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A New Decavanadate Dihydrate Templated by Ethylenediamine

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Abstract

$(C_2H_{10}N_2)_3[V_{10}O_{28}].2H_2O$, tris(ethylenediammonium) decavanadate dihydrate, crystallizes in the monoclinic system ($P2_1/n$). Its structure, solved by single-crystal X-ray diffraction with a final R value of 0.0237 for 5136 unique reflections, is characterized by a pseudo body-centred arrangement of the $[V_{10}O_{28}]^{6-}$ polyanions, between which are intercalated the ethylenediammonium cations and the water molecules.

Comment

We have recently described a new family of vanadyl vanadates intercalated by organic templates and formulated as $[(V^{IV}O)(V^{V}O_4)]_2$.diamine (Riou & Férey, 1995*a*,*b*). Their two-dimensional structures are built up from inorganic layers of corner-sharing $V^{V}O_4$ tetrahedra and $[V^{IV}_2O_8]$ units in the form of two square pyramids; the organic cations are intercalated between them. In these phases, it was thought that the deintercalation of the amines from the structures could lead to a new form of V_2O_5. The thermal degradation method failed, as did the *in situ* oxidation of the amine in aqueous medium by hydrogen peroxide using $VO(VO_4).0.5$(ethylenediamine) as the starting compound. We have not obtained a new form of V_2O_5 but a new member in the long list of decavanadates templated by organic cations (Zurkova & Vavra, 1993; Sucha, Sivak & Schwendt, 1993): $(C_2H_{10}N_2)_3[V_{10}O_{28}].2H_2O$ (Fig. 1). In this compound, the centrosymmetric decavanadate group is built up from five independent atoms. Its topology is very close to that recently described by Averbuch-Pouchot (1994). In the cell, the $[V_{10}O_{28}]^{6-}$ anions located around the origin and around the centre of the cell describe a pseudo body-centred arrangement. The electroneutrality is ensured by the ethylenediammonium cations, which also form strong hydrogen bonds with the water molecules and with some O atoms.

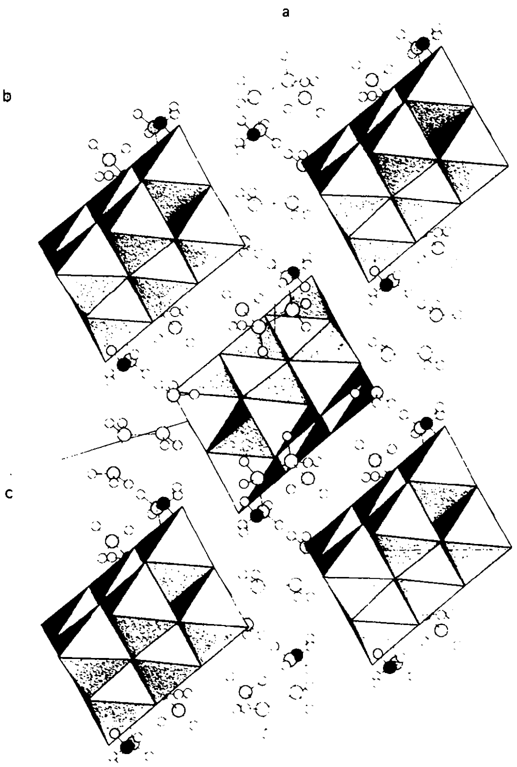

Fig. 1. Projection of the structure along the *b* axis. The N and C atoms are represented by dark and light shaded circles, respectively, *OW* by black circles and H by small circles.

Experimental

The title compound was prepared by dissolution then recrystallization at room temperature of $VO(VO_4).0.5(N_2C_2H_{10})$ (Riou & Férey, 1995*a*,*b*) (300 mg) in H_2O_2 (50 ml). In a first step, the vanadyl vanadate compound dissolved in 2–3 h to give an orange solution; after one day, small orange crystals were observed on the inner wall of the flask, their growth continuing until the decolouration of the solution. The density D_m was measured by multipycnometry (1305 micromeritics under He flow).

