Crystal structure of tris(piperazinium) hexakis[(μ_3-oxo)(μ_2-oxo)-dioxotungsten]tellurate(VI) hexahydrate, $[C_4H_{12}N_2]_3[TeW_6O_{24}] \cdot 6H_2O$

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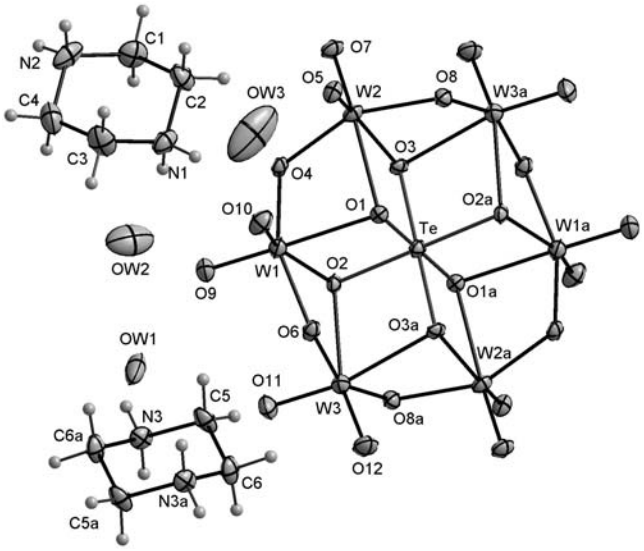

Abstract

$C_{12}H_{48}N_6O_{30}TeW_6$, monoclinic, $P2_1/n$ (no. 14), a = 9.486(2) Å, b = 11.709(2) Å, c = 17.242(3) Å, β = 100.37(3)°, V = 1883.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.046, T = 566 K.

Source of material

Hydrothermal reactions were carried out in 23 ml Teflon-lined stainless steel vessels at 150 °C for 2 d. Piperazine (0.086 g, 1.0 mmol), telluric acid (0.690 g, 3.0 mmol), WO_3 (0.696 g, 3 mmol) and H_2O (3 ml) were allowed to react. The pH values of the reaction mixture before and after the reaction were ~9 and ~7, respectively. The solid products were recovered by vacuum filtration and washed with water. Colorless polyhedral crystals suitable for X-ray analysis were obtained.

Experimental details

Hydrogen atoms associated with the piperazinium cations were placed geometrically and refined as riding. The hydrogen atoms of lattice water molecules were not located because of the large displacement parameters of oxygen atoms.

Discussion

The crystal structure of the title compound comprises discrete centrosymmetric heteronuclear $[TeW_6O_{24}]^{6-}$ anions, doubly protonated piperazinium cations and lattice water molecules. The Anderson-Evans type $[TeW_6O_{24}]^{6-}$ cluster anions is formed by close packing of oxygen atoms with tellurium and tungsten atoms in octahedral sites. The Te atom occupying the inversion center is coordinated by oxygen atoms in a nearly regular octahedral manner with a distances of 1.916(4) - 1.930(3) Å and the angles of 84.9(2)° - 95.1(2)° and 180°. The TeO_6 octahedron is condenced with six WO_6 octahedra by sharing its faces. Three crystallographically unique WO_6 octahedra are severely distorted and contain two short, two long, and two intermediate bond lengths. Each pair of short, intermediate and long bonds are in *cis*-configuration to each other and involve terminal, μ_2- and μ_3-oxygen atoms, respectively. The bond distances are similar to those in other tungstotellurate anions [1-4].

The crystal packing of the title complex is stabilized by extensive hydrogen bonds between the $[TeW_6O_{24}]^{6-}$ anions and piperazinium cations in the range of d(N···O) = 2.7941(4) - 2.9309(5) Å. In addition, three unique lattice water molecules are hydrogen bonded to $[TeW_6O_{24}]^{6-}$ anions, piperazinium cations or to each other in a complex arrangement.

Table 1. Data collection and handling.

Crystal:	colorless polyhedron, size 0.16 × 0.21 × 0.23 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	191.13 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID,
$2\theta_{max}$:	54.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17913, 4310
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3939
$N(param)_{refined}$:	251
Programs:	SHELXS-97, SHELXL-97 [5], DIAMOND [6]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	0.6493	0.0220	0.1878	0.039
H(1B)	4*e*	0.5047	–0.0143	0.1532	0.039
H(2A)	4*e*	0.3611	0.1665	0.2940	0.047
H(2B)	4*e*	0.2265	0.1205	0.2518	0.047
H(3A)	4*e*	0.6687	0.5306	0.0675	0.031
H(3B)	4*e*	0.7225	0.4281	0.0349	0.031
H(1C)	4*e*	0.3295	0.2424	0.1729	0.045
H(1D)	4*e*	0.3012	0.1205	0.1357	0.045
H(2C)	4*e*	0.5314	0.1750	0.1257	0.044
H(2D)	4*e*	0.5686	0.1987	0.2169	0.044
H(3C)	4*e*	0.5874	0.0394	0.3106	0.055
H(3D)	4*e*	0.5629	–0.0864	0.2792	0.055

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(4A)	4*e*	0.3215	–0.0511	0.2363	0.056
H(4B)	4*e*	0.3604	–0.0184	0.3259	0.056
H(5A)	4*e*	0.5534	0.3798	0.1086	0.037
H(5B)	4*e*	0.5073	0.3402	0.0207	0.037
H(6A)	4*e*	0.5911	0.4603	–0.0857	0.037
H(6B)	4*e*	0.6854	0.5683	–0.0586	0.037

