

A redox-triggered structural rearrangement in an iodate-templated polyoxotungstate cluster cage†

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The new tungstatoiodate, α -[H₅W₁₈O₅₉(IO₃)]⁶⁻, containing I^{VO}₃⁻ within a {W₁₈O₅₄} metal oxide framework has been prepared and shown by X-ray crystallography and mass spectrometry to be derived from the fully oxidised [H₃W₁₈O₅₆(IO₆)]⁶⁻ by two-electron reduction accompanied by a redox-triggered structural rearrangement where three I–O covalent bonds are broken.

Polyoxometalates (POMs) are attracting widespread attention because of emerging and anticipated applications arising from their uniquely diverse electronic and molecular properties.^{1–3} The physical and electronic properties of POMs are intimately linked to their structural features, but systematic synthesis and the reactivity studies required to understand these relationships remain a pressing challenge. Methods for metal substitution in Lindqvist hexametalates [(RO)MW₅O₁₈]³⁻ (M = Ti, Sn) enabled us to show how the frontier orbital energies vary with metal substitution and the remarkable effect on ¹⁸³W NMR spectra.⁴ Electronic properties can also be tuned by encapsulation of 'functional' template anions in place of the 'innocent' anions such as PO₄³⁻ and SO₄²⁻ more commonly used in POM synthesis,^{4–7} and by utilizing redox-active templates, we have isolated new types of XO₃ and XO₆-based POM clusters. The thermochromic Dawson-type α - and β -[Mo₁₈O₅₄(SO₃)₂]⁴⁻,⁸ and [W₁₈O₅₈(SO₃)₂(H₂O)₂]⁸⁻ contain SO₃²⁻ templates inside the cluster shell,^{9,10} and the first crystallographically characterized tungstatoiodate, [H₃W₁₈O₅₆(IO₆)]⁶⁻, was shown to be catalytically active.¹¹ We present herein the structure of a new type of {W₁₈} cluster, (C₆H₁₆NO₃)₅-Na[H₅W₁₈O₅₉(IO₃)]·5H₂O **1**, which is the first example of a POM with encapsulated IO₃⁻. Its formation from the fully oxidised {W₁₈O₅₆(IO₆)} core involves two-electron reduction and a redox-switched structural rearrangement.†

Compound **1** was prepared from an aqueous solution of Na₂WO₄, H₅IO₆ (molar ratio 14:1) and triethanolammonium chloride (TEAH⁺Cl⁻) under reflux and was precipitated as pale brown crystals. X-ray crystallographic structural analysis revealed a Dawson-type *D*_{3h}-symmetric {W₁₈O₅₄} cluster shell enclosing an IO₃ unit with average I–O and (I)O–W distances of 1.90(2) Å and 2.42(2) Å respectively. Two μ_3 -O atoms from the capping {W₃} groups, with average O–W distances of 2.23(2) Å, and three μ_2 -O atoms bridging pairs of belt W centers make up the remaining internal oxygen sites. The overall W and O positions are very close to those in Dawson-type anions containing tetrahedral template heteroatoms, but in contrast to the previously reported potassium salt of β^* -[H₃W₁₈O₅₆(IO₆)]⁶⁻,¹¹ in which the iodine is centrally located, the iodine in α -[H₅W₁₈O₅₉(IO₃)]⁶⁻ in **1** is displaced to one side of the cluster along the molecular C₃ axis, with a deviation of 0.53(2) Å from the centre (Fig. 1). The off-centre displacement of iodine lowers the cluster symmetry and increases the number of possible isomers from six for standard Dawson-type clusters [W₁₈O₅₄(PO₄)₂]⁶⁻ or the [H₄W₁₉O₆₂]⁶⁻ and [H₃W₁₈O₅₆(IO₆)]⁶⁻ systems^{11–13} to eight for this new anion [H₅W₁₈O₅₉(IO₃)]⁶⁻. The isomers can be defined as α , α^* , β_1 , β_2 , β_1^* , β_2^* , γ , γ^* , based on the six isomers of the parent [H₄W₁₉O₆₂]⁶⁻ and [H₃W₁₈O₅₆(IO₆)]⁶⁻ systems.^{11,13} In the α , α^* , γ

