

- Boughzala, H., Driss, A. & Jouini, T. (1993). *Acta Cryst.* **C49**, 425–427.
- Boughzala, H. & Jouini, T. (1995). *Acta Cryst.* **C51**, 179–181.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Dowty, E. (1993). *ATOMS*. Version 2.3. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, EU.
- Driss, A. & Jouini, T. (1994). *J. Solid State Chem.* **112**, 277–280.
- Duisenberg, A. J. M. (1992). *J. Appl. Cryst.* **25**, 92–96.
- Effenberger, H. & Pertlik, F. (1993). *Z. Kristallogr.* **207**, 223–236.
- Enjalbert, R., Hasselmann, G. & Galy, J. (1997). *Acta Cryst.* **C53**, 269–272.
- Eysel, W. & Jie, Y. C. (1992). Mineralogische und Petrographische Institut, Universität Heidelberg, Allemagne.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, Les Pays-Bas.
- Macíček, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.
- Mairesse, G., Drache, M., Nowogrocki, G. & Abraham, F. (1990). *Phase Transitions*, **27**, 91–105.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Universität de Göttingen, Allemagne.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Universität de Göttingen, Allemagne.
- Wang, S.-L., Wu, C.-H. & Liu, S.-N. (1994). *J. Solid State Chem.* **113**, 37–40.

Acta Cryst. (1998). **C54**, 1733–1735

(NH₄)₄Na₂[Mo₂V₂^{IV}V₆^VO₂₈].10H₂O

YAN XU,^a JI-QING XU,^{a*} GUO-YU YANG,^a YAN XING,^b
YONG-HUA LIN^b AND HENG-QING JIA^b

^aDepartment of Chemistry, Jilin University, Changchun, Jilin 130023, People's Republic of China, and ^bChangchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin 130022, People's Republic of China. E-mail: people@mail.jlu.edu.cn

(Received 5 January 1998; accepted 29 June 1998)

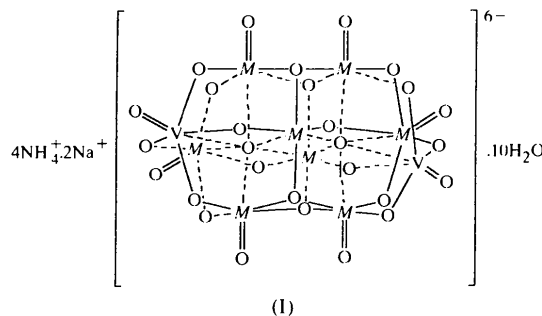
Abstract

The title compound, tetraammonium disodium octacosaoxo(dimolybdenumoctavanadium)ate decahydrate, is a mixed V/Mo salt which has a well known decavanadate structure. The centrosymmetric polyanion consists of eight (V/Mo)O₆ and two VO₆ edge-sharing distorted octahedra. Each of the two Na⁺ cations is surrounded by six water molecules in a distorted octahedral arrangement. The V—O and (V/Mo)—O distances are between 1.571 (6) and 2.432 (5) Å.

Comment

Numerous crystal structures of decavanadates have been reported, for example, Na₆V₁₀O₂₈.12H₂O (Xu *et al.*,

1996) and (C₄H₁₂N)₄[Li(H₂O)₄][V₁₀O₂₈].4H₂O (Zavalij *et al.*, 1997). However, only one example of the structure of a mixed decaoxometallate of vanadium with molybdenum, [(CH₃)₄N]₄[H₂MoV₉O₂₈].6H₂O, has been reported (Strukan *et al.*, 1997). We report here the single-crystal structure of the reduced V/Mo decaoxometallate (NH₄)₄Na₂(Mo₂V₂^{IV}V₆^VO₂₈).10H₂O, (I), where eight Mo/V-atom positions in the structure are occupied by six V and two Mo atoms.



The structure of the centrosymmetric polyanion [Mo₂V₂^{IV}V₆^VO₂₈]⁶⁻ is similar to that of the polyanions [V₁₀O₂₈]⁶⁻ (Xu *et al.*, 1996; Zavalij *et al.*, 1997) and [MoV₉O₂₈]⁵⁻ (Strukan *et al.*, 1997), and consists of eight Mo/VO₆ and two VO₆ edge-sharing octahedra. The O atoms in the anion can be divided into four groups, O_c, O_{3b}, O_{2b} and O_t, where O_t represents a terminal O atom bound to one metal atom (Mo/V or V atom), O_{2b} represents a doubly bridging O atom bound to two metal atoms, O_{3b} represents a triply bridging O atom bound to three metal atoms and O_c represents a central O atom coordinated to six metal atoms. The distances from metal M (Mo/V

