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Bis(trimethylenediammonium) hexaaquacopper(II) decavanadate heptahydrate

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Key indicators

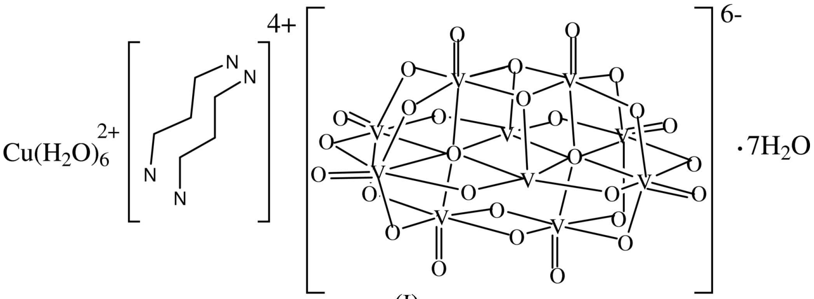
Single-crystal X-ray study
T = 253 K
Mean σ(C–C) = 0.003 Å
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 13.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $(C_3H_{12}N_2)_2[Cu(H_2O)_6][V_{10}O_{28}]\cdot 7H_2O$, contains $[V_{10}O_{28}]^{6-}$ polyanions, $[Cu(H_2O)_6]^{2+}$ cations, $H_3NCH_2CH_2CH_2NH_3^{2+}$ cations and non-coordinated water molecules. A variety of O—H···O and N—H···O hydrogen bonds generate a three-dimensional network. The asymmetric unit contains two half-anions; each anion is centrosymmetric.

Comment

The title compound, (I), contains $[V_{10}O_{28}]^{6-}$ polyanions, similar to those seen in $K_2[Zn(H_2O)_6]_2\ [V_{10}O_{28}]\cdot 4H_2O$ (Evans, 1966), $[Ni(H_2O)_6]_2[Na(H_2O)_3]_2[V_{10}O_{28}]\cdot 4H_2O$ (Higami *et al.*, 2002), $(NH_4)_2\{Co_2[V_{10}O_{28}]\}\cdot 16H_2O$ (Nowogrocki *et al.*, 1997) and $Na_4[Ni(H_2O)_6][[V_{10}O_{28}].17H_2O$ (Sun *et al.*, 2002). The asymmetric unit contains two half-anions; each anion is centrosymmetric.



(I)

In this polyanion, the ten V atoms and 28 O atoms form a condensed system of distorted VO_6 octahedra combined *via* shared edges (Evans, 1966), resulting in six V atoms arranged in an equatorial plane and the other four V atoms distributed above and below the plane (Fig. 1). Depending on their connectivity to vanadium neighbours, the O atoms in the $[V_{10}O_{28}]^{6-}$ anion fall into four categories: terminal, bridging, triply bridging or six-coordinate. The O—V—O angles in (I) span the ranges 74.54 (5)–103.74 (7)° and 153.42 (5)–175.55 (6)° for the *cis* and *trans* bonds, respectively.

The structure of (I) also contain $[Cu(H_2O)_6]^{2+}$ cations and doubly protonated 1,3-diaminopropane molecules, which combine to balance the negative charge of the cluster. A similar charge-balancing combination of a metal complex and an organic cation for the same cluster was seen in $(H_3NCH_2CH_2NH_3)_2[Na_2(H_2O)_{10}][V_{10}O_{28}]$ (Li *et al.*, 2004). Finally, seven uncoordinated water molecules of crystallization are present in the asymmetric unit of (I). A large number of O—H···O and N—H···O hydrogen bonds (Table 1 and Fig. 2) serve to connect the different chemical species into a three-dimensional network.

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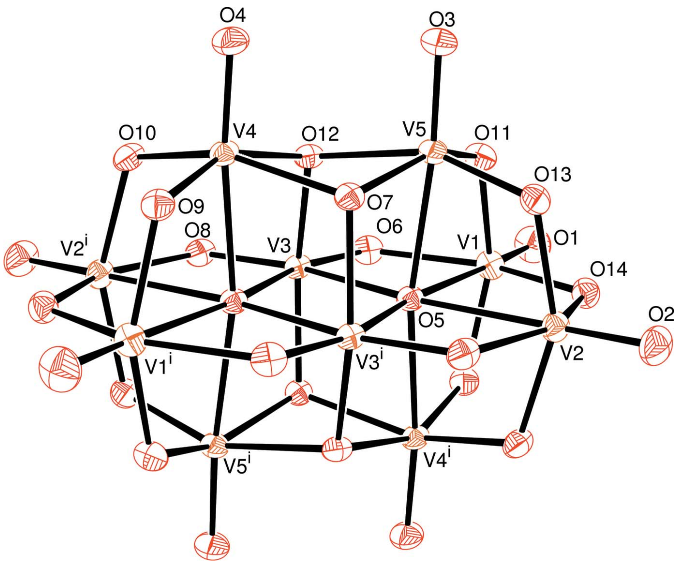

Figure 1
Detail of (I), showing one of the $[V_{10}O_{28}]^{6-}$ ions (50% displacement ellipsoids). The other polyanion is almost identical. [Symmetry code: (i) $2 - x, 1 - y, 1 - z$.]

