

Synthesis and Crystal Structure of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$

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A novel diperoxoheptatungstate was crystallised as a $\text{Cs}^+ - \text{CN}_3\text{H}_6^+ - (\text{C}_2\text{H}_5)_2\text{NH}_2^+$ salt and characterised by a single-crystal X-ray diffraction method. The anion has a Lindqvist heptametallate structure. The metal atoms are located in a bent 2-3-2 arrangement with the central W_3 section (W_3 , W_4 and W_5) as the hinge. The peroxo groups coordinate the tungsten atoms at both ends of the W_3 section (W_3 and

W_5). In the crystal polyanions, caesium and guanidinium cations, and water of crystallisation form tunnel-like cavities, and the diethylammonium cations are accommodated in the cavities, suggesting a clathrate-like feature for the compound.

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Introduction

Polyoxometallates are aggregates of oxo anions involving transition metals of groups 5 and 6. By substituting oxo groups in a polyoxometallate with peroxo groups, a peroxopolyoxometallate is formed. The peroxopolyoxometallates are known to be effective oxidising agents. Several peroxopolyoxometallates have thus been examined as oxidation catalysts, and epoxidation of alkene and hydroxylation of benzene are mentioned as examples of catalytic reactions.^[1–3]

Peroxopolyoxometallates constructed from only oxoanions of addenda atoms such as V, Mo and W are called peroxoisopolyoxometallates, and from both addenda and hetero atoms such as P, S and As are called peroxoheteropolyoxometallates. The catalytic properties of the peroxopolyoxometallates depend on their components; generally, peroxoheteropolyoxometallates are more active than peroxoisopolyoxometallates, and tungstates are more active than molybdates.^[4,5] Other than functioning as catalysts, the peroxopolyoxometallates have application in photoresist materials and as precursors of oxides.^[6]

While extensive research in the application of peroxopolyoxometallates has been done, the basic chemistry of peroxopolyoxometallates has not been well-investigated. Especially, the chemistry of peroxoisopolytungstates is not well-known and only four anionic structures, $[\text{W}(\text{O}_2)_4]^{2-}$,^[7] $[\text{W}_2\text{O}_3(\text{O}_2)_2(\text{H}_2\text{O})_2]^{2-}$,^[8] $[\text{W}_4\text{O}_6(\text{O}_2)(\text{OH})_2(\text{H}_2\text{O})_2]^{2-}$ ^[9] and $[\text{W}_4\text{O}_{12}(\text{O}_2)_2]^{4-}$ ^[10] have been reported so far, probably due to the instability of the system and compounds formed, and

the slow formation of the anions. On the other hand, a spectroscopic work has been reported and a number of structurally unknown species have been detected.^[11,12]

The authors have therefore been working with isolating peroxoisopolytungstates as single crystals to elucidate synthetic conditions and structures of the complexes. In the course of the investigation on peroxoisopolytungstates formed in aqueous medium, a novel diperoxoheptatungstate anion was isolated as a caesium/diethylammonium/guanidinium salt. The preparation and structure of this compound is described here.

Results and Discussion

An ORTEP^[13] diagram of all non-H atoms in the asymmetric unit is shown in Figure 1 with atom numbering. The anion has a Lindqvist heptametallate structure. The metal atoms are located in a bent 2-3-2 arrangement in which the central W_3 section (W_3 , W_4 and W_5) acts as a hinge. The dihedral angle between least-squares planes defined by $\text{W}_1 - \text{W}_2 - \text{W}_5 - \text{W}_4 - \text{W}_3$ and $\text{W}_3 - \text{W}_4 - \text{W}_5 - \text{W}_6 - \text{W}_7$ is $84.67(1)^\circ$. The peroxo groups coordinate the tungsten atoms at both ends of the W_3 section (W_3 and W_5), protruding from opposite sides of the W_2 units. The two W atoms are thus heptacoordinated with a pentagonal bipyramidal geometry. The other W atoms are hexacoordinate. Selected bond lengths are listed in Table 1. The ranges of the bond lengths of W–O (terminal) and W–O (bridge) are $1.713(4) - 1.751(4)$ Å and $1.758(4) - 2.324(4)$ Å, respectively.

