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Hexaaquadisodium Hexakis(tetramethylammonium) Bis[bis(3-acetylamino-4-hydroxyphenylarsonato)aquaoctadecaoxohexamolybdate] Decahydrate: $[Na_2(H_2O)_6][(CH_3)_4N]_6[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]_2.10H_2O$

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Abstract

Di-μ-aqua-tetraaquadisodium hexakis(tetramethylammonium) bis[μ_4-(3-acetylamino-4-hydroxyphenylarsonato)-1:2κ^2O,3$\kappa O'$,6$\kappa O''$-μ_6-(3-acetylamino-4-hydroxyphenylarsonato)-1:6κ^2O,2:3κ^2O',4:5κ^2O''-μ-aqua-4:5κ^2O-hexa-μ-oxo-1:2κ^2O;1:6κ^2O;2:3κ^2O;3:4κ^2O;4:5κ^2O;-5:6κ^2O-dodecaoxo-1κ^2O,O';2κ^2O,O';3κ^2O,O';4κ^2O,O';-5κ^2O,O';6κ^2O,O'-hexamolybdate decahydrate {dimer of $[Na(H_2O)_3][(CH_3)_4N]_3[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]$} has been crystallized. The unit cell contains two $[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]^{4-}$ complex anions linked by two Na^+ cations associated with six water molecules, six $[(CH_3)_4N]^+$ cations and another ten water molecules of hydration.

Comment

Polyoxomolybdates are oxo transfer catalysts, potential photosensitizers and electron relay species in the redox cycle. The synthesis, solution properties, and structure of a series of polymolybdate anions based on monoalkyl- and monoarylarsonates $(RAsO_3)^{2-}$ have been studied previously by Adams, Klemperer & Liu (1979), Zonnevijlle & Pope (1979), and You, Chen, Xu & Huang (1989).

The molecular structure consists of $[(CH_3)_4N]^+$ cations, $[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]^{4-}$ anions and Na^+ cations coordinated by water molecules and the carbonyls of the acetyl groups. The molybdate anions are linked by the $[Na_2(H_2O)_6]^{2+}$ cation *via* the carbonyl O atoms O(29) and O(29′) to form an $\{[Na_2(H_2O)_6][Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]_2\}^{6-}$ dimer lying on a centre of symmetry (Figs. 1 and 2).

The anion may be viewed as six distorted octahedra joined together by shared edges to form an approximately flat metal oxide ring, which is capped, top and bottom, by 3-acetylamino-4-hydroxyphenylarsonate ligands. The water molecule $H_2O(18)$ bridges the Mo atoms Mo(4) and Mo(5) in place of the arsonate O atoms O(14) and O(25), which only singly coordinate to Mo atoms Mo(3) and Mo(6), respectively [O(14)···Mo(4) = 4.342, O(25)···Mo(5) = 3.845 Å]. This results in the loss of the

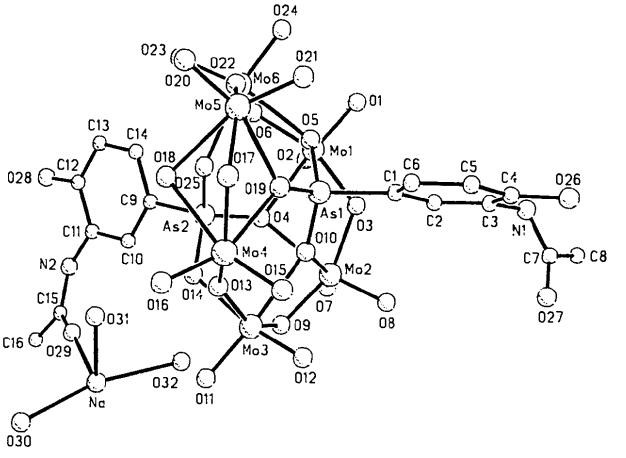

Fig. 1. Structure of the $[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]^{4-}$ anion.

