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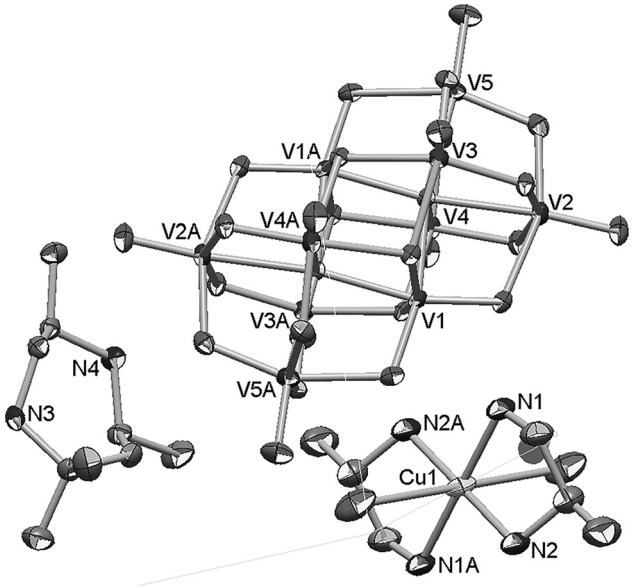
Crystal structure of bis(2,5,5,7-tetramethyl-1,4-diazepane-1,4-diium) diaqua-bis(1,2-diaminopropane)copper(II) bis(μ_6-oxido) tetrakis(μ_3-oxido)-tetradecakis(μ_2-oxido)-octaoxido-decavanadium(V) – water (1/4), $C_{24}H_{76}CuN_8V_{10}O_{34}$



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Abstract

$C_{24}H_{76}CuN_8V_{10}O_{34}$, monoclinic, $P2_1/n$ (no. 14), a = 22.416(4) Å, b = 11.7003(18) Å, c = 20.079(3) Å, β = 95.594(7)°, V = 5241.2(14) Å^3, Z = 4, $R_{gt}(F)$ = 0.0243, $wR_{ref}(F^2)$ = 0.1110, T = 296(2) K.

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Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.32 × 0.28 × 0.16 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.20 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.7°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	23,078, 6030, 0.017
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5457
$N(param)_{refined}$:	372
Programs:	BRUKER [1], SHELX [2, 3], Diamond [4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

An aqueous solution (10 mL) of NH_4VO_3 (117 mg, 1 mmol) was layered with an acetonitrile solution (10 mL) of $[Cu(1,2\text{-pn})_2](ClO_4)_2$ (42.3 mg, 0.1 mmol) (pn = diaminopropane) and 2,5,5,7-tetramethyl-1,4-diazepane (tmda, 15.6 mg, 0.1 mmol). The resultant solution was slowly and naturally diffused at room temperature. Crystals of the title compound were obtained within one week.

Experimental details

The structure was solved using Direct Methods, which yielded the positions of all non-hydrogen atoms. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters. The U_{iso} values of the hydrogen atoms of methyl groups were set to 1.5U_{eq}(C) and