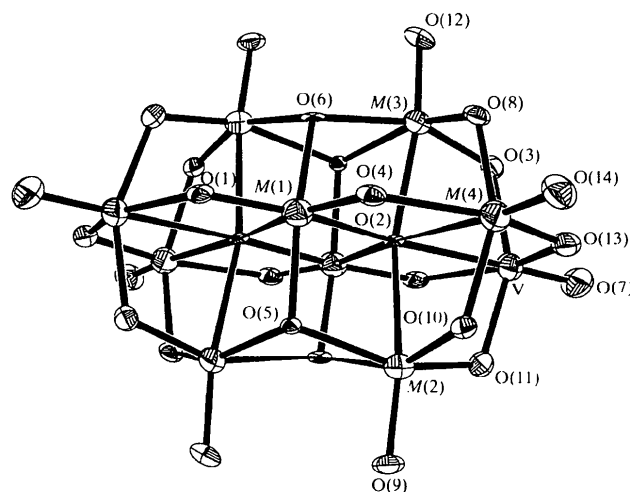


Fig. 1. The structure of [Mo₂V₂^{IV}V₆^VO₂₈]⁶⁻ drawn with 50% probability displacement ellipsoids. The eight metal (M) positions are randomly occupied by two Mo and six V atoms.

or V) to oxygen are $M-O_i$ 1.571 (6)–1.692 (6), $M-O_{2b}$ 1.660 (5)–2.175 (5), $M-O_{3b}$ 1.869 (4)–2.132 (5) and $M-O_c$ 2.049 (4)–2.432 (5) Å. A similar trend has been found in Na₆V₁₀O₂₈.12H₂O (Xu *et al.*, 1996), (C₄H₁₂N)₄[Li(H₂O)₄][V₁₀O₂₈].4H₂O (Zavalij *et al.*, 1997) and [(CH₃)₄N]₄[H₂MoV₉O₂₈].Cl.6H₂O (Strukan *et al.*, 1997). Each Na⁺ cation is coordinated by six water molecules, with Na—O distances between 2.289 (7) and 2.555 (7) Å.

Experimental

The title compound was synthesized by a hydrothermal method. A mixture of NH₄VO₃, Na₂MoO₄, H₂C₂O₄ and H₂O (pH = 6.0) was sealed in a 15 ml Teflon-lined reactor and kept at 433 K for 4 d. On cooling to room temperature, a blue solution resulted. After standing for 2 d, dark-brown single crystals suitable for X-ray diffraction studies were obtained.

Crystal data

(NH ₄) ₄ Na ₂ [Mo ₂ V ₈ O ₂₈].10H ₂ O	Mo $K\alpha$ radiation
$M_r = 1345.71$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 30 reflections
$P\bar{1}$	$\theta = 4.72$ – 12.82°
$a = 8.595$ (2) Å	$\mu = 2.904$ mm ⁻¹
$b = 10.449$ (2) Å	$T = 293$ (2) K
$c = 11.243$ (2) Å	Prism
$\alpha = 68.96$ (3) $^\circ$	$0.36 \times 0.28 \times 0.16$ mm
$\beta = 81.14$ (3) $^\circ$	Dark brown
$\gamma = 66.90$ (3) $^\circ$	
$V = 866.7$ (3) Å ³	
$Z = 1$	
$D_x = 2.578$ Mg m ⁻³	
D_m not measured	

Data collection

Siemens P4 diffractometer	$R_{int} = 0.019$
ω - 2θ scans	$\theta_{max} = 25.39^\circ$
Absorption correction: empirical via ψ scans (North <i>et al.</i> , 1968)	$h = -1 \rightarrow 9$
$T_{min} = 0.582$, $T_{max} = 0.628$	$k = -10 \rightarrow 11$
2975 measured reflections	$l = -13 \rightarrow 13$
2237 independent reflections	3 standard reflections
1965 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{max} = 0.695$ e Å ⁻³
$wR(F^2) = 0.151$	$\Delta\rho_{min} = -0.698$ e Å ⁻³
$S = 1.065$	Extinction correction: none
2237 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
244 parameters	
H atoms not located	
$w = 1/[\sigma^2(F_o^2) + (0.0807P)^2 + 6.9369P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j a_i \cdot a_j$$

