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A Trinuclear Tungsten(IV) Cluster Compound with a Capping Chlorine Atom and Three Bridging Oxygen Atoms

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Sharp and Schrock have reported that the reaction of $W_2Cl_4(PBu_3)_4$ with acetic acid produces a complex polynuclear product, neither the exact composition nor the structure of which could be inferred solely from analytical and other conventional data. A crystal structure analysis, which is here reported in full, showed that this compound consists of molecules containing equilateral, triangular clusters of tungsten(IV) atoms and has a molecular formula of $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$. One face of the W_3 triangle is capped by a chlorine atom, and the three edges are each bridged on the other side of the triangle by oxygen atoms. The coordination sphere of each tungsten atom is completed by three other ligand atoms so that the overall structure, consisting of three metal atoms and thirteen ligand atoms, is an example of the well-known M_3X_{13} type of cluster molecule. The molecule has no crystallographically imposed symmetry, but a virtual mirror plane passes through one W atom and the capping Cl atom, bisects a W–W bond, and passes through the C atoms of the acetate ion that bridges the bisected W–W bond. The bridged W–W bond has a length of 2.596 (1) Å while the other two W–W distances are 2.615 (1) Å. The compound crystallizes from toluene as $W_3O_3Cl_5(OCCH_3)(PBu_3)_3{\cdot}0.5C_6H_5CH_3$ in space group $P2_1/n$ with $a = 12.056$ (3) Å, $b = 20.248$ (4) Å, $c = 23.977$ (7) Å, $\beta = 92.17$ (2)°, $V = 5853$ (4) Å^3, and $Z = 4$. The structure has been refined with 16 atoms treated anisotropically and 43 atoms isotropically to residuals of $R_1 = 0.045$ and $R_2 = 0.056$.

Introduction

In only the past few years has it become clear that molybdenum and tungsten in oxidation state IV have a considerable chemistry and that much of this is based structurally on triangular clusters with M–M bonds of order 1. In fact, from a structural point of view there are two such chemistries, one based on the structural unit shown in Figure 1a and the other based on that shown in Figure 1b.

The type of structure shown in Figure 1b has been found in both molybdenum[1] and tungsten[2,3] compounds, all of which (so far) have been obtained by reactions of the hexacarbonyls with carboxylic acids. The tungsten compounds are known only with the metal atoms in oxidation state +4 and with two oxygen atoms as capping groups, but the molybdenum compounds afford a far more complicated, and fascinating, field since they may have either oxygen atoms or alkylidyne groups, or both, as caps and oxidation states from +4 to +4 $^2/_3$.

The other type of structure has been found in a number of compounds,[4-9] most of them isolated from the red solutions of the molybdenum(IV) aquo ion,[10] and is presumably the type of structure found in the aquo ion itself, despite earlier suggestions[10] that the aquo ion might be dinuclear. This $M_3(\mu_3\text{-}X)(\mu\text{-}Y)_3$ structural unit has also been found in two tungsten compounds[11,12] but has not so far assumed such importance for tungsten as for molybdenum. It is, therefore, important that another compound of tungsten(IV) with a structure of this type has now been established.

Table I. Summary of Crystallographic Data and Data Collection Procedures

formula	$W_3Cl_5P_3O_5C_{41.5}H_{88}$
space group	$P2_1/n$
a, Å	12.056 (3)
b, Å	20.248 (4)
c, Å	23.977 (7)
β, deg	92.17 (2)
V, Å^3	5853 (4)
d_{calcd}, g/cm^3	1.76
Z	4
fw	1548.95
cryst size, mm	0.15 × 0.35 × 0.35
μ (Mo Kα), cm^{-1}	65.851
radiation	graphite-monochromated Mo Kα ($\lambda_{\bar{\alpha}} = 0.710\,73$ Å)
scan type	ω-2θ
scan width ($\Delta\omega$), deg	$0.65 + 0.35 \tan\theta$
aperture width, mm	$1.5 + \tan\theta$
crystal–counter distance, mm	173
prescan rejection limit	2.0 (0.5σ)
prescan acceptance limit	0.02 (50σ)
max scan speed, deg/min	20.12
max counting time, s	30
data collection range	$+h, +k, \pm l$ $3° \leq 2\theta \leq 48°$
no. of unique data	9139
no. of data, $F_o^2 > 3\sigma(F_o^2)$	5727
p	0.05
X-ray exposure time, h	70.0
no. of intensity stds	3
time between measurements	3600
cryst decompn	negligible
no. of variables	318
R_1	0.045
R_2	0.056
esd	1.468
largest peak,[a] e/Å^3	0.75
Δ/σ[b]	0.26

[a] Largest peak in the final difference Fourier map. [b] Largest shift (Δ)-to-error (σ) ratio in the final least-squares cycle.

