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Novel cerium(IV) heteropolyoxotungstate containing two types of lacunary Keggin anions†

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A novel V-shaped polyoxotungstate is formed when Ce^{IV} metal centres bridge monolacunary $[PW_{11}O_{39}]^{7-}$ anions to an unusual 1,4-bilacunary $[PW_{10}O_{38}]^{11-}$ anion which appears with an unprecedented bridging structural motif.

Polyoxometalates are a unique family of metal–oxygen clusters[1] which exhibit a myriad of molecular architectures[2] and find applications in fields ranging from materials science to medicine.[3] Lanthanopolyoxometalates have been shown to exhibit catalytic activity[4,5] and have been used as luminescent centres in functional materials.[6] The first crystallographic report of a structure containing anions of the $[M(XW_{11}O_{39})_2]^{n-}$ type concerned $Cs_{12}[U(GeW_{11}O_{39})_2]\cdot 13–14H_2O$,[7] with the corresponding lanthanide undecamolybdophosphate analogues being only recently described by Gaunt *et al.*[8] which includes the Ce^{III} compound, $(NH_4)_{11}[Ce^{III}(PMo_{11}O_{39})_2]\cdot 16H_2O$. A handful of reports on monolacunary derived lanthanopolyoxometalates can be found in the literature, namely those by Peacok and Weakley (who have isolated the first Ce^{IV} and Ce^{III} complexes, $K_{10}[Ce^{IV}(PW_{11}O_{39})_2]\cdot 25H_2O$ and $K_{12}[Ce^{IV}(SiW_{11}O_{39})_2]\cdot 28H_2O$),[9] Griffith *et al.*,[5] Haraguchi *et al.* (1 : 2 complexes containing Ce^{III}, such as $K_{13}[Ce^{III}(GeW_{11}O_{39})_2]\cdot 21H_2O$ and $K_{15}[Ce^{III}(BW_{11}O_{39})_2]\cdot 20H_2O$),[10] Pope and collaborators (who have described the formation of polymeric chains of the 1 : 1 anionic complex $[Ce^{III}(\alpha\text{-}SiW_{11}O_{39})(H_2O)_3]^{5-}$),[11] Mialane *et al.* ($KCs_4[Yb(SiW_{11}O_{39})(H_2O)_2]\cdot 24H_2O$ and $K_{0.5}Nd_{0.5}[Nd_2(SiW_{11}O_{39})(H_2O)_{11}]\cdot 17H_2O$),[12] Wang *et al.* ($K_{11}H_2[Dy(SiMo_{11}O_{39})_2]\cdot 29H_2O$),[13] Shan *et al.* ($K_7H_6[Nd(GeMo_{11}O_{39})_2]\cdot 27H_2O$),[14] and Naruke and Yamase ($K_{8.5}H_{3.5}[Eu(BW_{11}O_{39})(W_5O_{18})]\cdot 25H_2O$).[15] Following our interest in the synthesis of novel lanthanide complexes containing Keggin-type monolacunary polyoxotungstophosphates or polyoxotungstoborates, which can be used in the preparation of thin films[16] and exhibit catalytic activity for oxidative processes,[4,5] here we describe the first Ce^{IV} complex with two distinct Keggin-type lacunary polyoxotungstophosphates (monolacunary $[PW_{11}O_{39}]^{7-}$ and bilacunary $[PW_{10}O_{38}]^{11-}$ anions, both derived from the α-isomer) $H_7K_{10}[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]\cdot 28H_2O$, belonging to a new class of lanthanide-substituted polyoxometalates in which the bilacunary $[PW_{10}O_{38}]^{11-}$ anions show an unprecedented bridging structural motif.‡ Of the five possible bilacunary α-Keggin anion isomers, the one observed here is the 1,4 isomer (C_2 symmetry), resulting from the removal of two W=O groups in the 1 and 4 positions, respectively, as defined by Pope and Scully.[17]

