

Synchrotron structure determination of an α -Keggin doubly Pt^{IV}-substituted silicotungstate, (CH₆N₃)₈[α -SiPt₂-W₁₀O₄₀] \cdot 6H₂O

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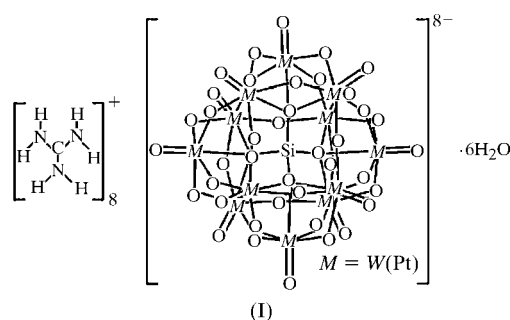
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The crystal structure of octaguanidinium α -silicodiplatino-decatungstate hexahydrate, (CH₆N₃)₈[α -SiPt₂W₁₀O₄₀] \cdot 6H₂O, has been analyzed *via* a high-energy X-ray diffraction experiment at the SPring-8 BL04B2 beamline. The title compound contains a novel α -Keggin heteropolyanion in which two of the addenda atoms are replaced by Pt atoms. W and Pt atoms occupy the same coordinates; the occupancy fractions are $\frac{5}{6}$ (W) and $\frac{1}{6}$ (Pt), and the α -Keggin anion has $\bar{4}$ symmetry. The two types of W(Pt)–W(Pt) distance are in the ranges 3.3565 (4)–3.3704 (4) and 3.7033 (4)–3.7100 (4) Å, the four types of W(Pt)–O bond length are in the ranges 1.721 (5)–1.725 (5), 1.910 (5)–1.932 (5), 1.934 (5)–1.956 (5) and 2.339 (4)–2.348 (4) Å, and the Si–O bond length is 1.646 (4) Å.

Comment

High-energy synchrotron radiation X-ray diffraction experiments are advantageous for structure determinations of inorganic crystals that would show very large absorption coefficients when analyzed with Mo K α radiation. With high-energy synchrotron radiation, systematic deviations of the diffraction intensities due to the effects of absorption and extinction are considerably reduced, leading to more accurate positional and displacement parameters for both the heavier and the lighter atoms in the crystal. This advantage has been demonstrated for the structure determinations of some isopolyoxotungstates (Ozeki, 2001; Ozeki *et al.*, 2001). In the present study, we have applied this strategy to a structure determination of a heteropolyoxotungstate containing Pt^{IV} atoms.

The Pt^{IV} ion shows a very rich chemical behavior when it forms heteropolyoxometalates with the Anderson structure (Lee *et al.*, 1983, 1984; Lee & Sasaki, 1994; Lee, 1994; Joo *et al.*, 1994). We assume that the diversity of the Pt^{IV}-containing heteropolyoxometalates is caused by the similarities in the oxidation states and the ionic radii of addenda atoms (Pt⁴⁺ = 0.76, Mo⁶⁺ = 0.73 and W⁶⁺ = 0.74 Å; Shannon, 1976) and by the electron configuration of Pt⁴⁺ (5d⁶), which preferentially forms six-coordinated octahedra. These results led us to attempt to synthesize Pt^{IV}-containing heteropolyoxometalates with the Keggin structure. As a first result of this research project, we have obtained the doubly Pt^{IV}-substituted silicotungstate (I), the crystal structure of which is reported here.



The systematic extinctions and the diffraction symmetry yielded three possible space groups, *viz.* $I4$, $I\bar{4}$ and $I4/m$, but a reasonable structure model could only be established with space group $I\bar{4}$. The α -Keggin [SiM₁₂O₄₀]ⁿ⁻ (M = W and Pt) anion is located at the $\bar{4}$ site of the crystal, with the result that one-quarter of the anion is crystallographically independent. Elemental EDXRF (energy-dispersive X-ray fluorescence) analysis and the requirement of the neutrality of the whole crystal indicated that there are two Pt atoms in the anion. None of the three independent heavy-atom sites showed preferred occupation of the Pt atoms. In addition, none of these three sites showed any feature indicating a deviation between the W and Pt positions. Therefore, each heavy-atom site was refined so that the W and Pt atoms share the same coordinates and anisotropic displacement parameters, and have fixed occupancy fractions of $\frac{5}{6}$ and $\frac{1}{6}$, respectively.

