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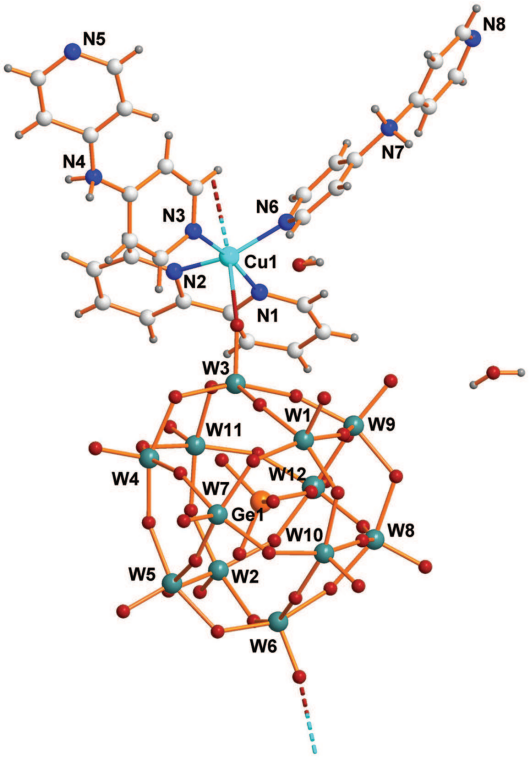
Crystal structure of *catena*-poly[bis(4,4′-dipyridylaminium-*kN*)-(μ_2-germanowolframato-κ^2O:O')-(2,2′-bipyridine-κ^2N,N')copper(II)] with a Keggin-type heteropolyoxoanion, $[Cu(C_{10}H_8N_2)(C_{10}H_{10}N_3)_2][GeW_{12}O_{40}]\cdot H_2O$



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Abstract

$C_{30}H_{30}GeW_{12}CuN_8O_{41}$, triclinic, $P\bar{1}$ (no. 2), $a = 12.095(2)$ Å, $b = 13.488(3)$ Å, $c = 19.220(4)$ Å, $\alpha = 90.221(3)°$, $\beta = 92.188(3)°$, $\gamma = 108.966(3)°$, $V = 2962.8(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0624$, $wR_{ref}(F^2) = 0.1622$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.18 × 0.12 × 0.09 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	24.1 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.9°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	16457, 11935, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8794
$N(param)_{refined}$:	848
Programs:	Olex2 [1], SHELX [2]

Source of material

A mixture of $K_4[GeW_{12}O_{40}]\cdot 14H_2O$ (0.1 mmol), $CuCl_2\cdot 2\ H_2O$ (0.2 mmol), 4,4′-dipyridylamine (0.1 mmol), 2,2′-bipyridine (0.1 mmol), and H_2O (10 mL) was stirred for 30 min at 25 °C, after the pH value of the solution was adjusted to 5.0 with diluted NaOH solution and then transferred to a 23 mL Teflon-lined stainless steel reactor. The solution was heated under autogenous pressure at 160 °C for 96 h. After the solution was slowly cooled to room termperature at a rate of 10 °C h^{-1}, blue block-shaped crystals were filtered off, washed with distilled water and dried in air.

Experimental details

The Olex2 program equipped with SHELXT and SHELXL were used for structure analysis [1, 2]. All the non-hydrogen atoms were located by SHELXT directly and refined anisotropicly by SHELXL with least squares methods. All the hydrogens on N and C were placed at calculated positions (0.93 Å) and refined with the riding model, with U_{iso}(H) set to 1.2 U_{eq}(C) or 1.2 U_{eq}(N). The H atoms of the solvent water molecule were located from the difference Fourier map and then allowed to ride on their parent O atom in the final cycles of refinement with d(O–H) = 0.850 Å and U_{iso}(H) = 1.5 U_{eq}(O). The occupancies of water molecules were refined as 0.5.