Sharp and Schrock[13] found that when the quadruply bonded $W_2Cl_4(PBu_3)_4$ compound was treated with acetic acid, under rather rigorous conditions (160 °C in a glyme solvent), they obtained an acetate-containing substance that also retained chlorine and phosphine ligands. The exact identity of this substance was not determinable from elemental analyses, but an X-ray crystallographic study, already reported in a preliminary communication,[14] showed it to be $W_3O_3Cl_5$-

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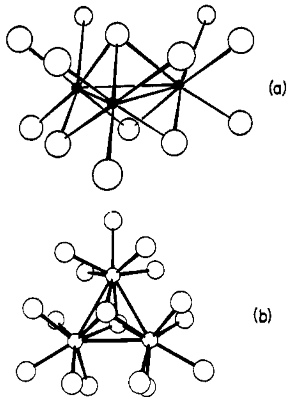

Figure 1. Two of the important general structures for metal atom cluster species containing equilateral triangular clusters: (a) M_3X_{13} structure; (b) M_3X_{17} structure.

$(O_2CCH_3)(PBu_3)_3$, based on a triangular cluster structure of the type shown in Figure 1a but with several novel features not previously seen in any structure of this kind. We report here the full details of this structure, which has since been further refined.

Experimental Section

A crystalline sample was provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. Several deep red prismatic crystals were selected for X-ray diffraction analysis, coated with epoxy cement, and mounted on glass fibers.

X-ray Crystallography. Collection of Data. Preliminary crystal examination and subsequent data collection were performed on a Enraf-Nonius CAD-4F autodiffractometer under the control of a PDP/8A computer at 26 ± 1 °C. Table I summarizes the data collection procedures. Further details have been given before for this diffractometer.[15] The final cell constants were obtained from a least-squares fit to 25 reflections in the range $25° < 2\theta < 32°$. Data were corrected for Lorentz and polarization effects as well as absorption. The absorption correction was based on an empirical method that uses ψ scans ($\psi = 0$–360° every 10°) for χ values near 90°. Eight sets of reflections ($\bar{5}\bar{2}3$, $\bar{4}\bar{1}2$, $\bar{3}\bar{1}1$, $\bar{3}\bar{2}2$, $\bar{6}\bar{1}3$, $\bar{6}\bar{1}2$, $\bar{3}\bar{1}0$, $\bar{3}\bar{2}1$) were averaged to produce an absorption profile for the crystal with maximum, minimum, and average transmission factors of 1.00, 0.46, and 0.73, respectively.

Structure Solution and Refinement.[16] Data were collected for a monoclinic crystal system and revealed systematic absences ($h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$) that uniquely determined the space group as $P2_1/n$, a nonstandard setting of $P2_1/c$-C_{2h}^5, No. 14. The observed cell volume was consistent with the presence of four trinuclear tungsten clusters in the unit cell. The positions of the three independent tungsten atoms were determined with use of the MULTAN direct-methods program. Four cycles of least-squares refinement of these three atom positions along with the associated isotropic temperature factors and an overall scale factor (determined from a Wilson plot) produced residuals of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.217$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.313$$

A difference Fourier map revealed as the highest peak an atom capping a face of the triangle of tungsten atoms. Because of the position of this atom in the map, it was assumed from the outset that the atom was a Cl atom. Subsequent refinement with satisfactory thermal parameters and reasonable W–Cl distances proved this assumption to be correct. The seven remaining Cl and P atoms could only be distinguished after the n-Bu carbon atoms were identified. Further least-squares refinement followed by difference Fourier maps led to the identification of all 54 atoms in the trinuclear cluster. Among the last atoms to be located were the three edge-bridging oxygen atoms, which were unexpected in the structure, and the terminal and penultimate carbon atoms of the n-Bu groups of the phosphine ligands. Particular difficulties were encountered in the refinement of the C(123), C(124), C(134), and C(224) atoms of the n-Bu groups. The relatively high thermal parameters of these atoms were suggestive of positional disorder. Persistent efforts were made to locate alternative positions with fractional occupancies for these atoms, but the positions ultimately were refined to convergence with full occupancy factors and high thermal parameters.

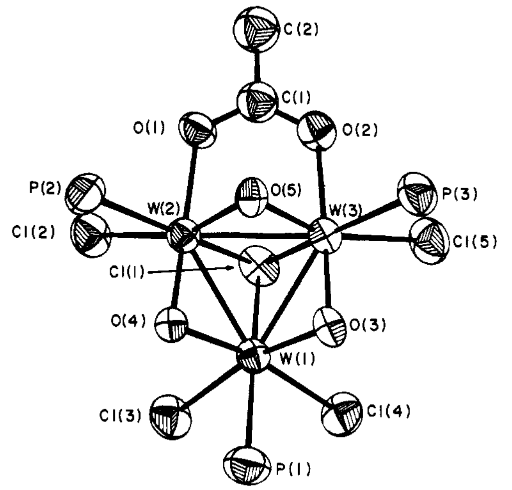

Figure 2. ORTEP drawing of the trinuclear cluster omitting the n-Bu groups of the phosphine ligands. Thermal ellipsoids are shown at the 50% probability level.

