distributed three on each tetrahedron apex and two on each Os atom of the inner octahedral frame.

A comparison of some relevant average structural parameters for $H_2Os_{10}C(CO)_{24}$ (1) and related species is made in Table I. Attention is focused on the isostructural and isoelectronic complexes [$HOs_{10}C(CO)_{24}$]$^-$,[1] [$Os_{10}C(CO)_{24}$]$^{2-}$,[2] and [$H_4Os_{10}(CO)_{24}$]$^{2-}$.[3] It can be seen that (i) the size of the inner octahedron is similar in the three carbides, while expectedly larger than in the tetrahydrido dianion [$H_4Os_{10}(CO)_{24}$]$^{2-}$, (ii) the "short" Os–Os outer bonds [mean 2.774 (2) Å] in 1 are not only comparable with the corresponding "short" bonds in [$H_4Os_{10}(CO)_{24}$]$^{2-}$ [2.750 (1) Å] but also with the average length of the tetrahedral edges in [$Os_{10}C(CO)_{24}$]$^{2-}$ [2.786 (1) Å], and (iii) the "long" edges, on the other hand, appear to be slightly longer than in [$H_4Os_{10}(CO)_{24}$]$^{2-}$ [2.891 (2) Å versus 2.852 (1) Å]. Os–C and C–O distances fall within the expected range.

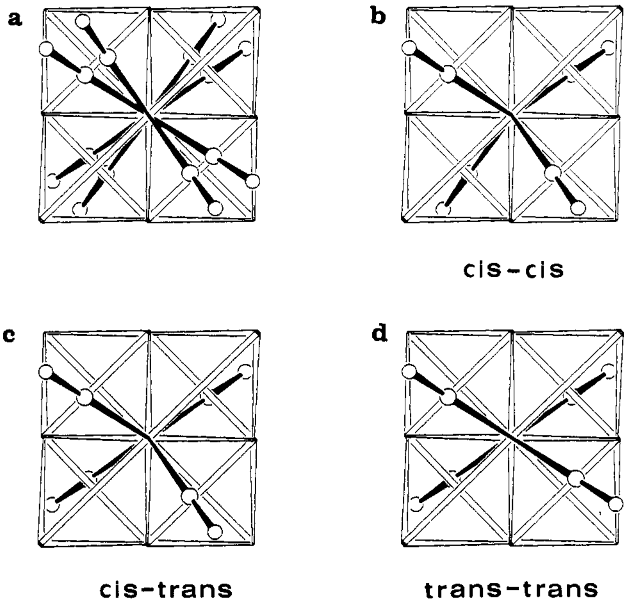

Figure 2. (a) Orientational disorder of the CO groups bound to Os(1) and Os(4) (50% occupancy on each site), (b) "cis–cis" structure, (c) "cis–trans" structure, and (d) "trans–trans" structure.

Disorder and H(hydride) Location. The crystal structure of 1 presents an interesting case of static disorder: the O atoms of the CO groups bound to the Os atoms on the 2-fold axis [Os(1) and Os(4)] occupy two distinct sites of 50% probability each. The separation between the disordered images of the two oxygen atoms is 0.90 Å for the pair O(1A,B) and 0.77 Å for the O(6A,B) pair. Assuming linear Os–C–O axes, a simple geometric calculation shows that the separation between the corresponding C atoms (ca. 0.40 Å) is below the resolution power of our diffraction data (ca. 0.8 Å) and cannot be distinguished. Because of the presence of the crystallographic 2-fold axis, the disorder model implies *four* distinct positions for each pair of CO's [O(1A) and O(1B) belonging to Os(1); O(6A) and O(6B) belonging to Os(4)], as sketched in Figure 2a. It is clear that the *actual* molecular structure of 1 may, in principle, possess any of the three basic combinations of the disordered ligands, which we have designated "cis–cis", "cis–trans", and "trans–trans" (see Figure 2b–d). We can now attempt to combine this observation with the fact that the Os–Os bond lengths along the two tetrahedron edges involving Os(1) and Os(4) as central atoms are noticeably longer than those of the other four edges [2.891 (2) versus 2.774 (3) Å].

