

Uk Lee,^{a*} Soon-Jung Jang,^a
Hea-Chung Joo^a and Ki-Min
Park^b

^aDepartment of Chemistry, Pukyong National University, 599-1 Daeyeon-3dong Nam-ku, Pusan 608-737, South Korea, and ^bResearch Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, South Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{N}-\text{C}) = 0.024\text{ \AA}$

R factor = 0.049

wR factor = 0.106

Data-to-parameter ratio = 17.0

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

Anhydrous octaguanidinium hexatungstoplatinate(IV)

Very stable crystals of the title compound, $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$, containing the well known A-type Anderson–Evans heteropolyoxotungstate structure, were obtained by hydrothermal reaction. All O atoms in the polyanion form strong $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds with all N atoms of the guanidinium ions. The $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion has $S_6(\bar{3})$ symmetry, with a Pt–O bond length of 2.016 (9) Å, and three types of W–O bonds, with distances of 1.74 (1) and 1.78 (1) (O_t), 1.95 (1) (O_b), and 2.17 (1) (O_c) Å.

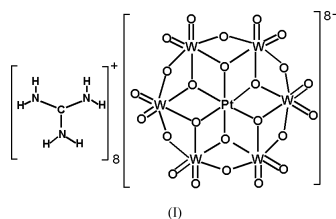
Received 4 February 2003

Accepted 14 February 2003

Online 21 February 2003

Comment

The guanidinium ion is useful in separating polyoxometalates because of the insolubility of its salts. Since all replaceable counter-cations in the polyoxometalate can be exchanged by guanidinium ions, it is possible to separate the polyoxometalate precipitate from aqueous solution. Good crystals of guanidinium polyoxometalates are not always obtained, but X-ray quality single crystals of the title compound, (I), were recrystallized from hot aqueous solution. Guanidinium polyoxometalates usually crystallize with little or no water of crystallization, *e.g.* $(\text{CH}_6\text{N}_3)_4[\text{GeMo}_{12}\text{O}_{40}]$ (Strandberg & Hedman, 1982), $(\text{CH}_6\text{N}_3)_2[\text{MoO}_4]$ (Ozeki *et al.*, 1987) and $(\text{CH}_6\text{N}_3)_4[\text{SiMo}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$ (Ichida *et al.*, 1980), but there is one particular case in which more water of crystallization is found, *viz.* $(\text{CH}_6\text{N}_3)_4[\text{As}_2\text{Mo}_{18}\text{O}_{62}]\cdot 9\text{H}_2\text{O}$ (Ichida & Sasaki, 1983).



Na or K salts of A-type Anderson–Evans heteropolytungstate structures (Anderson, 1937; Evans, 1948; Tsigdinos, 1978) containing heteroatoms of high oxidation state, such as $[\text{X}^{n+}\text{W}_6\text{O}_{24}]^{(12-n)-}$ [X^{n+} : Te^{6+} (Schmidt *et al.*, 1986), Sb^{5+} (Lee & Sasaki, 1988), Mn^{4+} (Sergienko *et al.*, 1979; Nolan *et al.*, 2000), Pt^{4+} (Lee *et al.*, 1984)] have been reported. The $[\text{PtW}_6\text{O}_{24}]^{8-}$ anion in $\text{Na}_2\text{K}_6[\text{PtW}_6\text{O}_{24}]\cdot 12\text{H}_2\text{O}$ (Lee *et al.*, 1984) has D_{3d} point symmetry, an ideal symmetry in Anderson–Evans polyoxometalate structures. The crystal structure of (I) is a good example of the packing found in polyoxometalates. Here we report the crystal structure of the anhydrous $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$, in which the Na and K cations

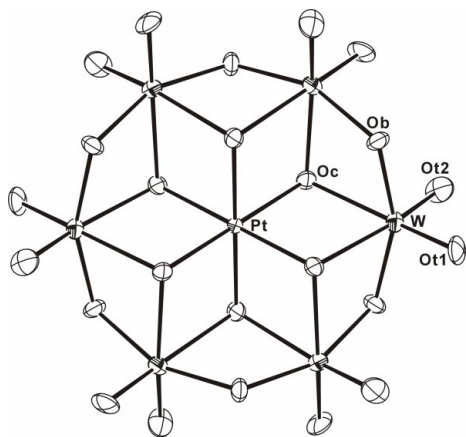


Figure 1
The anion structure in $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$. Displacement ellipsoids are drawn at the 50% probability level.