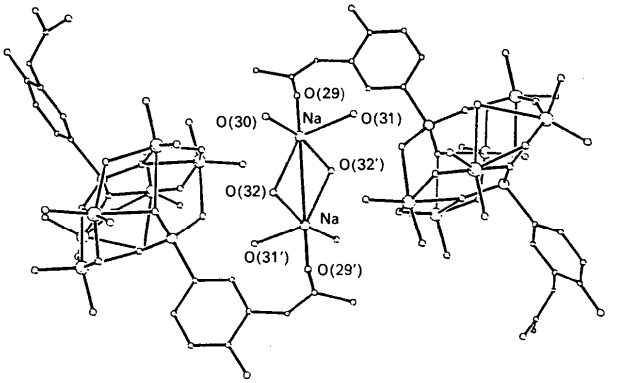

Fig. 2. View of the $\{[Na_2(H_2O)_6][Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]_2\}^{6-}$ dimer.

approximate D_{3d} symmetry of the anion. (The three O atoms of the other $RAsO_3$ group bridge two Mo atoms each.) The distances between the water molecule and the two Mo atoms are 2.506 (4) [O(18)—Mo(4)] and 2.502 (4) Å [O(18)—Mo(5)], longer than other Mo—O distances. O(30) and O(37) are water molecules. The average distances for Mo—O(terminal), Mo—O(doubly shared) and Mo—O(triply shared) bonds are 1.699 (4), 1.920 (3) and 2.314 (4) Å, respectively. The geometry around the As atoms is very close to tetrahedral with angles in the $RAsO_3$ group ranging from 106.5 (2) to 112.6 (2)°; the average As—C distance of 1.907 (5) Å and the average As—O distance of 1.686 (5) Å are consistent with values found in free organoarsonate.

Experimental

Crystal data

$[Na_2(H_2O)_6][(CH_3)_4N]_6$-$[Mo_6(C_8H_8AsNO_5)_2$-$O_{18}(H_2O)]_2.10H_2O$
M_r = 3634.70
Triclinic
$P\bar{1}$
a = 11.244 (3) Å
b = 12.775 (2) Å
c = 21.050 (5) Å
α = 97.26 (2)°
β = 103.03 (2)°
γ = 89.84 (2)°
V = 2921 (1) Å^3
Z = 1
D_x = 2.07 Mg m^{-3}
Mo radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3-12°
μ = 2.445 mm^{-1}
T = 295 K
Rectangular
Light yellow

Data collection

Nicolet $R3m/E$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none (Lorentz-polarization corrections were applied)
8324 measured reflections
8156 independent reflections
5165 observed reflections [$I \geq 3.0\sigma(I)$]
R_{int} = 0.0379
θ_{max} = 22.5°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -23 \rightarrow 23$
2 standard reflections monitored every 98 reflections
intensity variation: <1.5%

