Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
Dickson, R. S. (1985). In *Homogeneous Catalysis with Compounds of Rhodium and Iridium*. Dordrecht: D. Reidel.
Fernández, M. J., Esteruelas, M. A., Covarrubias, M., Oro, L. A., Apreda, M.-C., Foces-Foces, C. & Cano, F. H. (1989). *Organometallics*, **8**, 1158–1162.
Henrici-Olivé, G. & Olivé, S. (1977). *Coordination and Catalysis*, pp. 110–114. New York: Verlag Chemie.
Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
Steyn, G. J. J., Roodt, A. & Leipoldt, J. G. (1992). *Inorg. Chem.* **31**, 3477–3481.
Theron, M., Purcell, W. & Basson, S. S. (1995). *Inorg. Chim. Acta*. Submitted.

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Piperazine Metavanadate Trihydrate

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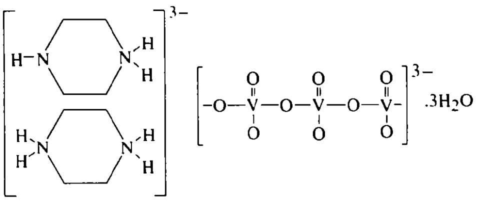
Abstract

The structure of piperazine-1,4-diium piperazin-1-ium metavanadate trihydrate, ($C_4H_{11}N_2$)($C_4H_{12}N_2$)V_3O_9.-$3H_2O$, is orthorhombic, space group *Pbca*, and contains infinite ($V_3O_9^{3-}$)$_n$ chains running along the *b* axis of the unit cell. These chains form layers running parallel to the (100) plane. The protonated piperazine molecules and three molecules of water are located between the ($V_3O_9^{3-}$)$_n$ chains, forming hydrogen bonds which contribute to the stabilization of the structure.

Comment

The common feature of the structures of the hydrated metavanadates that have been determined so far is the presence of chains formed by the linking of VO_5 polyhedra, as found in $KVO_3.H_2O$ (Christ, Clark & Evans, 1954), $Ca(VO_3)_2.2H_2O$ (Kelsey & Barnes, 1960), $Ca(VO_3)_2.4H_2O$ (Ahmed & Barnes, 1963), $Sr(VO_3)_2.4H_2O$ (Sedlacek & Dornberger-Schiff, 1965), $Cd(VO_3)_2.4H_2O$ (Ulická, 1988) and $Co(VO_3)_2.4H_2O$ (Avtamonova, Trunov & Bezrukov, 1990). The structures of $Ba(VO_3)_2.H_2O$ (Ulická, Pavelčík & Huml, 1987), $Co(VO_3)_2.2H_2O$ (Murashova, Velikodnii, Potapov & Trunov, 1988) and $Cu(VO_3)_2.2H_2O$ (Leblanc & Ferey, 1989) contain tetrahedrally coordinated V atoms. We describe here the structure of piperazine metavanadate trihydrate, (I).



(I)

The solution of the structure of piperazine metavanadate trihydrate shows that the asymmetric unit of the crystal structure consists of a $V_3O_9^{3-}$ unit, which is part of a polymeric anion, two piperazine cations unequally protonated (one cation is doubly protonated and the other is singly protonated) and three molecules of water. The metavanadate anions are infinite chains of VO_4 corner-sharing tetrahedra with each V atom in the centre of a tetrahedron formed by four O atoms. The V—O distances, 1.600 (4)–1.796 (4) Å, are within the range observed in other metavanadate anions. The O—V—O angles are in the range 107.5 (2)–111.5 (2)°, and give no indication of any strong distortion of the tetrahedral environment. The C—N distances in the piperazine cations are within the range observed in the cations in ethylenediammonium vanadate (Bensch, Hug, Reller & Oswald, 1987), *n*-hexylammonium metavanadate (Roman, Aranzabe, Luque & Gutiérrez-Zorrilla, 1991) and 3-aza-1,5-pentamethylenediammonium metavanadate (Roman,