Crystal data

$(C_2H_{10}N_2)_3[V_{10}O_{28}].2H_2O$
$M_r = 590.0$
Monoclinic
$P2_1/n$
$a = 10.5096\,(8)$ Å
$b = 10.8730\,(10)$ Å
$c = 14.3200\,(10)$ Å
$\beta = 106.261\,(8)°$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 38 reflections
$\theta = 14–16°$
$\mu = 3.119\ mm^{-1}$
$T = 293$ K
Truncated parallelepiped

$V = 1570.9\ (2)$ Å^3
$Z = 4$
$D_x = 2.496$ Mg m^{-3}
$D_m = 2.50\ (7)$ Mg m^{-3}

0.324 × 0.270 × 0.102 mm
Orange

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.32$, $T_{\max} = 0.95$
8682 measured reflections
6917 independent reflections

5136 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0248$
$\theta_{\max} = 35.02°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 2.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0237$
$wR(F^2) = 0.0625$
$S = 0.994$
5136 reflections
240 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0341P)^2 + 0.9607P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.564$ e Å^{-3}
$\Delta\rho_{\min} = -0.437$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0011 (2)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
V1	0.07550 (2)	0.96103 (2)	0.11266 (2)	0.01176 (5)
V2	−0.23043 (3)	0.91135 (2)	0.02515 (2)	0.01361 (5)
V3	0.12381 (3)	0.88083 (3)	0.82161 (2)	0.01598 (6)
V4	0.03275 (3)	0.24113 (2)	0.04924 (2)	0.01476 (5)
V5	0.23216 (3)	0.31050 (3)	0.46924 (2)	0.01602 (6)
O1	0.26258 (11)	0.79591 (12)	0.90172 (9)	0.0178 (2)
O2	0.16907 (10)	1.10898 (10)	0.09495 (8)	0.0131 (2)
O3	−0.05119 (11)	0.83307 (10)	0.07502 (8)	0.0135 (2)
O4	−0.21629 (11)	0.96607 (11)	0.14894 (8)	0.0163 (2)
O5	−0.34299 (11)	1.03131 (11)	−0.03807 (9)	0.0166 (2)
O6	0.03984 (12)	1.00722 (11)	0.21521 (8)	0.0165 (2)
O7	0.21170 (11)	0.86960 (11)	0.14927 (8)	0.0164 (2)
O8	0.37060 (12)	0.19896 (11)	0.48355 (9)	0.0176 (2)
O9	−0.00228 (12)	0.23983 (11)	0.16733 (9)	0.0169 (2)
O10	−0.32563 (13)	0.79379 (13)	0.01270 (11)	0.0242 (3)
O11	0.13067 (13)	0.35760 (12)	0.05540 (10)	0.0221 (2)
O12	0.14337 (14)	0.85183 (14)	0.71685 (9)	0.0250 (3)
O13	0.08495 (10)	0.93266 (10)	−0.03320 (8)	0.0126 (2)
O14	0.10706 (13)	0.22907 (13)	0.41218 (10)	0.0235 (3)
O*W*1	−0.07454 (13)	0.80374 (13)	0.30274 (10)	0.0240 (3)
N1	−0.5521 (2)	1.0632 (2)	−0.20378 (12)	0.0231 (3)
N2	0.3792 (2)	1.1607 (2)	0.25382 (12)	0.0244 (3)
N3	0.1136 (2)	−0.0344 (2)	0.42313 (11)	0.0215 (3)
C1	−0.5694 (2)	0.9889 (2)	−0.29382 (14)	0.0243 (3)
C2	0.4396 (2)	1.0496 (2)	0.31133 (14)	0.0260 (4)
C3	0.0714 (2)	−0.0218 (2)	0.51297 (12)	0.0209 (3)