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.03679 (12)	0.3798 (3)	−0.11290 (15)	0.0439 (7)
H1C	0.041899	0.302830	−0.095249	0.053*
H1D	0.057839	0.385277	−0.152761	0.053*
C2	0.02858 (13)	0.5957 (3)	0.13012 (15)	0.0442 (7)
H2	0.032544	0.520744	0.151916	0.053*
C3	0.05883 (17)	0.6850 (4)	0.17758 (17)	0.0671 (12)
H3C	0.099336	0.662042	0.191001	0.101*
H3D	0.037217	0.691690	0.216390	0.101*
H3E	0.058947	0.757501	0.155177	0.101*
C4	0.22262 (10)	0.1238 (2)	0.34069 (10)	0.0212 (4)
H4C	0.220476	0.107438	0.293150	0.025*
H4D	0.257242	0.083975	0.362235	0.025*
C5	0.23111 (10)	0.2504 (2)	0.35119 (10)	0.0203 (4)
H5	0.223193	0.268815	0.397133	0.024*
C6	0.29457 (11)	0.2863 (2)	0.34177 (11)	0.0259 (5)
H6A	0.302866	0.269932	0.296739	0.039*
H6B	0.322106	0.244917	0.372494	0.039*
H6C	0.299028	0.366784	0.350102	0.039*
C7	0.12320 (10)	0.2923 (2)	0.30476 (11)	0.0235 (5)
H7	0.113162	0.291251	0.351175	0.028*
C8	0.08911 (13)	0.3890 (3)	0.26745 (16)	0.0402 (7)
H8A	0.104640	0.461052	0.284166	0.060*
H8B	0.047362	0.383714	0.274081	0.060*
H8C	0.093811	0.383303	0.220551	0.060*
C9	0.10787 (11)	0.1762 (2)	0.27272 (11)	0.0252 (5)
H9A	0.134116	0.164361	0.237686	0.030*
H9B	0.067247	0.180431	0.251241	0.030*
C10	0.11213 (10)	0.0694 (2)	0.31806 (11)	0.0238 (5)
C11	0.05876 (13)	0.0598 (3)	0.35984 (14)	0.0400 (7)
H11A	0.065786	−0.001124	0.391673	0.060*
H11B	0.023032	0.044054	0.330931	0.060*
H11C	0.053996	0.130370	0.383109	0.060*
C12	0.11831 (14)	−0.0374 (2)	0.27630 (13)	0.0366 (6)
H12A	0.154152	−0.032351	0.253914	0.055*
H12B	0.084188	−0.044028	0.243714	0.055*
H12C	0.120487	−0.103342	0.304887	0.055*
Cu1	0.000000	0.500000	0.000000	0.03230 (13)
N1	0.06171 (10)	0.4632 (2)	−0.06247 (11)	0.0343 (5)
H1A	0.072299	0.526699	−0.082731	0.041*
H1B	0.094203	0.434248	−0.039550	0.041*
N2	0.05650 (10)	0.5898 (2)	0.06584 (11)	0.0344 (5)
H2A	0.091951	0.555133	0.071983	0.041*
H2B	0.061952	0.659872	0.050263	0.041*
N3	0.16745 (9)	0.07901 (17)	0.36767 (9)	0.0210 (4)
H3A	0.158773	0.124355	0.400988	0.025*
H3B	0.175620	0.010084	0.384969	0.025*
N4	0.18909 (8)	0.31918 (16)	0.30407 (10)	0.0222 (4)
H4A	0.199067	0.308583	0.262685	0.027*
H4B	0.194595	0.392849	0.313865	0.027*
O1	0.32906 (6)	0.13368 (13)	−0.00322 (7)	0.0158 (3)
O1W	0.36185 (9)	0.71604 (17)	0.01840 (9)	0.0330 (4)
H1WA	0.3423 (14)	0.7737 (17)	0.0027 (14)	0.050*
H1WB	0.3576 (15)	0.6611 (17)	−0.0093 (13)	0.050*
O2	0.33601 (7)	0.22691 (13)	0.12096 (7)	0.0189 (3)
O2W	0.01306 (11)	0.3186 (2)	0.07593 (14)	0.0528 (6)
H2WA	0.0502 (6)	0.302 (3)	0.086 (2)	0.079*
H2WB	−0.0020 (15)	0.264 (3)	0.0503 (19)	0.079*
O3	0.29706 (7)	0.01488 (13)	0.10366 (7)	0.0198 (3)
O3W	0.00836 (13)	0.8519 (3)	0.02340 (17)	0.0667 (7)
H3WA	0.0338 (16)	0.900 (3)	0.043 (2)	0.100*
H3WB	−0.0194 (15)	0.893 (3)	0.003 (2)	0.100*
O4	0.30296 (8)	0.09609 (16)	0.22751 (7)	0.0284 (4)
O5	0.19626 (7)	0.06776 (14)	0.15541 (7)	0.0213 (3)
O6	0.23562 (7)	0.27741 (13)	0.17502 (7)	0.0189 (3)
O7	0.13061 (7)	0.23931 (14)	0.10264 (7)	0.0197 (3)
O8	0.16435 (7)	0.45362 (14)	0.13021 (8)	0.0228 (3)
O9	0.26817 (7)	0.40191 (12)	0.06890 (7)	0.0154 (3)
O10	0.20803 (8)	0.59375 (14)	0.01466 (8)	0.0269 (4)
O11	0.30921 (7)	0.52044 (13)	−0.03272 (7)	0.0209 (3)
O12	0.41239 (8)	0.47772 (17)	−0.08858 (10)	0.0340 (4)
O13	0.37349 (7)	0.34949 (14)	0.01809 (8)	0.0210 (3)
O14	0.23194 (6)	0.18940 (12)	0.05115 (6)	0.0145 (3)
V1	0.31511 (2)	0.27377 (3)	0.04238 (2)	0.01411 (10)
V2	0.27020 (2)	0.13518 (3)	0.15649 (2)	0.01905 (11)
V3	0.19248 (2)	0.33928 (3)	0.10149 (2)	0.01578 (10)
V4	0.23405 (2)	0.47874 (3)	−0.01697 (2)	0.01670 (10)
V5	0.35161 (2)	0.41005 (3)	−0.07815 (2)	0.02052 (11)

the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C, N).

Comment

Similar substances to the title compound have been synthesized [5, 6], which exhibited three-dimensional structures formed by connections of polyoxovanadium clusters with $[Cu(1,2\text{-pn})_2]^{2+}$ groups.

X-ray crystal structural analysis reveals that the asymmetric unit of the title structure contains one half of a $[Cu(1,2\text{-pn})_2(H_2O)_2]^{2+}$, one half of a $[V_{10}O_{26}]^{6-}$, one 2,5,5,7-tetramethyl-1,4-diazepane-1,4-diium, $[tmda]^{2+}$ and two water molecules (see the figure; water molecules were omitted). The central Cu(II) atom displays a six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms of 1,2-pn, and two oxygen atoms of water.

The monomers of $[Cu(1,2\text{-pn})_2(H_2O)_2]^{2+}$, $[V_{10}O_{26}]^{6-}$, $[tmda]^{2+}$ and water molecules are connected through intermolecular hydrogen bonds to form a three-dimensional structure.

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