Refinement

Refinement on F (block-diagonal least squares)
Final R = 0.0380
wR = 0.0397
S = 1.365
5165 reflections
746 parameters
All H atoms calculated as idealized contributions (C—H = 0.96 Å)
$w = [\sigma^2(F) + 0.0004F^2]^{-1} \times \{1-\exp[-5(\sin\theta/\lambda)^2]\}$
$(\Delta/\sigma)_{max}$ = −0.140
$\Delta\rho_{max}$ = 0.994 e Å^{-3}
$\Delta\rho_{min}$ = −0.924 e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 0.00034
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Mo(1)	−0.1107 (1)	−0.2122 (1)	−0.1657 (1)	0.024 (1)
Mo(2)	0.0026 (1)	−0.4528 (1)	−0.1468 (1)	0.024 (1)
Mo(3)	0.2751 (1)	−0.4869 (1)	−0.1850 (1)	0.023 (1)
Mo(4)	0.3318 (1)	−0.3942 (1)	−0.3330 (1)	0.025 (1)
Mo(5)	0.1769 (1)	−0.1926 (1)	−0.3867 (1)	0.028 (1)
Mo(6)	0.0433 (1)	−0.0757 (1)	−0.2471 (1)	0.022 (1)
As(1)	0.0313 (1)	−0.3517 (1)	−0.2939 (1)	0.016 (1)
As(2)	0.2117 (1)	−0.2257 (1)	−0.1301 (1)	0.018 (1)
Na	0.5918 (3)	−0.3857 (2)	0.0065 (2)	0.053 (1)
N(1)	−0.3752 (5)	−0.5803 (3)	−0.3592 (2)	0.026 (1)
N(2)	0.4762 (5)	−0.0979 (3)	0.1118 (2)	0.029 (1)
N(3)	0.0332 (5)	0.2053 (4)	−0.3617 (2)	0.036 (1)
N(4)	−0.0758 (5)	0.1901 (4)	−0.0942 (2)	0.036 (1)
N(5)	0.3490 (6)	0.2019 (4)	−0.5528 (3)	0.058 (1)
O(1)	−0.2436 (5)	−0.1825 (3)	−0.2154 (2)	0.040 (1)
O(2)	−0.1370 (5)	−0.1891 (3)	−0.0889 (2)	0.038 (1)
O(3)	−0.1247 (4)	−0.3628 (3)	−0.1861 (2)	0.025 (1)
O(4)	0.0763 (4)	−0.2762 (2)	−0.1226 (2)	0.019 (1)
O(5)	−0.0342 (4)	−0.2406 (3)	−0.2686 (2)	0.020 (1)
O(6)	−0.0100 (4)	−0.0937 (3)	−0.1684 (2)	0.025 (1)
O(7)	−0.0266 (5)	−0.4501 (3)	−0.0710 (2)	0.041 (1)
O(8)	−0.0646 (5)	−0.5679 (3)	−0.1883 (2)	0.038 (1)
O(9)	0.1697 (4)	−0.4923 (3)	−0.1250 (2)	0.028 (1)
O(10)	0.0893 (4)	−0.4187 (3)	−0.2301 (2)	0.019 (1)
O(11)	0.4077 (4)	−0.5211 (3)	−0.1364 (2)	0.034 (1)
O(12)	0.2301 (4)	−0.5992 (3)	−0.2373 (2)	0.036 (1)
O(13)	0.3332 (4)	−0.4118 (3)	−0.2470 (2)	0.027 (1)
O(14)	0.3088 (4)	−0.3249 (3)	−0.1289 (2)	0.025 (1)
O(15)	0.2821 (5)	−0.5133 (3)	−0.3750 (2)	0.039 (1)
O(16)	0.4859 (5)	−0.3933 (4)	−0.3287 (2)	0.045 (1)
O(17)	0.2852 (4)	−0.3061 (3)	−0.4037 (2)	0.028 (1)
O(18)	0.3398 (4)	−0.2038 (3)	−0.2852 (2)	0.029 (1)
O(19)	0.1417 (4)	−0.3285 (2)	−0.3335 (2)	0.018 (1)
O(20)	0.2519 (5)	−0.0951 (4)	−0.4116 (2)	0.055 (1)
O(21)	0.0529 (5)	−0.2226 (3)	−0.4493 (2)	0.046 (1)
O(22)	0.1090 (4)	−0.1161 (3)	−0.3236 (2)	0.028 (1)
O(23)	0.1288 (4)	0.0369 (3)	−0.2169 (2)	0.033 (1)
O(24)	−0.0918 (4)	−0.0294 (3)	−0.2887 (2)	0.035 (1)
O(25)	0.1959 (4)	−0.1720 (3)	−0.2009 (2)	0.021 (1)
O(26)	−0.3503 (4)	−0.6331 (3)	−0.4866 (2)	0.038 (1)
O(27)	−0.3131 (6)	−0.7446 (4)	−0.3511 (3)	0.066 (1)
O(28)	0.4235 (4)	0.0989 (3)	0.1010 (2)	0.036 (1)
O(29)	0.5636 (5)	−0.2456 (3)	0.0765 (2)	0.048 (1)
O(30)	0.7969 (7)	−0.3908 (7)	0.0031 (4)	0.117 (1)
O(31)	0.5559 (5)	−0.3031 (3)	−0.0931 (2)	0.043 (1)
O(32)	0.3795 (5)	−0.4283 (3)	−0.0005 (2)	0.048 (1)
O(33)	−0.3645 (5)	−0.4246 (4)	−0.1960 (2)	0.050 (1)
O(34)	0.5360 (5)	−0.0629 (4)	−0.2446 (3)	0.049 (1)
O(35)	0.6374 (6)	−0.6150 (4)	−0.1336 (3)	0.069 (1)
O(36)	−0.3296 (6)	−0.9438 (4)	−0.3151 (3)	0.068 (1)
O(37)	0.4144 (9)	0.0656 (8)	0.3948 (6)	0.176 (1)
C(1)	−0.0904 (6)	−0.4381 (4)	−0.3555 (2)	0.021 (1)
C(2)	−0.1855 (6)	−0.4801 (4)	−0.3361 (2)	0.019 (1)
C(3)	−0.2729 (6)	−0.5434 (4)	−0.3804 (2)	0.023 (1)
C(4)	−0.2646 (6)	−0.5686 (4)	−0.4458 (2)	0.027 (1)
C(5)	−0.1682 (6)	−0.5257 (4)	−0.4654 (2)	0.027 (1)
C(6)	−0.0795 (6)	−0.4598 (4)	−0.4215 (2)	0.024 (1)
C(7)	−0.3876 (7)	−0.6757 (5)	−0.3417 (3)	0.042 (1)
C(8)	−0.4913 (8)	−0.6946 (6)	−0.3113 (4)	0.060 (1)
C(9)	0.2803 (6)	−0.1211 (4)	−0.0579 (2)	0.020 (1)
C(10)	0.3529 (6)	−0.1506 (4)	−0.0017 (2)	0.021 (1)
C(11)	0.4024 (6)	−0.0755 (4)	0.0514 (3)	0.022 (1)
C(12)	0.3757 (6)	0.0319 (4)	0.0472 (2)	0.024 (1)
C(13)	0.3023 (6)	0.0605 (4)	−0.0095 (3)	0.028 (1)
C(14)	0.2549 (6)	−0.0159 (4)	−0.0629 (2)	0.025 (1)
C(15)	0.5524 (6)	−0.1782 (4)	0.1212 (3)	0.032 (1)
C(16)	0.6213 (7)	−0.1806 (5)	0.1901 (3)	0.047 (1)
C(17)	0.0445 (8)	0.3054 (5)	−0.3894 (4)	0.069 (1)
C(18)	−0.0017 (7)	0.2292 (5)	−0.2970 (3)	0.052 (1)
C(19)	−0.0625 (8)	0.1342 (7)	−0.4065 (4)	0.082 (1)
C(20)	0.1528 (8)	0.1554 (7)	−0.3512 (4)	0.077 (1)