The structure of the title compound was elucidated by single-crystal X-ray diffraction§ and consists of discrete V-shaped anionic complexes, $[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]^{17-}$, *ca.* 1.5 × 2.2 nm in size and constructed from bilacunary $[PW_{10}O_{38}]^{11-}$ and monolacunary $[PW_{11}O_{39}]^{7-}$ polyanions bridged by Ce^{IV} cations (Fig. 1). Highly symmetric and unusual 1,4-bilacunary $[PW_{10}O_{38}]^{11-}$ species are located at the two-fold axis along the *c* direction, leading to two lacunae formed by the O(45), O(47), O(57) and O(58) atoms and occupied by the Ce^{IV} cations with $Ce(1)\cdots Ce(1)^i$ of *ca.* 6.10 Å [symmetry code: (i) $-x$, y, $1.5-z$] (Fig. 2). The residual available coordination sites of these cations establish a physical connection with a crystallographically independent monolacunary $[PW_{11}O_{39}]^{7-}$ polyanion [*via* the O(19), O(28), O(32) and O(39) atoms], resulting in a $\{CeO_8\}$ coordination environment, best described as a distorted bicapped trigonal prism. In Fig. 2, Ce–O(19) and Ce–O(39) bonds occupy the capped positions and the Ce–O bond lengths are within the 2.28(3) to 2.44(3) Å range. The PO_4 tetrahedra in the polyanions are almost regular with the P–O and O–P–O bond lengths and angles within the expected ranges [1.53(3)–1.57(3) Å and 1.55(3)–1.57(3) Å, 107.3(16)–111.4(16)° and 108(2)–113(2)° for the mono- and bilacunary polyanions, respectively]. Despite the observed bond ranges for W–O_a [2.31(3)–2.48(3) and 2.36(3)–2.48(3) Å], W–$O_{b/c}$ [1.76(3)–2.02(3) and 1.77(4)–2.05(3) Å]

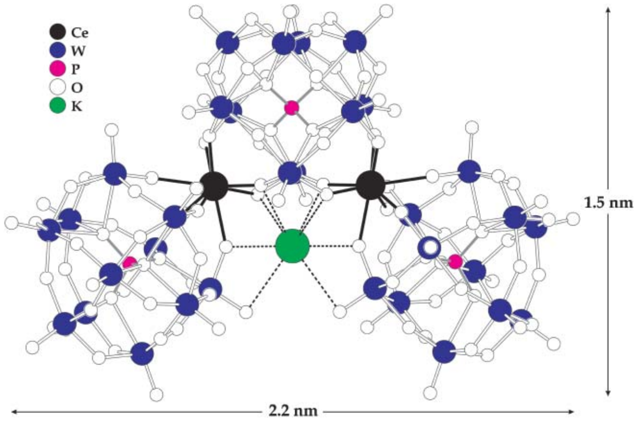

Fig. 1 Molecular structure of $H_7K_{10}[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]\cdot 28H_2O$.

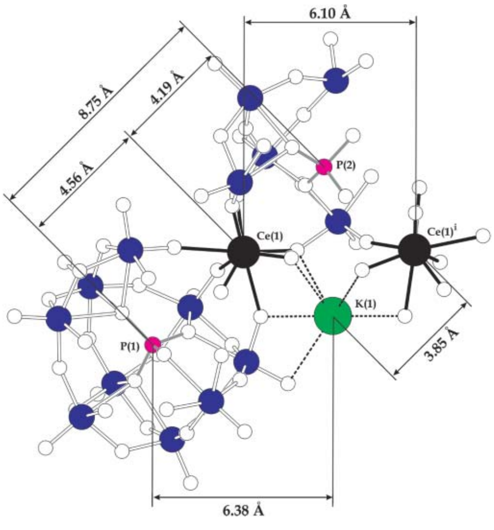

Fig. 2 Geometry of the molecular unit. Colour scheme as in Fig. 1. Distances not shown: $K(1)\cdots Ce(1)$ 3.85 Å; $P(1)\cdots P(1)^i$ 12.69 Å. Symmetry code used to generate equivalent atoms: (i) $-x$, y, $1.5-z$.

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† Electronic supplementary information (ESI) available: single-crystal X-ray diffraction: details on crystal structure solution and refinement. See http://www.rsc.org/suppdata/cc/b4/b409034a/

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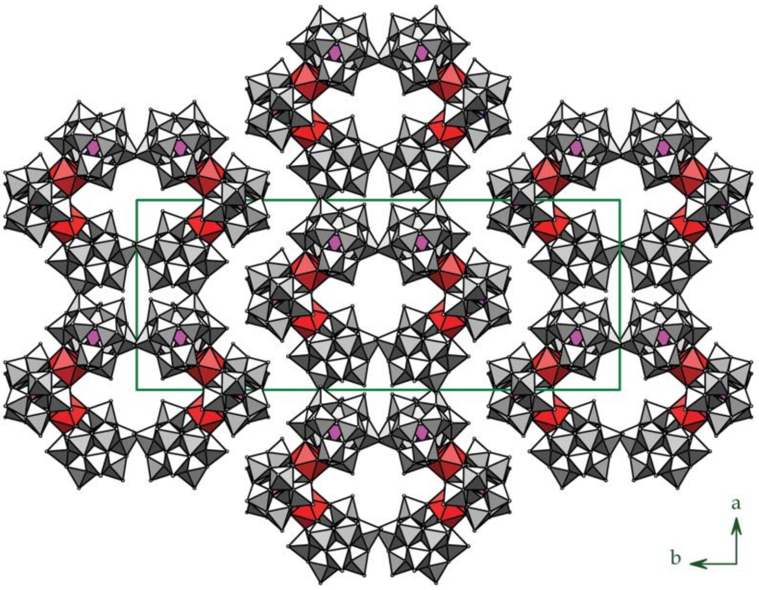