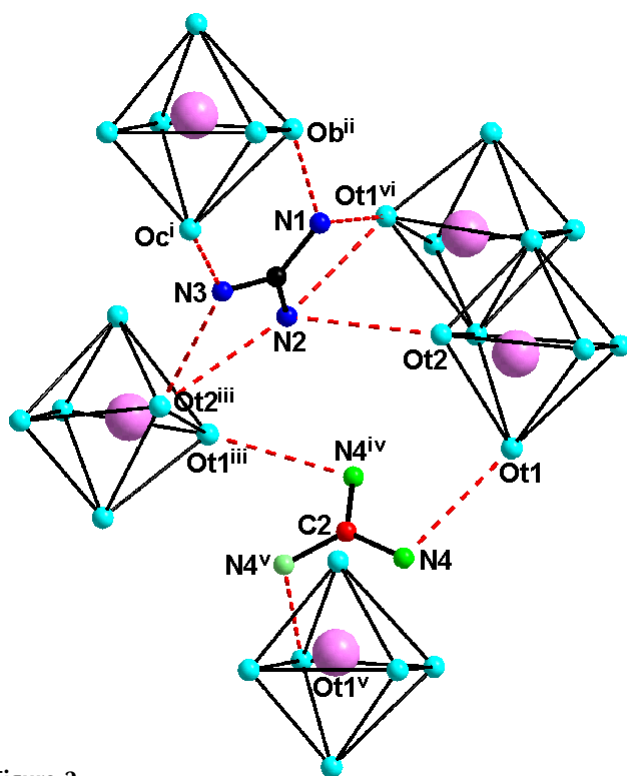


Figure 2
Formation of hydrogen bonds by guanidinium ions [symmetry codes: (i) $-1/3 + y, 1/3 - x + y, 1/3 - z$; (ii) $-1/3 - x + y, 1/3 - x, 1/3 + z$; (iii) $-y, 1 + x - y, z$; (iv) $-y, 1 + x - y, z$; (v) $-1 - x + y, -x, z$; (vi) $y, -x + y, -z$].

of $\text{Na}_2\text{K}_6[\text{PtW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$ are completely exchanged by guanidinium ions and the symmetry is reduced from $D_{3d}(\bar{3}m)$ to $S_6(\bar{3})$.

Fig. 1 shows the structure of the $[\text{PtW}_6\text{O}_{24}]^{8-}$ polyanion. The labelling of the O atoms in the polyanion is the same as the labelling in the previous structure (Lee *et al.*, 1984). The W—O and Pt—O bond distances of (I) agree well with those in $\text{Na}_2\text{K}_6[\text{PtW}_6\text{O}_{24}] \cdot 12\text{H}_2\text{O}$. The anion has a structure with point symmetry $S_6(\bar{3})$. The Pt...W and W...W distances are 3.2437 (7) and 3.2443 (7) Å, respectively. The Pt—O bond length is 2.016 (9) Å, and there are three types of W—O bond

