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$(NH_4)_2(NH_3(CH_2)_6NH_3)_4[H_2W_{12}O_{42}]\cdot 8H_2O$: a novel ammonium 1,6-hexanediammonium dodecatungstate

Graeme J. Gainsford,* Natalie Robinson and J. L. Tallon

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

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

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Key indicators

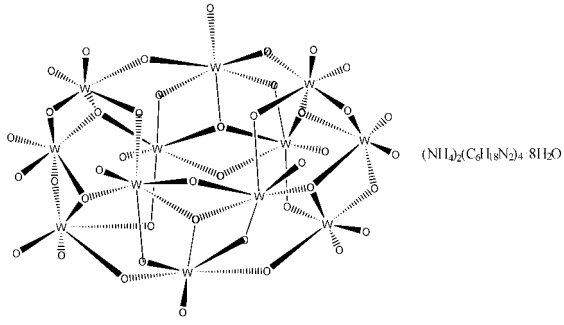
Single-crystal synchrotron study
T = 100 K
Mean σ(C–C) = 0.018 Å
H-atom completeness 49%
R factor = 0.038
wR factor = 0.103
Data-to-parameter ratio = 20.5

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

A novel ammonium 1,6-hexanediammonium dodecatungstate, $(NH_4)_2(NH_3(CH_2)_6NH_3)_4[H_2W_{12}O_{42}]\cdot 8H_2O$, contains centrosymmetric $[H_2W_{12}O_{42}]^{10-}$ anions separated by the ammonium and 1,6-hexanediammonium cations, and water molecules, in a pseudo-layer structure.

Comment

The title compound, (I), was prepared as part of a study into the use of organic amine inter-layer spacer molecules for inorganic oxide-layered compounds. The crystal structure comprises $[H_2W_{12}O_{42}]^{10-}$ anions bound in an infinite three-dimensional network through hydrogen bonding with 1,6-hexanediammonium^{2+} and NH_4^+ cations and water molecules, as shown in Fig. 1. There are at least 34 contacts between the anion O atoms, amine N atoms and water O atoms within normal hydrogen-bonding distances, *e.g.* O6···O3*W* 2.814 (12) Å. Other minor intermolecular interactions are also found, *e.g.* C11—H···O3 with C11···O3 3.38 (2) Å (Spek, 1990).



(I)

The anions are centrosymmetric, and the final cell composition is inferred from the analytical data and chemically reasonable refinement options, since the X-ray scattering of H atoms cannot be determined unambiguously in the presence of the W atoms. The atom-numbering scheme for the anion follows that in $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 10H_2O$ (Allmann, 1971). A closely related six-ammonium cation $(NH_4)_6[H_6W_{12}O_{42}]\cdot 10H_2O$ structure has been reported by Averbuch-Pouchot *et al.* (1979), and a decasodium diglycine $[H_2W_{12}O_{42}]^{10-}$ salt recently by Naruke *et al.* (2000).

The 1,6-hexanediammonium cations, which are aligned approximately along the *c* axial direction, can be considered to separate the anions by the length of the molecule along this axis. By contrast, the other 1,6-hexanediammonium cations, aligned along the *b* axis (end-on in Fig. 1), separate the anions

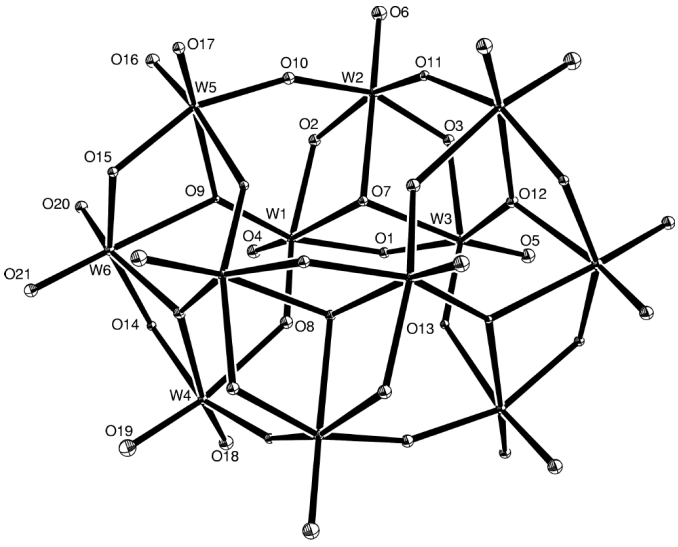


Figure 1
A view of the $[H_2W_{12}O_{42}]^{10-}$ anion, showing atom labels (Farrugia, 1997); centrosymmetrically related atoms are not labelled. Displacement ellipsoids are drawn at the 50% probability level. H atoms were not located.