C(21)	−0.1740 (8)	0.1654 (7)	−0.1552 (4)	0.071 (1)
C(22)	−0.1080 (7)	0.2847 (5)	−0.0529 (3)	0.050 (1)
C(23)	−0.0606 (7)	0.0987 (5)	−0.0561 (3)	0.048 (1)
C(24)	0.0426 (8)	0.2135 (6)	−0.1124 (4)	0.059 (1)
C(25)	0.3564 (10)	0.2949 (8)	−0.5011 (6)	0.127 (1)
C(26)	0.3386 (11)	0.2340 (9)	−0.6189 (6)	0.139 (1)
C(27)	0.2466 (10)	0.1330 (9)	−0.5539 (6)	0.127 (1)
C(28)	0.4621 (11)	0.1461 (10)	−0.5402 (8)	0.162 (1)

Table 2. *Geometric parameters* (Å, °)

Mo(1)—O(1)	1.692 (4)	Mo(1)—O(2)	1.697 (4)
Mo(1)—O(3)	1.917 (3)	Mo(1)—O(4)	2.287 (4)
Mo(1)—O(5)	2.491 (4)	Mo(1)—O(6)	1.907 (4)
Mo(2)—O(3)	1.937 (4)	Mo(2)—O(4)	2.359 (3)
Mo(2)—O(7)	1.696 (4)	Mo(2)—O(8)	1.698 (4)
Mo(2)—O(9)	1.913 (5)	Mo(2)—O(10)	2.275 (4)
Mo(3)—O(9)	1.924 (5)	Mo(3)—O(10)	2.308 (4)
Mo(3)—O(11)	1.698 (4)	Mo(3)—O(12)	1.697 (3)
Mo(3)—O(13)	1.938 (4)	Mo(3)—O(14)	2.237 (3)
Mo(4)—O(13)	1.849 (4)	Mo(4)—O(15)	1.688 (4)
Mo(4)—O(16)	1.715 (6)	Mo(4)—O(17)	1.955 (4)
Mo(4)—O(18)	2.506 (4)	Mo(4)—O(19)	2.292 (4)
Mo(5)—O(17)	1.942 (4)	Mo(5)—O(18)	2.502 (4)
Mo(5)—O(19)	2.263 (3)	Mo(5)—O(20)	1.705 (5)
Mo(5)—O(21)	1.695 (4)	Mo(5)—O(22)	1.851 (4)
Mo(6)—O(5)	2.235 (3)	Mo(6)—O(6)	1.923 (4)
Mo(6)—O(22)	1.932 (4)	Mo(6)—O(23)	1.702 (4)
Mo(6)—O(24)	1.718 (4)	Mo(6)—O(25)	2.223 (4)
As(1)—O(5)	1.679 (4)	As(1)—O(10)	1.690 (3)
As(1)—O(19)	1.690 (4)	As(1)—C(1)	1.903 (5)
As(2)—O(4)	1.703 (4)	As(2)—O(14)	1.669 (4)
As(2)—O(25)	1.692 (3)	As(2)—C(9)	1.912 (4)
Na—O(29)	2.240 (5)	Na—O(30)	2.324 (9)
Na—O(31)	2.418 (5)	Na—O(32)	2.417 (7)
Na—Na′	3.527 (6)	Na—O(32′)	2.388 (5)
N(1)—C(3)	1.425 (9)	N(1)—C(7)	1.334 (8)
N(2)—C(11)	1.415 (6)	N(2)—C(15)	1.340 (8)
N(2)—H(*n*2)	0.939 (19)	N(3)—C(17)	1.488 (9)
N(3)—C(18)	1.494 (9)	N(3)—C(19)	1.485 (9)
N(3)—C(20)	1.470 (11)	N(4)—C(21)	1.493 (8)
N(4)—C(22)	1.491 (8)	N(4)—C(23)	1.487 (8)
N(4)—C(24)	1.506 (11)	N(5)—C(25)	1.495 (13)
N(5)—C(26)	1.481 (15)	N(5)—C(27)	1.445 (14)