The following comments can be made: (i) the presence of "long" edges indicates that these might be spanned by the two H(hydride) bridges; (ii) since there are four such edges, the two H(hydride) atoms must be disordered over the two symmetry-equivalent bridging sites on the two pairs of Os–Os bonds [Os(1)–Os(5), Os(1)–Os(5′), Os(4)–Os(6), Os(4)–Os(6′)] constituting the "long" tetrahedron edges; (iii) the disorder in the CO's bound to Os(1) and Os(4) arises as a consequence of the presence of these hydrido ligands, which are expected to cause CO displacement around the bridged sites, as commonly observed among clusters carbonyls.

Along this line of reasoning it follows that the CO distribution of the kind cis–cis (see Figure 2b) is better suited for the accommodation of the bridging hydrides along the

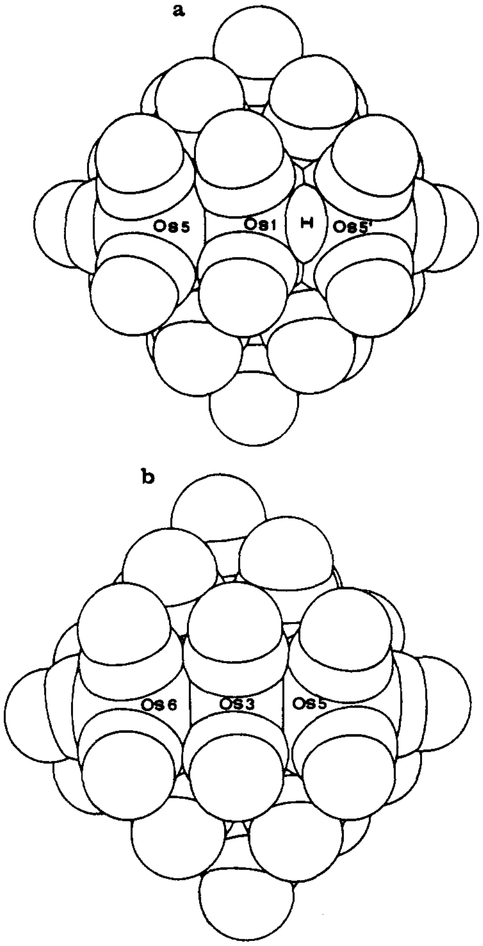

Figure 3. Comparison of the space-filling diagrams of (a) the hydrido-bridged Os(5)–Os(1)–Os(5′) edge and of (b) the unbridged edge Os(5)–Os(3)–Os(6). (The H(hydride) position is that afforded by XHYDEX.)

Os–Os edges than those of the kind trans–trans or trans–cis.

"Analogic" support for this interpretation comes from the comparison of the space-filling diagram of one (supposedly) bridged edge (Figure 3a) and that of an unbridged one (Figure 3b). Although the difference is somewhat obscured by the disorder (one should keep in mind that the Os–Os bond lengths also result from an average of "short" unbridged and "long" bridged edges), it is evident that the CO ligands around the "long" edges (with respect to those around the "short" edges) appear to be pushed away from the middle of the bond in accord with the well-ascertained fact that H atoms are sterically rather demanding ligands.[6]

We have also applied XHYDEX[7] to locate the sites of minimum repulsions within the CO-ligand envelope. We have found that these correspond to the bridging sites over the "long" tetrahedral edges.

In summary, we have converging evidence that the H(hydride) atoms in [$H_2Os_{10}(CO)_{24}$] are not interstitial but occupy disordered μ_2-bridging positions over the two sets of "long" Os–Os bonds and that the disorder in the CO ligands bound to Os(1) and Os(4) arises as a consequence of the presence of the H bridges. This conclusion is strongly supported by the recent neutron diffraction study of 4.[3b] In this work, McPartlin et al. have clearly shown that, contrary to earlier conclusions based on X-ray data,[3a] all H ligands in 4 are on the cluster surface, two in edge-bridging positions.

