Contribution from the Laboratoire de Chimie des Métaux de Transition,
ERA-CNRS No. 608, Université Pierre et Marie Curie, 75230 Paris Cedex 5, France

Synthesis and X-ray Structure of the First Mercury(I)-Containing Polytungstate, $[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]^{10-}$, with an Odd Open-Shell Structure

J. MARTIN-FRÈRE and Y. JEANNIN*

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The compound $K_5Cs_5[(Hg_2)_2WO(H_2O)(AsW_9O_{33})_2]$ was synthesized and its crystal structure determined. It crystallizes in the triclinic space group $P\bar{1}$. The lattice constants are as follows: $a = 28.99$ (1) Å; $b = 18.82$ (1) Å; $c = 16.88$ (1) Å; $\alpha = 78.49$ (7)°; $\beta = 84.36$ (8)°; $\gamma = 78.25$ (6)°; $Z = 4$. The structure has been refined by block full-matrix least squares to a final R factor of 0.054 for 6554 reflections included in the refinement. As confirmed by ^{183}W NMR, the heteropolyanion is made of two AsW_9O_{33} units joined by one WO_6 octahedron. This looks like a shell kept open by two dinuclear Hg_2^{2+} cations inserted between the two AsW_9 groups; each cation is coordinated to four oxygen atoms.

Introduction

Different polyoxotungstates of general shortened formula $As_2W_{18}M_n$ have been recently reported.[1–6] In these compounds arsenic is As(III), $n = 1$, 2, or 3 and M is a transition metal such as W(VI), Cu(II), or Co(II). Other compounds with analogous formulas containing phosphorus(V) have also been prepared.[7,8] Similar structures have been postulated for them. When the heteroatom is in oxidation state V, the XW_9 group (X = P) is of type A.[9] Weakley[10] has solved the structure of $P^V{}_2W_{21}$; the heteroatom is tetrahedrally surrounded by four oxygen atoms. When the heteroatom is in oxidation state III, the XW_9 group is of type B;[9] the heteroatom is bound to three oxygen atoms only, and it has a free lone pair.

The structures[4–6] of $[As_2W_{21}O_{69}(H_2O)]^{6-}$, $[As_2W_{18}Cu_3O_{66}(H_2O)_2]^{12-}$, and $[As_2W_{18}Co_3O_{66}(H_2O)_3]^{12-}$ have already been solved. They are made of two AsW_9 units linked together by three tungsten, three copper, or three cobalt atoms; indeed, if two AsW_9 moieties of type B are to be joined together, one must, however, keep them apart enough to avoid lone-pair interaction. In the As_2W_{21} structure the two AsW_9 units face each other; in $As_2W_{18}Cu_3$ they are slightly shifted away perpendicular to the longest dimension of the polyanion. Although the differences of the As–As distances are not significant within the estimated deviations (5.33 (6) Å in the copper compound, 5.39 (6) Å in the tungsten one), this might be attributed to the fact that copper is smaller than tungsten, bringing the arsenic atoms closer. Therefore, the lateral shift of the AsW_9 moieties give more space to the lone pairs of arsenic in the copper compound.

The bridge linking both AsW_9 moieties may be lacunary; for instance, it may have either one tungsten atom or two tungsten atoms.[3] This is shown by compounds such as $[As_2W_{19}O_{67}]^{14-}$ or $[As_2W_{20}O_{68}]^{10-}$. The vacancies may be filled by first-row transition-metal atoms, making mixed bridge compounds such as $[As_2W_{19}Z_2O_{67}]^{(14-2z)-}$ or $[As_2W_{20}ZO_{68}]^{(14-z)-}$; Z is a metal atom in the oxidation state z. However, up to now no structures of such compounds have been solved.

Thus, it is possible to separate two AsW_9 moieties by using the oxygen atoms linked to a metal atom such as tungsten or copper. The same goal could be reached by using the lone pairs of arsenic atoms ligated to a metal atom; Hg_2^{2+} has been considered, due to its known chemistry.

Actually, the prepared compound does not fulfill this expectation. It turned out to be a compound of the $[As_2W_{19}Z_2O_{67}]^{(14-z)-}$ type; a Hg_2^{2+} cation takes the place of Z.

Experimental Section

Crystal Synthesis and Chemical Analysis. Sodium tungstate (66 g) and diarsenic trioxide (2.2 g), i.e. one arsenic atom for nine tungsten atoms, were added to water (200 mL), and the mixture was boiled. After dissolution of the mixture, 17 mL of concentrated nitric acid ($d = 1.38$) was added slowly with stirring in order to lower the pH to 5. Then 6 g of mercurous nitrate dissolved in 20 mL of water acidified by 0.5 mL of the same concentrated nitric acid was poured into the mixture, and the new mixture was boiled. The pH dropped to 4. The potassium salt was formed by adding 25 g of potassium nitrate. On cooling, transparent crystals appeared after 2 or 3 days.

In order to prepare crystals of a mixed salt of cesium and potassium that are more suitable for the crystallographic study, we dissolved 3 g of this potassium salt in 75 mL of hot water, and 5 mL of a 10% cesium nitrate aqueous solution was poured into it. Slow evaporation led to transparent crystals, which were recrystallized in water.

Anal. Found (first sample): W, 50.26; Hg, 11.18; As, 1.91; Cs, 7.56; K, 1.62. Found (second sample): W, 51.41; Hg, 10.08; As, 2.00; Cs, 9.54; K, 3.06. Calcd from X-ray structure of $K_5Cs_5As_2W_{19}Hg_4O_{67}(H_2O)\cdot3H_2O$: W, 54.16; Hg, 12.44; As, 2.32; Cs, 10.30; K, 3.03. The number of water molecules measured by thermogravimetric analysis is 4.