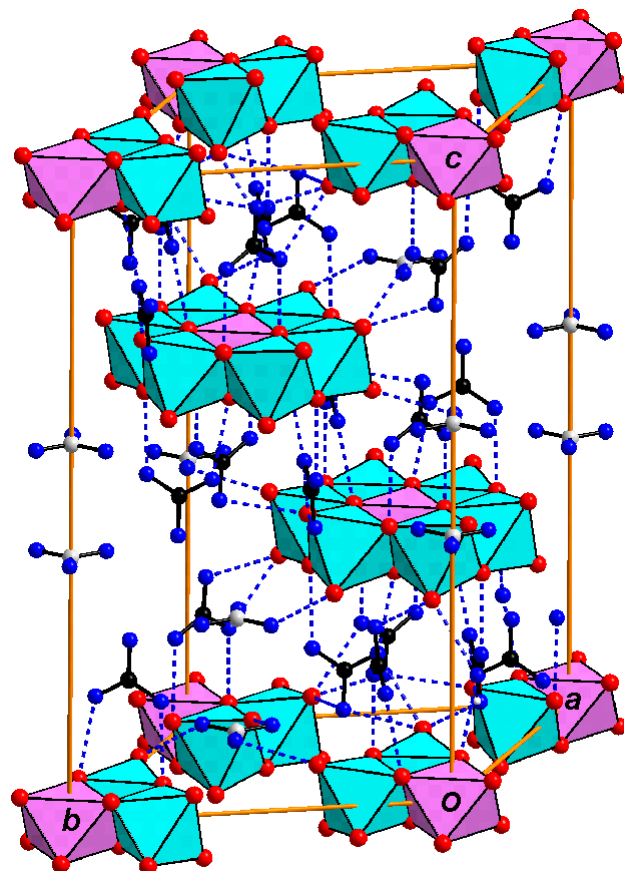


Figure 3
The crystal packing of $(\text{CH}_6\text{N}_3)_8[\text{PtW}_6\text{O}_{24}]$ in the unit cell, shown as a polyhedral model. Red circles are O, black circles are C1, grey circles are C2, and blue circles are N. Violet and cyan octahedra are $[\text{PtO}_6]$ and $[\text{WO}_6]$, respectively. Hydrogen bonds are shown as blue broken lines.

lengths are 1.74 (1) and 1.78 (1) (O_l), 1.95 (1) (O_b), and 2.17 (1) Å (O_c). The bond lengths and angles of the guanidinium ions agree well with those in $\text{CH}_6\text{N}_3\text{Cl}$ (Haas *et al.*, 1965) and $\text{CH}_6\text{N}_3(\text{NO}_3)$ (Katrusiak, 1994).

Fig. 2 shows the hydrogen-bonding interactions of guanidinium ions with O atoms of the anions. All O atoms in the polyanion form strong N—H...O hydrogen bonds with all N atoms of the guanidinium ions. A list of all hydrogen bonds with N...O distances within 3.1 Å is given in Table 2. There are two crystallographically independent guanidinium, $(\text{CH}_6\text{N}_3)^+$, ions in the asymmetric unit, one of which lies on a threefold axis. The two guanidinium ions are named Gu1 and Gu2 (the numbering is in accordance with the C atoms). The formula unit contains six Gu1 ions and two Gu2 ions. Almost all hydrogen bonds between anions and guanidinium ions involve Gu1 ions. All N...O hydrogen-bond distances fall into the range 2.83–3.10 Å, with the range of N—H...O angles varying between 109 and 175°. Fig. 3 shows the unit-cell packing with hydrogen bonding.

The crystal structure of (I) is stabilized by the formation of extensive N—H...O hydrogen-bond interactions involving N atoms of the guanidinium ions and by effective packing. As a result, the crystals are stable, even though water of crystallization is not present in the crystal structure.

Experimental

A pale-yellow powder of the title compound was obtained by adding a small excess stoichiometric quantity of CH₆N₃Cl to a solution of hexatungstoptatinate Na₂K₆[PtW₆O₂₄] (Lee *et al.*, 1984). Single crystals were obtained by recrystallizing the powdered crude sample from the boiling aqueous solution.

Crystal data

(CH₆N₃)₈[PtW₆O₂₄]
M_r = 2162.89
 Trigonal, R $\bar{3}$
a = 12.928 (2) Å
c = 21.981 (5) Å
V = 3181.6 (10) Å³
Z = 3
D_x = 3.387 Mg m⁻³

Mo *Kα* radiation
 Cell parameters from 25 reflections
 θ = 13.7–15.7°
 μ = 19.59 mm⁻¹
T = 298 (2) K
 Cube, yellow
 0.10 × 0.10 × 0.10 mm

Data collection

Stoe Stadi4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
T_{min} = 0.120, *T_{max}* = 0.143
 1629 measured reflections
 1629 independent reflections
 1108 reflections with *I* > 2σ(*I*)

θ_{\max} = 27.5°
h = -16 → 8
k = 0 → 16
l = 0 → 28
 3 standard reflections
 frequency: 60 min
 intensity decay: 3.5%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.049
wR(*F*²) = 0.106
S = 1.18
 1629 reflections
 96 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 60.3628P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -2.72 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å).

