

Decaammonium dodecatungstate nonahydrate, (NH₄)₁₀[H₂W₁₂O₄₂]·9H₂O: anionic 'isomorphism'

Graeme J. Gainsford,* S. V.
Chong, B. Ingham and J. L. Tallon

Industrial Research Limited, PO Box 31-310,
Lower Hutt, New Zealand

Correspondence e-mail: g.gainsford@irl.cri.nz

Key indicators

Single-crystal X-ray study

T = 168 K

Mean $\sigma(W-O)$ = 0.012 Å

H-atom completeness 0%

Disorder in solvent or counterion

R factor = 0.051

wR factor = 0.128

Data-to-parameter ratio = 28.5

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

The title salt crystallizes in an almost identical cell to that of (NH₄)₆[H₆W₁₂O₄₂]·10H₂O [Averbuch-Pouchot, Tordjman, Durif & Guitel (1979). *Acta Cryst.* B35, 1675–1677]. While the centrosymmetric anion coordinates are isomorphous, refinement confirms the different ammonium cation and water content, even though the H atoms cannot be unambiguously determined.

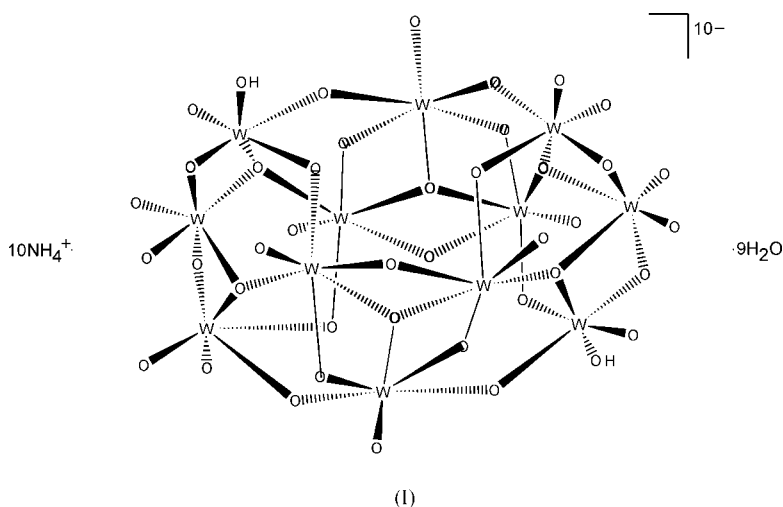
Received 3 September 2002

Accepted 18 September 2002

Online 27 September 2002

Comment

The title compound, (I), was prepared as a by-product while attempting to use aniline as an organic amine inter-layer spacer molecule for new inorganic oxide-layered compounds. The crystal structure comprises [H₂W₁₂O₄₂]^{10−} anions (Fig. 1) bound in an infinite three-dimensional network through hydrogen bonding with NH₄⁺ cations and water molecules. There are at least 42 contacts between the anion O atoms, amine N atoms and water O atoms within normal hydrogen-bonding distances, *e.g.* O22···O2W 2.76 (2) Å.



The two independent anions in the asymmetric unit are centrosymmetric and are essentially identical (truly isomorphous) with those in (NH₄)₆[H₆W₁₂O₄₂]·10H₂O (Averbuch-Pouchot *et al.*, 1979, hereafter AVEPOU). The final cell composition is inferred from the consistency of the refined displacement parameters of the water O atoms and ammonium cation N atoms, the analytical data, and the proximity of cations to each other, since the positions of the H atoms cannot be determined unambiguously in the presence of the W atoms. The atom-numbering scheme for the anions follows that in AVEPOU, with the coordinates transformed into one asymmetric unit. The cell volume here is slightly larger [2542 (2) Å³ at 168 K compared with 2540 Å³ at 293 K for

AVEPOU], as expected from the greater total number of cations and water molecules. Other structures found in the Cambridge Structural Database [Allen & Kennard, 1993; *Conquest* (CCDC, 2002)] containing the same $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anion are the closely related $(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 10\text{H}_2\text{O}$, which crystallizes in space group *Pbca*, as reported by Allmann (1971), and a decasodium diglycine salt (Naruke *et al.*, 2000). A summary of the expected geometry of the anions is given in the paper reporting $\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 20\text{H}_2\text{O}$ (Evans & Rollins, 1976). The internally self-consistent range of W—O distances is indicated in Table 1 by those found for W1.

A larger crystal from another preparation was also examined; it had a slightly smaller cell [$2510(1) \text{ \AA}^3$ at 168 K], but the diffraction data were not as good, with an internal agreement R_{int} of 0.068, and the subsequent refinement was less stable. The isomorphism of the anion coordinates reported here with those in the six-cation structure AVEPOU suggests that this larger crystal could be made up of plate-like twins, possibly with variable cation/water composition.