With the cluster atoms now completely found, anisotropic temperature factors were assigned, first to the tungsten atoms and then to all noncarbon atoms in the cluster. After least-squares refinement of 54 atoms with 297 variable parameters, a difference Fourier map revealed the presence of a solvent molecule in the lattice located about an inversion center. Since the compound was recrystallized from a toluene solution and the analytical data were most consistent with the presence of toluene,[17] a model was sought that would refine with a toluene solvate disordered about a crystallographic center of inversion. A disordered toluene molecule about an inversion center was recently encountered in the structure of an ytterbium organometallic compound,[18] and the toluene molecule found here displays a similar, but not identical, type of disorder. Numerous attempts were made to define accurately a disordered model for the toluene, but the five atom positions defined by C(10)–C(13) and C(20) represent the only positions that would refine to convergence. All solvate atoms were refined with full occupancy factors except C(20), which was given half-occupancy. The entire structure was now refined with 317 variable parameters for the 59 atoms.

An inspection of several low-angle reflections at this point revealed the need for a secondary extinction correction. This correction was made according to the equation $|F_o| = |F_c|(1 + gI_c)^{-1}$, where the value of g as determined from least-squares refinement was 9.55×10^{-9}. The entire structure was now refined to the residuals given in Table I. The largest shift in the final least-squares cycle occurred in the B value for C(134). The final difference Fourier map revealed that the top three peaks were located about the W atoms. No attempt was made to include hydrogen atom contributions in the refinement. A table of observed and calculated structure factor amplitudes for those reflections with $I > 3\sigma(I)$ is available.[19]

Results and Discussion

Table II presents the atomic positional and thermal parameters for the asymmetric unit. A total of sixteen atoms were treated anisotropically, namely, the three tungsten atoms and the thirteen atoms directly attached to them to form the

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(16) All crystallographic computing was done on PDP 11/45 or 11/60 computers at the Molecular Structure Corp., College Station, Texas, with the Enraf-Nonius structure determination package with local modifications.

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(19) Supplementary material.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3 \cdot 0.5C_7H_8$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	0.39107 (4)	0.03814 (2)	0.23486 (2)	3.24 (2)	2.94 (2)	3.54 (2)	0.19 (2)	−0.19 (2)	−0.02 (2)
W(2)	0.31507 (4)	−0.05254 (2)	0.30093 (2)	2.81 (2)	3.61 (2)	3.25 (2)	0.10 (2)	0.20 (2)	−0.10 (2)
W(3)	0.50600 (4)	0.00200 (2)	0.32441 (2)	3.03 (2)	3.54 (2)	3.30 (2)	0.10 (2)	−0.20 (2)	−0.32 (2)
Cl(1)	0.3316 (3)	0.0647 (2)	0.3294 (1)	4.6 (2)	4.4 (1)	4.4 (2)	1.1 (1)	−0.1 (1)	−1.0 (1)
Cl(2)	0.1222 (3)	−0.0418 (2)	0.3088 (2)	3.3 (2)	7.6 (2)	5.3 (2)	0.2 (2)	0.5 (1)	−0.3 (2)
Cl(3)	0.2192 (3)	0.0809 (2)	0.1958 (2)	4.4 (2)	5.1 (2)	6.9 (2)	1.1 (1)	−1.1 (2)	0.8 (2)
Cl(4)	0.4584 (3)	0.1498 (2)	0.2298 (2)	6.1 (2)	3.2 (1)	6.7 (2)	−0.5 (1)	−0.3 (2)	0.3 (1)
Cl(5)	0.6006 (3)	0.0936 (2)	0.3645 (2)	6.0 (2)	5.0 (2)	5.9 (2)	−1.0 (2)	−1.1 (2)	−1.1 (2)
P(1)	0.4479 (4)	0.0183 (2)	0.1358 (2)	6.4 (2)	5.0 (2)	3.4 (2)	−0.4 (2)	−0.0 (2)	0.2 (2)
P(2)	0.2744 (3)	−0.1715 (2)	0.2772 (2)	4.4 (2)	4.0 (2)	4.6 (2)	−0.9 (1)	0.5 (2)	0.2 (1)
P(3)	0.6952 (3)	−0.0516 (2)	0.3305 (2)	3.2 (2)	5.3 (2)	4.7 (2)	0.4 (1)	−0.3 (1)	0.2 (2)
O(1)	0.3110 (7)	−0.0717 (4)	0.3892 (3)	3.4 (4)	6.5 (5)	3.1 (4)	−0.0 (4)	0.0 (3)	0.3 (4)
O(2)	0.4740 (7)	−0.0222 (4)	0.4095 (4)	4.1 (4)	5.2 (4)	3.6 (4)	0.3 (4)	0.3 (4)	−0.6 (4)
O(3)	0.5432 (6)	0.0070 (4)	0.2469 (3)	2.9 (4)	3.8 (4)	3.9 (4)	0.1 (3)	−0.7 (3)	−0.4 (3)
O(4)	0.3358 (6)	−0.0510 (4)	0.2227 (3)	2.9 (3)	3.4 (3)	3.2 (4)	−0.2 (3)	−0.0 (3)	0.0 (3)
O(5)	0.4628 (6)	−0.0895 (4)	0.3131 (3)	1.9 (3)	3.6 (3)	3.7 (4)	0.3 (3)	0.7 (3)	−0.4 (3)