W...W ⁱ	3.2443 (7)	W—Oc	2.17 (1)
Pt...W	3.2437 (7)	C1—N1	1.32 (2)
Pt—Oc	2.016 (9)	C1—N2	1.33 (2)
W—Or1	1.78 (1)	C1—N3	1.32 (2)
W—Or2	1.74 (1)	C2—N4	1.33 (2)
W—Ob	1.95 (1)		

Symmetry code: (i) *y*, -*x* + *y*, -*z*.

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1A...Ob ⁱⁱ	0.86	1.97	2.83 (2)	175
N1—H1B...Or1 ⁱ	0.86	2.37	3.10 (2)	142
N2—H2A...Or1 ⁱ	0.86	2.30	3.04 (3)	145
N2—H2B...Or2 ⁱⁱⁱ	0.86	2.18	2.94 (2)	147
N2—H2A...Or2	0.86	2.59	2.99 (2)	109
N3—H3A...Oc ^{iv}	0.86	1.99	2.83 (2)	165
N3—H3B...Or2 ⁱⁱⁱ	0.86	2.18	2.94 (2)	148
N4—H4A...Or1	0.86	2.13	2.91 (2)	150

Symmetry codes: (i) *y*, -*x* + *y*, -*z*; (ii) $-\frac{1}{3} - x + y, \frac{1}{3} - x, \frac{1}{3} + z$; (iii) -*y*, 1 + *x* - *y*, *z*; (iv) $y - \frac{1}{3}, \frac{1}{3} - x + y, \frac{1}{3} - z$.

The highest peak in the difference map is 1.49 Å from H2A and the largest hole is 0.89 Å from Pt. All H atoms were placed in calculated positions, with N—H distances of 0.88 Å and H—N—H angles of 120°. They were included in the refinement in riding model approximation, with *U*_{iso} = 1.2*U*_{eq}(N).

Data collection: *Stadi4* (Stoe & Cie, 1996); cell refinement: *Stadi4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

References

Anderson, J. S. (1937). *Nature (London)*, **150**, 850.
 Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
 Evans, H. T. Jr (1948). *J. Am. Chem. Soc.* **70**, 1291–1292.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Haas, D. J., Harris, D. R. & Mills, H. H. (1965). *Acta Cryst.* **19**, 676–679.
 Ichida, H., Kobayashi, A. & Sasaki, Y. (1980). *Acta Cryst.* **B36**, 1382–1387.
 Ichida, H. & Sasaki, Y. (1983). *Acta Cryst.* **C39**, 529–533.
 Katrusiak, A. (1994). *Acta Cryst.* **C50**, 1161–1163.
 Lee, U., Ichida, H., Kobayashi, A. & Sasaki, Y. (1984). *Acta Cryst.* **C40**, 5–7.
 Lee, U. & Sasaki, Y. (1988). *Bull. Korean Chem. Soc.* **8**, 1–3.
 Nolan, A. L., Burns, R. C., Lawrance, G. A. & Craig, D. C. (2000). *Acta Cryst.* **C56**, 729–730.
 Ozeki, T., Ichida, H. & Sasaki, Y. (1987). *Acta Cryst.* **C43**, 2220–2221.
 Schmidt, K. J., Schrobilgen, G. J. & Sawyer, J. F. (1986). *Acta Cryst.* **C42**, 1115–1118.
 Sergienko, V. S., Molchanov, V. N., Porai-Koshits, M. A. & Torchenkova, E. A. (1979). *Sov. J. Coord. Chem.* **5**, 740–746.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Strandberg, R. & Hedman, B. (1982). *Acta Cryst.* **B38**, 773–778.
 Stoe & Cie (1996). *Stadi4*, *X-RED* and *X-SHAPE*. Stoe & Cie GmbH, Darmstadt, Germany.
 Tsigdinos, G. A. (1978). *Top. Curr. Chem.* **76**, 36–41.