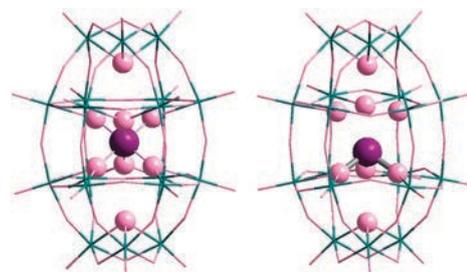


Fig. 1 Representation of the structure of β^* -[H₃W₁₈O₅₆(IO₆)]⁶⁻ in its K⁺ salt (left), IO₆ having octahedral geometry, and α -[H₅W₁₈O₅₉(IO₃)]⁶⁻ in **1** (right), three O atoms of IO₃ being eclipsed with the three μ_2 -O atoms above the iodine atom. The {W₁₈O₅₄} frameworks are shown in stick mode. The central iodine atoms and interior oxo ligands are highlighted as large spheres (I: purple; O: pink).

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and γ^* isomers of the $\{W_{18}O_{62}\}$ structure, the two ends are geometrically equivalent, so movement of the central iodine atom towards either end would give a single isomer in each case. However, in the β and β^* isomers the two ends are inequivalent, so movement of the iodine in different directions generates the β_1 , β_2 , β_1^* and β_2^* isomers. The $\{W_{18}O_{59}(IO_3)\}$ structure in **1** is the α isomer in which the $\{W_{18}O_{54}\}$ cluster shell has a D_{3h} symmetry with a horizontal mirror plane and the three oxygen atoms bonded to iodine are eclipsed with the three μ_2 -O atoms above the iodine atom (Fig. 1). The presence of iodine lowers the symmetry to C_{3v} .

$[H_3W_{18}O_{59}(IO_3)]^{6-}$ in **1** and the periodate cluster $[H_3W_{18}O_{56}(IO_6)]^{6-}$ represent different redox states of the $\{W_{18}O_{62}\}^{n-}$ core, where $n = 11$ and 9 respectively and the additional two electrons in **1** are localized on iodine. The difference between these two clusters was verified by use of mass spectrometry coupled with the X-ray single crystal structure determination and elemental analysis. Exchange of the TEAH⁺ cations in **1** with tetrabutylammonium (TBA⁺) gave $(TBA)_6[H_5W_{18}O_{59}(IO_3)]$ **2**.¹⁴ Fig. 2 shows the mass spectrum of **2** in acetonitrile in which all major peaks are derived from $[H_5W_{18}O_{59}(IO_3)]^{6-}$ and m/z values can be assigned as follows: 1720.3 $\{TBA_3[H_5IW_{18}O_{62}]\}^{3-}$, 1800.7 $\{TBA_4[H_4IW_{18}O_{62}]\}^{3-}$, 2580.4 $\{TBA_3[H_6IW_{18}O_{62}]\}^{2-}$, 2701.6 $\{TBA_4[H_5IW_{18}O_{62}]\}^{2-}$, 2822.2 $\{TBA_5[H_4IW_{18}O_{62}]\}^{2-}$, 3683.5 $\{TBA_9[H_5IW_{18}O_{62}]\}^{3-}$. In contrast, the TBA⁺ salt of $[H_3W_{18}O_{56}(IO_6)]^{6-}$ in acetonitrile shows a quite different mass spectrum in this m/z range, and peaks can be assigned as follows: 2570.8 $\{TBA_3[H_2IW_{18}O_{61}]\}^{2-}$, 2700.5 $\{TBA_4[H_3IW_{18}O_{62}]\}^{2-}$, 2822.1 $\{TBA_5[H_2IW_{18}O_{62}]\}^{2-}$.¹¹ The combined mass spectral and elemental analyses therefore clearly show the relationship between the $I^V O_3^-$ and $I^{VI} O_6^{5-}$ POMs, and confirm that **2** contains the redox active center with encapsulated iodine(v), *i.e.* $[H_5W_{18}O_{59}(IO_3)]^{6-}$.

The main peaks in the mass spectrum of **2** can be assigned to species of the type $\{(TBA)_{9-n}[H_nW_{18}O_{59}(IO_3)]\}^{2-}$ where $n = 4, 5$ or 6 . Of these, the five-fold protonated form is predominant, *i.e.* the most intense peak at 2701.6 in Fig. 2 corresponds to $\{(TBA)_4[H_5IW_{18}O_{62}]\}^{2-}$. These results suggest that addition of two electrons to $[H_3W_{18}O_{56}(IO_6)]^{6-}$ is accompanied by additional double protonation to balance the increased charge.