Comment

The significant contemporary interest in the crystal engineering of inorganic-organic hybrid materials not only originates from their diversely structural flexibility, but also from

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
W1	0.40968(6)	1.01560(6)	0.25592(3)	0.01614(17)
W2	0.18792(7)	1.43847(6)	0.21179(4)	0.02087(18)
W3	0.09213(6)	0.96399(6)	0.21505(4)	0.01726(18)
W4	0.15391(6)	1.11328(6)	0.07249(3)	0.01787(18)
W5	0.35750(6)	1.38706(6)	0.08883(3)	0.01868(18)
W6	0.47650(7)	1.48535(6)	0.24480(4)	0.02123(18)
W7	0.47307(6)	1.16409(6)	0.11303(3)	0.01614(17)
W8	0.40702(7)	1.32170(6)	0.40380(3)	0.02084(18)
W9	0.22299(6)	1.07260(6)	0.38941(3)	0.01743(18)
W10	0.59278(6)	1.26331(6)	0.26990(4)	0.01994(18)
W11	−0.01308(6)	1.16422(6)	0.19447(4)	0.02128(19)
W12	0.11872(7)	1.27214(6)	0.36868(4)	0.02035(18)
Ge1	0.28985(15)	1.22169(14)	0.23592(8)	0.0137(4)
Cu1	−0.1781(2)	0.71904(18)	0.24552(10)	0.0222(5)
O1	0.0130(10)	1.1382(10)	0.0991(5)	0.019(3)
O2	0.3809(12)	1.4366(10)	0.0076(6)	0.028(3)
O3	0.2305(12)	1.2607(11)	0.0684(6)	0.026(3)
O4	0.1674(10)	1.1406(10)	0.1921(5)	0.018(3)
O5	0.5168(11)	1.2745(11)	0.3526(6)	0.025(3)
O6	0.3443(11)	1.0426(10)	0.3399(6)	0.023(3)
O7	0.4055(10)	1.1774(10)	0.2224(5)	0.017(2)
O8	0.2496(10)	0.9670(9)	0.2173(5)	0.016(3)
O9	0.0262(10)	1.1958(10)	0.2914(6)	0.021(3)
O10	0.2617(12)	1.3420(10)	0.4228(6)	0.024(3)
O11	0.2681(10)	1.2224(9)	0.3232(5)	0.011(2)
O12	0.3434(11)	1.1806(11)	0.4410(5)	0.022(3)
O13	0.4348(11)	1.4305(10)	0.3358(6)	0.025(3)
O14	0.3202(10)	1.3463(9)	0.2051(5)	0.012(2)
O15	0.3108(10)	1.1020(10)	0.0848(5)	0.018(3)
O16	0.2449(11)	1.4525(9)	0.1168(6)	0.018(3)
O17	0.4319(12)	0.8980(10)	0.2722(6)	0.026(3)
O18	0.5573(11)	1.1148(11)	0.2860(6)	0.026(3)
O19	0.1105(13)	1.5242(11)	0.2087(7)	0.033(3)
O20	0.4768(10)	1.4895(10)	0.1453(6)	0.022(3)
O21	0.4586(10)	1.0342(10)	0.1623(5)	0.018(3)
O22	0.0968(10)	0.9763(9)	0.1160(5)	0.018(3)
O23	−0.0336(11)	1.0168(10)	0.2116(6)	0.023(3)
O24	0.0164(11)	0.8330(11)	0.2229(6)	0.028(3)
O25	0.1244(11)	1.0087(10)	0.3113(5)	0.019(3)
O26	0.1892(12)	0.9760(10)	0.4489(6)	0.026(3)
O27	0.4502(10)	1.2940(10)	0.0954(5)	0.018(3)
O28	0.5638(10)	1.3897(10)	0.2425(5)	0.018(3)
O29	0.6079(11)	1.2349(10)	0.1724(5)	0.019(3)
O30	0.5372(11)	1.1427(11)	0.0396(6)	0.028(3)
O31	0.3420(12)	1.5301(10)	0.2419(6)	0.029(3)
O32	0.5844(11)	1.6026(10)	0.2656(6)	0.028(3)
O33	0.4913(12)	1.3828(11)	0.4738(6)	0.030(3)
O34	0.1134(11)	1.1435(11)	0.4124(6)	0.025(3)
O35	0.1223(10)	1.0781(11)	−0.0118(6)	0.027(3)
O36	0.7344(13)	1.3097(12)	0.2969(7)	0.034(3)
O37	−0.1555(12)	1.1621(12)	0.1871(7)	0.038(4)
O38	0.0714(11)	1.3092(10)	0.1816(6)	0.021(3)
O39	0.0164(13)	1.3026(12)	0.4171(7)	0.037(4)
O40	0.1674(10)	1.3857(10)	0.3036(6)	0.020(3)
N1	−0.1850(14)	0.8330(13)	0.3089(7)	0.025(3)
N2	−0.2759(13)	0.7797(12)	0.1849(7)	0.019(3)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