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	4*e*	–0.06078(2)	–0.08669(2)	0.17118(1)	0.0172(1)	0.0203(1)	0.0172(1)	0.00158(8)	0.00638(9)	0.00156(9)
W(2)	4*e*	–0.06380(2)	0.18681(2)	0.13026(1)	0.0130(1)	0.0178(1)	0.0178(1)	0.00248(8)	0.00410(8)	–0.00186(8)
W(3)	4*e*	–0.00588(2)	–0.27569(2)	0.03743(1)	0.0174(1)	0.0155(1)	0.0224(1)	0.00042(8)	0.00708(9)	0.00132(9)
Te	2*a*	0	0	0	0.0111(2)	0.0147(2)	0.0151(2)	0.0004(2)	0.0040(2)	–0.0007(2)
N(1)	4*e*	0.5561(5)	0.0299(5)	0.1907(3)	0.021(2)	0.041(3)	0.038(4)	0.000(2)	0.007(2)	–0.010(3)
N(2)	4*e*	0.3221(5)	0.1194(5)	0.2547(4)	0.015(2)	0.055(4)	0.046(4)	0.002(2)	0.002(2)	–0.022(3)
N(3)	4*e*	0.6452(5)	0.4735(4)	0.0326(3)	0.015(2)	0.028(3)	0.033(3)	0.003(2)	0.001(2)	0.002(2)
C(1)	4*e*	0.3565(7)	0.1626(6)	0.1792(5)	0.023(3)	0.041(4)	0.043(4)	0.007(3)	–0.003(3)	0.003(3)
C(2)	4*e*	0.5130(7)	0.1507(6)	0.1767(5)	0.029(3)	0.033(3)	0.049(5)	–0.006(3)	0.007(3)	0.006(3)
C(3)	4*e*	0.5319(7)	–0.0079(7)	0.2700(5)	0.035(4)	0.045(4)	0.055(5)	0.007(3)	0.003(4)	0.019(4)
C(4)	4*e*	0.3754(8)	0.0020(7)	0.2735(5)	0.049(4)	0.053(5)	0.042(5)	–0.014(4)	0.017(4)	0.008(4)
C(5)	4*e*	0.5263(6)	0.4065(5)	0.0547(4)	0.025(3)	0.027(3)	0.037(4)	0.001(2)	–0.001(3)	0.015(3)
C(6)	4*e*	0.6068(6)	0.5218(6)	–0.0474(4)	0.017(3)	0.039(4)	0.037(4)	–0.001(3)	0.007(3)	0.009(3)
O(1)	4*e*	0.0698(4)	0.0305(3)	0.1094(2)	0.015(2)	0.017(2)	0.014(2)	0.001(1)	0.002(2)	0.000(2)
O(2)	4*e*	–0.1245(4)	–0.1084(3)	0.0382(2)	0.015(2)	0.021(2)	0.019(2)	–0.004(2)	0.008(2)	–0.000(2)
O(3)	4*e*	–0.1243(4)	0.1293(3)	0.0048(2)	0.012(2)	0.016(2)	0.023(2)	0.004(1)	0.004(2)	–0.001(2)
O(4)	4*e*	–0.1707(4)	0.0539(3)	0.1530(2)	0.012(2)	0.022(2)	0.022(2)	0.003(2)	0.006(2)	0.002(2)
O(5)	4*e*	0.0387(4)	0.2062(3)	0.2239(2)	0.020(2)	0.029(2)	0.021(2)	–0.001(2)	0.007(2)	–0.002(2)
O(6)	4*e*	0.0584(4)	–0.2072(3)	0.1414(2)	0.018(2)	0.024(2)	0.019(2)	0.005(2)	0.005(2)	0.003(2)
O(7)	4*e*	–0.2006(4)	0.2852(3)	0.1227(3)	0.020(2)	0.026(2)	0.031(3)	0.007(2)	0.008(2)	–0.003(2)
O(8)	4*e*	0.0642(4)	0.2672(3)	0.0743(2)	0.020(2)	0.019(2)	0.023(2)	–0.001(2)	0.006(2)	–0.002(2)
O(9)	4*e*	–0.2050(5)	–0.1661(4)	0.1897(3)	0.032(2)	0.028(2)	0.038(3)	–0.002(2)	0.018(2)	0.006(2)
O(10)	4*e*	0.0417(5)	–0.0585(4)	0.2618(3)	0.031(2)	0.040(3)	0.023(2)	0.006(2)	0.005(2)	–0.001(2)
O(11)	4*e*	–0.1449(5)	–0.3566(4)	0.0593(3)	0.039(2)	0.031(2)	0.038(3)	–0.013(2)	0.019(2)	–0.002(2)
O(12)	4*e*	0.1385(5)	–0.3680(4)	0.0448(3)	0.037(2)	0.027(2)	0.036(3)	0.012(2)	0.011(2)	0.002(2)
OW(1)	4*e*	–0.3567(7)	–0.3715(5)	0.1609(4)	0.074(4)	0.067(4)	0.058(4)	–0.038(3)	0.048(3)	–0.035(3)
OW(2)	4*e*	0.3939(6)	–0.1518(6)	0.1067(5)	0.044(3)	0.071(4)	0.114(6)	–0.004(3)	–0.013(4)	–0.040(4)
OW(3)	4*e*	–0.4238(7)	–0.105(1)	0.0003(5)	0.031(3)	0.23(1)	0.100(7)	0.009(5)	–0.007(4)	–0.065(7)

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