The TEAH⁺ salt of the periodate-templated cluster $(TEAH)_6[H_3W_{18}O_{56}(IO_6)]^{11}$ was synthesized from the same reaction mixture as **1** but with a shorter heating and reflux time (about 30 minutes compared with one hour for **1**). From the reaction sequence and the cluster structure similarity, we argue that **1** is

the reduction product of $(TEAH)_6[H_3W_{18}O_{56}(IO_6)]^{11}$, *i.e.* upon extended heating, the initial periodate product is reduced to iodate product by the protonated organic amine TEAH⁺. This argument is based on the fact that purple iodine vapor is produced from the system after longer reflux periods confirming that iodine can be reduced from higher oxidation states during the reaction. Furthermore, an analogous reaction using iodic rather than periodic acid under the same reaction conditions did not produce **1**, which further supports the intermediacy of the fully oxidized $[H_3W_{18}O_{56}(IO_6)]^{6-}$ in the formation of **1**.

The isomer configuration of the periodate cluster $[H_3W_{18}O_{56}(IO_6)]^{6-}$ in the previously reported K⁺ salt $K_6[H_3W_{18}O_{56}(IO_6)]$ was undoubtedly determined as β^* by crystallography,¹¹ but that in $(TEAH)_6[H_3W_{18}O_{56}(IO_6)]^{11}$ was not clear due to heavy disorders of the IO_6 template and $\{W_{18}O_{54}\}$ cluster shell in the crystal structure which result from either cluster packing disorder or irresolvable isomer co-crystallization. Evidently the α isomer configuration of the iodate cluster $[H_5W_{18}O_{59}(IO_3)]^{6-}$ in **1** is clear, but it is not possible to conclude whether the isomer configuration is conserved from the parent cluster during the reaction while three I-O covalent bonds of the IO_6 template are broken to form IO_3 upon the reduction. The isopolytungstate $[H_4W_{19}O_{62}]^{6-}$ is unavoidably produced as an impurity in this reaction system. This is not unexpected, as this anion is produced quantitatively from the same reaction mixture in the absence of periodic acid after heating under reflux for three days.

The compounds reported here are the first examples of tungstatoiodates,¹⁵ and the synthesis of **1** represents the first time that the $I^V O_3^-$ ion has been captured within a POM cage, and the first incorporation of I(v) into a POM. Notably, this is also the first example of a Dawson-like $\{W_{18}\}$ cluster cage containing pyramidal XO_3 templates to adopt an 'olive' shape with a $\{XW_{18}\}$ composition. All previous examples of the $\{XW_{18}\}$ composition have 'peanut' shape, *e.g.* the $[H_2SbW_{18}O_{60}]^{7-}$ and $[H_2Te^{IV}W_{18}O_{60}]^{6-}$ anions.¹⁶ $[H_2Te^{IV}W_{18}O_{60}]^{6-}$ was produced by the reduction of $[H_3Te^{VI}W_{18}O_{62}]^{7-}$ with the loss of two internal oxo ligands.^{16a} Interestingly, the non-hydrogen composition is retained after reduction of $[H_3W_{18}O_{56}(IO_6)]^{6-}$ to $[H_5W_{18}O_{59}(IO_3)]^{6-}$, suggesting the possibility to design a reversible, proton-coupled redox process. This also provides an opportunity to expand our design and synthesis of POMs with redox-switchable physical properties, and complements our work on the reductive synthesis of capped Keggin-type structures *e.g.* $[PMo_{12}O_{40}\{Co(MeCN)_2\}]^{3-}$ and $[PMo_{12}O_{40}(VO)_2]^{3-}$.¹⁷

In summary, we have discovered a new type of tungstatoiodate, $[H_5W_{18}O_{59}(IO_3)]^{6-}$, which contains iodine(v) within a $\{W_{18}O_{54}\}$ Dawson-type shell and is the first example of an α -isomer of this family. We have characterized this polyanion using single crystal structure analysis and confirmed the assignment of the central atom of the template anion as iodine, as well as the degree of cluster protonation using mass spectrometry. Electrochemical, catalytic and DFT studies are being performed to compare with conventional Dawson-type polyoxotungstates.

