Crystal structure of bis[hexaaqua-copper(II)] dodecatungstate-germanate hexahydrate, $[\{Cu(H_2O)_6\}_2]GeW_{12}O_{40} \cdot 6H_2O$

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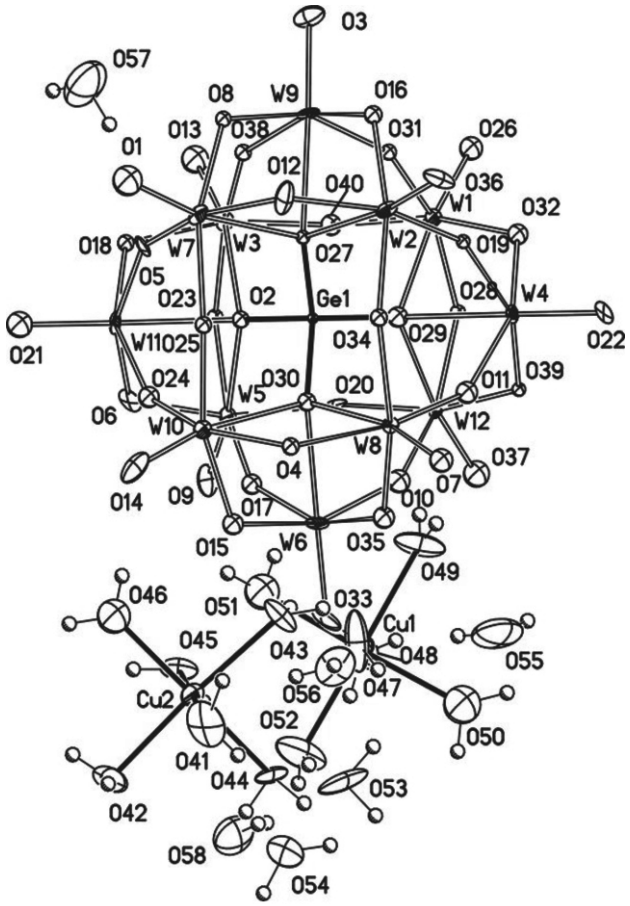

Abstract

$Cu_2GeO_{58}H_{36}W_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 13.114(3) Å, b = 13.799(3) Å, c = 14.033(3) Å, α = 90.23(3)°, β = 104.05(3)°, γ = 107.63(3)°, V = 2339.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.065, $wR_{ref}(F^2)$ = 0.161, T = 293 K.

Source of material

$CuSO_4 \cdot 5H_2O$ (0.2509 g, 1.00 mmol) was dissolved in appropriate amount of water and then 1M NaOH solution was added. $Cu(OH)_2$ was separated by filtration, then washed with distilled water 5 times. The freshly prepared $Cu(OH)_2$, 4-bromobenzoic acid (0.2456 g, 1.22 mmol), $H_4GeW_{12}O_{40} \cdot nH_2O$ (1.2395 g, 0.40 mmol), CH_3OH/H_2O (v/v = 1:2, 15 ml) were mixed and stirred for 2 h. Subsequently, the resulting suspension was heated in a 23 ml Teflon-lined stainless steel autoclave at 433 K for 5800 minutes. After the autoclave was cooled to room temperature in 2600 minutes, the solid was filtered off. The resulting filtrate was allowed to stand at room temperature, and the slow evaporation for 8 weeks afforded light-blue block-shaped single crystals.

Experimental details

For a tungstens cluster, *R*-values are expected to be high. They markedly mend when W1 and W10 atoms are refined as disordered over two sites with occupancy factors of 0.60 and 0.40. These positions and all O atoms were refined in isotropic approximation of atomic displacement. The largest peak in the final difference Fourier map is 0.59 Å from atom W10 and the deepest hole is 0.92 Å from atom W9.