atom	x	y	z	B, Å²	atom	x	y	z	B, Å²
C(1)	0.388 (1)	−0.0546 (7)	0.4231 (6)	4.9 (3)	C(214)	0.014 (2)	−0.2293 (12)	0.1313 (10)	11.8 (7)
C(2)	0.376 (1)	−0.0746 (8)	0.4840 (7)	6.3 (4)	C(221)	0.380 (1)	−0.2036 (7)	0.2324 (6)	5.0 (3)
C(10)	0.556 (3)	0.5594 (15)	0.0163 (13)	16.4 (11)	C(222)	0.355 (2)	−0.2761 (9)	0.2132 (8)	8.2 (5)
C(11)	0.431 (3)	0.4519 (14)	0.0351 (12)	15.0 (10)	C(223)	0.446 (2)	−0.3015 (12)	0.1726 (11)	12.7 (8)
C(12)	0.474 (2)	0.4966 (12)	0.0427 (10)	12.5 (8)	C(224)	0.419 (4)	−0.2774 (20)	0.1266 (18)	23.8 (16)
C(13)	0.504 (4)	0.4544 (22)	−0.0728 (20)	25.3 (18)	C(231)	0.268 (1)	−0.2258 (7)	0.3379 (7)	5.9 (4)
C(20)	0.594 (4)	0.6177 (25)	0.0418 (22)	13.0 (16)	C(232)	0.381 (1)	−0.2372 (8)	0.3662 (7)	6.8 (4)
C(111)	0.549 (2)	0.0853 (11)	0.1069 (9)	10.2 (6)	C(233)	0.361 (2)	−0.2792 (10)	0.4210 (9)	9.8 (6)
C(112)	0.474 (2)	0.1371 (13)	0.0886 (12)	13.7 (8)	C(234)	0.466 (2)	−0.2963 (14)	0.4490 (12)	14.0 (9)
C(113)	0.570 (2)	0.1954 (12)	0.0691 (11)	11.8 (7)	C(311)	0.807 (1)	−0.0031 (7)	0.3042 (7)	5.9 (4)
C(114)	0.504 (3)	0.2566 (15)	0.0601 (14)	16.9 (11)	C(312)	0.798 (1)	0.0088 (8)	0.2378 (7)	6.7 (4)
C(121)	0.347 (2)	0.0018 (12)	0.0806 (10)	11.7 (7)	C(313)	0.902 (2)	0.0445 (10)	0.2185 (9)	9.5 (6)
C(122)	0.278 (2)	−0.0484 (12)	0.0876 (11)	12.6 (8)	C(314)	0.894 (2)	0.0485 (10)	0.1546 (10)	10.3 (6)
C(123)	0.215 (4)	−0.0804 (20)	0.0176 (17)	22.6 (16)	C(321)	0.694 (1)	−0.1315 (7)	0.2950 (6)	5.1 (3)
C(124)	0.149 (4)	−0.0365 (19)	0.0199 (16)	22.0 (15)	C(322)	0.809 (1)	−0.1655 (8)	0.2968 (7)	7.2 (4)
C(131)	0.545 (2)	−0.0560 (9)	0.1398 (9)	9.1 (5)	C(323)	0.794 (2)	−0.2352 (11)	0.2588 (11)	12.0 (7)
C(132)	0.586 (2)	−0.0750 (13)	0.0864 (12)	13.7 (9)	C(324)	0.742 (2)	−0.2768 (13)	0.2851 (11)	14.0 (9)
C(133)	0.672 (2)	−0.1377 (13)	0.1019 (11)	13.6 (9)	C(331)	0.749 (1)	−0.0658 (8)	0.4038 (7)	6.4 (4)
C(134)	0.713 (3)	−0.1596 (21)	0.0616 (17)	23.7 (16)	C(332)	0.688 (2)	−0.1236 (9)	0.4310 (8)	7.5 (4)
C(211)	0.141 (1)	−0.1859 (7)	0.2404 (6)	5.3 (3)	C(333)	0.732 (2)	−0.1165 (11)	0.4975 (10)	11.4 (7)
C(212)	0.132 (1)	−0.1461 (8)	0.1851 (7)	6.6 (4)	C(334)	0.678 (2)	−0.1699 (14)	0.5254 (12)	14.9 (9)
C(213)	0.011 (2)	−0.1594 (9)	0.1563 (8)	8.3 (5)					