Crystallographic Data. Preliminary precession photographs showed a triclinic unit cell.

A crystal shaped as a parallelepiped with approximate dimensions 0.02 × 0.1 × 0.2 mm was put into a sealed Lindemann tube and set up on an automatic Philips PW 1100 diffractometer.

Lattice constants refined by least squares from 25 reflections: $a = 28.99$ (1) Å; $b = 18.82$ (1) Å; $c = 16.88$ (1) Å; $\alpha = 78.49$ (7)°; $\beta = 84.36$ (8)°; $\gamma = 78.25$ (6)°; $V = 8818$ Å^3. The density of crystals was measured by pycnometry in cyclohexane. The obtained value of 4.9 g cm^{-3} led to a value of 4 molecules per unit cell. The calculated value is 4.86 if the formula is $K_5Cs_5[As_2W_{19}Hg_4O_{67}(H_2O)]\cdot3H_2O$. As the space group is triclinic, the asymmetrical unit contains two $[As_2W_{19}Hg_4O_{67}(H_2O)]^{10-}$ anions. This point will be discussed later on.

A total of 14 025 independent reflections were collected at room temperature: radiation Mo Kα; scan type θ–2θ; scan speed 0.01 deg s^{-1}; scan length $(0.80 + 0.30 \tan\theta)$°, if θ is the Bragg angle; background measurement, in fixed position before and after every scan during a time equal to half of the scan time; maximum recording angle, $\theta_{Bragg} = 20°$; standard reflections, $38\bar{1}$, 006, and $\bar{3}\bar{8}1$, measured every 2 h. No decrease of standards was observed. Only 6554 reflections

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Table I. Atomic Coordinates of Hg and W Atoms

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Hg(1)	0.1842 (1)	0.3773 (2)	0.1947 (2)	W(16)	0.4887 (1)	0.1131 (2)	0.1247 (3)
Hg(2)	0.2552 (1)	0.3847 (2)	0.1044 (3)	W(17)	0.4184 (1)	0.1518 (2)	−0.0611 (2)
Hg(3)	0.2545 (1)	0.3248 (2)	0.3827 (2)	W(18)	0.4737 (1)	0.2980 (2)	−0.0095 (2)
Hg(4)	0.3243 (1)	0.3376 (2)	0.2910 (3)	W(19)	0.2708 (1)	0.1365 (2)	0.2440 (2)
Hg(5)	0.1619 (1)	0.5335 (2)	0.2647 (2)	W(20)	0.2176 (1)	0.8575 (2)	0.0906 (2)
Hg(6)	0.2120 (1)	0.4987 (2)	0.3873 (2)	W(21)	0.2564 (1)	0.7337 (2)	−0.0318 (2)
Hg(7)	0.2687 (2)	0.5499 (2)	0.1323 (3)	W(22)	0.1908 (1)	0.5898 (2)	−0.0502 (2)
Hg(8)	0.3202 (2)	0.5163 (2)	0.2513 (3)	W(23)	0.0944 (1)	0.5711 (2)	0.0677 (2)
W(1)	0.1374 (1)	0.3492 (2)	0.5049 (2)	W(24)	0.0535 (1)	0.6960 (2)	0.2097 (2)
W(2)	0.2173 (1)	0.1700 (2)	0.5519 (2)	W(25)	0.1096 (1)	0.8363 (2)	0.2201 (2)
W(3)	0.2248 (1)	0.0394 (2)	0.4362 (2)	W(26)	0.1557 (1)	0.8649 (2)	−0.0739 (2)
W(4)	0.1538 (1)	0.0852 (2)	0.2491 (2)	W(27)	0.0896 (1)	0.7171 (2)	−0.0881 (2)
W(5)	0.0867 (1)	0.2559 (2)	0.2008 (2)	W(28)	0.0487 (1)	0.8459 (2)	0.0535 (2)
W(6)	0.0744 (1)	0.3905 (2)	0.3357 (2)	W(29)	0.3340 (1)	0.7701 (2)	0.3679 (2)
W(7)	0.0549 (1)	0.1291 (2)	0.3591 (2)	W(30)	0.4091 (1)	0.6154 (2)	0.3350 (2)
W(8)	0.0450 (1)	0.2657 (2)	0.4944 (2)	W(31)	0.3945 (1)	0.4305 (2)	0.4382 (2)
W(9)	0.1251 (1)	0.0829 (2)	0.5449 (2)	W(32)	0.3000 (1)	0.4126 (2)	0.5594 (2)
W(10)	0.4275 (1)	0.3788 (2)	0.1481 (2)	W(33)	0.2137 (1)	0.5763 (2)	0.5884 (2)
W(11)	0.4433 (1)	0.1971 (2)	0.2829 (2)	W(34)	0.2294 (1)	0.7485 (2)	0.5045 (2)
W(12)	0.3983 (1)	0.0568 (2)	0.2376 (2)	W(35)	0.4044 (1)	0.6710 (2)	0.5173 (2)
W(13)	0.3277 (1)	0.0954 (2)	0.0506 (2)	W(36)	0.3878 (1)	0.4838 (2)	0.6212 (2)
W(14)	0.3101 (1)	0.2665 (2)	−0.0637 (2)	W(37)	0.3005 (1)	0.6499 (2)	0.6524 (2)
W(15)	0.3664 (1)	0.4127 (2)	−0.0217 (2)	W(38)	0.2264 (1)	0.7329 (2)	0.2888 (2)

with an observed structure factor greater than 12.0 were kept for refinement. Lorentz and polarization corrections were applied.