The crystal structures of silicododecatungstates with the α - and β -Keggin structures (Keggin, 1934; Tézé & Hervé, 1977) were reported by Kobayashi & Sasaki (1975) and Matsumoto *et al.* (1975). The substitution of secondary heteroatoms for two of the 12 W atoms has been reported for [γ -SiW₁₀Mn₂^{III}O₄₀H₆]⁴⁻ (Zhang *et al.*, 1996) and [{" β -SiNi₂W₁₀O₃₆(OH)₂(H₂O)]₂]¹²⁻ (Kortz *et al.*, 1999). However, complete studies have not yet been conducted on the crystal structures of α -Keggin silicotungstates that contain two secondary heteroatoms, with the formula [α -SiM₂ⁿ⁺W₁₀O₄₀]⁽¹⁶⁻²ⁿ⁾⁻ (where M is a transition element).

Fig. 1 shows a perspective view of the anion. The O atoms in the polyanion are classified as Ot, Oc, Oe or Od, where Ot represents terminal O atoms, Oc represents bridging O atoms at corner-sharing linkages, Oe represents O atoms at edge-

sharing linkages, and *Od* represents O atoms coordinating to one Si and three W(Pt) atoms. The structure has an almost *Td* symmetry, and the $W_{10}Pt_2$ framework is very close to a regular cuboctahedron. When the $W(Pt)O_6$ octahedra share edges, the $W(Pt)-W(Pt)$ distances vary between 3.3565 (4) and 3.3704 (4) Å, while, when sharing corners, they increase to 3.7033 (4)–3.7100 (4) Å. The $W(Pt)-O$ distances are in the ranges 1.721 (5)–1.725 (5) (*Ot*), 1.910 (5)–1.932 (5) (*Oc*), 2.339 (4)–2.348 (4) (*Od*) and 1.934 (5)–1.956 (5) Å (*Oe*). The central $[SiO_4]$ group is a tetrahedron with an Si–*Od* distance of 1.646 (4) Å and *Od*–Si–*Od* angles of 109.2 (3) and 109.6 (2)°. The bond distances and angles in the $[\alpha-SiPt_2W_{10}O_{40}]^{8-}$ anion clearly show the character of a typical α -Keggin structure (Table 1).

Fig. 2 shows the unit-cell packing and hydrogen bonding. There are two crystallographically independent guanidinium ions ($CH_6N_3^+$) and two water molecules in the asymmetric unit. The structural character of the guanidinium ions agrees well with those in CH_6N_3Cl (Haas *et al.*, 1965) and $CH_6N_3(NO_3)$ (Katrusiak, 1994). The connecting links between the anions are strong hydrogen bonds effected by the guanidinium ions, and the N atoms of the guanidinium ions do not form hydrogen bonds with water molecules. A list of all probable hydrogen-bond distances below 3.1 Å is given in Table 2. The interactions of water molecules are not shown. Atom *Ow2* forms a weak hydrogen bond with atom *Oe5* of the anion. The TGA (thermogravimetric analysis) trace of (I)

