

## Synthesis and characterisation of a lanthanide-capped dodecavanadate cage†

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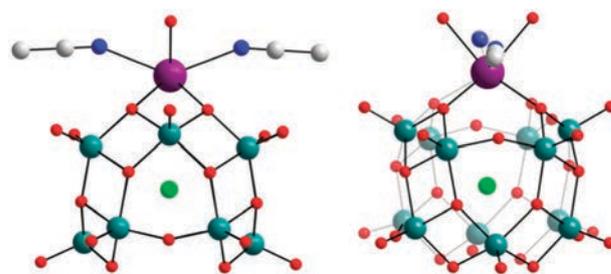
**The synthesis of a series of discrete lanthanide-capped polyoxovanadate cages is presented along with magnetic and electrochemical measurements which reveal a redox active dodecavanadate cluster with potential as a new functional building unit in polyoxovanadate chemistry.**

Polyoxometalates (POMs) represent a vibrant and expanding field in inorganic chemistry due not only to their interesting electronic, catalytic and material properties but also thanks to their potential to support the formation of discrete, high-nuclearity heterometallic clusters.<sup>1</sup> Whilst the majority of reported POM structures are constructed from W<sup>VI</sup> or Mo<sup>VI</sup> based building units, so-called polyoxovanadates (POVs) have attracted increasing interest for their unique structural motifs and rich photochemical and electronic properties.<sup>2</sup> Consequently, mixed-valence and highly reduced POVs have been the subject of intense study, particularly due to their rich magnetic behaviour.<sup>3</sup>

Expanding the study of POVs to include novel assemblies incorporating additional transition metal sub-units has, however, proved relatively difficult, largely owing to the structural lability of the vanadium ions which can readily adopt a mixture of tetrahedral, square pyramidal and octahedral coordination geometries. This structural flexibility leads to a tendency towards closed, cage-like structures and inhibits the isolation of lacunary clusters which can be thought of as excellent building units in the formation of nanoscale, supramolecular architectures. Whilst there are numerous examples of discrete POVs linked into networks through coordinated heterometal ions,<sup>4</sup> only limited success has been achieved in directly introducing 3d- or 4f-metal moieties into POV frameworks.<sup>5</sup>

Interest in 4f-ions in particular has grown significantly in recent years and they have emerged as excellent candidates for magnetic studies owing to their large number of unpaired electrons and high axial anisotropy.<sup>6</sup> In some well-documented cases, clusters containing a single 4f-ion have been shown to exhibit slow-relaxation behaviour, allowing for the isolation of 'single ion magnets'.<sup>7</sup> Similarly, incorporation of trivalent lanthanide ions into mixed metal 3d-4f clusters has been an active area of research and has driven a new direction in the study of molecular magnetism.<sup>8</sup> In this regard, W-based POMs in particular have shown excellent promise for the construction of both mono- and mixed-metal systems.<sup>9</sup> Directly combining 4f-ions with electronically interesting vanadium-based POMs however, has proved challenging and such examples remain rare.<sup>4c</sup>

Herein, we present the first example, to our knowledge, of the direct incorporation of lanthanide ions into a classical cage-like POV framework as a series of mono-substituted dodecavanadate clusters; (TBA)<sub>2</sub>[Ln(V<sub>12</sub>O<sub>32</sub>(Cl))(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (Ln = Gd (1), Tb (2), Dy (3), Ho (4) and Er (5)) (Fig. 1). The system was fully characterised *via* single crystal X-ray diffraction, elemental analysis, thermogravimetric analysis, electrospray ionisation mass spectrometry (ESI-MS) and infrared spectroscopy. The magnetic properties of the complexes were compared and electrochemical measurements of **1** were undertaken to probe the redox chemistry of the dodecavanadate cage.



**Fig. 1** Ball and stick representations of the [Ln(V<sub>12</sub>O<sub>32</sub>(Cl))(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>]<sup>2-</sup> cluster in **1–5**. Colour code: V = teal, Ln = purple, Cl = green, O = red, N = blue and C = grey (hydrogen atoms have been omitted for clarity).