The absorption coefficient was equal to 341 cm^{-1}. Corrections were calculated[11] and applied. Transmission factors varied from 0.06 to 0.58.

Structure Determination. The unit cell contains $As_8W_{76}Hg_{16}$. Statistical tests[12] were used and applied to the whole set of collected reflections. They showed centrosymmetry.

Ten atoms of an AsW_9 group were first localized with use of the MULTAN program.[12] Subsequent Fourier syntheses and refinements gave the positions of all the other heavy atoms of the polyanions. Ten cesium atoms and the oxygen atoms of the anions were found by difference Fourier syntheses. Moreover, eight peaks were ascribed to potassium or disordered cesium cations. It has not been possible to locate all cations required by charge balance. No attempt was made to find water molecules.

Refinements were made by the least-squares method minimizing $R = (\sum|F_o - kF_c|^2/\sum F_o^2)^{1/2}$, where k is the scale factor. Because of the large number of parameters, each anion refinement was made by dividing it into 13 blocks. The isotropic temperature factors of structurally similar oxygen atoms were kept equal by using the constraints of the SHELX program.[13] A final R value of 0.054 was obtained by using anisotropic temperature factors for tungsten and mercury. ($R = \sum|F_o - kF_c|/\sum F_o$.) Atomic form factors were taken from Cromer and Waber.[14] The real and imaginary parts of the anomalous dispersion correction for tungsten, mercury, cesium, and arsenic were taken into account.

Final atomic coordinates, vibrational parameters, and corresponding standard deviations are given in Tables I, II (supplementary material), and III.

Description of the Structure

The cell is centrosymmetric, and the asymmetrical unit contains two $[As_2W_{19}Hg_4O_{67}(H_2O)]^{10-}$ anions.

Each anion (Figure 1) is made of two AsW_9O_{33} units of type B.[9] The arsenic is the apex of an AsO_3 pyramid; each oxygen is the common vertex of three octahedra of a W_3O_{13} group. These two units are joined by a WO_6 octahedron. Four among these six oxygen atoms make the square basal plane; they are shared with the AsW_9O_{33} moieties, two per unit. The two other oxygen atoms are in a trans position with regard to this basal plane. The two AsW_9O_{33} units look like the two shells of a half-opened clam, the tungsten atom that links them acting as the hinge. In each AsW_9 unit there is a plane containing six tungsten atoms. The dihedral angles of the two planes of both AsW_9 units are 39.2 and 41.4° for the two anions of the asymmetric unit.

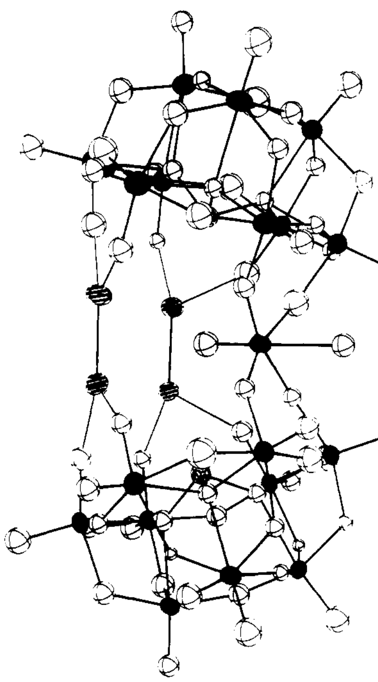

Figure 1. ORTEP[19] plot of the $[As_2W_{19}Hg_4O_{67}(H_2O)]^{10-}$ anion (with 20% probability ellipsoids): black circles, tungsten atoms; striped circles, mercury atoms; spotted circles, arsenic atoms.

Keeping the clam opened are the two Hg_2^{2+} cations. The four mercury atoms are in the same plane located at the four vertices of a rectangle. The short sides are 2.490 (6) Å long: they correspond to the Hg–Hg bonds. The average length of the long sides, 3.738 (6) Å, shows clearly that there is no Hg–Hg bond in this direction.

Each of the two $[As_2W_{19}Hg_4O_{67}(H_2O)]^{10-}$ polyanions of one asymmetric unit has two perpendicular noncrystallographic symmetry planes. The hinge tungsten atom is on their in-

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Table III. Atomic Coordinates and Isotropic Temperature Factors of As, O, Cs, and K Atoms[a]