N(5)—C(28)	1.444 (14)	O(26)—C(4)	1.341 (7)
O(26)—H(*o*26)	0.949 (24)	O(27)—C(7)	1.242 (9)
O(28)—C(12)	1.338 (6)	O(28)—H(*o*28)	0.913 (20)
O(29)—C(15)	1.221 (7)	C(1)—C(6)	1.414 (7)
C(1)—C(2)	1.361 (9)	C(2)—H(2)	0.970 (24)
C(2)—C(3)	1.374 (7)	C(4)—C(5)	1.381 (10)
C(3)—C(4)	1.398 (7)	C(5)—H(5)	1.014 (24)
C(5)—C(6)	1.397 (7)	C(7)—C(8)	1.484 (12)
C(6)—H(6)	0.974 (22)	C(9)—C(14)	1.386 (7)
C(9)—C(10)	1.372 (7)	C(10)—H(10)	1.032 (17)
C(10)—C(11)	1.389 (6)	C(12)—C(13)	1.378 (7)
C(11)—C(12)	1.413 (7)	C(13)—H(13)	0.966 (17)
C(13)—C(14)	1.399 (6)	C(15)—C(16)	1.486 (8)
C(14)—H(14)	0.964 (21)		
O(1)—Mo(1)—O(2)	104.1 (2)	O(1)—Mo(1)—O(3)	98.0 (2)
O(2)—Mo(1)—O(3)	103.8 (2)	O(1)—Mo(1)—O(4)	165.4 (2)
O(2)—Mo(1)—O(4)	89.5 (2)	O(3)—Mo(1)—O(4)	73.4 (1)
O(1)—Mo(1)—O(5)	84.9 (2)	O(2)—Mo(1)—O(5)	170.1 (2)
O(3)—Mo(1)—O(5)	78.6 (2)	O(4)—Mo(1)—O(5)	81.9 (1)
O(1)—Mo(1)—O(6)	101.0 (2)	O(2)—Mo(1)—O(6)	102.6 (2)
O(3)—Mo(1)—O(6)	142.4 (2)	O(4)—Mo(1)—O(6)	80.6 (2)
O(5)—Mo(1)—O(6)	71.2 (1)	O(3)—Mo(2)—O(4)	71.4 (1)
O(3)—Mo(2)—O(7)	100.2 (2)	O(4)—Mo(2)—O(7)	91.4 (2)
O(3)—Mo(2)—O(8)	95.8 (2)	O(4)—Mo(2)—O(8)	161.9 (2)
O(7)—Mo(2)—O(8)	103.8 (2)	O(3)—Mo(2)—O(9)	151.7 (2)
O(4)—Mo(2)—O(9)	86.7 (2)	O(7)—Mo(2)—O(9)	97.9 (2)
O(8)—Mo(2)—O(9)	100.8 (2)	O(3)—Mo(2)—O(10)	83.9 (2)
O(4)—Mo(2)—O(10)	72.8 (1)	O(7)—Mo(2)—O(10)	161.6 (2)
O(8)—Mo(2)—O(10)	93.5 (2)	O(9)—Mo(2)—O(10)	72.4 (2)
O(9)—Mo(3)—O(10)	71.5 (2)	O(9)—Mo(3)—O(11)	99.1 (2)
O(10)—Mo(3)—O(11)	167.4 (2)	O(9)—Mo(3)—O(12)	100.9 (2)
O(10)—Mo(3)—O(12)	87.3 (2)	O(11)—Mo(3)—O(12)	103.0 (2)
O(9)—Mo(3)—O(13)	148.9 (2)	O(10)—Mo(3)—O(13)	83.7 (2)
O(11)—Mo(3)—O(13)	102.0 (2)	O(12)—Mo(3)—O(13)	96.3 (2)
O(9)—Mo(3)—O(14)	79.6 (2)	O(10)—Mo(3)—O(14)	83.0 (1)
O(11)—Mo(3)—O(14)	87.1 (2)	O(12)—Mo(3)—O(14)	169.6 (2)
O(13)—Mo(3)—O(14)	78.9 (1)	O(13)—Mo(4)—O(15)	103.2 (2)