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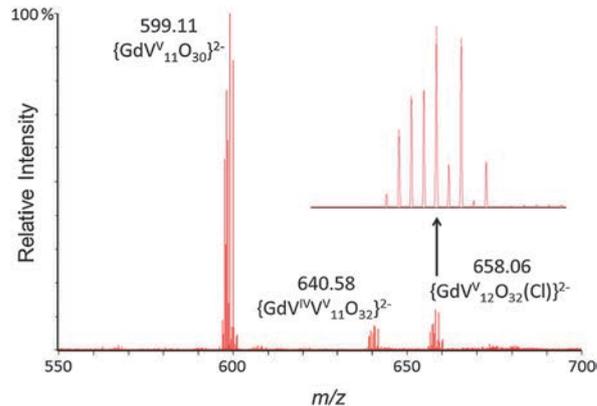
† Electronic supplementary information (ESI) available: Full experimental procedures, crystallographic data, bond valence sums, mass spectrometry and thermogravimetric analysis. CCDC 913544. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc40912k

Complexes 1–5 were synthesised by the facile reaction of the bowl-shaped dodecavanadate inclusion complex (TBA)<sub>4</sub>[V<sub>12</sub>O<sub>32</sub>(CH<sub>3</sub>CN)]<sup>10</sup> with different lanthanide chloride salts in acetonitrile. The high affinity of lanthanide ions towards oxygen donors renders them a good match for POM-type ligands, and this has been exploited to great effect, particularly when using W-based POMs. Based on this we hypothesised that the oxygen rich ‘lip’ of the V<sub>12</sub> bowl might provide a good binding site for lanthanide ions. Instead, we observed a complete rearrangement of the V<sub>12</sub> precursor upon addition of the lanthanide ions, forming an open-ended cage-like framework which is directly related to the previously reported [V<sub>15</sub>O<sub>36</sub>(Cl)]<sup>6-</sup> parent compound.<sup>11</sup> Interestingly, the role of the chloride ion appears crucial to the success of the synthesis – acting as an anionic template for the formation of the vanadate cage and potentially helping to drive the inclusion of the lanthanide ion directly into the framework of the POV shell.<sup>12</sup>

Crystallographic analysis reveals that **1** crystallises in an orthorhombic system with space group *P*2<sub>1</sub>2<sub>1</sub>2, where the anion complex has crystallographically imposed twofold symmetry with the Gd and Cl atoms located on the twofold axis. The Gd ion possesses a distorted square antiprismatic geometry and caps the dodecavanadate unit through four nearly identical coordinative bonds (with *d*<sub>O–Gd</sub> = 2.363(4) Å and 2.384(4) Å).<sup>‡</sup> Two disordered water ligands and two acetonitrile ligands make up the remainder of the lanthanide ions’ coordination sphere (although elemental analysis confirms that the acetonitrile ligands are rapidly lost upon removal of the crystals from the supernatant mother liquor). The chloride ion is electrostatically bound within the centre of the cage (average *d*<sub>V–Cl</sub> = 3.352(17) Å). Charge balance considerations in conjunction with the intense orange colour of the crystals (indicative of the LMCT bands of fully oxidised polyoxovanadates) and bond valence sum calculations confirm that all twelve V centres are in the +5 oxidation state and all lanthanide ions are present in their expected +3 oxidation state. Subsequent crystallographic analysis revealed that compounds 2–5 can be considered to be directly isostructural with compound 1.

High resolution negative-mode ESI-MS was used in conjunction with the structural analysis to confirm the identity of products 1–5. Peaks in the *m/z* region of 550–700 could be unambiguously assigned in each case to well-resolved anionic fragments of the dodecavanadate cage, with each compound easily distinguishable by both its mass and the characteristic isotopic distribution pattern of its constituent lanthanide ion. For compound **1**, the peak centred at *m/z* = 658.06 corresponds to the intact cluster fragment [GdV<sup>V</sup><sub>12</sub>O<sub>32</sub>(Cl)]<sup>2-</sup> whilst additional peaks located at *m/z* = 640.58 and 599.11 can be assigned to [GdV<sup>IV</sup>V<sup>V</sup><sub>11</sub>O<sub>32</sub>]<sup>2-</sup> and [GdV<sup>V</sup><sub>11</sub>O<sub>30</sub>]<sup>2-</sup> species respectively (Fig. 2). Compounds 2–5 exhibited similar trends with peaks corresponding to the fragment [LnV<sup>V</sup><sub>12</sub>O<sub>32</sub>(Cl)]<sup>2-</sup> appearing in the region of *m/z* ≈ 660, with additional peaks in close agreement to those reported for compound **1** (see ESI<sup>†</sup>). It should be noted that it was also possible to observe singly charged species including (TBA)[LnV<sup>V</sup><sub>12</sub>O<sub>32</sub>(Cl)]<sup>-</sup> (*m/z* ≈ 1560) in the mass spectra of 1–5 but in most cases the intensity was very low and the resolution too poor to unambiguously assign the isotopic envelope.