atom	x/a	y/b	z/c	B(iso), Å^2
As(1)	0.1588 (3)	0.2241 (4)	0.3677 (5)	2.5 (2)
As(2)	0.3674 (3)	0.2421 (5)	0.1181 (5)	2.5 (2)
As(3)	0.1612 (3)	0.7006 (4)	0.1000 (5)	2.0 (2)
As(4)	0.3071 (3)	0.5898 (4)	0.4477 (5)	2.0 (2)
O(1,6,8,As(1))	0.115 (1)	0.285 (2)	0.415 (2)	2.7 (7)
O(2,3,9,As(1))	0.175 (2)	0.148 (3)	0.452 (3)	2.2 (11)
O(4,5,7,As(1))	0.123 (2)	0.186 (3)	0.315 (3)	2.2 (7)
O(10,15,18,As(2))	0.403 (2)	0.307 (3)	0.075 (3)	2.7 (11)
O(11,12,16,As(2))	0.413 (2)	0.169 (3)	0.173 (3)	2.2 (11)
O(13,14,17,As(2))	0.364 (2)	0.204 (3)	0.033 (3)	2.2 (7)
O(20,21,26,As(3))	0.188 (2)	0.770 (3)	0.036 (3)	1.9 (11)
O(22,23,27,As(3))	0.140 (2)	0.664 (2)	0.027 (3)	3.5 (10)
O(24,25,28,As(3))	0.110 (2)	0.755 (3)	0.129 (3)	1.9 (7)
O(29,30,35,As(4))	0.349 (2)	0.647 (3)	0.431 (3)	1.9 (10)
O(31,32,36,As(4))	0.341 (2)	0.509 (3)	0.506 (3)	3.5 (12)
O(33,34,37,As(4))	0.276 (2)	0.630 (3)	0.526 (3)	1.9 (8)
O(5,Hg(1))	0.139 (2)	0.285 (3)	0.180 (3)	3.1 (12)
O(6,Hg(1))	0.129 (2)	0.402 (3)	0.283 (3)	2.3 (11)
O(14,Hg(2))	0.274 (2)	0.300 (3)	0.013 (4)	4.8 (15)
O(15,Hg(2))	0.313 (2)	0.417 (3)	0.041 (3)	1.8 (10)
O(1,Hg(3))	0.187 (2)	0.360 (3)	0.440 (3)	3.2 (12)
O(2,Hg(3))	0.252 (2)	0.218 (3)	0.478 (3)	2.5 (11)
O(10,Hg(4))	0.372 (2)	0.382 (3)	0.194 (4)	4.0 (14)
O(11,Hg(4))	0.385 (2)	0.239 (3)	0.318 (3)	3.6 (13)
O(23,Hg(5))	0.135 (2)	0.538 (3)	0.146 (3)	3.2 (13)
O(24,Hg(5))	0.102 (2)	0.634 (3)	0.265 (4)	4.4 (15)
O(32,Hg(6))	0.272 (2)	0.437 (3)	0.473 (3)	2.1 (10)
O(33,Hg(6))	0.196 (2)	0.567 (2)	0.492 (3)	1.8 (10)
O(21,Hg(7))	0.273 (2)	0.667 (3)	0.052 (3)	2.8 (11)
O(22,Hg(7))	0.225 (2)	0.549 (3)	0.038 (3)	2.5 (11)
O(30,Hg(8))	0.363 (3)	0.599 (4)	0.276 (5)	7.0 (20)
O(31,Hg(8))	0.354 (2)	0.458 (3)	0.356 (4)	4.3 (14)
O(1,2)	0.167 (2)	0.257 (3)	0.560 (3)	2.2 (10)
O(1,6)	0.095 (2)	0.418 (3)	0.429 (3)	2.3 (11)
O(1,8)	0.078 (2)	0.316 (3)	0.554 (3)	3.2 (12)
O(2,3)	0.246 (2)	0.073 (3)	0.513 (4)	4.9 (15)
O(2,9)	0.168 (1)	0.110 (2)	0.603 (3)	0.8 (8)
O(3,4)	0.187 (2)	0.044 (3)	0.348 (4)	4.2 (14)
O(3,9)	0.173 (2)	0.009 (3)	0.508 (3)	1.9 (11)
O(3,19)	0.259 (2)	0.100 (3)	0.352 (3)	2.3 (11)
O(4,5)	0.122 (2)	0.148 (3)	0.184 (4)	4.2 (14)
O(4,7)	0.098 (2)	0.062 (2)	0.303 (3)	1.5 (9)
O(4,19)	0.208 (2)	0.132 (3)	0.227 (3)	2.1 (11)
O(5,6)	0.064 (2)	0.319 (3)	0.270 (3)	2.0 (12)
O(5,7)	0.039 (2)	0.197 (2)	0.260 (3)	1.1 (9)
O(6,8)	0.026 (2)	0.348 (3)	0.408 (4)	3.9 (13)
O(7,8)	0.036 (2)	0.207 (3)	0.413 (3)	2.9 (11)
O(7,9)	0.093 (2)	0.081 (2)	0.451 (3)	1.5 (10)
O(8,9)	0.091 (2)	0.170 (3)	0.546 (4)	3.8 (14)
O(10,11)	0.456 (2)	0.291 (4)	0.216 (4)	4.0 (16)
O(10,15)	0.399 (2)	0.446 (3)	0.051 (3)	3.5 (12)
O(10,18)	0.484 (2)	0.346 (3)	0.068 (3)	3.6 (13)
O(11,12)	0.425 (2)	0.091 (3)	0.316 (4)	3.9 (13)
O(11,16)	0.498 (2)	0.141 (3)	0.225 (3)	3.2 (12)
O(12,13)	0.372 (2)	0.056 (3)	0.137 (3)	1.9 (10)
O(12,16)	0.459 (2)	0.034 (3)	0.187 (3)	2.4 (11)
O(12,19)	0.338 (2)	0.110 (3)	0.263 (3)	2.7 (12)
O(13,14)	0.296 (2)	0.166 (3)	−0.027 (3)	2.4 (11)
O(13,17)	0.375 (2)	0.074 (3)	−0.023 (3)	3.2 (12)
O(13,19)	0.283 (2)	0.140 (3)	0.132 (4)	4.4 (14)
O(14,15)	0.348 (2)	0.341 (4)	−0.077 (4)	4.9 (16)
O(14,17)	0.365 (2)	0.208 (3)	−0.117 (3)	2.5 (11)
O(15,18)	0.432 (2)	0.378 (3)	−0.066 (3)	3.1 (12)
O(16,17)	0.458 (2)	0.105 (3)	0.036 (4)	2.9 (14)
O(16,18)	0.494 (2)	0.209 (3)	0.062 (3)	1.9 (10)
O(17,18)	0.445 (2)	0.230 (4)	−0.062 (4)	5.6 (15)
O(20,21)	0.263 (2)	0.817 (3)	0.025 (3)	3.1 (12)
O(20,25)	0.158 (2)	0.873 (3)	0.143 (3)	2.3 (11)
O(20,26)	0.185 (2)	−0.088 (3)	−0.009 (3)	1.8 (10)
O(20,38)	0.235 (2)	0.778 (4)	0.181 (4)	5.4 (16)
O(21,22)	0.225 (2)	0.671 (3)	−0.079 (4)	4.4 (14)
O(21,26)	0.215 (2)	0.819 (3)	−0.109 (3)	1.9 (10)
O(22,23)	0.141 (2)	0.535 (3)	−0.009 (3)	2.9 (12)