Table 2. *Selected geometric parameters (Å, °)*

V1—O6	1.6903 (12)	V4—O11	1.6186 (13)
V1—O7	1.7005 (12)	V4—O8$^{\rm v}$	1.8209 (12)
V1—O3	1.8966 (11)	V4—O9	1.8287 (12)
V1—O2	1.9388 (11)	V4—O2$^{\rm vi}$	2.0051 (11)
V1—O13$^{\rm i}$	2.0976 (11)	V4—O3$^{\rm vii}$	2.0119 (11)
V1—O13	2.1410 (11)	V4—O13$^{\rm vii}$	2.2348 (11)
V2—O10	1.6021 (13)	V5—O14	1.6057 (13)
V2—O5	1.8221 (12)	V5—O1$^{\rm viii}$	1.8399 (12)
V2—O4	1.8360 (12)	V5—O8	1.8609 (12)
V2—O3	2.0074 (11)	V5—O5$^{\rm ix}$	1.8834 (12)
V2—O2$^{\rm i}$	2.0108 (11)	V5—O7$^{\rm x}$	2.0500 (12)
V2—O13$^{\rm i}$	2.2647 (11)	V5—O13$^{\rm x}$	2.3048 (11)
V3—O12	1.6016 (13)	N1—C1	1.489 (3)
V3—O1	1.8327 (13)	N2—C2	1.499 (3)
V3—O9$^{\rm ii}$	1.8684 (12)	N3—C3	1.480 (2)
V3—O4$^{\rm iii}$	1.9142 (12)	C1—C2$^{\rm i}$	1.513 (3)
V3—O6$^{\rm iii}$	2.0518 (12)	C3—C3$^{\rm xi}$	1.517 (3)
V3—O13$^{\rm iv}$	2.2984 (11)		
O6—V1—O7	106.15 (6)	O9$^{\rm ii}$—V3—O6$^{\rm iii}$	83.95 (5)
O6—V1—O3	98.98 (5)	O4$^{\rm iii}$—V3—O6$^{\rm iii}$	83.00 (5)
O7—V1—O3	97.02 (5)	O12—V3—O13$^{\rm iv}$	175.98 (6)
O6—V1—O2	96.38 (5)	O1—V3—O13$^{\rm iv}$	82.48 (5)
O7—V1—O2	96.40 (5)	O9$^{\rm ii}$—V3—O13$^{\rm iv}$	78.27 (5)
O3—V1—O2	155.91 (5)	O4$^{\rm iii}$—V3—O13$^{\rm iv}$	78.19 (4)
O6—V1—O13$^{\rm i}$	88.13 (5)	O6$^{\rm iii}$—V3—O13$^{\rm iv}$	74.84 (4)
O7—V1—O13$^{\rm i}$	165.65 (5)	O11—V4—O8$^{\rm v}$	103.71 (6)
O3—V1—O13$^{\rm i}$	81.74 (5)	O11—V4—O9	104.19 (6)
O2—V1—O13$^{\rm i}$	80.32 (4)	O8$^{\rm v}$—V4—O9	94.53 (6)
O6—V1—O13	166.52 (5)	O11—V4—O2$^{\rm vi}$	99.07 (6)
O7—V1—O13	87.22 (5)	O8$^{\rm v}$—V4—O2$^{\rm vi}$	154.80 (5)
O3—V1—O13	80.66 (4)	O9—V4—O2$^{\rm vi}$	90.18 (5)
O2—V1—O13	80.10 (4)	O11—V4—O3$^{\rm vii}$	98.32 (6)
O13$^{\rm i}$—V1—O13	78.46 (5)	O8$^{\rm v}$—V4—O3$^{\rm vii}$	89.69 (5)
O10—V2—O5	102.56 (7)	O9—V4—O3$^{\rm vii}$	155.37 (5)
O10—V2—O4	104.19 (6)	O2$^{\rm vi}$—V4—O3$^{\rm vii}$	76.37 (5)
O5—V2—O4	96.52 (6)	O11—V4—O13$^{\rm vii}$	172.91 (5)
O10—V2—O3	101.29 (6)	O8$^{\rm v}$—V4—O13$^{\rm vii}$	80.70 (5)
O5—V2—O3	153.41 (5)	O9—V4—O13$^{\rm vii}$	80.77 (5)
O4—V2—O3	88.84 (5)	O2$^{\rm vi}$—V4—O13$^{\rm vii}$	75.64 (4)
O10—V2—O2$^{\rm i}$	99.03 (6)	O3$^{\rm vii}$—V4—O13$^{\rm vii}$	75.98 (4)
O5—V2—O2$^{\rm i}$	88.44 (5)	O14—V5—O1$^{\rm viii}$	104.69 (7)
O4—V2—O2$^{\rm i}$	154.52 (5)	O14—V5—O8	101.55 (6)
O3—V2—O2$^{\rm i}$	76.35 (5)	O1$^{\rm viii}$—V5—O8	91.75 (6)
O10—V2—O13$^{\rm i}$	174.18 (6)	O14—V5—O5$^{\rm ix}$	101.80 (6)
O5—V2—O13$^{\rm i}$	79.88 (5)	O1$^{\rm viii}$—V5—O5$^{\rm ix}$	91.65 (6)
O4—V2—O13$^{\rm i}$	80.63 (5)	O8—V5—O5$^{\rm ix}$	154.70 (5)
O3—V2—O13$^{\rm i}$	75.32 (4)	O14—V5—O7$^{\rm x}$	97.82 (6)
O2$^{\rm i}$—V2—O13$^{\rm i}$	75.65 (4)	O1$^{\rm viii}$—V5—O7$^{\rm x}$	157.49 (5)
O12—V3—O1	101.47 (7)	O8—V5—O7$^{\rm x}$	84.15 (5)
O12—V3—O9$^{\rm ii}$	102.19 (7)	O5$^{\rm ix}$—V5—O7$^{\rm x}$	83.17 (5)
O1—V3—O9$^{\rm ii}$	92.08 (6)	O14—V5—O13$^{\rm x}$	173.16 (6)
O12—V3—O4$^{\rm iii}$	100.79 (7)	O1$^{\rm viii}$—V5—O13$^{\rm x}$	82.15 (5)
O1—V3—O4$^{\rm iii}$	91.97 (6)	O8—V5—O13$^{\rm x}$	78.02 (5)
O9$^{\rm ii}$—V3—O4$^{\rm iii}$	155.36 (5)	O5$^{\rm ix}$—V5—O13$^{\rm x}$	77.63 (5)
O12—V3—O6$^{\rm iii}$	101.21 (6)	O7$^{\rm x}$—V5—O13$^{\rm x}$	75.34 (4)
O1—V3—O6$^{\rm iii}$	157.31 (5)		