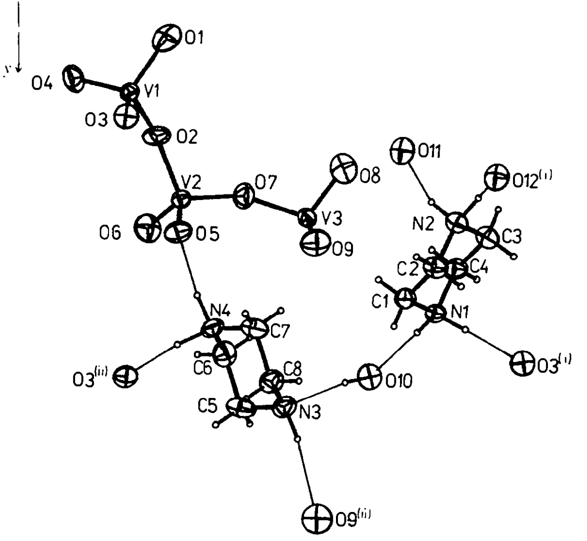


Fig. 1. A fragment of the structure of the title compound showing hydrogen-bonding contacts. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}-x$, $1-y$, $\frac{1}{2}+z$; (ii) $\frac{1}{2}-x$, $\frac{1}{2}+y$, z.]

Macias, Luque & Gutiérrez-Zorrilla, 1992), with bond distances in the range 1.446 (7)–1.479 (7) Å. The structure of metavanadate piperazine trihydrate is stabilized by an extended hydrogen-bond network between the non-corner-sharing O atoms in the metavanadate anion, the N atoms of the piperazine cations and the molecules of water.

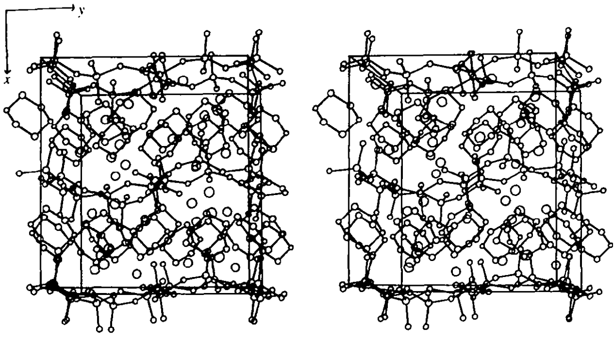


Fig. 2. A stereoscopic view of the title compound.

Experimental

Piperazine metavanadate trihydrate was prepared by dissolving V_2O_5 in an aqueous solution of piperazine. The resulting colourless solution (pH 8.5) was filtered and then acetone was added slowly. This solution was allowed to stand in a refrigerator. After several days colourless crystals of piperazine metavanadate trihydrate were obtained. The crystal density D_m was measured by flotation in dioxane.

Crystal data

$(C_4H_{11}N_2)(C_4H_{12}N_2)V_3O_9.3H_2O$
$M_r = 526.17$
Orthorhombic
Pbca
$a = 14.301\ (6)$ Å
$b = 13.037\ (5)$ Å
$c = 20.981\ (14)$ Å
$V = 3911.9\ (35)$ Å^3
$Z = 8$
$D_x = 1.79$ Mg m^{-3}
$D_m = 1.81\ (2)$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 15 reflections
$\theta = 6.25$–$10.15°$
$\mu = 1.468$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.55 × 0.35 × 0.2 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
ω–2θ scans
Absorption correction: none
4456 measured reflections
4456 independent reflections
2880 observed reflections $[F_o^2 > 2\sigma(F_o^2)]$

$\theta_{max} = 27.57°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 25$
2 standard reflections monitored every 98 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0568$
$wR(F^2) = 0.1261$

$(\Delta/\sigma)_{max} = 0.128$
$\Delta\rho_{max} = 0.513$ e Å^{-3}
$\Delta\rho_{min} = -0.764$ e Å^{-3}

$S = 1.125$
4443 reflections
292 parameters
H atoms were located by difference Fourier syntheses and were refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0666P)^2 + 3.7679P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0016 (2)
Atomic scattering factors from *SHELXL*93 (Sheldrick, 1993)