Discussion

The crystal structure of the title compound is similar to the structure of a novel Keggin units-supported complex $[(CH_3)_2NH_2]_6[Cu(DMF)_4(GeW_{12}O_{40})_2] \cdot 2DMF$ [1], metal-oxo transition metal complex $[\{Cu(phen)_2\}_2SiW_{12}O_{40}]$ [2], bis[bis((1,10-phenanthroline-*N*,*N'*)-copper(I)]μ_6-oxido-dodecakis-μ_2-oxidohexaoxidohexatungsten(VI) [3]. It consists of two $[Cu(H_2O)_6]^{2+}$ cations, one $[GeW_{12}O_{40}]^{4-}$ polyanion and lattice water molecules. The $[GeW_{12}O_{40}]^{4-}$ anion consists of twelve WO_6 octahedra and one GeO_4 tetrahedron. For the latter, d(Ge—O) varies from 1.71(2) to 1.75(1) Å with an average of 1.73 Å, 0.01 Å shorter than in a previous report [1]. The average ∠O–Ge–O of 109.47° is 0.12° larger than that in [1]. The GeO_4 tetrahedron shares its oxygen atoms with four $\{W_3O_{13}\}$ groups, each of which is made up of three edge-sharing WO_6 octahedra. W_3O_{13} subunits are joined by corner sharing. Oxygen atoms in $[GeW_{12}O_{40}]^{4-}$ can be divided into four groups according to their coordination number; terminal oxygen atoms O_t connect to one W atom, O_b atoms share corners between twe W_3O_{13} unit, O_c atoms interconnect edge-sharing WO_6 octahedra in the same W_3O_{13} unit and O_a atoms connect the Ge and three W atoms. Relevant d(W—O) in the anion can be classified into three groups: d(W—O_t) = 1.68(2) - 1.74(2) Å, mean 1.70 Å, d(W—$O_{b,c}$) = 1.87(2) - 1.97 Å, and d(W—O_a) = 2.28(2) - 2.33(2) Å, mean 2.30 Å. In the $[Cu(H_2O)_6]^{2+}$ cations, each Cu(II) is coordinated by six H_2O molecules to a distorted CuO_6 octahedral environment. In the octahedron, all adjacaent bond angels are between 88.3(7)° and 93.5(9)°, and opposite angles range from 176.0(8) - 178.4(9)°, close to ideal octahedral values (90° and 180°). Moreover, the $[Cu(H_2O)_6]^{2+}$ cations, $[GeW_{12}O_{40}]^{4-}$ anions are connected to each other by hydrogen bonds between the coordinated water molecules, lattice water molecules and dodecatungstate-germanate clusters with d(O–H···O) = 2.771 - 3.402 Å, ∠(O–H···O) = 113.6 - 177.6°. Through the hydrogen interactions, the compounds are interlinked to a 3D network.

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Table 1. Data collection and handling.

Crystal:	light-blue block, size 0.240 × 0.350 × 0.360 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	310.19 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18588, 8215
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7212
$N(param)_{refined}$:	360
Program:	SHELXS-97 [4]

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

Atom	Site	Occ.	x	y	z	U_{iso}
Ge(1)	2*i*		0.0137(2)	0.2538(1)	0.2613(1)	0.0025(4)
W(1)	2*i*	0.60	0.0007(2)	–0.0030(1)	0.2998(1)	0.0013(2)
W(1')	2*i*	0.40	–0.0004(2)	0.0005(2)	0.3164(2)	0.0013(2)
W(10)	2*i*	0.60	0.0499(2)	0.5153(1)	0.2287(1)	0.0022(2)
W(10')	2*i*	0.40	0.0460(2)	0.5105(2)	0.2109(2)	0.0022(2)
O(1)	2*i*		–0.272(1)	0.353(1)	–0.019(1)	0.019(3)
O(2)	2*i*		–0.069(1)	0.2554(9)	0.3399(9)	0.007(3)
O(3)	2*i*		–0.307(1)	–0.049(1)	0.048(1)	0.019(3)
O(4)	2*i*		0.165(1)	0.5181(9)	0.1592(8)	0.007(3)
O(5)	2*i*		–0.218(1)	0.314(1)	0.1818(9)	0.010(3)
O(6)	2*i*		–0.103(1)	0.374(1)	0.4572(9)	0.012(3)
O(7)	2*i*		0.335(1)	0.463(1)	0.1155(9)	0.014(3)
O(8)	2*i*		–0.266(1)	0.1614(9)	0.0413(9)	0.007(3)
O(9)	2*i*		0.033(1)	0.332(1)	0.629(1)	0.016(3)
O(10)	2*i*		0.257(1)	0.3269(9)	0.4308(9)	0.008(3)
O(11)	2*i*		0.259(1)	0.287(1)	0.2131(9)	0.013(3)
O(12)	2*i*		–0.099(1)	0.278(1)	–0.027(1)	0.018(3)
O(13)	2*i*		–0.313(1)	0.024(1)	0.388(1)	0.017(3)
O(14)	2*i*		0.034(1)	0.630(1)	0.198(1)	0.017(3)
O(15)	2*i*		0.166(1)	0.5538(9)	0.3443(9)	0.009(3)
O(16)	2*i*		–0.119(1)	0.0783(9)	0.0019(9)	0.009(3)
O(17)	2*i*		0.112(1)	0.408(1)	0.4661(9)	0.011(3)
O(18)	2*i*		–0.270(1)	0.2229(9)	0.3397(8)	0.007(3)
O(19)	2*i*		0.099(1)	0.1413(9)	0.1002(8)	0.005(2)
O(20)	2*i*		0.092(1)	0.2180(9)	0.4950(9)	0.007(3)
O(21)	2*i*		–0.272(1)	0.423(1)	0.323(1)	0.017(3)
O(22)	2*i*		0.304(1)	0.103(1)	0.175(1)	0.019(3)
O(23)	2*i*		–0.126(1)	0.1779(9)	0.4890(9)	0.008(3)
O(24)	2*i*		–0.056(1)	0.4586(9)	0.2938(9)	0.008(3)
O(25)	2*i*		–0.056(1)	0.4269(9)	0.1143(9)	0.009(3)
O(26)	2*i*		–0.047(1)	–0.132(1)	0.3146(9)	0.012(3)
O(27)	2*i*		–0.068(1)	0.2168(9)	0.1415(8)	0.003(2)
O(28)	2*i*		0.114(1)	0.0453(9)	0.4269(8)	0.006(3)
O(29)	2*i*		0.086(1)	0.1708(9)	0.2996(9)	0.009(3)
O(30)	2*i*		0.107(1)	0.3760(9)	0.2652(8)	0.005(2)
O(31)	2*i*		–0.096(1)	0.0103(9)	0.1843(8)	0.006(3)
O(32)	2*i*		0.114(1)	0.0075(9)	0.2412(9)	0.009(3)
O(33)	2*i*		0.338(1)	0.534(1)	0.497(1)	0.016(3)
O(34)	2*i*		0.115(1)	0.3269(9)	0.0688(8)	0.006(3)
O(35)	2*i*		0.310(1)	0.467(1)	0.3054(9)	0.013(3)
O(36)	2*i*		0.040(1)	0.188(1)	–0.0961(9)	0.014(3)