Fig. 3 Crystal packing. WO_6 polyhedra are represented in grey and CeO_8 polyhedra in red.

and W–O_t [1.65(3)–1.76(3) and 1.70(3)–1.75(3) Å for the mono- and bilacunary polyanions, respectively] of the $\{WO_6\}$ octahedra being approximately identical to the expected values, the heterogeneity of bond lengths seems to indicate a generalised distortion of the $[Ce_2(PW_{10}O_{38})(PW_{11}O_{39})_2]^{17-}$ anionic complex which is, consequently, reflected in the previously described coordination environment of the Ce^{IV} metal centres. Interestingly, the complex has an internal molecular cavity occupied by a K^+ cation with K(1)···O interactions ranging from 2.59(3) to 3.24(3) Å. The cation can simultaneously stabilise the complex and contribute to the observed distortions. Further geometric details of the complex are given in Fig. 2.

Individual complexes close-pack in the *ab* plane, with the steric hindrance imposed by the unusual V-shape leading to several types of channels filled with crystallisation water molecules (Fig. 3). These are, in turn, involved in a complex and extended hydrogen-bonding network (not shown).

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Notes and references

‡ *Synthesis*: Reagents were readily available from commercial sources and were used as received without further purification. Phosphotungstic acid hydrate (4.3 g, 1.5 mmol) was dissolved in hot water (*ca.* 5 cm^3) followed by the addition of an aqueous solution of $(NH_4)_2[Ce(NO_3)_6]$ (0.41 g, 0.75 mmol in *ca.* 2 cm^3 of water). A concentrated solution of potassium acetate (5.0 g, 50 mmol in *ca.* 5 cm^3 of water; pH adjusted to *ca.* 7 with acetic acid) was added dropwise with vigorous magnetic stirring. The mixture was filtered and the resulting aqueous solution refrigerated. The precipitate formed after one week was manually separated and identified as $K_{10}[Ce^{IV}(PW_{11}O_{39})_2]\cdot 8H_2O$ (1.87 g; 41% yield) according to Haraguchi *et al.*[10] [Elemental composition (in %) calculated: K 6.48, P 1.03, W 67.08, Ce 2.32. Found (in %): K 6.97, P 1.01, W 66.40, Ce 2.56. Selected FT-IR data (in cm^{-1}): ν(W–O) at 956, ν(W–O–W) at 892, 813 and 746, and ν(P–O) at 1105 and 1051.] Yellow crystals of the title compound suitable for X-ray measurements were obtained by slow evaporation of the aqueous solution over several weeks (0.35 g, 10% yield). Elemental composition (in %) calculated (based on crystallographic data): K 4.34, P 1.03, W 65.26, Ce 3.11. Found (in %): K 4.43, P 0.5, W 65.00, Ce 2.73. Selected FT-IR data (from KBr disk; Aldrich 99%+): ν(W–O) at 953, ν(W–O–W) at 889, 827, 764 and 721 cm^{-1}, and ν(P–O) at 1105, 1090, 1051 and 1022 cm^{-1}.

§ *Crystal data*: $H_{63}Ce_2K_{10}O_{144}P_3W_{32}$ (including the 63 H-atoms from the charge balancing H^+ and crystallisation water molecules), $M = 9014.85$, monoclinic, space group $C2/c$, $Z = 4$, $a = 21.035(4)$ Å, $b = 53.449(16)$ Å, $c = 12.472(3)$ Å, $\beta = 91.67(3)^\circ$, $V = 14016(6)$ Å^3, μ(Mo–Kα) = 27.221 mm^{-1}, $D_c = 4.272$ g cm^{-3}. Of a total of 21642 reflections collected, 6872 were independent ($R_{int} = 0.0738$). Final $R1 = 0.0752$ [$I > 2\sigma(I)$] and $wR2 = 0.1723$ (all data). Data completeness to $\theta = 20.58^\circ$, 96.5%. Details for crystal structure solution and refinement are given as Supporting Information.† CCDC 243257. See http://www.rsc.org/suppdata/cc/b4/b409034a/ for crystallographic data in .cif or other electronic format.

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