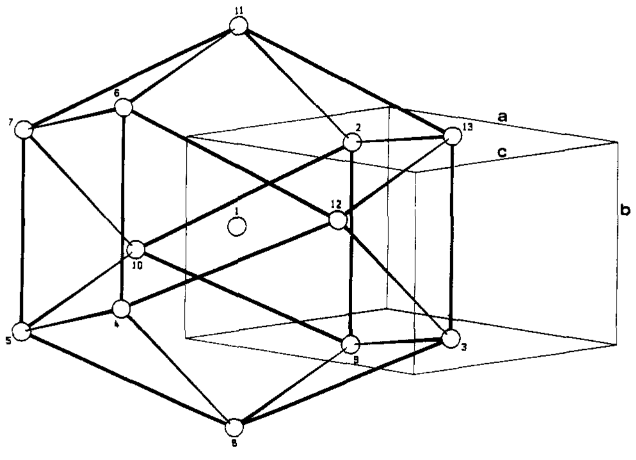

Figure 4. Quasi-cubooctahedral distribution of the FNM in the lattice of 1. The numbering refers to the sequence of symmetry operation generating the molecular distribution from the reference molecule (1).[4]

The bridging location for the H(hydride) atoms in 1 is also in agreement with the presence of a μ_2-$AuPPh_3$ ligand in the mixed-metal derivative [$Os_{10}C(CO)_{24}(AuPPh_3)$]$^-$.[8a] This observation is in keeping with the recognition that the $AuPPh_3$ fragment and hydrogen are isolobal[8b,c] and often occupy the same coordination site when bound to transition-metal clusters.

Molecular Organization in Crystalline 1. In spite of the dimensions of the cluster, the overall packing arrangement in crystalline 1 does not differ from the closest packing arrangements observed for mononuclear and binuclear binary carbonyl complexes.[4b,c] The orientation of the unit cell axes and the quasi-cubooctahedral distribution of the molecular centers of mass around the reference molecule are shown in Figure 4. Although this observation merely confirms that neutral polynuclear carbonyls form van der Waals-type crystals,[4] there are a number of aspects arising from the topology of the CO-ligand distribution around the metal framework which deserve closer examination. The outer shape of the cluster is defined by essentially three "shape elements": (i) the tricarbonyl units on the apices; (ii) the six "grooves" formed by the two sets of three parallel CO's at almost right angle along the cluster edges; (iii) the layer of six parallel CO's covering the triangular faces. It can be anticipated that this latter shape element will contribute very little to molecular interlocking due to the closest packing distribution of the CO's over the triangular faces (which forbids efficient compenetration with CO ligands of neighboring molecules).

Following the procedure successfully employed to decode the crystal construction process in solid [$Ru_3(CO)_{12}$] and [$Fe_3(CO)_{12}$],[4c] we will use these shape elements to construct, first, a "one-dimensional crystal" (a row of molecules). Such rows will then be coupled to form a layer, and layers will be stacked in order to build the observed tridimensional molecular assemblage.

We can start by recognizing that molecules labeled 1, 8, and 11 in Figure 4 pile up around the crystallographic

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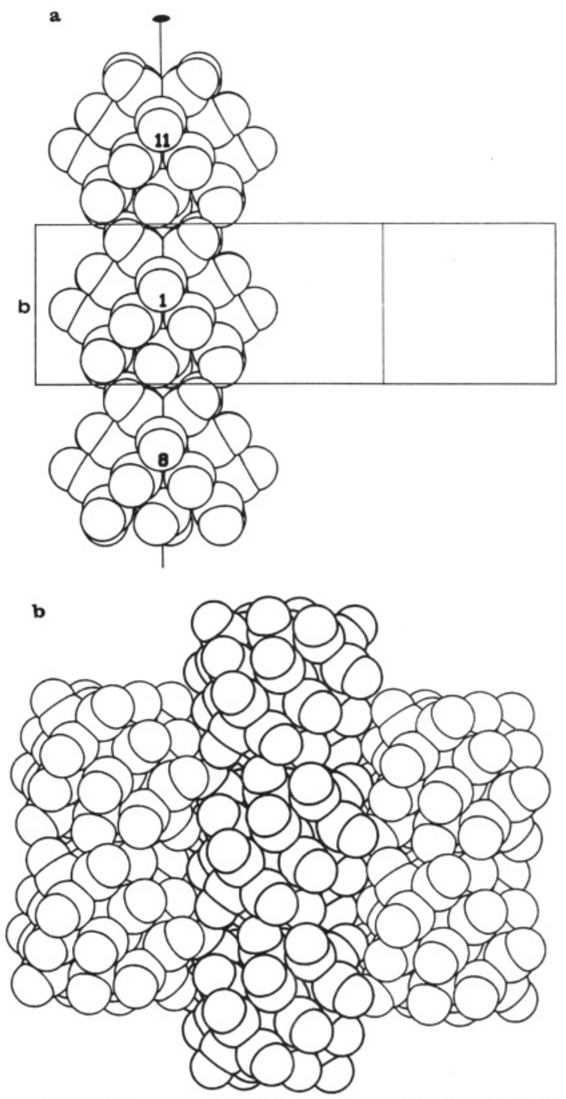