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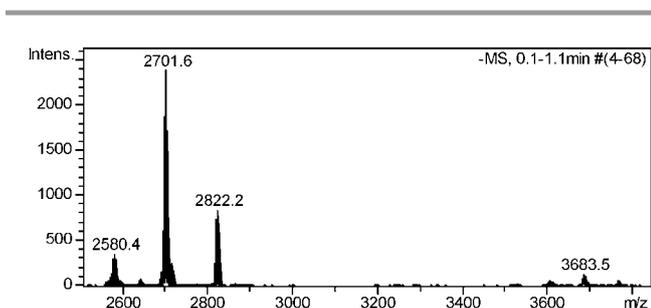


Fig. 2 Negative mode mass spectrum of $(TBA)_6[H_5W_{18}O_{59}(IO_3)]$ **2** in acetonitrile.

Notes and references

‡ **Caution:** care should be taken when using IO_6^{5-} based materials since there is a risk of explosion or combustion.

§ Synthesis of $(\text{TEAH})_5\text{Na}[\text{H}_5\text{W}_{18}\text{O}_{59}(\text{IO}_3)] \cdot 5\text{H}_2\text{O}$ **1**: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (10.0 g, 30.3 mmol) and triethanolamine hydrochloride (7.0 g, 37.7 mmol) were dissolved in water (20 mL) and H_5IO_6 (0.5 g, 2.2 mmol) in water (5 mL) was added. The solution pH was adjusted to 1.3 by dropping in 6 M HCl and the solution was heated to reflux and stirred for about 1.0 h until the solution turned to light brown and purple I_2 vapour just started to appear in the flask. Light brown crystalline product was then isolated in three days. Yield: 3.2 g. Elemental analysis, calc. for $\text{C}_{30}\text{H}_{85}\text{IN}_5\text{NaO}_{77}\text{W}_{18}$ (dried sample): C 6.91, H 1.65, I 2.44, N 1.34, Na 0.44%. Found: C 7.80, H 1.81, I 2.46, N 1.46, Na 0.76%. Cation exchange to produce $(\text{TBA})_6[\text{H}_5\text{W}_{18}\text{O}_{59}(\text{IO}_3)] \cdot 2$: $(\text{C}_6\text{H}_{16}\text{NO}_3)_5\text{Na}[\text{H}_5\text{W}_{18}\text{O}_{59}(\text{IO}_3)] \cdot 5\text{H}_2\text{O}$ **1** (1.0 g) was dissolved in water (20 mL). Tetrabutylammonium bromide (1.0 g) dissolved in water (10 mL) was added with stirring. The precipitate was centrifuged and washed with water, ethanol and ether, and dried in vacuum. Yield: 0.7 g. Elemental analysis, calc. for $\text{C}_{96}\text{H}_{221}\text{IN}_6\text{O}_{62}\text{W}_{18}$: C 19.58, H 3.78, I 2.16, N 1.43%. Found: C 19.80, H 3.73, I 2.21, N 1.50%.

¶ Crystallographic data and structure refinements for $(\text{TEAH})_5\text{Na}[\text{H}_5\text{W}_{18}\text{O}_{59}(\text{IO}_3)] \cdot 5\text{H}_2\text{O}$ **1**: $\text{C}_{30}\text{H}_{85}\text{IN}_5\text{NaO}_{77}\text{W}_{18}$, $M_r = 5297.29$ g mol⁻¹; block crystal: $0.19 \times 0.15 \times 0.05$ mm³; $T = 150(2)$ K; triclinic, space group $P\bar{1}$, $a = 14.1743(3)$, $b = 18.6898(4)$, $c = 21.2836(5)$ Å, $\alpha = 89.751(2)^\circ$, $\beta = 87.320(2)^\circ$, $\gamma = 70.905(2)^\circ$, $V = 5321.9(2)$ Å³, $Z = 2$, $\rho = 3.306$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 19.76$ mm⁻¹, $F(000) = 4724$, 86 475 reflections collected, 19 759 unique, 1101 refined parameters, $R_1 = 0.0591$, $wR_2 = 0.1782$. The cluster is well defined in the asymmetric unit. One Na^+ site is identified by the coordination environment around the site. Four TEAH^+ sites are roughly modelled in the structure. The fifth TEAH^+ molecule (or a little more according chemical analysis) is believed to be located in the heavily disordered solvent area. Crystal data were measured on a Oxford Gemini A Ultra Atlas CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) at 150(2) K. Twin data process and structure refinement were applied in this structure determination. CCDC 951761 (**1**) contains the crystallographic data.

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