Experimental

NH_4VO_3 (0.5 mmol, 0.061 g) was dissolved in an acidic aqueous solution (pH = 1–2), before adding aqueous $Cu(CH_3COO)_2$ (1 ml, 0.01 mmol l^{-1}) and a concentrated aqueous 1,3-diaminopropane solution (1 ml, 0.1 mol l^{-1}) to the vanadate solution. The mixture was stirred for about 30 min and left in the dark at room temperature for several weeks. Green crystals of (I) suitable for diffraction studies were obtained.

Crystal data

$(C_3H_{12}N_2)_2[Cu(H_2O)_6]$-$[V_{10}O_{28}]\cdot 7H_2O$
$M_r = 1407.44$
Triclinic, $P\overline{1}$
$a = 10.351$ (2) Å
$b = 11.125$ (2) Å
$c = 18.536$ (4) Å
$\alpha = 92.62$ (3)°
$\beta = 103.14$ (3)°
$\gamma = 100.17$ (3)°
$V = 2037.7$ (8) Å^3
$Z = 2$
$D_x = 2.294$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5958 reflections
$\theta = 2.1$–28.2°
$\mu = 2.82$ mm^{-1}
$T = 253$ (2) K
Block, green
0.20 × 0.15 × 0.12 mm

Data collection

Bruker SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.605$, $T_{max} = 0.710$
24545 measured reflections
9825 independent reflections
8442 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 28.2°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.079$
$S = 1.01$
9825 reflections
713 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2 + 0.0005P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.53$ e Å^{-3}
$\Delta\rho_{min} = -1.81$ e Å^{-3}