O(13)—Mo(4)—O(16)	99.4 (2)	O(15)—Mo(4)—O(16)	103.9 (2)
O(13)—Mo(4)—O(17)	147.1 (2)	O(15)—Mo(4)—O(17)	99.7 (2)
O(16)—Mo(4)—O(17)	97.6 (2)	O(13)—Mo(4)—O(18)	81.2 (1)
O(15)—Mo(4)—O(18)	162.55 (2)	O(16)—Mo(4)—O(18)	91.8 (2)
O(17)—Mo(4)—O(18)	70.3 (1)	O(13)—Mo(4)—O(19)	84.1 (2)
O(15)—Mo(4)—O(19)	96.0 (2)	O(16)—Mo(4)—O(19)	158.3 (2)
O(17)—Mo(4)—O(19)	70.3 (2)	O(18)—Mo(4)—O(19)	67.4 (1)
O(17)—Mo(5)—O(18)	70.6 (1)	O(17)—Mo(5)—O(19)	71.2 (2)
O(18)—Mo(5)—O(19)	67.9 (1)	O(17)—Mo(5)—O(20)	97.3 (2)
O(18)—Mo(5)—O(20)	93.8 (2)	O(19)—Mo(5)—O(20)	160.6 (2)
O(17)—Mo(5)—O(21)	101.9 (2)	O(18)—Mo(5)—O(21)	161.5 (2)
O(19)—Mo(5)—O(21)	93.8 (2)	O(20)—Mo(5)—O(21)	104.1 (2)
O(17)—Mo(5)—O(22)	145.2 (2)	O(18)—Mo(5)—O(22)	79.0 (2)
O(19)—Mo(5)—O(22)	82.3 (1)	O(20)—Mo(5)—O(22)	101.1 (2)
O(21)—Mo(5)—O(22)	101.8 (2)	O(5)—Mo(6)—O(6)	77.2 (1)
O(5)—Mo(6)—O(22)	83.7 (2)	O(6)—Mo(6)—O(22)	157.1 (1)
O(5)—Mo(6)—O(23)	165.9 (2)	O(6)—Mo(6)—O(23)	97.3 (2)
O(22)—Mo(6)—O(23)	98.3 (2)	O(5)—Mo(6)—O(24)	90.6 (2)
O(6)—Mo(6)—O(24)	96.5 (2)	O(22)—Mo(6)—O(24)	96.1 (2)
O(23)—Mo(6)—O(24)	102.9 (2)	O(5)—Mo(6)—O(25)	76.0 (1)
O(6)—Mo(6)—O(25)	81.3 (2)	O(22)—Mo(6)—O(25)	81.9 (1)
O(23)—Mo(6)—O(25)	90.5 (2)	O(24)—Mo(6)—O(25)	166.6 (2)
O(5)—As(1)—O(10)	111.0 (2)	O(5)—As(1)—O(19)	112.6 (2)
O(10)—As(1)—O(19)	109.7 (2)	O(5)—As(1)—C(1)	108.2 (2)
O(10)—As(1)—C(1)	108.8 (2)	O(19)—As(1)—C(1)	106.5 (2)
O(4)—As(2)—O(14)	107.2 (2)	O(4)—As(2)—O(25)	111.4 (2)
O(14)—As(2)—O(25)	110.1 (2)	O(4)—As(2)—C(9)	111.9 (2)
O(14)—As(2)—C(9)	107.4 (2)	O(25)—As(2)—C(9)	108.8 (2)
O(29)—Na—O(30)	108.9 (3)	O(29)—Na—O(31)	98.6 (2)
O(30)—Na—O(31)	87.6 (3)	O(29)—Na—O(32)	85.0 (2)
O(30)—Na—O(32)	165.2 (2)	O(31)—Na—O(32)	95.7 (2)
O(29)—Na—Na′	118.0 (2)	O(30)—Na—Na′	123.2 (2)
O(31)—Na—Na′	113.6 (2)	O(32)—Na—Na′	42.5 (1)
O(29)—Na—O(32′)	141.4 (2)	O(30)—Na—O(32′)	80.2 (3)
O(31)—Na—O(32′)	119.5 (2)	O(32)—Na—O(32′)	85.6 (2)