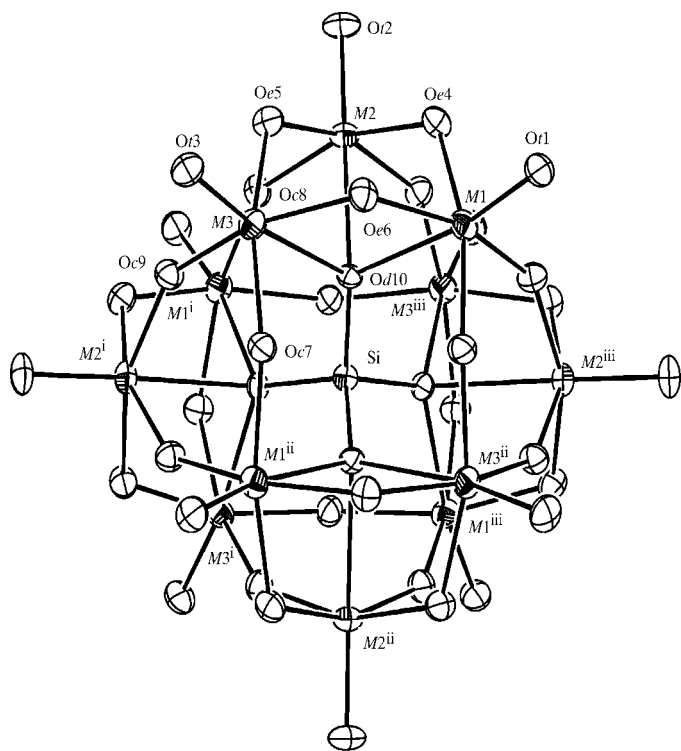


Figure 1
The structure of the $[\alpha-SiPt_2M_{10}O_{40}]^{8-}$ anion. Displacement ellipsoids are shown at the 50% probability level. *M* represents atom sites occupied by $\frac{5}{6}W$ and $\frac{1}{6}Pt$. [Symmetry codes: (i) $y, 1-x, 1-z$; (ii) $1-x, 1-y, z$; (iii) $1-y, x, 1-z$.]

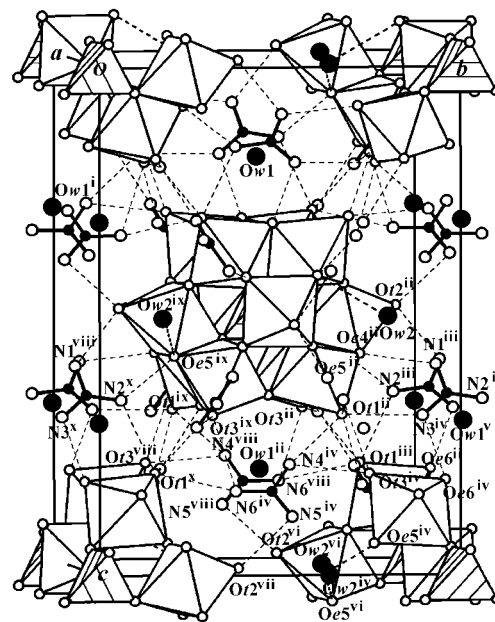


Figure 2
The crystal packing of (I), with the $[\alpha-SiPt_2M_{10}O_{40}]^{8-}$ anions shown as a polyhedral model. Possible hydrogen bonds are indicated by broken lines. [Symmetry codes: (i) $\frac{1}{2} + y, \frac{1}{2} - x, \frac{1}{2} - z$; (ii) $y, 1 - x, 1 - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, \frac{3}{2} - y, \frac{1}{2} + z$; (v) $-\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} + z$; (vi) $\frac{3}{2} - y, \frac{1}{2} + x, \frac{3}{2} - z$; (vii) $-\frac{1}{2} + y, \frac{1}{2} - x, \frac{3}{2} - z$; (viii) $\frac{1}{2} + x, -\frac{1}{2} + y, \frac{1}{2} + z$; (ix) $1 - y, x, 1 - z$; (x) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$.]

dwindled very slowly as the temperature was increased from room temperature to 515 K, without any sudden change, suggesting that the crystalline water molecules of (I) disintegrate gradually between room temperature and 515 K. These crystalline water molecules seem to behave as zeolitic water.

Experimental

The pH of a mixture of aqueous solutions of $K_2Pt(OH)_6$ (0.2 g per 20 ml; Lee *et al.*, 1983) and $K_8[\alpha-SiW_{11}O_{39}] \cdot 13H_2O$ (2.8 g per 30 ml; Contant, 1990) was adjusted first to 11.5 by the addition of KOH (3 M), and then to 7.0 by the addition of HNO_3 (3 M). The mixture was then concentrated to about 30 ml on a water bath. Compound (I) was obtained in the form of a pale yellow powder by adding an aqueous solution (30 ml) containing $CH_5N_3 \cdot HCl$ (0.3 g) to the reaction mixture. Yellow truncated-tetrahedral crystals of (I) were obtained by recrystallization of a powdered crude sample from a boiling aqueous solution.

Elemental analysis for W and Pt was carried out by regression analysis of EDXRF (Jordan Vally, Spectrometer EX310) using standard samples with Pt:W ratios of 1:6, 1:5 and 1:4. The molar ratio of Pt:W in (I) was estimated to be 1:5.3. Standard samples with Pt:W equal to 1:4 and 1:5 were prepared by mixing WO_3 and K_2PtCl_6 , and the sample with Pt:W equal to 1:6 had the formula $Na_5[H_3PtW_6O_{24}] \cdot 22H_2O$ (Lee *et al.*, 1983). Elemental analysis, calculated: C 2.75, H 1.72, N 9.64%; found: C 2.95, H 1.94, N 9.86%. Thermogravimetric analysis for H_2O , calculated: 3.10%; found: 2.23%. The FT-IR (Perkin-Elmer Spectrum 2000) absorption peaks in the range 500–1000 cm^{-1} show a pattern typical of an α -Keggin silicotungstate. [KBr disk; 994.24 (s), 937.72 (s), 871.59 (s), 794.26 (s), 727.34 (s), 520.64 (s)].