O(22,27)	0.139 (2)	0.658 (3)	−0.123 (3)	3.3 (13)
O(23,24)	0.059 (2)	0.639 (3)	0.127 (3)	2.6 (11)
O(23,27)	0.064 (2)	0.638 (2)	−0.030 (3)	1.5 (9)
O(25,38)	0.159 (2)	0.759 (2)	0.277 (3)	1.1 (9)
O(26,27)	0.126 (2)	0.793 (3)	−0.105 (3)	1.8 (10)
O(26,28)	0.100 (2)	0.885 (3)	−0.008 (3)	2.4 (12)
O(27,28)	0.057 (2)	0.777 (3)	−0.018 (4)	4.2 (14)
O(29,30)	0.380 (2)	0.727 (3)	0.301 (3)	2.6 (11)
O(29,34)	0.284 (2)	0.779 (2)	0.449 (3)	1.8 (10)
O(29,35)	0.380 (2)	0.763 (3)	0.455 (4)	3.9 (15)
O(29,38)	0.287 (2)	0.740 (3)	0.306 (3)	2.5 (11)
O(30,31)	0.420 (2)	0.516 (3)	0.399 (3)	2.9 (12)
O(30,35)	0.440 (2)	0.641 (3)	0.424 (3)	3.3 (12)
O(31,32)	0.354 (2)	0.366 (3)	0.504 (3)	3.0 (12)
O(31,36)	0.421 (1)	0.429 (2)	0.550 (3)	1.0 (9)
O(32,33)	0.257 (2)	0.484 (3)	0.605 (3)	2.9 (11)
O(32,36)	0.342 (2)	0.419 (3)	0.644 (4)	4.3 (15)
O(33,34)	0.191 (2)	0.686 (3)	0.559 (3)	2.0 (10)
O(33,37)	0.244 (2)	0.606 (3)	0.680 (3)	2.1 (10)
O(34,37)	0.257 (2)	0.740 (3)	0.603 (3)	2.3 (11)
O(34,38)	0.218 (2)	0.729 (2)	0.396 (3)	1.4 (9)
O(35,36)	0.410 (2)	0.576 (3)	0.567 (4)	3.9 (14)
O(35,37)	0.346 (2)	0.688 (3)	0.586 (3)	2.6 (11)
O(36,37)	0.341 (2)	0.555 (3)	0.662 (3)	2.7 (11)
O(1)	0.139 (2)	0.401 (3)	0.582 (4)	4.1 (10)
O(2)	0.242 (2)	0.166 (3)	0.636 (3)	2.0 (8)
O(3)	0.258 (2)	−0.043 (3)	0.435 (3)	3.0 (8)
O(4)	0.166 (2)	0.015 (3)	0.198 (3)	3.0 (8)
O(5)	0.057 (2)	0.286 (3)	0.116 (4)	2.0 (13)
O(6)	0.041 (2)	0.472 (3)	0.294 (3)	4.1 (12)
O(7)	0.006 (2)	0.087 (3)	0.371 (3)	4.2 (8)
O(8)	−0.005 (2)	0.264 (3)	0.548 (3)	2.0 (11)
O(9)	0.098 (2)	0.029 (3)	0.614 (3)	4.2 (12)
O(10)	0.451 (2)	0.440 (3)	0.186 (4)	4.1 (14)
O(11)	0.475 (2)	0.189 (3)	0.362 (3)	2.0 (11)
O(12)	0.398 (2)	−0.027 (3)	0.290 (3)	3.0 (8)
O(13)	0.302 (2)	0.023 (3)	0.045 (3)	3.0 (8)
O(14)	0.279 (2)	0.295 (3)	−0.145 (3)	2.0 (8)
O(15)	0.352 (2)	0.489 (3)	−0.097 (4)	4.1 (10)
O(16)	0.539 (2)	0.067 (3)	0.105 (3)	4.2 (11)
O(17)	0.450 (2)	0.114 (2)	−0.131 (3)	4.2 (7)
O(18)	0.525 (2)	0.304 (3)	−0.063 (3)	2.0 (12)
O(19)	0.265 (2)	0.229 (3)	0.244 (4)	3.8 (13)
O(19)′	0.279 (2)	0.003 (3)	0.243 (3)	3.0 (12)
O(20)	0.242 (2)	0.922 (3)	0.115 (3)	2.3 (8)
O(21)	0.305 (2)	0.735 (3)	−0.091 (4)	4.6 (11)
O(22)	0.220 (2)	0.536 (3)	−0.116 (4)	3.6 (9)
O(23)	0.058 (2)	0.506 (3)	0.069 (3)	3.6 (12)
O(24)	0.001 (2)	0.680 (2)	0.257 (3)	4.6 (10)
O(25)	0.105 (2)	0.894 (3)	0.288 (3)	2.3 (8)
O(26)	0.140 (2)	0.938 (3)	−0.154 (3)	4.5 (12)
O(27)	0.058 (2)	0.738 (3)	−0.168 (4)	3.6 (14)
O(28)	0.004 (2)	0.913 (4)	0.012 (4)	4.5 (11)
O(29)	0.327 (2)	0.860 (3)	0.320 (3)	2.3 (8)
O(30)	0.458 (2)	0.610 (3)	0.270 (3)	4.8 (12)
O(31)	0.437 (2)	0.362 (3)	0.416 (3)	3.6 (10)
O(32)	0.281 (2)	0.336 (3)	0.610 (4)	4.6 (11)
O(33)	0.168 (2)	0.554 (3)	0.649 (4)	3.6 (9)
O(34)	0.190 (2)	0.831 (3)	0.500 (3)	2.3 (8)
O(35)	0.444 (2)	0.698 (3)	0.563 (4)	4.5 (14)
O(36)	0.419 (2)	0.456 (3)	0.697 (4)	3.6 (13)
O(37)	0.312 (2)	0.670 (3)	0.747 (4)	4.5 (9)
O(38)	0.239 (2)	0.638 (3)	0.285 (4)	4.0 (13)
O(38)′	0.218 (2)	0.867 (3)	0.305 (3)	3.5 (13)
Cs(1)	0.1978 (4)	0.2983 (6)	0.7274 (7)	10.4 (3)
Cs(2)	−0.1100 (2)	0.3189 (3)	0.5717 (4)	4.3 (1)
Cs(3)	0.3561 (4)	0.7219 (6)	0.1240 (7)	10.3 (3)
Cs(4)	0.4430 (3)	0.9246 (4)	0.0762 (5)	5.8 (2)
Cs(5)	0.0204 (3)	0.5613 (4)	−0.1482 (5)	5.7 (2)
Cs(6)	0.2861 (3)	0.4570 (4)	0.7890 (5)	6.4 (2)
Cs(7)	0.0983 (3)	0.0384 (5)	0.0532 (5)	6.9 (2)
Cs(8)	0.1908 (4)	0.2189 (7)	0.0401 (8)	11.0 (3)
Cs(9)	0.3478 (5)	0.1187 (8)	0.4502 (9)	13.5 (4)
Cs(10)	0.0885 (5)	0.8803 (7)	0.7190 (9)	7.5 (3)
Cs(11)	0.1881 (8)	0.752 (1)	−0.258 (1)	5.7 (5)
K(1)	0.3204 (8)	−0.138 (1)	0.575 (1)	4.6 (5)
K(2)	0.0154 (9)	0.120 (1)	0.693 (2)	5.9 (6)
K(3)	0.1267 (8)	0.933 (1)	0.418 (1)	4.8 (5)
K(4)	0.032 (1)	0.427 (1)	0.640 (2)	6.4 (6)