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

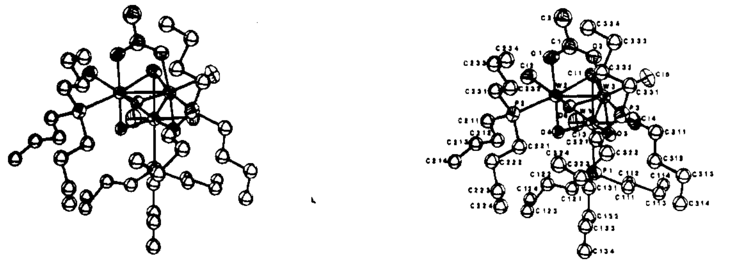

Figure 3. Stereoview of $W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3$ with vibrational ellipsoids of all but the *n*-Bu carbon atoms given at the 50% probability level. The *n*-Bu carbon atoms are represented as spheres with B_{iso} values arbitrarily reduced to 4.0 Å² for clarity.

M_3Y_{13} structural unit. All others, including the five making up the solvent of crystallization molecule (which resides on an inversion center and has only five crystallographically distinct atoms), were treated isotropically. The latter five atoms are labeled C(10)–C(13) and C(20). The carbon atoms of the butyl groups attached to P(*n*) are labeled C(*n*11), C(*n*12), C(*n*13), C(*n*14); C(*n*21), C(*n*22), ..., C(*n*34), etc. The labels for the anisotropically refined atoms are defined in Figure 2, which shows the M_3X_{13} core plus the two carbon atoms, C(1) and C(2), that form part of the acetate ion. Figure 3 presents a stereoview of the complete $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$ molecule and identifies by number each of the butyl carbon atoms.

While the general features of the $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$ structure are the familiar ones for the M_3X_{13} type of cluster compound, one of the details specific to this compound is a distinctly novel feature, namely, the capping—or triply bridging—chlorine atom. Among trinuclear clusters of the group 6 elements this has not been seen before. The usual arrangement has oxygen atoms at both capping and bridging positions, the only previous exception having been the $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$ ion, which has an oxygen atom cap but chlorine atoms at the bridging positions.[5] It may be noted, of course, that in the (nondiscrete) Nb_3Cl_{13} unit that occurs in Nb_3Cl_8[20] both capping and bridging atoms are chlorine atoms. Thus, there are now examples of all four combinations, viz., $(\mu_3\text{-O})(\mu\text{-O})_3$, $(\mu_3\text{-O})(\mu\text{-Cl})_3$, $(\mu_3\text{-Cl})(\mu\text{-O})_3$, and $(\mu_3\text{-Cl})(\mu\text{-Cl})_3$, although no discrete cluster compound with the last combination is yet known.

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Table III. Bond Distances (Å) and Angles (Deg) for the Trinuclear Cluster in $W_3O_3Cl_5(CH_3CO_2)(PBu_3)_3 \cdot 0.5C_7H_8$