Figure 5. Building a crystal of 1. (a) A row of molecules is shown piled along the crystallographic 2-fold axis. The molecular interlocking is based on the "orthogonal" interaction of the two groups of six CO groups along the Os(5)–Os(1)–Os(5′) and Os(6)–Os(4)–Os(6′) tetrahedron edges. (b) Two molecular rows are linked side by side via parallel interlocking to the molecular row shown in (a) (thick space-filling outline).

2-fold axis (see Figure 5a). These molecules establish an interesting packing pattern: as shown in Scheme Ia, two such molecules are "interlocked" via insertion of the six CO's belonging to one tetrahedron edge in the cavities left among the six CO's of a neighbor molecule ("orthogonal mode"). This very interaction involves exclusively the two "long" tetrahedral edges that are bridged by the H(hydride) atoms, so that these atoms result selectively located between the molecules piled up along the unit cell *b* axis.

The alternative possibility to make use of the "grooves" along the tetrahedral edges is based on the interlocking of two such units in "parallel mode" (see Scheme Ib). The parallel mode can be used to put side by side three molecular rows to form a layer (see Figure 5b). Figure 6 shows that the outermost packing motif above (and below) the surface of the layer is again based on "grooved" tetrahedral edges, which can be used to link up in parallel mode the molecules belonging to layers above and below to form the crystal. It is worth mentioning that the distance between the centers of mass of the molecules linked in orthogonal mode is much shorter than that between molecules linked in parallel mode (9.890 versus a minimum of 10.412 Å). Unfortunately, the approximate nature of the packing potential energy calculations used to "decode" the molecular packing in crystalline 1 (see methodology) does not allow one to discuss this difference on energetic grounds.

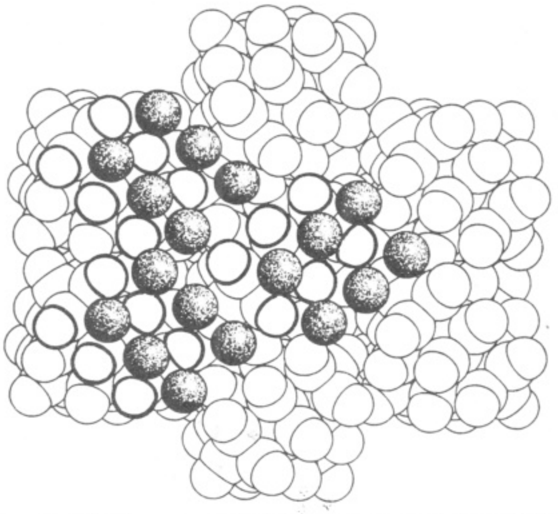
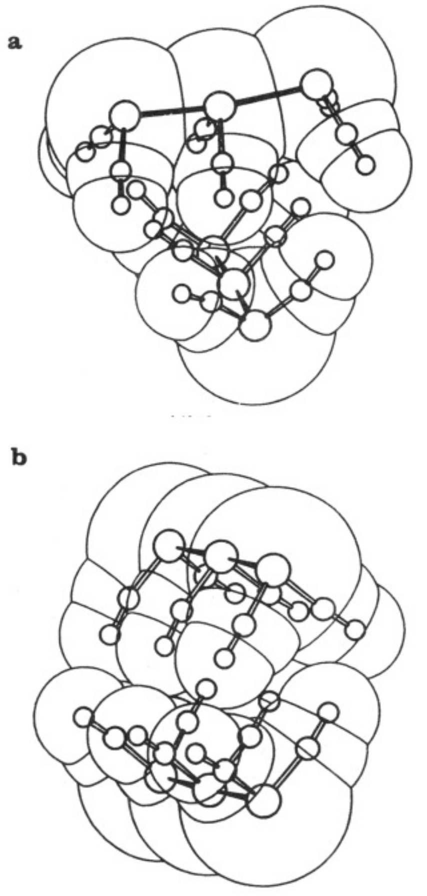