Table III (*Continued*)

atom	x/a	y/b	z/c	B(iso), Å^2	atom	x/a	y/b	z/c	B(iso), Å^2
O(24,25)	0.067 (2)	0.775 (3)	0.262 (4)	4.4 (14)	K(5)	0.381 (1)	0.629 (2)	−0.135 (2)	11.8 (10)
O(24,28)	0.017 (2)	0.788 (2)	0.135 (3)	1.4 (9)	K(6)	0.483 (1)	0.467 (2)	−0.177 (2)	11.8 (10)
O(25,28)	0.065 (1)	0.890 (2)	0.144 (3)	0.8 (8)	K(7)	0.5	0.5	0.5	6.5 (9)

[a] O atoms indexed (*i,j*) are bonded to W(*i*) and W(*j*); O atoms indexed (*i,j,k*, As(*n*)) are bonded to W(*i*), W(*j*), W(*k*), and As(*n*); O atoms indexed (*i*, Hg(*n*)) are bonded to W(*i*) and Hg(*n*); O atoms indexed (*i*)′ are bonded to W(*i*) and belong to a H_2O molecule.

Table V. Distances (Å) between Mercury Atoms

Hg(1)–Hg(2)	2.450 (5)	Hg(3)–Hg(6)	3.267 (5)
Hg(1)–Hg(3)	3.796 (6)	Hg(4)–Hg(8)	3.275 (6)
Hg(1)–Hg(5)	3.303 (6)	Hg(5)–Hg(6)	2.545 (6)
Hg(2)–Hg(4)	3.760 (6)	Hg(5)–Hg(7)	3.664 (6)
Hg(2)–Hg(7)	3.340 (6)	Hg(6)–Hg(8)	3.732 (6)
Hg(3)–Hg(4)	2.446 (6)	Hg(7)–Hg(8)	2.521 (6)

tersection. The intersections of the two polyanions of the same asymmetric unit are collinear, and the symmetry planes are common. Both polyanions face each other by the opening of the clam, but they are turned by 90° with regard to each other. Thus, one understands why the unit cell contains four polyanions and why the asymmetric unit contains two polyanions.

Discussion

The main bond distances and angles are given in Tables IV (supplementary material) and V.