Distances

W(1)-W(2)	2.614 (1)	O(1)-C(1)	1.26 (1)	W(3)-Cl(1)	2.464 (3)	C(221)-C(222)	1.57 (2)
-W(3)	2.615 (1)	O(2)-C(1)	1.28 (1)	-Cl(5)	2.363 (3)	C(222)-C(223)	1.58 (2)
-Cl(1)	2.462 (3)	C(1)-C(2)	1.53 (2)	-P(3)	2.525 (3)	C(223)-C(224)	1.24 (4)
-Cl(3)	2.403 (3)	C(111)-C(112)	1.44 (3)	-O(2)	2.147 (7)	C(231)-C(232)	1.52 (2)
-Cl(4)	2.407 (3)	C(112)-C(113)	1.72 (3)	-O(3)	1.931 (7)	C(232)-C(233)	1.59 (2)
-P(1)	2.529 (3)	C(113)-C(114)	1.48 (3)	-O(5)	1.941 (6)	C(233)-C(234)	1.45 (3)
-O(3)	1.950 (6)	C(121)-C(122)	1.33 (3)	P(1)-C(111)	1.97 (2)	C(311)-C(312)	1.61 (2)
-O(4)	1.941 (6)	C(122)-C(123)	1.93 (4)	-C(121)	1.79 (2)	C(312)-C(313)	1.53 (2)
W(2)-W(3)	2.596 (1)	C(123)-C(124)	1.20 (5)	-C(131)	1.90 (2)	C(313)-C(314)	1.54 (2)
-Cl(1)	2.477 (3)	C(131)-C(132)	1.44 (3)	P(2)-C(211)	1.83 (1)	C(321)-C(322)	1.56 (2)
-Cl(2)	2.351 (3)	C(132)-C(133)	1.67 (3)	-C(221)	1.82 (1)	C(322)-C(323)	1.69 (2)
-P(2)	2.518 (3)	C(133)-C(134)	1.19 (4)	-C(231)	1.83 (1)	C(323)-C(324)	1.24 (3)
-O(1)	2.153 (7)	C(211)-C(212)	1.55 (2)	P(3)-C(311)	1.80 (1)	C(331)-C(332)	1.54 (2)
-O(4)	1.901 (6)	C(212)-C(213)	1.61 (2)	-C(321)	1.83 (1)	C(332)-C(333)	1.67 (2)
-O(5)	1.944 (6)	C(213)-C(214)	1.54 (2)	-C(331)	1.87 (1)	C(333)-C(334)	1.44 (3)

Angles

W(2)-W(1)-W(3)	59.52 (2)	Cl(1)-W(3)-P(3)	171.7 (1)	W(3)-W(2)-Cl(1)	58.06 (7)	W(2)-O(1)-C(1)	122.7 (8)
-Cl(1)	58.32 (7)	-O(2)	83.5 (2)	-Cl(2)	144.59 (8)	W(3)-O(2)-C(1)	122.4 (8)
-Cl(3)	99.91 (8)	-O(3)	104.4 (2)	-P(2)	128.27 (8)	W(1)-O(3)-W(3)	84.7 (3)
-Cl(4)	144.80 (8)	-O(5)	105.9 (2)	-O(1)	85.2 (2)	W(1)-O(4)-W(2)	85.7 (3)
-P(1)	124.84 (8)	Cl(5)-W(3)-P(3)	83.8 (1)	-O(4)	93.3 (2)	W(2)-O(5)-W(3)	83.8 (2)
-O(3)	91.9 (2)	-O(2)	83.9 (2)	-O(5)	48.0 (2)	O(1)-C(1)-O(2)	124 (1)
-O(4)	46.5 (2)	-O(3)	102.9 (2)	Cl(1)-W(2)-Cl(2)	87.6 (1)	-C(2)	116 (1)
W(3)-W(1)-Cl(1)	57.96 (7)	-O(5)	158.3 (2)	-P(2)	172.7 (1)	O(2)-C(1)-C(2)	119 (1)
-Cl(3)	147.46 (9)	P(3)-W(3)-O(2)	92.4 (2)	-O(1)	84.7 (2)	P(1)-C(111)-C(112)	103 (2)
-Cl(4)	97.75 (8)	-O(3)	80.6 (2)	Cl(1)-W(2)-O(4)	104.1 (2)	C(111)-C(112)-C(113)	100 (2)
-P(1)	124.93 (9)	-O(5)	80.5 (2)	-O(5)	105.3 (2)	C(112)-C(113)-C(114)	105 (2)