Figure 6. Building a crystal of 1. The outermost packing motif (thick space-filling outlines) over the molecular layer is depicted; dotted atom circles show how a second layer of molecules is linked via "parallel" interlocking to generate the tridimensional crystal.

Scheme I. (a) "Orthogonal" Interlocking Mode and (b) "Parallel" Interlocking Mode



Concluding Remarks

In this paper we have studied *both the molecular and crystal structures* of [$H_2Os_{10}C(CO)_{24}$]. We have shown that, although the approximate spherical shape of the molecule leads to a closest packed molecular arrangement

Table II. Crystal Data and Details of Measurements for $H_2Os_{10}C(CO)_{24}$

formula	$C_{25}H_2O_{24}Os_{10}$
M_r	2585.6
cryst size, mm	0.25 × 0.30 × 0.35
system	monoclinic
space group	$C2/c$
a, Å	21.479 (6)
b, Å	9.890 (3)
c, Å	20.807 (4)
β, deg	120.42 (2)
V, Å^3	3811.4
Z	4
$F(000)$	4414
D_{calcd}, g cm^{-3}	4.5
λ(Mo Kα), Å	0.710 69
μ(Mo Kα), cm^{-1}	319.9
2θ range, deg	4–56
ω-scan width, deg	1.3
requested counting $\sigma(I)/I$	0.02
prescan rate, deg min^{-1}	6
max scan time, s	120
no. of mesd reflcns	4989
no. of unique obsd reflcns $[I_0 > 2.0\sigma(I_0)]$ $(n)^b$	2077
no. of refined params $(m)^b$	150
R, R_w,[a] S,[b] K[a]	0.058, 0.047, 1.08, 2.7

[a] $R_w = \sum[(F_o - F_c)w^{1/2}]/\sum F_o w^{1/2})$, where $w = K[\sigma(F) + |g|F^2]$. [b] $S = \sum[(F_o - F_c)/\sigma]^2/(n - m)$.

Table III. Fractional Atomic Coordinates for 1

atom	x	y	z
Os(1)	0.0	0.73067 (26)	0.25
Os(2)	−0.10541 (7)	0.52170 (20)	0.16963 (8)
Os(3)	−0.02919 (8)	0.52249 (20)	0.32817 (8)
Os(4)	0.0	0.31418 (27)	0.25
Os(5)	0.07763 (9)	0.70917 (18)	0.41187 (9)
Os(6)	−0.13376 (8)	0.32926 (18)	0.24931 (9)
C(1)	−0.0686 (19)	0.8513 (37)	0.2526 (20)
O(1A)[a]	−0.0940 (36)	0.9213 (80)	0.2778 (30)
O(1B)[a]	−0.1118 (37)	0.9377 (14)	0.2290 (32)
C(2)	−0.1569 (21)	0.4123 (45)	0.0858 (22)
O(2)	−0.1833 (18)	0.3452 (42)	0.0337 (21)
C(3)	−0.1889 (21)	0.6232 (47)	0.1547 (23)
O(3)	−0.2364 (18)	0.6815 (38)	0.1482 (19)
C(4)	0.0016 (19)	0.4117 (40)	0.4136 (20)
O(4)	0.0173 (14)	0.3595 (30)	0.4679 (16)
C(5)	−0.0980 (18)	0.6243 (40)	0.3427 (19)
O(5)	−0.1379 (15)	0.6858 (32)	0.3470 (16)
C(6)	0.0411 (28)	0.1846 (41)	0.3281 (21)
O(6A)[a]	0.0416 (49)	0.1174 (92)	0.3736 (45)
O(6B)[a]	0.0777 (39)	0.1100 (85)	0.3744 (44)
C(7)	0.1242 (22)	0.6392 (45)	0.5082 (24)
O(7)	0.1467 (16)	0.5877 (34)	0.5633 (17)
C(8)	0.0281 (20)	0.8210 (43)	0.4400 (21)
O(8)	−0.0045 (16)	0.8929 (35)	0.4523 (17)
C(9)	0.1549 (21)	0.8264 (45)	0.4408 (22)
O(9)	0.2001 (17)	0.9003 (37)	0.4609 (19)
C(10)	−0.1925 (22)	0.2153 (48)	0.1744 (24)
O(10)	−0.2229 (19)	0.1187 (41)	0.1341 (21)
C(11)	−0.2092 (20)	0.4027 (44)	0.2509 (21)
O(11)	−0.2636 (17)	0.4620 (35)	0.2458 (18)
C(12)	−0.1201 (23)	0.2050 (51)	0.3230 (26)
O(12)	−0.1110 (17)	0.1472 (36)	0.3745 (18)
C(99)	0.0	0.5211 (71)	0.25
H(1)[b]	0.0439	0.8313	0.3356
H(2)[b]	0.0704	0.2084	0.2476