The title compound was prepared as follows: a solution of sodium molybdate (10.9 g, 0.045 mol) and 4-hydroxy-3-acetylarsanilic acid (3.7 g, 0.013 mol) in 100 ml of water was adjusted to pH 4.7 with dilute sulfuric acid; after the solution had been boiled for 20 min, tetramethylammonium chloride (6.6 g, 0.06 mol) was dissolved in the warm solution; the pH of the resulting solution was adjusted to 4.7 with dilute sulfuric acid, then the solution was boiled for a further 10 min; the hot solution was filtered and allowed to evaporate at room temperature, yielding a large number of well shaped light-yellow crystals within a few days. Analysis calculated for $[Na_2(H_2O)_6]$ $[(CH_3)_4N]_6[Mo_6(C_8H_8AsNO_5)_2O_{18}(H_2O)]_2 \cdot 10H_2O$: C 18.50, H 3.88, N 3.85, Mo 31.7, As 8.2, Na 1.3%. Analysis found: C 18.31, H 3.44, N 4.11, Mo 32.0, As 7.9, Na 1.3%. The structure was solved by Patterson methods; all non-H atoms were located by direct methods and difference Fourier synthesis. All calculations were performed using *SHELXTL* (Sheldrick, 1985) on an Eclipse S/140 computer.