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

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

	x	y	z	U_{eq}
V1	0.06405 (5)	0.25265 (6)	0.10441 (4)	0.0235 (2)
V2	0.03059 (5)	0.48844 (6)	0.17178 (4)	0.0241 (2)
V3	0.02021 (5)	0.52991 (6)	0.33081 (4)	0.0251 (2)
O1	0.0430 (3)	0.1451 (3)	0.1505 (2)	0.0512 (11)
O2	0.0133 (2)	0.3620 (3)	0.1401 (2)	0.0407 (9)
O3	0.1775 (2)	0.2651 (3)	0.0971 (2)	0.0350 (8)
O4	0.0190 (3)	0.2395 (3)	0.0345 (2)	0.0440 (10)
O5	0.1395 (2)	0.5209 (3)	0.1656 (2)	0.0387 (9)
O6	−0.0298 (3)	0.5698 (3)	0.1313 (2)	0.0477 (10)
O7	−0.0061 (3)	0.4937 (3)	0.2515 (2)	0.0435 (10)
O8	−0.0122 (3)	0.4384 (3)	0.3770 (2)	0.0515 (11)
O9	0.1305 (3)	0.5456 (3)	0.3393 (2)	0.0503 (11)
O10	0.1719 (3)	0.8143 (3)	0.4088 (2)	0.0354 (9)
O11	0.1323 (3)	0.3532 (3)	0.4470 (2)	0.0405 (10)
O12	0.0963 (3)	0.6821 (3)	0.0598 (2)	0.0424 (10)
N1	0.2277 (3)	0.6614 (3)	0.4893 (2)	0.0302 (10)
N2	0.2742 (3)	0.4548 (3)	0.5137 (2)	0.0323 (10)
N3	0.2713 (3)	0.8440 (4)	0.2989 (2)	0.0380 (11)
N4	0.2285 (3)	0.6937 (4)	0.2085 (2)	0.0399 (12)
C1	0.2953 (4)	0.6076 (4)	0.4492 (2)	0.0321 (11)
C2	0.3437 (4)	0.5260 (4)	0.4859 (3)	0.0365 (12)
C3	0.2064 (4)	0.5090 (4)	0.5541 (3)	0.0341 (12)
C4	0.1579 (3)	0.5911 (4)	0.5168 (3)	0.0314 (11)
C5	0.2097 (4)	0.8669 (4)	0.2462 (3)	0.0421 (14)
C6	0.1593 (4)	0.7720 (4)	0.2259 (3)	0.0432 (14)
C7	0.2932 (4)	0.6718 (4)	0.2602 (3)	0.0410 (14)
C8	0.3407 (4)	0.7678 (4)	0.2809 (3)	0.0381 (13)

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

V1—O4	1.612 (4)	N1—C1	1.460 (6)
V1—O3	1.638 (3)	N1—C4	1.473 (6)
V1—O1	1.729 (4)	N2—C3	1.470 (6)
V1—O2	1.767 (4)	N2—C2	1.479 (7)
V2—O6	1.610 (4)	N3—C5	1.446 (7)
V2—O5	1.619 (3)	N3—C8	1.454 (7)
V2—O7	1.754 (4)	N4—C7	1.454 (8)
V2—O2	1.794 (4)	N4—C6	1.467 (7)
V3—O9	1.600 (4)	C1—C2	1.485 (7)
V3—O8	1.605 (4)	C3—C4	1.497 (7)
V3—O7	1.771 (4)	C5—C6	1.493 (8)
V3—O1^{i}	1.796 (4)	C7—C8	1.489 (7)
O4—V1—O3	108.8 (2)	O7—V3—O1^{i}	108.7 (2)
O4—V1—O1	110.7 (2)	V1—O1—V3^{ii}	152.6 (3)
O3—V1—O1	107.8 (2)	V1—O2—V2	147.3 (2)
O4—V1—O2	107.9 (2)	V2—O7—V3	147.5 (3)
O3—V1—O2	111.5 (2)	C1—N1—C4	112.1 (4)
O1—V1—O2	110.2 (2)	C3—N2—C2	111.7 (4)
O6—V2—O5	107.5 (2)	C5—N3—C8	111.0 (4)
O6—V2—O7	108.5 (2)	C7—N4—C6	112.3 (4)
O5—V2—O7	110.7 (2)	N1—C1—C2	110.7 (4)
O6—V2—O2	109.6 (2)	N2—C2—C1	109.9 (4)
O5—V2—O2	110.0 (2)	N2—C3—C4	110.3 (4)
O7—V2—O2	110.3 (2)	N1—C4—C3	109.6 (4)
O9—V3—O8	108.2 (2)	N3—C5—C6	110.0 (5)
O9—V3—O7	110.4 (2)	N4—C6—C5	108.8 (5)

O8—V3—O7	107.9 (2)	N4—C7—C8	110.1 (4)
O9—V3—O1^i	111.4 (2)	N3—C8—C7	109.8 (4)
O8—V3—O1^i	110.2 (2)		
N1—C1—C2—N2	56.1 (6)	N3—C5—C6—N4	−57.8 (6)
C1—C2—N2—C3	−56.8 (6)	C5—C6—N4—C7	56.8 (6)
C2—N2—C3—C4	57.2 (6)	C6—N4—C7—C8	−56.5 (6)
N2—C3—C4—N1	−56.2 (6)	N4—C7—C8—N3	56.2 (6)
C3—C4—N1—C1	57.0 (6)	C7—C8—N3—C5	−59.2 (6)
C4—N1—C1—C2	−57.5 (6)	C8—N3—C5—C6	60.4 (6)