N3	−0.1527(14)	0.6235(13)	0.1706(7)	0.024(4)
N4	−0.1713(15)	0.4420(13)	−0.0078(7)	0.028(4)
H4A	−0.2234	0.4606	−0.0339	0.033*
H4B	−0.1033	0.4686	−0.0281	0.033*
N5	−0.2633(18)	0.1220(17)	−0.0528(9)	0.044(4)
N6	−0.1455(15)	0.6313(13)	0.3237(7)	0.026(4)
N7	−0.1352(15)	0.4036(14)	0.4674(8)	0.030(3)
H7A	−0.1417	0.3483	0.4401	0.036*
H7B	−0.0613	0.4256	0.4838	0.036*
N8	−0.327(2)	0.2658(16)	0.6375(10)	0.055(6)
C1	−0.3266(19)	0.7417(17)	0.1226(9)	0.032(5)
H1	−0.3170	0.6808	0.1050	0.038*
C2	−0.3943(19)	0.7913(18)	0.0827(9)	0.031(5)
H2	−0.4349	0.7606	0.0419	0.037*
C3	−0.3977(17)	0.8887(17)	0.1074(10)	0.030(4)
H3	−0.4348	0.9270	0.0808	0.036*
C4	−0.3447(18)	0.9271(16)	0.1721(10)	0.029(5)
H4	−0.3480	0.9906	0.1892	0.034*
C5	−0.2859(16)	0.8697(15)	0.2119(8)	0.021(4)
C6	−0.2352(15)	0.9001(15)	0.2802(8)	0.020(4)
C7	−0.241(2)	0.989(2)	0.3176(11)	0.047(6)
H7	−0.2805	1.0324	0.2992	0.056*
C8	−0.184(2)	1.008(2)	0.3851(10)	0.043(6)
H8	−0.1851	1.0654	0.4117	0.051*
C9	−0.1264(18)	0.9431(18)	0.4106(9)	0.032(5)
H9	−0.0881	0.9559	0.4543	0.038*
C10	−0.1262(17)	0.8612(18)	0.3721(8)	0.030(5)
H10	−0.0831	0.8199	0.3893	0.036*
C11	−0.1970(16)	0.5215(16)	0.1738(10)	0.029(5)
H11	−0.2267	0.4933	0.2159	0.035*
C12	−0.2031(18)	0.4530(18)	0.1199(9)	0.030(4)
H12	−0.2342	0.3808	0.1251	0.036*
C13	−0.1589(16)	0.4981(15)	0.0545(8)	0.019(4)
C14	−0.1068(16)	0.6071(15)	0.0528(9)	0.021(4)
H14	−0.0718	0.6384	0.0126	0.026*
C15	−0.1073(16)	0.6674(15)	0.1096(8)	0.022(4)
H15	−0.0760	0.7399	0.1069	0.027*
C16	−0.209(2)	0.1581(19)	0.0075(13)	0.045(6)
H16	−0.1912	0.1117	0.0380	0.055*
C17	−0.178(2)	0.2648(19)	0.0272(11)	0.037(5)
H17	−0.1415	0.2870	0.0706	0.045*
C18	−0.2013(17)	0.3362(15)	−0.0166(8)	0.022(4)
C19	−0.256(2)	0.293(2)	−0.0839(10)	0.042(6)
H19	−0.2717	0.3373	−0.1171	0.051*
C20	−0.283(2)	0.191(2)	−0.0982(12)	0.050(6)
H20	−0.3166	0.1656	−0.1417	0.060*
C21	−0.0608(16)	0.5881(15)	0.3251(9)	0.021(4)
H21	−0.0039	0.6086	0.2921	0.025*
C22	−0.0533(18)	0.5168(17)	0.3716(10)	0.031(5)
H22	0.0087	0.4903	0.3718	0.037*
C23	−0.1418(17)	0.4828(16)	0.4201(10)	0.026(4)
C24	−0.2356(18)	0.5229(18)	0.4171(9)	0.039(6)
H24	−0.2974	0.4978	0.4466	0.047*
C25	−0.235(2)	0.5990(18)	0.3704(10)	0.038(5)
H25	−0.2944	0.6291	0.3697	0.045*
C26	−0.261(2)	0.219(2)	0.6012(12)	0.054(6)
H26	−0.2572	0.1547	0.6159	0.065*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C27	−0.203(3)	0.263(2)	0.5454(13)	0.069(10)
H27	−0.1641	0.2261	0.5204	0.083*
C28	−0.1986(18)	0.3617(17)	0.5240(9)	0.028(4)
C29	−0.259(2)	0.4105(17)	0.5635(8)	0.035(5)
H29	−0.2556	0.4784	0.5524	0.042*
C30	−0.323(3)	0.363(2)	0.6190(10)	0.058(8)
H30	−0.3642	0.3979	0.6437	0.070*
O1W[a]	−0.463(3)	0.888(3)	0.4476(15)	0.052(9)
H1WA[a]	−0.5044	0.8959	0.4797	0.077*
H1WB[a]	−0.4108	0.8663	0.4667	0.077*
O2W[a]	0.405(3)	0.903(3)	0.5585(15)	0.061(10)
H2WA[a]	0.4220	0.9063	0.6003	0.091*
H2WB[a]	0.3719	0.9433	0.5382	0.091*