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
O(37)	2*i*		0.297(1)	0.184(1)	0.5586(9)	0.015(3)
O(38)	2*i*		–0.242(1)	0.0876(9)	0.2175(9)	0.009(3)
O(39)	2*i*		0.277(1)	0.1582(9)	0.3563(8)	0.005(2)
O(40)	2*i*		–0.099(1)	0.044(1)	0.3617(9)	0.010(3)
O(41)	2*i*		0.402(2)	0.941(1)	0.217(1)	0.037(4)
H(41A)	2*i*		0.3757	0.8950	0.1718	0.056
H(41B)	2*i*		0.4628	0.9424	0.2520	0.056
O(42)	2*i*		0.340(2)	0.974(1)	0.396(1)	0.030(4)
H(42A)	2*i*		0.2752	0.9637	0.3952	0.046
H(42B)	2*i*		0.3525	1.0095	0.3509	0.046
O(43)	2*i*		0.340(1)	0.720(1)	0.240(1)	0.021(3)
H(43A)	2*i*		0.3780	0.698	0.2116	0.032
H(43B)	2*i*		0.3321	0.6767	0.2792	0.032
O(44)	2*i*		0.488(1)	0.857(1)	0.400(1)	0.030(4)
H(44A)	2*i*		0.4981	0.8975	0.4467	0.045
H(44B)	2*i*		0.5534	0.8764	0.3980	0.045
O(45)	2*i*		0.272(1)	0.757(1)	0.415(1)	0.024(3)
H(45A)	2*i*		0.3254	0.7587	0.4607	0.035
H(45B)	2*i*		0.2258	0.7791	0.4285	0.035
O(46)	2*i*		0.182(1)	0.835(1)	0.235(1)	0.027(4)
H(46A)	2*i*		0.1487	0.8762	0.2337	0.041
H(46B)	2*i*		0.1432	0.7748	0.2280	0.041
O(47)	2*i*		0.350(2)	0.409(1)	0.717(1)	0.038(4)
H(47A)	2*i*		0.4064	0.4440	0.7042	0.058
H(47B)	2*i*		0.2889	0.4125	0.6871	0.058
O(48)	2*i*		0.321(1)	0.269(1)	0.968(1)	0.020(3)
H(48A)	2*i*		0.3329	0.2156	0.9854	0.029
H(48B)	2*i*		0.3480	0.3045	1.0206	0.029
O(49)	2*i*		0.287(2)	0.198(1)	0.764(1)	0.032(4)
H(49A)	2*i*		0.2476	0.1455	0.7794	0.048
H(49B)	2*i*		0.2887	0.1928	0.7062	0.048
O(50)	2*i*		0.497(2)	0.339(1)	0.864(1)	0.035(4)
H(50A)	2*i*		0.5281	0.2985	0.8525	0.052
H(50B)	2*i*		0.5427	0.3927	0.8913	0.052
O(51)	2*i*		0.181(1)	0.341(1)	0.816(1)	0.029(4)
H(51A)	2*i*		0.1499	0.2799	0.8172	0.044
H(51B)	2*i*		0.133	0.3600	0.7791	0.044
O(52)	2*i*		0.389(2)	0.482(1)	0.921(1)	0.037(4)
H(52A)	2*i*		0.4098	0.4896	0.9810	0.055
H(52B)	2*i*		0.4175	0.5170	0.8814	0.055
O(53)	2*i*		0.513(2)	0.657(1)	0.661(1)	0.042(5)
H(53A)	2*i*		0.5082	0.6094	0.6234	0.062
H(53B)	2*i*		0.5802	0.6697	0.6846	0.062
O(54)	2*i*		0.501(2)	0.669(1)	0.865(1)	0.037(4)
H(54B)	2*i*		0.5404	0.6421	0.8444	0.056
H(54A)	2*i*		0.5222	0.7208	0.9022	0.056
O(55)	2*i*		0.493(2)	0.360(2)	0.625(2)	0.054(6)
H(55A)	2*i*		0.5023	0.3071	0.6468	0.081
H(55B)	2*i*		0.4515	0.3700	0.6566	0.081
O(56)	2*i*		0.485(2)	0.852(1)	0.084(1)	0.034(4)
H(56A)	2*i*		0.4516	0.8714	0.1188	0.051
H(56B)	2*i*		0.4920	0.8821	0.0341	0.051
O(57)	2*i*		–0.458(2)	0.146(2)	0.136(2)	0.053(5)
H(57A)	2*i*		–0.3920	0.1727	0.1607	0.079
H(57B)	2*i*		–0.4896	0.1508	0.1789	0.079
O(58)	2*i*		0.486(2)	0.846(1)	0.600(1)	0.043(5)
H(58A)	2*i*		0.5059	0.8442	0.5495	0.064
H(58B)	2*i*		0.4990	0.7940	0.6186	0.064