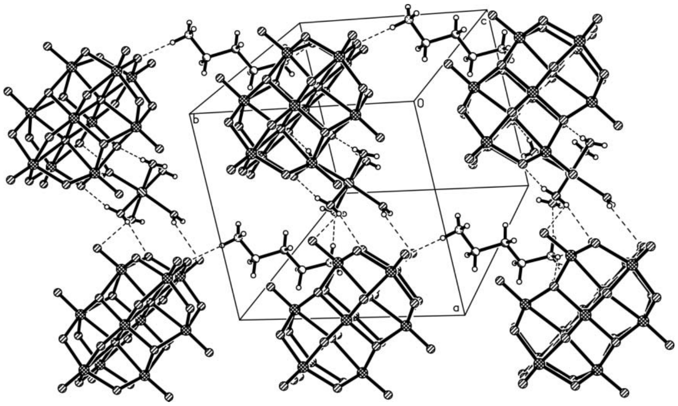

Figure 2
The packing of (I), with hydrogen bonds indicated by dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O*W*1—H*W*1···O19^{i}	0.83 (2)	1.946 (17)	2.756 (3)	163 (2)
O*W*1—H*W*1*A*···O*W*12	0.82 (2)	2.009 (19)	2.731 (3)	146 (2)
O*W*2—H*W*2*A*···O16^{ii}	0.83 (3)	2.31 (3)	2.993 (3)	140 (2)
O*W*2—H*W*2*A*···O28^{ii}	0.83 (3)	2.58 (3)	3.293 (3)	144 (2)
O*W*2—H*W*2···O6	0.84 (2)	1.873 (16)	2.712 (3)	173 (2)
O*W*3—H*W*3*A*···O25	0.86 (2)	1.902 (18)	2.744 (3)	166.5 (18)
O*W*3—H*W*3···O28^{ii}	0.84 (3)	2.10 (3)	2.893 (3)	155.7 (2)
O*W*3—H*W*3···O20^{ii}	0.84 (3)	2.46 (3)	2.937 (3)	117.31 (2)
O*W*4—H*W*4*A*···O7^{iii}	0.84 (2)	1.808 (15)	2.641 (3)	170 (2)
O*W*4—H*W*4···O*W*12	0.83 (2)	1.940 (17)	2.738 (3)	162 (2)
O*W*5—H*W*5*A*···O9^{iii}	0.85 (3)	1.849 (19)	2.689 (3)	168 (2)
O*W*5—H*W*5···O10^{iv}	0.85 (3)	2.02 (3)	2.816 (3)	157 (2)
O*W*6—H*W*6*A*···O22	0.84 (2)	1.819 (15)	2.654 (3)	173.5 (18)
O*W*6—H*W*6···O*W*9	0.83 (2)	1.884 (18)	2.714 (3)	176 (3)
O*W*7—H7*A*···O24	0.80 (2)	2.055 (14)	2.812 (3)	157 (2)
O*W*7—H7···O20^{ii}	0.80 (2)	2.03 (2)	2.805 (3)	167 (2)
O*W*7—H7···O15^{ii}	0.80 (2)	2.59 (2)	2.961 (3)	110.29 (2)
O*W*8—H8*A*···O14	0.83 (2)	2.022 (14)	2.837 (3)	167 (2)
O*W*8—H8···O4^{iv}	0.82 (2)	2.03 (2)	2.844 (3)	170.45 (2)
O*W*9—H9···O*W*7^{ii}	0.81 (2)	2.026 (16)	2.816 (3)	166.36 (2)
O*W*10—H10*A*···O17	0.80 (2)	2.00 (2)	2.792 (3)	167.4 (19)
O*W*10—H10···O27^{v}	0.80 (2)	2.177 (18)	2.962 (3)	165 (2)
O*W*10—H10···O15^{v}	0.80 (2)	2.574 (19)	3.113 (3)	126 (2)
O*W*11—H11*A*···O3^{vi}	0.81 (2)	2.28 (2)	3.006 (3)	149 (2)
O*W*11—H11···O11	0.81 (2)	1.95 (2)	2.742 (3)	167 (3)
O*W*12—H12*A*···O*W*8^{vii}	0.80 (2)	2.003 (19)	2.750 (3)	156 (2)
O*W*12—H12···O*W*13^{viii}	0.80 (2)	2.019 (19)	2.804 (3)	166 (2)
N101—H1*C*···O14^{ix}	0.89 (2)	2.013 (14)	2.890 (3)	170 (2)
N101—H1*C*···O13^{ix}	0.89 (2)	2.645 (17)	3.148 (3)	117 (2)
N101—H1*D*···O*W*11^{iv}	0.89 (2)	1.981 (15)	2.868 (3)	175 (2)
N101—H1*E*···O*W*8	0.89 (2)	2.211 (19)	3.021 (3)	151.8 (19)
N101—H1*E*···O3^{iv}	0.89 (2)	2.35 (2)	2.956 (3)	125 (2)
N301—H3*C*···O23^{i}	0.89 (2)	2.32 (2)	3.028 (3)	137 (2)
N301—H3*C*···O16^{i}	0.89 (2)	2.541 (18)	3.288 (3)	142 (2)
N301—H3*D*···O*W*6	0.88 (2)	2.04 (2)	2.915 (3)	174 (2)
N301—H3*E*···O10^{iv}	0.88 (2)	2.190 (17)	3.024 (3)	157.83
N301—H3*E*···O12^{iv}	0.88 (2)	2.419 (17)	3.050 (3)	129.21
N401—H4*C*···O24^{x}	0.89 (2)	1.901 (15)	2.788 (3)	176 (2)
N401—H4*D*···O*W*13^{viii}	0.89 (2)	2.082 (17)	2.904 (3)	154 (2)
N401—H4*E*···O*W*7	0.88 (2)	2.009 (18)	2.892 (3)	176 (2)
N601—H6*C*···O8	0.88 (2)	2.30 (2)	2.983 (3)	135.2 (15)
N601—H6*D*···O*W*4	0.88 (2)	2.02 (2)	2.892 (3)	170 (2)
N601—H6*E*···O26^{ii}	0.88 (2)	2.204 (16)	2.918 (3)	138 (2)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z$; (iii) $-x+2, -y+1, -z+1$; (iv) $x-1, y, z$; (v) $-x, -y, -z$; (vi) $-x+2, -y, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $x, y+1, z$; (ix) $-x+1, -y, -z+1$; (x) $-x+1, -y+2, -z$.

The C-bound H atoms were placed in idealized locations and refined as riding [C—H = 0.97 Å and $U_{\rm iso}$(H)=1.2$U_{\rm eq}$(C)]. All other H atoms were located in difference maps and were included in the refinement with O—H and N—H distances restrained to 0.80 (2)–0.86 (2) and 0.88 (2)–0.89 (2) Å, respectively. Some of the water H-atom positions should be regarded as less certain. The deepest hole is located 0.11 Å from atom V3.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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