-O(3)	47.3 (2)	O(2)-W(3)-O(3)	169.5 (3)	Cl(2)-W(2)-P(2)	85.5 (1)	P(1)-C(121)-C(122)	117 (2)
-O(4)	91.8 (2)	-O(5)	81.8 (3)	-O(1)	83.0 (2)	C(121)-C(122)-C(123)	112 (2)
Cl(1)-W(1)-Cl(3)	90.2 (1)	O(3)-W(3)-O(5)	89.2 (3)	-O(4)	104.2 (2)	C(122)-C(123)-C(124)	87 (3)
-Cl(4)	87.2 (1)	W(1)-Cl(1)-W(2)	63.90 (7)	-O(5)	158.0 (2)	P(1)-C(131)-C(132)	113 (2)
-P(1)	176.2 (1)	-W(3)	64.14 (7)	P(2)-W(2)-O(1)	92.2 (2)	C(131)-C(132)-C(133)	104 (2)
-O(3)	103.8 (2)	W(2)-Cl(1)-W(3)	63.39 (7)	-O(4)	79.9 (2)	C(132)-C(133)-C(134)	112 (3)
-O(4)	103.3 (2)	W(1)-P(1)-C(111)	114.5 (6)	-O(5)	80.5 (2)	P(2)-C(211)-C(212)	111.2 (9)
Cl(3)-W(1)-Cl(4)	86.0 (1)	W(1)-P(1)-C(121)	121.5 (7)	O(1)-W(2)-O(4)	168.7 (3)	C(211)-C(212)-C(213)	108 (1)
-P(1)	87.2 (1)	-C(131)	105.4 (6)	-O(5)	80.7 (3)	C(212)-C(213)-C(214)	107 (1)
-O(3)	165.1 (2)	C(111)-P(1)-C(121)	106 (1)	O(4)-W(2)-O(5)	90.0 (3)	P(2)-C(221)-C(222)	111.8 (9)
-O(4)	89.4 (2)	-C(131)	100.1 (8)	W(1)-W(3)-W(2)	60.20 (2)	C(221)-C(222)-C(223)	110 (1)
Cl(4)-W(1)-P(1)	89.9 (1)	C(121)-P(1)-C(131)	106.6 (9)	-Cl(1)	57.90 (7)	C(222)-C(223)-C(224)	105 (3)
-O(3)	89.6 (2)	W(2)-P(2)-C(211)	114.9 (4)	-Cl(5)	110.31 (8)	P(2)-C(231)-C(232)	112 (1)
-O(4)	168.5 (2)	-C(221)	109.8 (4)	-P(3)	128.11 (8)	C(231)-C(232)-C(233)	107 (1)
P(1)-W(1)-O(3)	78.5 (2)	-C(231)	114.2 (4)	-O(2)	137.3 (2)	C(232)-C(233)-C(234)	111 (2)
-O(4)	79.3 (2)	C(211)-P(2)-C(221)	106.5 (6)	-O(3)	47.9 (2)	P(3)-C(311)-C(312)	113.9 (9)
O(3)-W(1)-O(4)	92.2 (3)	-C(231)	102.9 (6)	-O(5)	91.2 (2)	C(311)-C(312)-C(313)	110 (1)
W(1)-W(2)-W(3)	60.27 (2)	C(221)-P(2)-C(231)	108.0 (6)	W(2)-W(3)-Cl(1)	58.55 (7)	C(312)-C(313)-C(314)	108 (2)
-Cl(1)	57.78 (7)	W(3)-P(3)-C(311)	115.6 (4)	-Cl(5)	146.39 (9)	P(3)-C(321)-C(322)	112.6 (9)
-Cl(2)	110.76 (9)	-C(321)	111.1 (4)	-P(3)	128.42 (8)	C(321)-C(322)-C(323)	106 (1)
-P(2)	127.21 (8)	-C(331)	113.6 (4)	-O(2)	85.4 (2)	C(322)-C(323)-C(324)	110 (2)
-O(1)	138.0 (2)	C(311)-P(3)-C(321)	108.3 (6)	-O(3)	92.9 (2)	P(3)-C(331)-C(332)	111 (1)
-O(4)	47.8 (2)	-C(331)	100.1 (6)	-O(5)	48.1 (2)	C(331)-C(332)-C(333)	102 (1)
-O(5)	91.2 (2)	C(321)-P(3)-C(331)	107.4 (6)	Cl(1)-W(3)-Cl(5)	88.6 (1)	C(332)-C(333)-C(334)	104 (2)