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}
Cu(1)	2*i*	0.3385(2)	0.3413(2)	0.8411(2)	0.010(1)	0.015(1)	0.022(1)	0.003(1)	0.002(1)	0.006(1)
Cu(2)	2*i*	0.3351(2)	0.8467(2)	0.3146(2)	0.011(1)	0.011(1)	0.024(1)	0.003(1)	0.002(1)	0.000(1)
W(2)	2*i*	0.00508(6)	0.20144(6)	0.01150(5)	0.0054(4)	0.0096(4)	0.0079(4)	–0.0006(3)	0.0014(3)	0.0010(3)
W(3)	2*i*	–0.20487(6)	0.11218(5)	0.35960(5)	0.0058(4)	0.0028(4)	0.0148(4)	–0.0007(3)	0.0057(3)	0.0045(3)
W(4)	2*i*	0.20861(6)	0.14073(5)	0.21697(5)	0.0061(4)	0.0026(4)	0.0137(4)	0.0026(3)	0.0036(3)	0.0028(3)
W(5)	2*i*	0.00053(7)	0.30205(6)	0.50514(5)	0.0084(4)	0.0061(4)	0.0088(4)	0.0028(3)	0.0024(3)	0.0015(3)
W(6)	2*i*	0.23237(7)	0.45649(5)	0.40757(5)	0.0080(4)	0.0019(4)	0.0121(4)	–0.0027(3)	–0.0007(3)	0.0006(3)
W(7)	2*i*	–0.17894(7)	0.30621(6)	0.05986(5)	0.0061(4)	0.0076(4)	0.0104(4)	0.0031(3)	–0.0011(3)	0.0050(3)

Table 3. Continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W(8)	2*i*	0.23311(6)	0.41157(5)	0.17135(5)	0.0044(4)	0.0013(4)	0.0145(4)	–0.0014(3)	0.0047(3)	0.0025(3)
W(9)	2*i*	–0.20193(6)	0.06087(5)	0.09929(5)	0.0048(4)	0.0031(4)	0.0107(4)	–0.0032(3)	–0.0014(3)	0.0021(3)
W(11)	2*i*	–0.18200(7)	0.35756(5)	0.32005(5)	0.0063(4)	0.0047(4)	0.0148(4)	0.0047(3)	0.0053(3)	0.0062(3)
W(12)	2*i*	0.20352(6)	0.18539(5)	0.45203(5)	0.0046(4)	0.0044(4)	0.0107(4)	0.0032(3)	–0.0022(3)	0.0014(3)

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