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 2-y, 1-z$; (iv) $x, y, 1+z$; (v) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (vi) $x, y-1, z$; (vii) $-x, 1-y, -z$; (viii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (ix) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (x) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (xi) $-x, -y, 1-z$.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *MOLVIEW* (Cense, 1992).

The authors thank Professor M. Leblanc (Université du Maine) for his help in data collection.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1141). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(dimethyl sulfoxide-*O*)copper(II) Bis(perchlorate)

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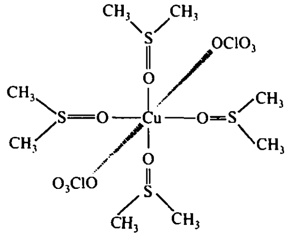
Abstract

The four dimethyl sulfoxide ligands of the title complex, $[Cu(C_2H_6OS)_4]^{2+}.2ClO_4^-$, adopt a tetrahedrally distorted square-planar arrangement around the central Cu^{II} ion, with all Cu—O bond lengths falling within the range 1.934 (6)–1.954 (6) Å. One O atom from each of the axial perchlorate anions interacts weakly at distances of 2.466 (8) and 2.640 (8) Å.

Comment

The dimethyl sulfoxide (DMSO) ligands of the title complex, (I), were found to form a distorted square-planar arrangement around the central Cu^{II} ion, with all angles around the Cu ion close to 90° [O31—Cu—O21 92.1 (3), O11—Cu—O31 86.8 (3), O21—Cu—O41 88.2 (3), O41—Cu—O11 93.5 (3)°]. The Cu ion was found to lie exactly in the mean plane of the four coordinating O atoms; however, there is a tetrahedral distortion at the metal centre, with O11 and O21 lying above [both by 0.105 (3) Å], and O31 and O41 falling below [by 0.106 (4) and 0.104 (3) Å, respectively] this plane. The four S atoms lie on the same side of the O_4 plane, but their deviations from it vary widely: for S1, S2, S3 and S4 these are 0.978 (8), 0.209 (8), 0.582 (9) and 0.092 (9) Å, respectively. There is, in addition, an interaction between the ligands themselves, with each S atom interacting weakly with the O atom of a neighbouring ligand at distances of 2.873 (6)–3.188 (6) Å.



(I)

The C—S bond lengths within the complex [1.754 (10)–1.789 (10) Å] are apparently shorter and the S—O bond lengths [1.505 (6)–1.534 (6) Å] somewhat longer than in uncoordinated sulfoxides [1.81 (3) and 1.497 (13) Å, respectively (Allen *et al.*, 1987)]. Any difference is presumably due to the withdrawal of electron density from the S atom and the diminishing of the S—O double-bond character on coordination.

The structure of (I) differs from the structures of $Cu(DMSO)_2Cl_2$ (Willett & Chang, 1970) and $Cu(DMSO)_2Br_2$ (Willett, Jardine & Roberts, 1977), both of which exhibit five-coordinate geometry around the Cu-atom centre. Both structures contain four normal

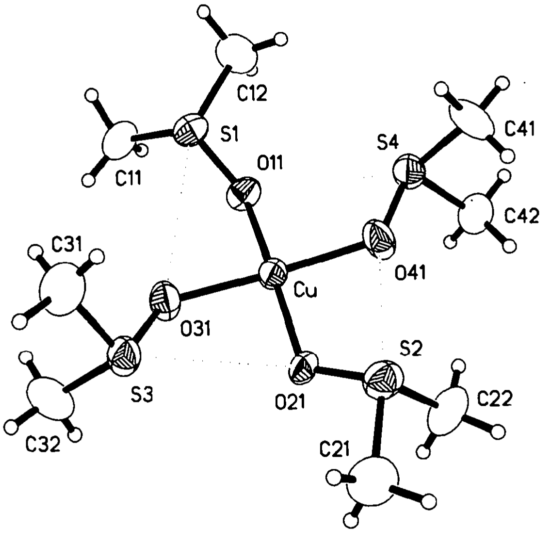


Fig. 1. A view of the complex (I) with atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii. Dotted lines indicate interactions between adjacent coordinated DMSO ligands. The axially coordinated perchlorate anions have been omitted for clarity.

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