Experimental

The compound was prepared as a by-product of the reaction of H_2WO_4 with aniline in an ammonia (0.1 N) solution and recrystallized from water [N content calculated for $(\text{H}_{60}\text{N}_{10}\text{O}_{51}\text{W}_{12})$, 4.35%; found 4.33%].

Crystal data

$(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 9\text{H}_2\text{O}$	$Z = 2$
$M_r = 3222.78$	$D_x = 4.211 \text{ Mg m}^{-3}$
Triclinic, <i>P1</i>	Mo $K\alpha$ radiation
$a = 11.945(4) \text{ \AA}$	Cell parameters from 8000 reflections
$b = 13.225(5) \text{ \AA}$	$\theta = 2.3\text{--}26.3^\circ$
$c = 16.780(6) \text{ \AA}$	$\mu = 26.20 \text{ mm}^{-1}$
$\alpha = 76.159(5)^\circ$	$T = 168(2) \text{ K}$
$\beta = 80.985(5)^\circ$	Plate, colourless
$\gamma = 88.763(5)^\circ$	$0.44 \times 0.14 \times 0.06 \text{ mm}$
$V = 2541.6(15) \text{ \AA}^3$	

Data collection

Siemens SMART CCD area-detector diffractometer	10192 independent reflections
φ and ω scans	7208 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.047$
$T_{\text{min}} = 0.355$, $T_{\text{max}} = 0.592$	$\theta_{\text{max}} = 26.5^\circ$
32370 measured reflections	$h = -14 \rightarrow 14$
	$k = -16 \rightarrow 16$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 6.04 \text{ e \AA}^{-3}$
10192 reflections	$\Delta\rho_{\text{min}} = -5.45 \text{ e \AA}^{-3}$
357 parameters	

Table 1

Selected interatomic distances (\AA).

W1—O38	1.764 (12)	W1—O37	2.168 (10)
W1—O34	1.768 (12)	W1—O1	2.258 (12)
W1—O10 ⁱ	1.874 (12)	W6—O1	2.400 (12)
W1—O35	1.947 (12)		

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

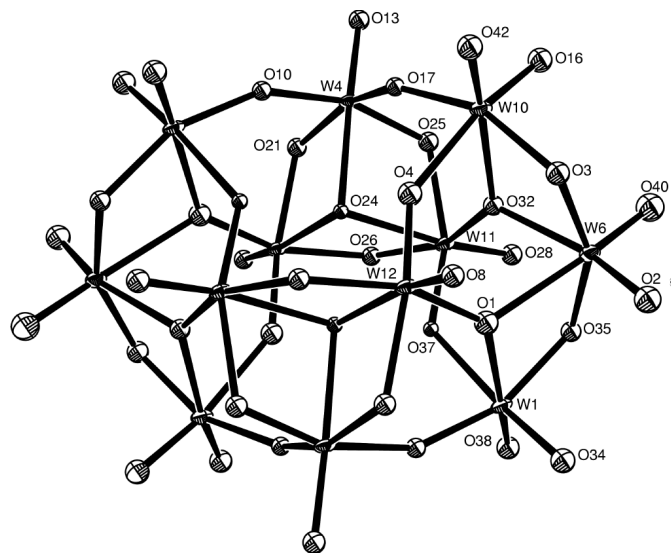


Figure 1

The molecular structure of one of the two independent $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anions. Displacement ellipsoids are drawn at the 50% probability level (Farrugia, 1997) and labels for centrosymmetrically related atoms have been omitted.

No H atoms were included in the refinement. One disordered water O atom (O9WA) was refined over two sites with final occupancies 0.52 (3)/0.48 (3) and a common U value of $0.045(6) \text{ \AA}^2$. The largest residual electron-density peak was located 0.99 \AA from W6 and the deepest hole 1.07 \AA from W7.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank Dr J. Wikaira and Professor Ward T. Robinson of the University of Canterbury for their assistance.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Allmann, Von R. (1971). *Acta Cryst.* **B27**, 1393–1404.
- Averbuch-Pouchot, M. T., Tordjman, I., Durif, A. & Guitel, J. C. (1979). *Acta Cryst.* **B35**, 1675–1677.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- CCDC (2002). *ConQuest*. Version 1.3. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Evans, H. T. & Rollins, O. W. (1976). *Acta Cryst.* **B32**, 1565–1567.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Naruke, H., Fukuda, N. & Yamase, T. (2000). *Acta Cryst.* **C56**, 177–178.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.