[a]Occupancy: 0.5.

their widely promising potential applications in catalysis, medicine, photochemistry and electromagnetism [3–5]. Up to now, although a number of inorganic-organic hybrid compounds containing polyoxomolybdates have been reported [6, 7]. Design and synthesis of novel hybrid materials with highly specific and cooperative functions are still a challenging work. A widely used approach to the synthesis of these materials is the hydrothermal crystallization in the presence of organic amines, which are used as templates or structure-directing agents to facilitate the formation of various networks [8, 9].

The title crystal structure is composed of $[GeW_{12}O_{40}]^{4-}$ Keggin-type polyoxoanions, $[Cu(C_{10}H_8N_2)(C_{10}H_{10}N_3)_2]^{4+}$ copper complex cations and water molecules. The polyoxoanion $[GeW_{12}O_{40}]^{4-}$ is a well known α-Keggin structure composed of 12 corner- or edge-sharing WO_6 octahedra with the central germanium ordered and coordinated to four oxygen atoms in a tetrahedral fashion (*cf.* the figure). The Ge—O distances are in the range of 1.708(9)–1.718(11) Å and the O—Ge—O angles are in the range of 108.9(5)–110.5(5)°. The W—O distances can be grouped into three sets according to the kind of oxygen atoms bound to the tungsten atoms: W—O_t = 1.681(12)−1.726(13) Å, W—O_b = 1.877(12)−1.964(11) Å and W—O_c = 2.291(12)−2.331(12) Å. The O—W—O angles are between 71.2(5) and 170.6(5)° and are in accord with the literature [10]. In the copper complex $[Cu(C_{10}H_8N_2)(C_{10}H_{10}N_3)_2]^{4+}$, each of the Cu^{2+} is six-coordinated by two nitrogen atoms from two 4,4′-dipyridylaminium cations (dpa) (N3 and N6), two nitrogen atoms from one 2,2′-bipyridine molecule (bipy, N1 and N2) and two oxygen atoms from adjacent POMs anions (O24 and O32), respectively, resulting a distorted octahedral geometry. The Cu—O distances were in the ranges of 2.412(13)−2.833(14) Å, and the Cu—N distances ranges from 1.982(16) to 2.026(14) Å. The dpa and bpy molecules act as a monodentate and bidentate ligand respectively coordinated to a copper atom with its nitrogen atoms. The most remarkable structural feature of the title compound is that the adjacent Keggin $[GeW_{12}O_{40}]^{4-}$ clusters are interconnected through $[Cu(C_{10}H_8N_2)(C_{10}H_{10}N_3)_2]^{4+}$ bridging groups to form a one-dimensional infinite anionic chain (*cf.* the figure; dashed lines). Furthermore, the adjacent one-dimensional chains are linked up by extensive hydrogen bonding interactions of the polyoxoanions, 4,4′-dipyridylamine, 2,2′-bipyridine and lattice water molecules to form a three-dimensional supramolecules framework. There are three types of intermolecular hydrogen bonds (O—H···O, C—H···O, N—H···O).

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