Crystal structure of diammonium hexaaquazinc(II) bis[(μ_{12}-molybdato)-tetracosa(μ_2-oxo)-dodecaoxo-dodecatungsten] — ammonia — water (1:4:36), $[NH_4]_2[Zn(H_2O)_6][(MoW_{12}O_{40})_2] \cdot 4NH_3 \cdot 36H_2O$

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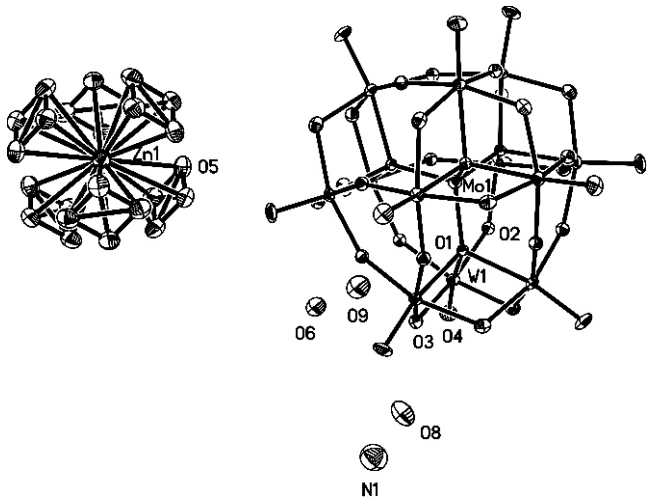

Abstract

$H_{104}Mo_2N_6O_{122}W_{24}Zn$, cubic, $Fm\bar{3}m$ (no. 225), a = 22.540(2) Å, V = 11452(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.126, T = 298 K.

Source of material

A mixture of $Zn(Ac)_2$ (0.1 mmol, 0.021 g), diphenylamine (0.1 mmol, 0.017 g), $(NH_4)_2MoO_4$ (0.1 mmol, 0.03 g), and $(NH_4)_2WO_4$ (0.1 mmol, 0.037 g) were added into 20 mL water with 20 % (v/v) ethanol and heated for 10 h at 313 K with stirring. The solution was obtained by filtration after cooling the reaction mixture to room temperature. Colorless block-shaped single crystals suitable for X-ray diffraction experiments were obtained after a few weeks.

Experimental details

The H atoms were generated geometrically and refined using a riding model, with d(N—H) and d(O—H) of 0.85 - 0.90 Å, and U_{iso}(H) = 1.2 - 1.5 U_{eq}(N,O).

Discussion

Keggin-type polyoxometalates $[XM_{12}O_{40}]^{n-}$ (X = B, P, Si, etc.; M = Mo, W) and their derivatives have been investigated for over a century because of their rich structural chemistry and diverse physicochemical properties [1]. Of the wide applications of Keggin anions, potential activities as catalysts attract special attention [2-5]. Recently, several successful strategies have been developed to design materials based on POMs. In the field of modified POMs, more attention has been paid to polyoxoanion-supported transition metal complexes, especially POMs containing Cu and Fe are of interest for their magnetic properties.

The crystal structure of the title compound consists of the Keggin anion, $[Zn(H_2O)_6]^{2+}$ and ammonium cations, lattice water and ammonia molecules. A regular tetrahedron is formed by four O1 atoms and a Mo atom at the center of the anion group. Mo and W atoms are interlinked by O1 atoms. Each O1 atom is connected to three W atoms. W atoms are coordinated by six O atoms to form a distorted octahedron. Two O2 atoms and two O3 atoms are located in the equatorial plane. Four of six O atoms bridge the neighboring W atoms. The bonds lengths are d(W1—O1) = 2.16(1) Å and d(W1—O4) = 1.77(2) Å. The bond angles of O1–Mo1–O1, O2–W1–O3 are 109.5(1)° and 162.2(6)°, respectively. The distance from W1 atom to the equatorial plane (formed by O2 and O3) is 0.30 Å. The O4 atom is a terminating atom. Mo and W atoms form a cage-like structure with Mo atom being the center, and W atoms rowing outside. There are intermolecular hydrogen bonds in the complex. The lattice NH_3 and H_2O molecules are connected to anions and cations by hydrogen bonds. The Zn atom is coordinated by O atoms of water molecules. There is a hydrogen bond at atom O7 but not at atom O8. A stable three-dimensional network structure is formed by the help of the O–H···O and O–H···N intermolecular hydrogen bonds.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.09 × 0.10 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	245.34 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.06°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11936, 568
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 488
$N(param)_{refined}$:	56
Programs:	SHELXS-97, SHELXL-97, SHELXTL [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	192*l*	0.17	0.4695	0.4806	0.7752	0.051
H(1B)	24*e*		½	½	0.8235	0.051
H(1C)	96*i*	0.25	½	0.5336	0.7688	0.051
H(5)	192*l*	0.25	0.4408	0.4844	0.1001	0.039
H(6)	96*k*	0.50	0.2343	0.5305	0.7343	0.063
H(7)	96*k*		0.3584	0.4694	0.8584	0.020
H(8C)	192*l*	0.25	0.1723	0.4772	0.8685	0.086
H(8D)	48*i*		0.1175	½	0.8825	0.086
H(9C)	96*j*	0.50	0.0273	½	0.9300	0.097

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(1)	96*k*		0.25708(4)	0.36025(3)	½+*y*	0.0247(6)	0.0198(5)	U_{22}	0.0004(2)	U_{12}	–0.0053(3)
Mo(1)	8*c*		¼	¼	¾	0.025(2)	U_{11}	U_{11}	0	0	0
Zn(1)	4*a*		½	½	0	0.030(3)	U_{11}	U_{11}	0	0	0
N(1)	24*e*		½	½	0.786(2)	0.04(2)	U_{11}	0.05(3)	0	0	0
O(1)	32*f*		0.2993(6)	*x*	½+*x*	0.021(5)	U_{11}	U_{11}	–0.001(6)	U_{12}	U_{12}
O(2)	96*k*		0.2018(4)	½–*x*	0.8803(6)	0.023(5)	U_{11}	0.023(7)	0.000(6)	0.001(4)	–0.001(4)
O(3)	96*k*		0.3194(5)	0.4066(7)	½+*x*	0.033(5)	0.029(8)	U_{11}	0.000(5)	–0.004(7)	U_{12}
O(4)	96*k*		0.2385(7)	0.4142(5)	½+*y*	0.05(1)	0.033(6)	U_{22}	0.000(5)	U_{12}	–0.012(8)
O(5)	96*k*	0.25	0.475(2)	*x*	0.088(3)	0.03(2)	U_{11}	U_{11}	0.00(2)	U_{12}	U_{12}
O(6)	24*d*		¼	½	¾	0.05(2)	0.05(3)	U_{11}	0	0.00(2)	0
O(7)	48*h*		0.3741(9)	½	½+*x*	0.05(1)	0.04(2)	U_{11}	0	0.01(1)	0
O(8)	48*i*		0.146(1)	½	1–*x*	0.07(1)	0.07(2)	U_{11}	0	0.00(2)	0
O(9)	48*i*	0.50	0.065(2)	½	1–*x*	0.08(3)	0.08(5)	U_{11}	0	0.00(4)	0

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