	Occupancy	x	y	z	U_{eq}
Mo1	0.22 (1)	0.68924 (14)	0.00360 (11)	0.47916 (11)	0.0261 (3)
V1	0.78 (1)	0.68924 (14)	0.00360 (11)	0.47916 (11)	0.0261 (3)
Mo2	0.38 (2)	0.52453 (13)	-0.00647 (10)	0.74361 (9)	0.0262 (3)
V2	0.62 (2)	0.52453 (13)	-0.00647 (10)	0.74361 (9)	0.0262 (3)
V	1	0.4722 (2)	-0.29089 (14)	0.76315 (13)	0.0261 (4)
Mo3	0.31 (2)	0.62224 (13)	-0.28588 (10)	0.50293 (10)	0.0246 (3)
V3	0.69 (2)	0.62224 (13)	-0.28588 (10)	0.50293 (10)	0.0246 (3)
Mo4	0.10 (1)	0.8258 (2)	-0.28573 (12)	0.72318 (12)	0.0263 (4)
V4	0.90 (1)	0.8258 (2)	-0.28573 (12)	0.72318 (12)	0.0263 (4)
Na	1	1.0681 (4)	-0.1668 (3)	0.1280 (3)	0.0280 (8)
O1	1	0.7391 (6)	0.1315 (5)	0.3598 (5)	0.0181 (11)
O2	1	0.5666 (5)	-0.1244 (5)	0.6056 (4)	0.0106 (10)
O3	1	0.5170 (6)	-0.3712 (5)	0.6313 (5)	0.0197 (11)
O4	1	0.8711 (6)	-0.1199 (5)	0.5732 (5)	0.0173 (11)
O5	1	0.6025 (6)	0.1205 (5)	0.5842 (4)	0.0117 (10)
O6	1	0.6822 (6)	-0.1145 (5)	0.3843 (4)	0.0128 (10)
O7	1	0.3897 (7)	-0.3973 (6)	0.8623 (5)	0.0334 (14)
O8	1	0.8270 (6)	-0.3638 (5)	0.5965 (5)	0.0177 (11)
O9	1	0.4924 (7)	0.1001 (5)	0.8266 (5)	0.0234 (12)
O10	1	0.7469 (6)	-0.1340 (5)	0.7942 (4)	0.0160 (11)
O11	1	0.4385 (6)	-0.1397 (5)	0.8318 (5)	0.0196 (11)
O12	1	0.6576 (7)	-0.3810 (5)	0.4108 (5)	0.0246 (12)
O13	1	0.7035 (7)	-0.3815 (5)	0.8239 (5)	0.0255 (13)
O14	1	1.0205 (7)	-0.3805 (6)	0.7877 (5)	0.0298 (13)
N1	1	1.1775 (9)	-0.2915 (7)	0.4933 (7)	0.028 (2)
N2	1	0.7212 (10)	-0.3250 (7)	0.0729 (7)	0.038 (2)
OW1	1	0.2067 (7)	-0.0143 (6)	0.9879 (5)	0.0320 (14)
OW2	1	0.9702 (8)	-0.3174 (7)	0.2987 (6)	0.045 (2)
OW3	1	0.6569 (8)	-0.6826 (6)	0.7533 (6)	0.042 (2)
OW4	1	1.0708 (9)	-0.3275 (7)	0.0252 (6)	0.044 (2)
OW5	1	1.0207 (8)	-0.0069 (7)	0.2425 (6)	0.044 (2)

Table 2. Selected geometric parameters (Å, $^\circ$)

M1—O1	1.660 (5)	V—O2	2.297 (4)
M1—O4	1.781 (5)	M3—O12	1.600 (5)
M1—O5	1.869 (4)	M3—O3	1.733 (5)
M1—O6	1.920 (4)	M3—O8	1.923 (5)
M1—O2	2.049 (4)	M3—O6	2.012 (5)
M1—O2'	2.223 (5)	M3—O5'	2.104 (5)
M2—O9	1.617 (5)	M3—O2	2.237 (4)
M2—O11	1.749 (5)	M4—O14	1.692 (6)
M2—O10	1.883 (5)	M4—O13	1.742 (5)
M2—O5	2.010 (4)	M4—O10	1.873 (5)
M2—O6'	2.132 (5)	M4—O8	1.875 (5)
M2—O2	2.215 (4)	M4—O4	2.056 (5)
M2—V	3.103 (2)	M4—O2	2.432 (5)
M2—M4	3.105 (2)	Na—OW2	2.289 (7)
V—O7	1.571 (6)	Na—OW5	2.338 (6)
V—O3	1.874 (5)	Na—OW4	2.346 (7)
V—O11	1.903 (5)	Na—OW1''	2.356 (6)
V—O13	1.947 (6)	Na—OW3'''	2.527 (7)
V—O1'	2.175 (5)	Na—OW1'	2.555 (7)
OW2—Na—OW5	89.8 (2)	M1—O2—M3	96.8 (2)
OW2—Na—OW4	83.6 (2)	M2—O2—M3	167.9 (2)
OW5—Na—OW4	170.5 (3)	M1—O2—V	170.4 (2)
M1—O2—M2	92.2 (2)		

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1+x, y, z-1$; (iii) $2-x, -1-y, 1-z$.

The occupancy factors of V and Mo on each of the M1, M2, M3 and M4 sites were refined as least-squares parameters, with the sum constrained to be 1.0.