Although O10 and O12 are asymmetrically bridging, the short bond lengths $\text{W}_4 - \text{O}_{10}$ [$1.784(4)$ Å] and $\text{W}_4 - \text{O}_{12}$ [$1.758(4)$ Å] indicate that these O atoms behave like the terminal oxygen atoms of W_4 . The long W–O bond lengths *trans* to $\text{W}_4 - \text{O}_{10}$ and $\text{W}_4 - \text{O}_{12}$, $\text{W}_4 - \text{O}_{13}$ [$2.222(4)$ Å]

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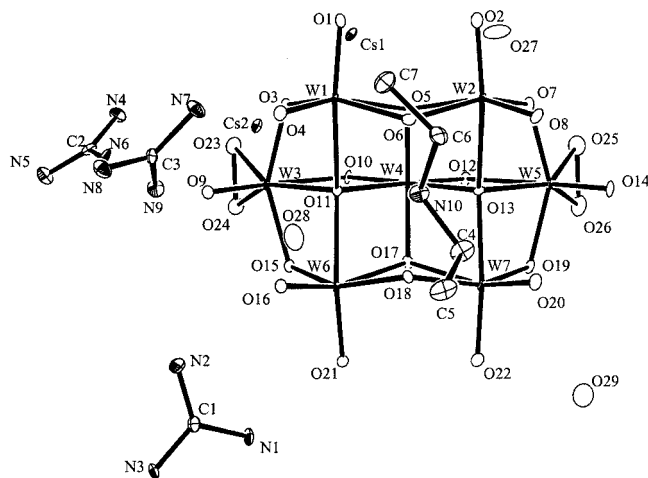


Figure 1. An ORTEP view of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$, displacement ellipsoids are drawn at the 50% probability level; selected bond lengths (Å) and angles (°): W(1)–O(1) 1.742(4), W(1)–O(4) 1.742(4), W(2)–O(2) 1.747(5), W(2)–O(8) 1.732(4), W(3)–O(9) 1.723(4), W(5)–O(14) 1.713(4), W(6)–O(16) 1.745(4), W(6)–O(21) 1.751(4), W(7)–O(20) 1.744(5), W(7)–O(22) 1.744(5), W(1)–O(3) 1.947(4), W(1)–O(6) 1.938(4), W(1)–O(5) 2.283(4), W(1)–O(11) 2.208(4), W(2)–O(5) 2.285(4), W(2)–O(6) 1.953(4), W(2)–O(7) 1.947(4), W(2)–O(13) 2.207(4), W(3)–O(3) 1.973(4), W(3)–O(10) 2.3237(4), W(3)–O(11) 2.081(4), W(3)–O(15) 1.984(4), W(4)–O(5) 1.883(4), W(4)–O(10) 1.784(4), W(4)–O(11) 2.252(4), W(4)–O(12) 1.758(4), W(4)–O(13) 2.222(4), W(4)–O(17) 1.898(4), W(5)–O(7) 1.964(4), W(5)–O(12) 2.367(4), W(5)–O(13) 2.110(4), W(5)–O(19) 1.993(4), W(6)–O(11) 2.204(4), W(6)–O(15) 1.950(4), W(6)–O(17) 2.227(4), W(6)–O(18) 1.935(4), W(7)–O(13) 2.174(4), W(7)–O(17) 2.280(4), W(7)–O(18) 1.930(4), W(7)–O(19) 1.951(4), W(3)–O(23) 1.955(5), W(3)–O(24) 1.943(5), W(5)–O(25) 1.948(5), W(5)–O(26) 1.942(5), O(23)–O(24) 1.479(7), O(23)–O(24) 1.468(7), O(23)–W(3)–O(24) 44.3(2), O(25)–W(5)–O(26) 44.6(2)

and W4–O11[2.252(4) Å], are the result of the *trans* influence of O10 and O12. The same phenomenon has been observed in peroxoheptamolybdates.^[14–16]