The bridging acetate ion is not a novelty, having been found in the aforementioned $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2+}$ ion and in all cluster species of the bicapped type. What is slightly novel is the presence of only one such bridging carboxylate, thus making one edge of the M_3 triangle different from the other two. This W(2)-W(3) edge is, in fact, slightly but significantly (0.018 (1) Å) shorter than the other two, which are of identical length within the esd's.

There are surprisingly few other distortions away from 3-fold symmetry in the rest of the structure. Thus, the W-P distances are all equal within the 3σ criterion with a mean value of 2.524 (4) Å, and the maximum differences among the three W-Cl(1) distances are just at the 3σ borderline; a mean W-Cl distance of 2.468 (6) Å may be considered valid. The other W-Cl bonds show differences, the average of W(1)-Cl(3) and W(1)-Cl(4), 2.405 (3) Å, being longer by 0.048 (7) Å than the average of W(2)-Cl(2) and W(3)-Cl(5), 2.357 (6) Å. The W-Cl(1)-W angles differ slightly, running from 63.39 (7) to 64.14 (7)° with an average of 63.8 ± 0.3°.

Certain features of this structure are to be compared with those of the $[W_3O_4F_9]^{5-}$ ion.[11] The chief difference is in the W-W distances, which have a mean value of 2.513 (2) Å in the fluoro anion as compared to 2.61 (1) Å in the present case. Since the two clusters are isoelectronic, this difference is most likely due to the different steric requirements of the capping atoms. In $[W_3O_4F_9]^{5-}$ the mean W-O-W angle at the capping oxygen atom is 74.9 (8)°. In our compound, even with the larger W-W distance, the mean angle at the large Cl capping atom is only 63.8 (3)°. It is our hypothesis that it is the resistance of the capping Cl atom to have even smaller angles that forces the W-W distances to be larger. Given the greater length of the W-W bonds, it follows that if the W-O bonds to the bridging oxygen atoms are to be about the same in both compounds (as they are, with average values of 1.95 (2) Å in the fluoro anion and 1.94 (1) Å in the present case), the W-O-W angles must be somewhat larger in the present case. In the $[W_3O_4F_9]^{5-}$ ion these angles have an average value of 80.1 (8)° while in the $W_3O_3Cl_5(PBu_3)_3$ molecule the mean value is 84.7 (7)°.

Comparison of the present structure with that of McCarley's $W(OCH_2CMe_3)O_3Cr_3(O_2CCMe_3)_{12}$[12] cannot be carried very far because of the many differences in detail between the two molecules. The mean W–W distances are equal, within the esd's, being 2.610 (3) Å for McCarley's molecule and 2.61 (1) Å for the present case.

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Registry No. $W_3O_3Cl_5(O_2CCH_3)(PBu_3)_3$, 73470-14-1.

Supplementary Material Available: Table IV (least-squares planes and dihedral angles) and tables of observed and calculated structure factors for the compound (26 pages). Ordering information is given on any current masthead page.

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Metal Ion Interactions with 8-Azapurines. Synthesis and Structure of Dichlorobis(8-azaadenine)mercury(II) and Tetraaquabis(8-azahypoxanthinato)mercury(II)

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The crystal and molecular structures of dichlorobis(8-azaadenine)mercury(II), $Hg(C_4N_6H_4)_2Cl_2$, and tetraaquabis(8-azahypoxanthinato)mercury(II), $Hg(C_4N_5OH_2)_2(H_2O)_4$, have been determined from three-dimensional X-ray data collected on an automatic diffractometer. The mercury–8-azaadenine complex crystallizes in space group *Ima*2 of the orthorhombic system with four formula units in a cell of dimensions $a = 27.68$ (3) Å, $b = 6.97$ (1) Å, and $c = 7.21$ (1) Å. The observed and calculated densities are 2.57 (2) and 2.596 g cm^{-3}, respectively. Full-matrix, least-squares refinement of the structure using 587 independent intensities has converged to a final value of the conventional R factor (on F) of 0.082. The crystal structure contains sheets of a two-dimensional Hg–Cl lattice, which lie parallel to the crystallographic *bc* plane, with the 8-azaadenine ligands extending above and below. The mercury ion sits on the crystallographic twofold axis and is coordinated to two trans purines via N(3) (2.72 (2) Å) and to four chloride ions—two coordinating strongly (2.39 (1) Å) and two weakly (2.92 (1) Å)—resulting in an approximate (2 + 4) octahedral arrangement. The mercury–8-azahypoxanthinato complex crystallizes in space group *C*2/*c* of the monoclinic system with four formula units in a cell of dimensions $a = 6.459$ (5) Å, $b = 11.233$ (8) Å, $c = 20.276$ (17) Å, and $\beta = 94.97$ (5)°. The observed and calculated densities are 2.45 (2) and 2.469 g cm^{-3}, respectively. Refinement of 1522 independent data converged to a final value of R of 0.070. The crystallographic twofold axis generates a linear chain of the formula units parallel to the *c* axis. The monomers are linked together by strong base-stacking interactions, and adjacent chains are held together through extensive hydrogen bonding. The mercury atom sits on the crystallographic inversion center and is coordinated to two trans purines through N(9) (2.04 (1) Å) and four water molecules (2.68 (1) and 2.80 (1) Å). Again, the coordination geometry around mercury approximates the (2 + 4) octahedral arrangement but with a cis O–Hg–O angle of 65.0 (4)°.

Introduction

Nucleic acids are the basis on which cells exist, function, and reproduce. Consequently, a large amount of effort is being devoted to the study of these polymers. But because of the difficulty inherent with obtaining precise structural information about even the smallest of these (transfer RNAs),[1-3] a great deal of effort has also been put toward the study of nucleic acid constituents[4]—nucleotides, nucleosides, and bases. Much has been learned from these studies concerning the hydrogen-bonding and stacking interactions[5] that occur as well as the conformational effects that exist within all nucleic acids.

The study of metal ion interactions with these same nucleic acid constituents[6-12] is also of great importance due to the variety of metal ion–nucleic acid interactions observed in biological systems.[13-18] These range from simple interactions such as those with Mg^{2+} and Mn^{2+}, which primarily stabilize the highly anionic nucleic acids, to complex interactions involving metalloenzymes such as the polymerases. Indications are that all nucleotidyl transferases contain Zn^{2+} ions,[19-22]

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