Crystal data

(CH₆N₃)₈[Pt₂W₁₀O₄₀Si]-6H₂O
M_r = 3485.57
 Tetragonal, *I* $\bar{4}$
a = 13.276 (1) Å
c = 18.959 (1) Å
V = 3341.6 (4) Å³
Z = 2
D_x = 3.464 Mg m⁻³
 Synchrotron radiation
 λ = 0.3282 Å

Data collection

MacScience DIP LABO
 diffractometer
 Oscillation method ω scans
 Absorption correction: multi-scan
 (PLATON; Spek, 2003)
T_{min} = 0.522, *T_{max}* = 0.555
 42 373 measured reflections

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.029
wR(*F*²) = 0.068
S = 1.26
 7980 reflections
 207 parameters
 H-atom parameters constrained

Cell parameters from 12 596
 reflections
 θ = 2.0–15.8°
 μ = 2.86 mm⁻¹
T = 293 (2) K
 Truncated-tetrahedron, yellow
 0.15 × 0.15 × 0.15 mm
 7980 independent reflections
 7961 reflections with *I* > 2σ(*I*)
R_{int} = 0.032
 θ_{max} = 15.8°
h = -22 → 22
k = -22 → 22
l = -31 → 31

w = 1/[σ²(*F*_o²) + 65.1125*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δσ)_{max} = 0.001
 Δρ_{max} = 2.09 e Å⁻³
 Δρ_{min} = -2.55 e Å⁻³
 Absolute structure: (Flack, 1983),
 3878 Friedel pairs
 Flack parameter = 0.08 (5)

Table 1

Selected geometric parameters (Å, °).

O_t represents terminal O atoms, O_c represents bridging O atoms at corner-sharing linkages, O_e represents O atoms at edge-sharing linkages, and O_d represents O atoms coordinating to one Si and three W(Pt) atoms. *M* represents atom sites occupied by $\frac{5}{6}$ W and $\frac{1}{6}$ Pt.

<i>M1</i> — <i>M2</i>	3.3565 (4)	<i>M3</i> —O _c 7	1.910 (5)
<i>M1</i> — <i>M3</i>	3.3631 (4)	<i>M3</i> —O _c 9	1.920 (5)
<i>M2</i> — <i>M3</i>	3.3704 (4)	<i>M3</i> —O _e 6	1.943 (5)
<i>M1</i> — <i>M2</i> ⁱⁱⁱ	3.7100 (4)	<i>M3</i> —O _e 5	1.945 (5)
<i>M1</i> — <i>M3</i> ⁱⁱⁱ	3.7033 (4)	<i>M3</i> —O _d 10	2.339 (4)
<i>M2</i> — <i>M3</i> ⁱⁱⁱ	3.7051 (4)	Si—O _d 10	1.646 (4)
<i>M1</i> —O _t 1	1.721 (5)	C1—N3	1.268 (13)
<i>M1</i> —O _c 8 ⁱⁱⁱ	1.921 (5)	C1—N2	1.324 (13)
<i>M1</i> —O _c 7 ⁱⁱ	1.932 (5)	C1—N1	1.344 (12)
<i>M1</i> —O _e 6	1.948 (5)	C2—N6	1.308 (17)
<i>M1</i> —O _e 4	1.956 (5)	C2—N5	1.342 (18)
<i>M1</i> —O _d 10	2.339 (4)	C2—N4	1.342 (17)
<i>M2</i> —O _t 2	1.722 (4)	Ow1—O _e 6 ⁱⁱ	3.174 (13)
<i>M2</i> —O _c 8	1.919 (5)	Ow1—O _c 7	3.204 (14)
<i>M2</i> —O _c 9 ⁱⁱⁱ	1.922 (5)	Ow1—O _e 6	3.174 (13)
<i>M2</i> —O _e 4	1.934 (5)	Ow1—O _e 6	3.174 (13)
<i>M2</i> —O _e 5	1.948 (5)	Ow2—O _e 5	3.043 (17)
<i>M2</i> —O _d 10	2.348 (4)	Ow2—O _c 8	3.123 (19)
<i>M3</i> —O _t 3	1.725 (5)	N5—O _t 2 ⁱ	3.132 (13)
<i>M3</i> ⁱⁱ — <i>M1</i> — <i>M2</i> ⁱⁱⁱ	59.974 (7)	<i>M1</i> — <i>M2</i> — <i>M3</i> ⁱⁱⁱ	90.066 (9)
<i>M2</i> — <i>M1</i> — <i>M3</i>	60.209 (8)	O _d 10 ⁱⁱⁱ —Si—O _d 10	109.63 (15)
<i>M1</i> — <i>M2</i> — <i>M3</i>	59.992 (8)	O _d 10—Si—O _d 10 ⁱⁱ	109.2 (3)
<i>M2</i> — <i>M1</i> — <i>M2</i> ⁱⁱⁱ	90.149 (9)	<i>M1</i> — <i>M3</i> — <i>M2</i>	59.799 (8)