In the vicinity of the peroxo groups (O23–O24 and O25–O26), the W–O bond lengths are in the range of 1.942(5)–1.955(5) Å, and the O23–O24 and O25–O26 bond lengths are 1.479(7) Å and 1.467(7) Å, respectively. The angles O23–W3–O24 and O25–W5–O26 of the peroxo group are 44.6(2)° and 44.3(2)°, respectively. These values are normal for compounds of this type.

The existence of such a polyanion has been predicted by an ^{17}O NMR study.^[11,12] However, this is the first example of the isolation and structural analysis of this type of anion. On the other hand, the corresponding molybdates have already been isolated and structurally analysed.^[14] Structures of heptatungstates without peroxo groups have also been

reported.^[17,18] The bond lengths in peroxoheptamolybdate, heptatungstate and the present peroxoheptatungstate are compared in Table 1;^[17–21] no significant differences are observed, and any discrepancies may be partly due to the accuracy of the measurements. The slightly shorter bond lengths in the present compound are a result of the low temperature at the time of the measurement.

Packing diagrams are shown in Figures 2 and 3. Three H_2O molecules, three CN_3H_6^+ and two Cs^+ ions, and one $(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ ion surround the anion. The polyanions, cations and water of crystallisation are linked by hydrogen bonds and electrostatic interactions (Table 2) to stabilise the whole crystal structure. Generally, the peroxoheptatungstate was considered to be difficult to isolate in the solid state and it has not been achieved before, although the existence of the anion in aqueous solution has been determined by spectroscopic methods.^[11,12] The reason for the isolation of the peroxoheptatungstate as single crystals this time may have depended on the stabilisation of the whole crystal structure by the coexistence of not a single but several kinds of cations in the composition. As can be seen in Figure 3, the polyanions, the caesium and guanidinium cations, and the water of crystallisation form tunnel-like cavities, and the diethylammonium cations are accommodated in these cavities. The ammonium cation is held in the structure by hydrogen bonds with the polyanion and water of crystallisation in the walls of the tunnels. The bond lengths are listed in Table 2. The compound thus has a

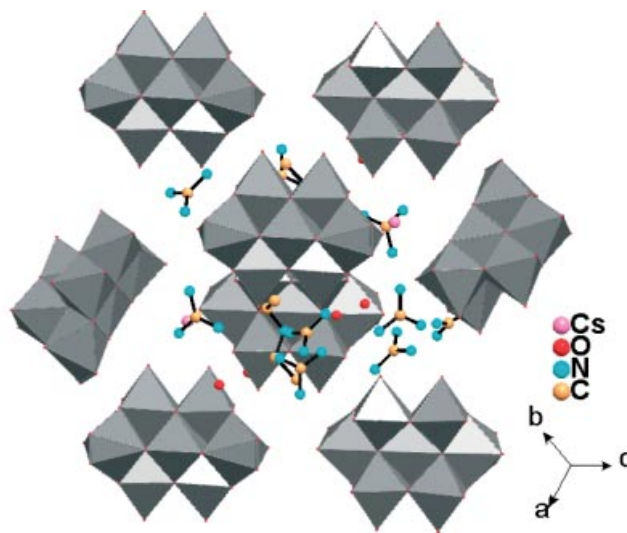


Figure 2. A packing diagram of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$

Table 1. Comparison of bond lengths (Å) in heptametallates

	M–O (terminal)	M–O–M (bridging)	Peroxo M–O	Peroxo O–O	Ref.
Peroxoheptatungstate	1.713(4)–1.751(4)	1.758(4)–2.324(4)	1.942(5)–1.955(5)	1.467(7)–1.479(7)	this work
Heptatungstate	1.523–1.884	1.661–2.616	—	—	[17,18]
Peroxoheptamolybdate	1.640–1.757	1.743–2.509	1.864–1.975	1.376–1.511	[19–21]

clathrate nature. This suggests that these compounds may be obtained with other monovalent cations in combination with caesium and guanidinium cations. We are therefore attempting to obtain such compounds with monovalent cations having various features; the results will be published elsewhere.