Inside an AsW_9O_{33} unit, As–O and W–O distances are those generally found in other Keggin-like structures. Let us consider the hinge WO_6 octahedra. They contain particularly long W–O bonds between the hinge tungsten atoms W_{19} and W_{38} and the terminal oxygen atoms located outside the surface of the clam, i.e. opposite mercury atoms (2.48 (6) and 2.55 (6) Å, respectively). The length of such W–O bonds strongly suggests that these oxygen atoms belong to water molecules. Trans to these, two oxygen atoms are located inside the clam. The W–O distances are 1.71 (6) and 1.76 (6) Å. Such distances are typical of a W═O double bond pointing inside the polyanion, i.e. toward the mercury atoms. The same arrangement of a doubly bonded oxygen inside the polyanion and a water molecule trans to it has been already found in the $[As_2W_{21}O_{69}(H_2O)]^{6-}$ anion.[4] Without a water molecule, there would be a tungsten atom with two doubly bonded oxygen atoms in trans positions, which has never been observed.

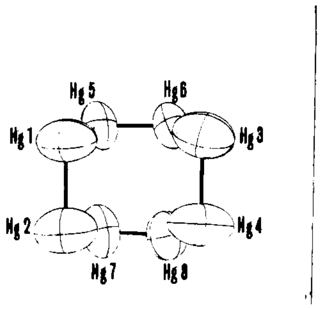

Figure 2. ORTEP[19] plot of the eight mercury atoms of the two anions.

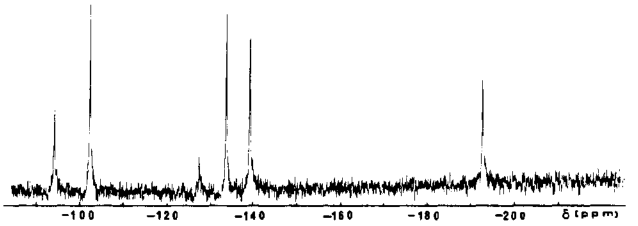

Figure 3. ^{183}W NMR spectrum of $[As_2W_{19}Hg_4O_{67}(H_2O)]^{10-}$ in deuterated dimethyl sulfoxide. Chemical shifts are given with respect to a 1 M solution of WO_4Na_2 in dimethyl sulfoxide.

The Hg_2^{2+} cation keeps the clam opened by Hg–O bonds, with oxygen atoms located on the upper part of the clam if the hinge is the lower part. Thus the two AsW_9 units are joined by a double O–Hg–Hg–O bridge. The bond length corresponding to Hg_2^{2+} is that one commonly observed for this dinuclear cation. Besides, each mercury atom is linked to two oxygen atoms of an AsW_9O_{33} unit belonging to two different W_3O_{13} groups. The values of these two different Hg–O distances averaged over the whole structure are 2.16 (5) and 2.34 (6) Å. The O–Hg–Hg angle corresponding to the shorter distance is 161.7 (15)°. Such a O–Hg–Hg–O group occurs in other Hg(I) compounds;[15-18] in mercurous nitrate, $Hg_2(NO_3)_2{\cdot}2H_2O$, and in mercurous perchlorate, $Hg_2(ClO_4)_2{\cdot}4H_2O$, it belongs to a discrete H_2O–Hg–Hg–H_2O unit. In the bromate, sulfate, selenate, or phthalate it links different BrO_3^-, SO_4^{2-}, SeO_4^{2-}, or $C_6H_4(CO_2)_2^{2-}$ anions in a similar O–Hg–Hg–O arrangement. The observed angles for O–Hg–Hg fluctuate between 160° for the selenate and 180° for the perchlorate. In all cases such geometry is ascribed to a covalent bond between Hg_2^{2+} and oxygen. Figure 2 represents all eight mercury atoms of an asymmetric unit. It is a distorted cube. Its sides alternately correspond to a covalent Hg–Hg bond and to a Hg···Hg distance of 3.26 Å, slightly longer than the sum of the van der Waals radii (1.5 Å). The four mercury atoms of an $As_2W_{19}Hg_4$ anion are roughly equidistant from the oxygen atom doubly bonded to the hinge tungsten: the average distance is 3.25 Å.

As pointed out earlier, 18 peaks of the difference Fourier synthesis have been ascribed to cations in the structure refinement whereas the charge balance led to 20 cations for one asymmetrical unit. Due to the difficulty of getting an accurate chemical analysis, these 18 peaks' attribution to cesium or potassium was made according to intensity and to environment. Occupation factors less than 1 were assigned to two sites too close to each other to be simultaneously occupied by two cesium atoms. No more cations were located.

A ^{183}W NMR study was carried out by using D_2O as solvent with a Bruker WM 400 NMR spectrophotometer. In order to obtain a concentrated enough solution, 1.2 g of the mixed cesium–potassium salt was shaken with a 3-mL sample of D_2O saturated in lithium perchlorate. The solution was then filtered to eliminate cesium and potassium perchlorates. The spectrum shown in Figure 3 was recorded at room temperature: scan number 21 000; acquisition time 2.7 s; spectral width 6000 Hz. Six different signals were observed: they are given by six different kinds of tungsten atoms. The peak area ratio is close to 2/4/1/4/4/4, which perfectly agrees with the crystallographic result.

Conclusion

This odd structure is made of two AsW_9O_{33} shells. It looks like a dead clam with a WO_6 octahedron as a hinge. It is kept

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opened by two Hg_2^{2+} binuclear cations. The asymmetrical unit contains two such moieties facing each other, the mercury atoms making a distorted cube.

Acknowledgment. We are indebted to Dr. C. Knobler for valuable advice and helpful discussions.