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

The *checkCIF* program suggested a higher symmetry, *I4/m*, for this structure, because every atom except O_d10 is either located close to the new mirror plane or related to a potential symmetry equivalent. However, a refinement in which all atoms were constrained to conform to the additional symmetry operations was very unstable,

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—H1B...O _t 2 ^{iv}	0.86	2.11	2.957 (10)	166
N1—H1A...O _e 4 ^v	0.86	2.01	2.864 (10)	175
N2—H2A...O _t 1	0.86	2.24	3.036 (12)	155
N2—H2B...O _e 5 ^{iv}	0.86	2.02	2.865 (12)	168
N3—H3B...O _t 1 ^v	0.86	2.11	2.945 (11)	164
N3—H3A...O _e 6	0.86	2.02	2.884 (11)	178
N4—H4B...O _t 1 ^v	0.86	2.57	3.045 (13)	116
N4—H4A...O _t 3	0.86	2.17	2.991 (12)	159
N5—H5A...O _t 2 ^{vi}	0.86	2.17	2.984 (12)	158
N6—H6B...O _t 1 ^{vii}	0.86	2.55	3.029 (13)	116
N6—H6A...O _t 3 ^{viii}	0.86	2.27	3.050 (14)	151

Symmetry codes: (iv) *y* - $\frac{1}{2}$, $\frac{1}{2}$ - *x*, $\frac{1}{2}$ - *z*; (v) $\frac{1}{2}$ - *y*, $\frac{1}{2}$ + *x*, $\frac{1}{2}$ - *z*; (vi) 1 - *y*, 1 + *x*, 1 - *z*; (vii) *x*, 1 + *y*, *z*; (viii) *y* - $\frac{1}{2}$, $\frac{1}{2}$ - *x*, $\frac{1}{2}$ - *z*.

leading to a sudden increase of *R*₁ to 0.1915, with maximum and minimum difference electron densities of 9.35 and -41.71 e Å⁻³, respectively. Therefore, the deviation from the higher symmetry is significant. Space group *I4/m* could also be adopted by interpreting the structure as a 1:1 disorder comprising 50% of the current chiral structure and 50% of its enantiomorph (although *checkCIF* did not suggest this interpretation), which is equivalent to treating the structure as a 1:1 racemic twin of the current chiral structure. Refinement of the fractional contributions of the potential twin components converged to 92 (5)% for the current enantiomorph and 8% for the inverted structure, indicating that the racemic twin model with an approximately equal amount of the two enantiomer pairs (which approximates to the disordered centrosymmetric structure with *I4/m*) should be excluded. Thus, the structure was concluded to be chiral having the space group *I4*.

Anomalous scattering factors were taken from Sasaki (1989). All H atoms, except water H atoms, were inserted at calculated positions, with N—H distances of 0.86 Å and H—N—H angles of 120°, and treated as riding atoms with constrained isotropic displacement parameters [*U*_{iso} = 1.2*U*_{eq}(N)]. The highest peak in the difference map is 3.21 Å from Ow1 and the largest hole is 0.90 Å from Ow1. Solvent-accessible voids of 96 Å³, which are equivalent to a space that approximately two water molecules could occupy, seem to be empty. Only two independent water molecules were confirmed in a separate low-temperature measurement.

Data collection: *DIP XPRESS* (MacScience, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1100). Services for accessing these data are described at the back of the journal.

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