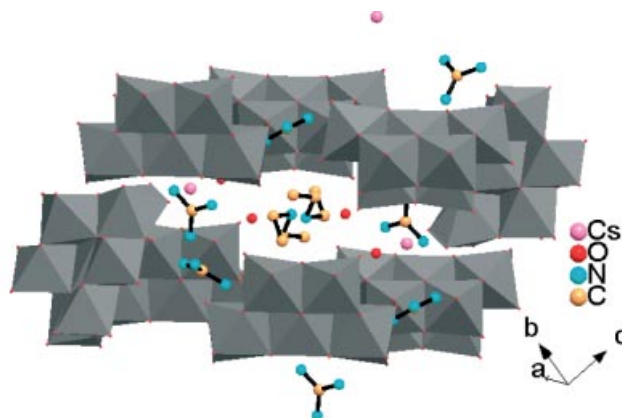


Figure 3. A packing diagram of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$; the tunnel-like cavity formed by polyanions, caesium and guanidinium cations and water is shown

Table 2. Distances involved in hydrogen bonding and electrostatic interactions (Å)

	Oaq	Oani	Cs
Gu–N ^[a]	2.868(8)–3.315(8)	2.827(7)–3.159(8)	3.403(6)–3.868(6)
Am–N ^[b]	2.731(8)	2.873(7)	—
Oaq ^[c]	2.730(8)	2.734(7)–2.878(7)	3.503(6)
Oani ^[d]		2.990(4)–3.712(5)	

[a] Gu–N...nitrogen of guanidinium. [b] Am–N...nitrogen of ammonium. [c] Oaq...oxygen of water molecule. [d] Oani...oxygen of anion.

Experimental Section

Preparation of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$: Tungsten powder (1.83 g) was slowly dissolved in 30% hydrogen peroxide (25 mL), and the mixture was diluted to 100 mL with H_2O . Care must be taken here because of a vigorous reaction. The pH of the solution was adjusted to ca. 4.0 with aqueous LiOH (2.7 M). CsCl , $(\text{CN}_3\text{H}_5)\cdot\text{HCl}$, $(\text{C}_2\text{H}_5\text{NH})\cdot\text{HCl}$ (molar ratio W/cation = 1:0.5 for each) were then added to the resulting solution. Colourless plate-shaped crystals appeared at room temperature in about 40 days.

Crystallographic Data for $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$: $M_r = 2276.77$, monoclinic, $P2_1/c$, $a = 13.4459(3)$, $b = 11.3009(2)$, $c = 25.0294(2)$ Å, $\beta = 90.4760(10)^\circ$, $V = 3803.11(11)$ Å³, $Z = 4$, $D_x = 3.977$ g/cm³, $T = 100(2)$ K, μ (Mo- K_α) = 23.08 mm⁻¹, $R_1 [F_o > 4.0\sigma(F_o)] = 0.0270$, wR_2 (all data) =

0.0627, goodness of fit = 0.998, $R(\text{int.}) = 0.0643$, reflections measured 63317, unique reflection 11647, parameter 497.

Intensity data of $\text{Cs}_2(\text{CN}_3\text{H}_6)_3[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{W}_7\text{O}_{22}(\text{O}_2)_2]\cdot 3\text{H}_2\text{O}$ was collected on SMART CCD SYSTEM. Data reduction and absorption correction based on psi-scans were applied with TEXSAN.^[22] All calculations were performed with SHELX97.^[23] Cs and W atoms were located by a direct method and all other atoms by successive Fourier syntheses. All non-H atoms were refined anisotropically by full-matrix least-squares based on F^2 . CCDC-227357 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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