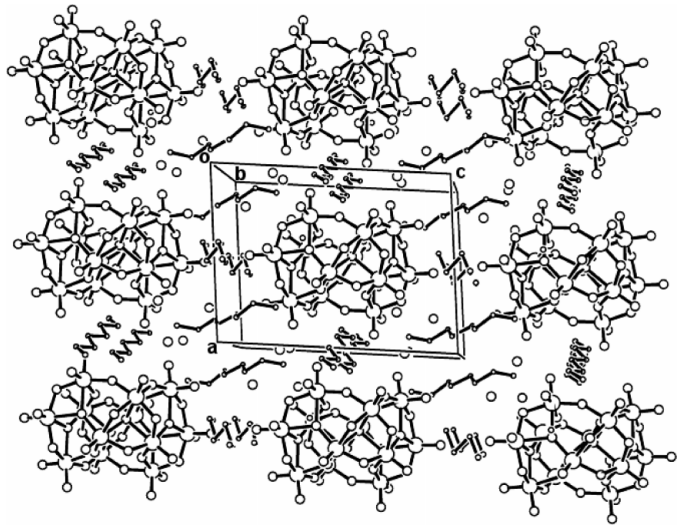


Figure 2
Cell packing diagram of (I), viewed down the *b* axis. (Farrugia, 1997). All atoms have arbitrary radii, in reducing size order W,O,N,C. H atoms on the 1,6-hexanediammonium cations are excluded for clarity.

by the width of the molecule. This pseudo-layer packing is reflected in the platy nature of the crystals.

Experimental

The compound was prepared by the reaction of H_2WO_4 with diaminohexane in an ammonia (0.1 *N*) solution under flowing nitrogen gas. The product was precipitated by evaporating to dryness at 353 K [Calc. N 3.96%, Found 3.71, 3.90%].

Crystal data

$(NH_4)_2(C_6H_{18}N_2)_4[H_2W_{12}O_{42}]\cdot 8H_2O$
M_r = 1766.66
Triclinic, $P\overline{1}$
a = 10.987 (2) Å
b = 10.980 (2) Å
c = 14.681 (3) Å
α = 85.99 (3)°
β = 84.85 (3)°
γ = 87.69 (3)°
V = 1758.6 (6) Å^3
Z = 2
D_x = 3.319 Mg m^{-3}
Synchrotron radiation
λ = 0.9204 Å
Cell parameters from 340 reflections
θ = 3.8–22.5°
μ = 37.82 mm^{-1}
T = 100 (2) K
Plate, colourless
0.35 × 0.08 × 0.03 mm

Data collection

Quantum4 CCD detector diffractometer
φ scans
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.033, T_{max} = 0.389
3953 measured reflections
3953 independent reflections
3937 reflections with $I>2\sigma(I)$
R_{int} = 0.066
θ_{max} = 30.0°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.09
3953 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 33.4374P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.74 e Å^{-3}
$\Delta\rho_{min}$ = −2.77 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

W1—O4	1.729 (8)	W1—O2	2.042 (8)
W1—O8	1.824 (8)	W1—O7	2.263 (7)
W1—O9	1.927 (7)	W6—O12^{i}	2.298 (8)
W1—O1	1.935 (7)	O11—W4^{i}	1.880 (8)
O4—W1—O8	104.6 (3)	O4—W1—O1	99.6 (3)
O4—W1—O9	100.8 (3)	O8—W1—O1	92.7 (3)
O8—W1—O9	93.8 (3)	O9—W1—O1	156.3 (3)

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

All non-H atoms were refined with isotropic displacement parameters. H atoms on the 1,6-hexanediammonium C atoms were constrained in calculated positions (C—H 0.99 Å) to ride on their parent atom, with a U_{iso} 1.2 × U_{eq} of the parent atom. No other H atoms were located. The largest residual electron density peak was located 0.61 Å from W3 and the deepest hole 0.59 Å from W1.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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