[a] Labels A and B indicate the disordered (sof = 0.5) O atoms of the CO groups bound to Os(1) and Os(4). [b] Positions optimized via XHYDEX.[7]

of the kind usually observed for globular organic molecules, the molecular assemblage in the lattice is controlled by specific interactions arising from the topology of the ligand distribution. The formation of rows of molecules via "orthogonal" interactions seems to play a fundamental role in determining the stability of the crystalline edifice. We can anticipate here that the same basic packing motif is present in the "ionic" crystals of $[Os_{10}C(CO)_{24}]^{2-}$ and of $[H_4Os_{10}(CO)_{24}]^{2-}$ as their $[PPN]^+$ salts. The structural relationship between ionic and molecular crystals of high-nuclearity clusters is currently under investigation and will be the matter of a future report.

The second question addressed in this paper is that of the H(hydride) location. Although a definite answer can only be expected to come from a neutron diffraction study, we have gathered enough evidence to assert that the H(hydride) atoms are in this case (and not necessarily in other decaosmium hydrides) on the periphery of the metal frame and not interstitial. In this respect the magnetic and spectroscopic properties of crystalline 1 might have to be reexamined.

Finally, it is interesting to note that the "grouping" of H atoms belonging to different molecules in the lattice of 1 seems to be quite a general feature of the crystals of neutral carbonyl hydrides, as it has been observed also in other polynuclear (such as $[H_2Os_3(CO)_{11}]$[9a]) and mononuclear complexes (such as $[HMn(CO)_5]$[9b]). This aspect of the crystal structures of transition-metal hydrides also deserves further investigation.

Experimental Section

General Data. IR spectra were recorded using a Perkin-Elmer 1760 FTIR spectrophotometer. Elemental analysis was performed using a Perkin-Elmer 240C elemental analyzer. The osmium content was determined by weighing after thermal decomposition of the crystals under a reducing atmosphere. $[Os_3(CO)_{12}]$ was synthesized according to Bradford et al.[10] Cyclohexane was a commercial product, dried on metallic sodium and distilled under nitrogen.

Synthesis and Characterization of $[H_2Os_{10}C(CO)_{24}]$. Route 1. To a solution of $[PPN]_2[Os_{10}C(CO)_{24}]$ in MeCN was added dropwise with stirring concentrated H_2SO_4. The black precipitate was separated by filtration, washed with several portions of water and then ethanol, and dried in a desiccator for several days.

Route 2. $Os_3(CO)_{12}$ (0.1 g) and cyclohexane (10 mL) were introduced in a glass vial and closed under nitrogen. The vial was placed in a rocking autoclave containing cyclohexane and heated at 300 °C for 1 h. The autoclave was slowly cooled and the vial recovered, and black crystals of $[H_2Os_{10}C(CO)_{24}]$ (0.05 g) separated from the solution were collected by filtration and characterized. Anal. Calcd for $C_{25}H_2O_{24}Os_{10}$: C, 11.49; H, 0.08; Os, 72.81. Found: C, 11.00; H, 0.10; Os, 72.00. The IR spectra (KBr pellet) shows peaks in the 2200–1800-cm^{-1} region at 2110 (w), 2095 (sh), 2066 (vs), 2012 (vs), 1955 (vw), and 1946 cm^{-1} (vw). These spectra are in agreement with the X-ray analysis and also show that no carbonyl groups are placed in bridging positions.