Data collection: P4 (Siemens, 1994a). Cell refinement: P4 and XSCANS (Siemens, 1994b). Data reduction: XSCANS. Program(s) used to solve structure: SHELXL86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-

Plus (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL93*.

This work was supported by grants from the Natural Science Foundation of China (Nos. 29733090 and 29671012) and the State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1273). Services for accessing these data are described at the back of the journal.

References

- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.
- Sheldrick, G. M. (1990). *SHELXTL-Plus. Structure Determination Software Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Siemens (1994a). *P4. Program for Data Collection*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994b). *XSCANS. X-ray Single Crystal Analytical System*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Strukan, N., Cindrić, M. & Kamenar, B. (1997). *Polyhedron*, **16**, 629–634.
- Xu, J. N., Yang, G. Y., Sun, H. R., Wang, T. G. & Xu, J. Q. (1996). *J. Struct. Chem.* **15**, 253–256.
- Zavalij, P. Y., Chirayil, T., Whittingham, M. S., Pecharsky, V. K. & Jacobson, R. A. (1997). *Acta Cryst.* **C53**, 170–171.

Acta Cryst. (1998). **C54**, 1735–1737

Bis(trichlorophosphine)iminium Hexachlorophosphate

FERDINAND BELAJ

*Institut für Anorganische Chemie, Karl-Franzens-Universität
Graz, Schubertstraße 1, A-8010 Graz, Austria. E-mail:
belaj@kfunigraz.ac.at*

(Received 22 April 1998; accepted 16 July 1998)

Abstract

The structure of the title compound, trichloro[(trichlorophosphoranylidene)iminio]phosphorus(V) hexachlorophosphate, $(\text{NP}_2\text{Cl}_6)\text{PCl}_6$ or $[\text{N}(\text{PCl}_3)_2]^+\cdot\text{PCl}_6^-$, contains two formula units in the asymmetric unit. The cations show slightly distorted C_{2v} symmetry. The P—N dis-

tances range from 1.556 (3) to 1.562 (3) Å and the P—N—P bonding angles are 133.3 (2) and 135.8 (2)°.

Comment

The crystal structure of the title compound, (I), was previously determined by Faggiani *et al.* (1980). They isolated the compound from a complex mixture of solid products of the reaction of S_7NH with PCl_5 . Since they collected reflection data at room temperature using $\text{Mo K}\alpha$ radiation only to a maximum θ of 17.5°, the P—N distances in the two cations of the asymmetric unit range from 1.513 (13) to 1.561 (10) Å. In the course of our work on trichlorophosphazenes, more accurate structural data of this fundamental substance were desirable.

In principle, the structure determination of (I) performed at 95 K confirmed the earlier structure analysis. The atomic labelling scheme was retained. The P—N distances in the two cations of the asymmetric unit are now much more reliable; as expected, the P—N distances within a cation are equal. According to the correlation between the P—N distance and the P—N—P bonding angle in acyclic compounds (Belaj, 1995a), the mean value of these distances is larger by about two standard deviations in the cation which is more bent by packing forces. Both cations show only slightly distorted *trans-trans* conformations [the groupings of Cl—P—N—P—Cl display a 'W' form, with torsion angles Cl—P—N—P ≥ 174.0 (2)°], as observed in $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$ (Belaj, 1993) or in $\text{SO}_2(\text{NPCl}_3)_2$ (Belaj, 1995b). As discussed in the latter work, the N—P—Cl angles including a Cl atom of the 'W' fragment (namely Cl14, Cl18, Cl20 and Cl22) are significantly smaller [109.36 (12)–110.04 (12)°] than the others [112.76 (12)–113.97 (12)°], whereas the opposite is true for the Cl—P—Cl angles [106.80 (6)–107.64 (6) versus 105.60 (6)–106.20 (6)°].

In the PCl_6^- anions, the P—Cl distances range from 2.1212 (12) to 2.1624 (12) Å, the *cis* Cl—P—Cl angles range from 89.32 (5) to 90.85 (5)° and no *trans* angle is smaller than 179.0 (6)°.

There are two remarkably short inter-ionic Cl \cdots Cl distances between the anions [Cl2 \cdots Cl11 3.182 (2) and Cl7 \cdots Cl17 3.194 (2) Å, compared with the sum of the van der Waals radii of 3.50 Å (Bondi, 1964)]. They are also present but not mentioned in the room-temperature structure determination of Faggiani *et al.* (1980) [3.186 (8) and 3.260 (7) Å, respectively]. In contrast, the shortest inter-ionic Cl \cdots Cl distances are 3.335 (1) Å between a cation and an anion, and 3.630 (2) Å between two cations. This strange situation, in which contacts between counter-ions are larger than between anions, shows that a simple inspection of short interionic Cl \cdots Cl contacts is not sufficient, and that an examination of the arrangement of the P atoms at the centre of the anions and in the NPCl_3 groups of the cations is necessary.