A computer output including lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry and difference map data, has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55828 (76 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1006]

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Structures of Hexachloroniobate(V) Salts of the 1-Methylimidazole/1-Methylimidazolium and 2-Methylimidazolium Cations

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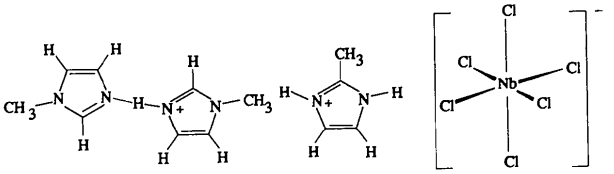
Abstract

Both salts contain approximately octahedral $[NbCl_6]^-$ anions with Nb—Cl bond lengths ranging from 2.326 (2) to 2.378 (2) Å. The 1-methylimidazole salt (I) contains the proton-bridged 1-methylimidazole/1-methylimidazolium cation, whereas the fully N-protonated 2-methylimidazolium ion is present in the 2-methylimidazole compound (II). Cohesion in the crystals is achieved by dipolar interactions between Cl atoms of $[NbCl_6]^-$ and imidazole C—H groups for (I) and (II), as well as N—H···Cl hydrogen bonds for (II).

Comment

The reactions of $NbCl_5$ with N-heterocycles are currently being investigated in this laboratory. Two reaction pathways have been identified with pyridine (McCarley, Hughes, Boatman & Torp, 1963) and 7-azaindole (Poitras & Beauchamp, 1992), namely the formation of Nb^V adducts $NbCl_5(L)$ and the reduction to Nb^{IV} with concomitant ligand oxidation. The two title compounds, (I) $[(1\text{-MeIm})_2H][NbCl_6]$ and (II) [2-MeImH][$NbCl_6$], were among the products isolated from the reactions with 1-methylimidazole (1-MeIm) and 2-methylimidazole (2-MeIm). An X-ray investigation was undertaken in order to explain their different stoichiometries despite very similar chemical properties.



These compounds were present in the filtrates from reactions of $NbCl_5$ (~1 g) with the imidazole ligand in a 2:7 ratio in ~50 ml of benzene (I) or toluene (II). The reactions were run under a dry argon atmosphere in a Schlenk system, from $NbCl_5$ (Aldrich, stored in glove box) and 1-MeIm (Aldrich, dried over molecular sieves) or 2-MeIm (Aldrich, sublimed). Solvents were dried by distillation over Na. Red crystals of the 1-MeIm compound (I) appeared after two weeks in the benzene filtrate. Brown crystals of the 2-MeIm compound (II) were isolated after two months from the toluene filtrate. Both compounds are extremely moisture sensitive.

The single $[NbCl_6]^-$ anion in (I) occupies the inversion center at the cell origin. In (II), the eight anions are distributed over equipoints 4(*e*) [Nb(1), twofold axis] and 4(*c*) [Nb(2), inversion center]. These three independent $[NbCl_6]^-$ anions have a nearly octahedral geometry. The octahedron is very regular for the two types of anions sitting on inversion centers: the *cis* Cl—Nb—Cl angles are in the region of 90.0 (5)°, whereas the *trans* angles are 180° by symmetry. The anion lying on a twofold axis [Nb(1) of (II)] is slightly more distorted, with *cis* angles ranging from 87.80 (6) to 91.98 (6)° and *trans* angles of 177.55 (6) and 177.46 (6)°. The Nb—Cl distances, ranging from 2.326 (2) to 2.378 (2) Å (mean 2.349 Å), compare well with literature values (Hubert-Pfalzgraf, Postel & Riess, 1987; von Dübgen, Müller, Weller & Dehnicke, 1980; Preiss, 1971; Preiss & Reich, 1971; Shibaeva & Lobkovskaya, 1985).

Compound (I) contains the 1-methylimidazole/1-methylimidazolium cation shown in Fig. 1. The two nearly coplanar 1-MeIm units are related by an inversion center. The bridging H(3) proton, whose position was deduced from a ΔF map, is disordered over two sites slightly off the inversion center. Thus, each of the imidazole units about the inversion center actually corresponds to equal populations of the neutral and monocationic forms. Attempts to refine a non-disordered model in space group $P\bar{1}$