X-ray Structure Determination. All X-ray measurements were made on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 69 Å). The intensities were collected in the $\omega/2\theta$ scan mode at room temperature. Crystal data and details of measurements are summarized in Table II. The structure was solved by using direct methods followed by difference Fourier syntheses and subsequent least-squares refinement. Scattering factors for neutral atoms taken from ref.[11a] For all calculations the SHELX76 program was

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used.[11b] The absorption correction was applied by the Walker and Stuart method[11c] once a complete structural model was available and all atoms refined isotropically. Considering the extremely large absorption coefficient, the effect of the correction was dramatic, allowing not only a drop of ca. 15% of the *R* factor but also detection of the O atom disorder discussed above. Only the Os atoms, however, could be treated anisotropically.

Because of the disorder, the possibility that the structural model could be treated in the noncentrosimmetric space group *Cc* was also tested: after refinement by blocked full-matrix least squares the Os–Os bond lengths, related by the 2-fold axis in the space group *C*2/*c*, remained strictly equivalent, indicating that the static disorder was not an artifact of the centric refinement. Fractional atomic coordinates are reported in Table III.

Crystal Packing Investigation: Methodology. In our approach to crystal packing use is made of the expression ppe = $\sum_i\sum_j[A\ \exp(-Br_{ij}) - Cr_{ij}^{-6}]$, where ppe represents the packing potential energy[12a] and r_{ij} represents the nonbonded atom–atom intermolecular distance. Index i in the summation runs over all atoms of one molecule (chosen as the reference molecule), and index j, over the atoms of the surrounding molecules distributed according to crystal symmetry. A cutoff of 15 Å has been adopted in our calculations. The values of the coefficients A, B, and C used in this work have been taken from the literature[12b] and discussed in previous papers.[4] The results of ppe calculations are used to select the first-neighboring molecules (FNM) among the molecules surrounging the one chosen as reference (RM) on the basis of the contribution to ppe. It should be stressed that this procedure is used only as a convenient means to investigate the molecular environment within the crystalline lattice without pretentions of obtaining "true" (or even approximate) crystal potential energy values. All calculations were carried out with the aid of the computer program OPEC.[13] SCHAKAL88[14] was used for the graphical representation of the results.

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Registry No. $[PPN]_2[Os_{10}C(CO)_{24}]$, 75117-74-7; $Os_3(CO)_{12}$, 15696-40-9; $H_2Os_{10}C(CO)_{24}$, 77908-36-2; Os, 7440-04-2.

Supplementary Material Available: Tables of anisotropic thermal parameters, fractional atomic coordinates and thermal parameters, and complete bonds and angles (9 pages); an F_o/F_c table (13 pages). Ordering information is given on any current masthead page.

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Crystal Construction and Molecular Interplay in Solid Ferrocene, Nickelocene, and Ruthenocene

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The molecular organization in crystals of nickelocene, ruthenocene, and the monoclinic, orthorhombic, and triclinic modifications of ferrocene has been investigated by means of packing potential energy calculations and computer graphic analysis. The relationship between the various phases has been explored showing that small differences in molecular geometries and in intermolecular nonbonding interactions account for relevant differences in crystal properties. Potential energy barriers to ring reorientations have been calculated and compared with those obtained from anisotropic displacement parameters and from spectroscopic sources.

Introduction

Over the last 30 or 40 years a great deal of progress has been made in understanding the packing modes of molecules and the relationship between crystal packing and molecular shape. The occurrence of dynamic phenomena in molecular crystals has also been extensively investigated.[1] However, virtually all the work in this area has been on organic molecules,[2] leaving the neighboring field of organometallic solid-state chemistry almost totally unexplored. In an attempt to broaden this perspective we have recently begun an investigation of the molecular organization and of the recognition process which leads to the self-assembling of organometallic molecules in a crystal.[3] The dynamic behavior, from small-amplitude librations to large amplitude motions and reorientations of molecular fragments, shown by a number of neutral organometallic species in the solid state has also been studied.[4]

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