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···A	H···A	D···A	D—H···A
N1—H18···O10	1.93 (4)	2.732 (6)	170 (6)
N1—H17···O3^i	1.96 (4)	2.806 (6)	173 (6)
N2—H19···O12^i	2.00 (4)	2.748 (6)	150 (6)
N2—H20···O11	2.05 (5)	2.799 (6)	149 (6)
N3—H21···O9^{ii}	2.30 (4)	3.098 (6)	174 (6)
N4—H23···O5	1.89 (4)	2.740 (6)	170 (6)
N4—H22···O3^{ii}	1.99 (4)	2.852 (6)	174 (6)
O10—H25···N3	1.89 (5)	2.737 (6)	162 (6)
O11—H26···O8	1.99 (5)	2.768 (6)	169 (6)
O11—H27···O4^{iii}	2.04 (5)	2.730 (6)	175 (8)
O12—H28···O6	2.04 (5)	2.765 (6)	168 (7)
O12—H29···O4^{iv}	2.11 (5)	2.770 (6)	155 (7)

Symmetry codes: (i) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iv) $-x, 1-y, -z$.

Data reduction: *XP*21 (Pavelčík, unpublished). Program(s) used to solve structure: *XFPS* (Pavelčík, Sivý, Rizzoli & Andreetti, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ahmed, F. R. & Barnes, W. H. (1963). *Can. Mineral.* **7**, 713–726.

Avtamonova, N. V., Trunov, V. K. & Bezrukov, J. I. (1990). *Neorg. Mater.* **26**, 346–349.

Bensch, W., Hug, P., Reller, A. & Oswald, H. R. (1987). *Mater. Res. Bull.* **22**, 577–583.

Christ, C. L., Clark. J. R. & Evans, H. T. Jr (1954). *Acta Cryst.* **7**, 801–807.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kelsey, C. A. & Barnes, W. H. (1960). *Can. Mineral.* **6**, 448–466.

Leblanc, M. & Ferey, G. (1989). *Acta Cryst.* **C46**, 15–18.

Murashova, E. V., Velikodnii, J. A., Potapov, M. A. & Trunov, V. K. (1988). *Neorg. Mater.* **24**, 519–521.

Pavelčík, F., Sivý, J., Rizzoli, C. & Andreetti, G. D. (1992). *J. Appl. Cryst.* **25**, 328–329.

Roman, P., Aranzabe, A., Luque, A. & Gutiérrez-Zorrilla, J. M. (1991). *Mater. Res. Bull.* **26**, 19–27.

Roman, P., Macias, R., Luque, A. & Gutiérrez-Zorrilla, J. M. (1992). *Mater. Res. Bull.* **27**, 573–580.

Sedlacek, P. & Dornberger-Schiff, K. (1965). *Acta Cryst.* **18**, 407–410.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Ulická, Ľ. (1988). *Chem. Zvesti*, **42**, 11–19.

Ulická, Ľ., Pavelčík, F. & Huml, K. (1987). *Acta Cryst.* **C43**, 2266–2268.

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$Me_2Cd(dabco)$

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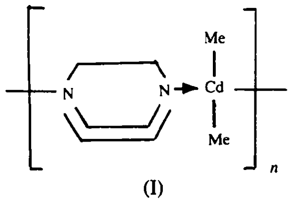
Abstract

The title compound, *catena*-poly[dimethylcadmium-μ-1,4-diazabicyclo[2.2.2]octane], $[Cd(CH_3)_2(C_6H_{12}N_2)]$, was synthesized and the crystal structure determined by X-ray diffraction methods. The complex was found to be a 1:1 linear polymer with four coordinated Cd atoms per unit cell. The Cd atom has distorted tetrahedral coordination.

Comment

The development of high-purity precursors for the preparation of II–VI semiconductor materials has been of critical importance for successful device fabrication. The realisation of techniques such as metal-organic chemical vapour deposition (MOCVD) and organometallic vapour-phase epitaxy (OMVPE) has been delayed by the inadequacy of the source materials available. We report here the synthesis and crystal structure of $Me_2Cd(dabco)$, (I) (where dabco is 1,4-diazabicyclo[2.2.2]octane), as a new MOCVD precursor (Bradley & Hursthouse, 1992; Jones & Rushworth, 1989).



(I)

The molecular structure and molecular arrangement in the unit cell are illustrated in Fig. 1. The complex consists of a 1:1 molecular adduct of dimethylcadmium bonded to dabco and has a linear polymeric structure. The Cd atom in the complex is coordinated in a distorted tetrahedral arrangement by two N atoms of two different

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