Registry No. $K_5Cs_5[As_2W_{19}Hg_4O_{67}(H_2O)]\cdot 3H_2O$, 92014-65-8; Hg, 7439-97-6.

Supplementary Material Available: Table II (anisotropic thermal parameters of Hg and W atoms), Table IV (selected bond distances and angles), and a listing of structure factor amplitudes (44 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica and Istituto di Mineralogia e Cristallografia,
Università di Perugia, 06100 Perugia, Italy

Exchange Interaction in Multinuclear Transition-Metal Complexes. 6.[1] Nature of Metal-Metal Coupling in Dinuclear Iron(III) Systems Containing Fe-O-Fe-O Bridging Units

B. CHIARI, O. PIOVESANA,* T. TARANTELLI, and P. F. ZANAZZI

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The crystal structures of the new complex bis(μ-ethoxy)dichloro[1,4-piperazinediylbis(*N*-ethylenesalicylaldiminato)]diiron(III), $Fe_2L(OC_2H_5)_2Cl_2$, $C_{26}H_{36}N_4O_4Cl_2Fe_2$, and of the already known bis(μ-ethoxy)bis[bis(2,4-pentanedionato)iron(III)], $Fe_2(acac)_4(OC_2H_5)_2$, $C_{24}H_{50}O_{10}Fe_2$, have been determined by X-ray methods. The L^{2-} derivative crystallizes in the orthorhombic space group *Pccn* with 4 molecules in a cell of dimensions $a = 10.840$ (3) Å, $b = 13.414$ (3) Å, and $c = 19.850$ (4) Å. Least-squares refinement of 1066 observed reflections and 173 parameters has led to a final *R* factor of 0.035. $Fe_2(acac)_4(OC_2H_5)_2$ crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$. Lattice constants are $a = 9.761$ (3) Å, $b = 14.627$ (3) Å, $c = 10.485$ (3) Å, and $\beta = 105.83$ (2)°. The least-squares refinement converged to an *R* value of 0.052 for 1526 observed reflections and 161 parameters. Both complexes consist of two iron(III) ions that are symmetrically bridged by two ethoxide groups. The coordination around each iron center is roughly octahedral. In $Fe_2L(OC_2H_5)_2Cl_2$, three coordination sites are occupied by one oxygen and two nitrogens (cis) of hexadentate L^{2-} and the remaining three by the two bridging ethoxy groups and a terminal chloride atom. The average Fe-O (bridging) bond length is 1.991 Å, the Fe-Fe separation is 3.144 (1) Å, and the FeOFe angle is 104.3 (1)°. The Fe_2O_2 ring is buckled, the dihedral angle between FeO_2 planes being 169°. In $Fe_2(acac)_4(OC_2H_5)_2$, the coordination sites are occupied by the two bridging alkoxide groups and the oxygen atoms of two cis bidentate $acac^-$ ligands. The Fe_2O_4 bridging unit is perfectly planar, owing to inversion symmetry. The average Fe-O (bridging) bond length is 1.982 Å, the Fe-Fe separation is 3.116 (1) Å, and the FeOFe angle is 103.6 (3°). The magnetic susceptibility of powdered samples of $Fe_2L(OC_2H_5)_2Cl_2$ has been examined in the temperature range 4-300 K. The compound exhibits an antiferromagnetic exchange interaction, with the best fit to the Van Vleck equation yielding $J = -15.40$ cm^{-1}, with $g = 2.00$ and TIP = 0. The data for the L^{2-} derivative are compared to those for the previously characterized $Fe_2L(OCH_3)_2Cl_2$, $J = -16.30$ cm^{-1}, and to those for $Fe_2(acac)_4(OC_2H_5)_2$, $J = -11.0$ cm^{-1}. Attempts to describe the relative magnetic properties of these compounds in terms of structural parameters or qualitative molecular orbital theory have been made.

Introduction

How the exchange coupling constants for dinuclear iron(III) compounds containing the Fe_2O_2 bridging system are influenced by variations in the geometrical and chemical features of the bridging and nonbridging ligands is not yet understood.[2-5]

In a recent paper[2] we have shown that, in qualitative agreement with predictions of MO theory[6] regarding the effect on *J* of variations in the electron density at the bridging atoms, a change in the bridging unit from Fe-OMe-Fe-OPh to Fe-OH-Fe-OPh, with no other structural change, brings about a decrease in the magnitude of the antiferromagnetic interaction. This datum seems to represent the strongest evidence so far available in support of the view[6] that exchange coupling problems presented by iron(III) systems can be analyzed with the same MO formalism as that which has been widely and successfully used to rationalize structure-magnetism correlations observed for exchange-coupled copper(II)[6] or chromium(III)[7,8] systems.

Continuing our efforts[2-4] to clarify the mechanism of spin-spin interaction in iron(III) compounds of the aforementioned type, we have now synthesized the bis(ethoxy)-bridged compound $Fe_2L(OC_2H_5)_2Cl_2$, where L^{2-} is the anion of the hexadentate Schiff base 1,4-piperazinediylbis(*N*-ethylenesalicylaldimine), and investigated its X-ray structure as well its magnetic properties down to 4.2 K.

In addition, we have determined the X-ray structure of $Fe_2(acac)_4(OC_2H_5)_2$ ($acac^-$ = 2,4-pentanedionato), also diethoxy-bridged, whose synthesis and magnetic behavior, between ca. 10 and 300 K, have been previously reported by other workers.[9]

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* To whom correspondence should be addressed at the Dipartimento di Chimica.

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