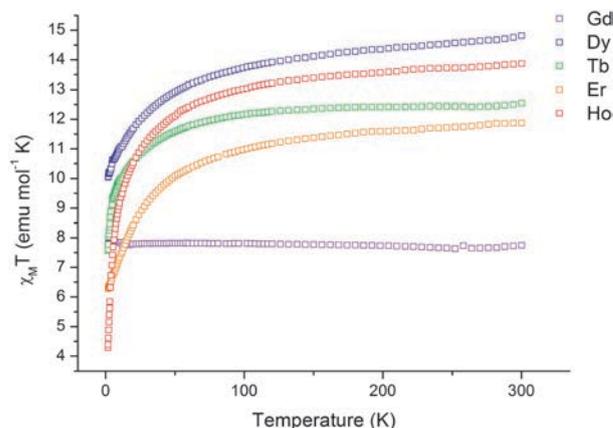
Low temperature SQUID measurements were performed on powdered samples of compounds 1–5 in order to study their



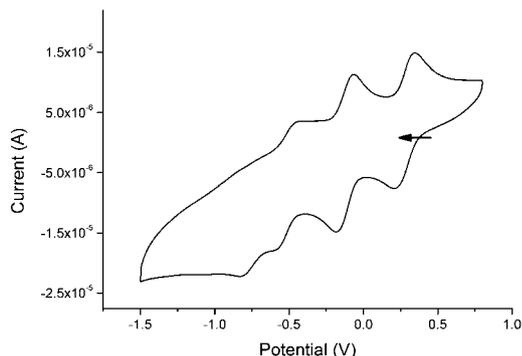
**Fig. 2** Negative mode mass spectrum of **1** shown in the 550 to 700 *m/z* range highlighting the three primary 2<sup>-</sup> peaks. Expansion of the peak centred at *m/z* = 658.06 is shown inset.

magnetic properties. Magnetic susceptibility measurements conducted from 1.8 to 300 K under a field of 0.05 T revealed that the behaviour of each complex conformed with that expected for the free lanthanide ion and  $\chi_m T$  vs. *T* plots found that the room temperature product for each ion was close to those reported in the literature<sup>13</sup> (previously reported values given in brackets); Gd: 7.73(7.88), Tb: 12.50(11.82), Dy: 14.82(14.17), Ho: 13.87(14.07) and Er: 11.87(11.48) (Fig. 3). The  $\chi_m T$  value observed for **1** remained more or less consistent as *T* decreased due to the magnetic isotropy of Gd(III), whilst 2–5 show a slight decrease in  $\chi_m T$  between 300 K and 50 K before declining sharply as a result of the thermal depopulation of the higher energy levels. In-phase ac susceptibility measurements of compounds 2–5 showed no frequency dependent response down to 1.8 K and negligible signal could be observed in the corresponding out-of-phase measurements allowing us to conclude that there is no significant barrier to reversal of the magnetisation in all four compounds measured.

Cyclic voltammetry of **1** performed in *N,N*-dimethylformamide (DMF) over the potential range +800 to –1500 mV at a scan rate of 100 mV s<sup>-1</sup> in the negative direction showed three redox waves with mean peak potentials (reported vs. Ag/AgCl) located at +0.28 V, –0.13 V and –0.52 V respectively, along with



**Fig. 3** Plot of  $\chi_m T$  vs. *T* for compounds 1–5 measured over the temperature range 1.8 to 300 K.



**Fig. 4** Cyclic voltammogram of a 1 mM solution of **1** taken in dimethylformamide with TBAPF<sub>6</sub> electrolyte at a scan rate of 100 mV s<sup>-1</sup>. The arrow indicates the starting potential and direction of the scan.

an additional ill-defined wave centred at approximately  $-0.75$  V, each of which may be attributed to the reduction and subsequent re-oxidation of the V<sub>12</sub>-cage via the V<sup>IV/V</sup> redox couple (Fig. 4).<sup>14</sup> The  $\Delta E_p$  values of around 0.12 V for the three well-defined redox waves are significantly higher than the theoretical value of 0.059 V for a reversible one-electron transfer suggesting that these are in fact quasi-reversible processes, typical of those associated with type I POMs.<sup>15</sup> Subsequent measurements of compound **2** provided nearly identical spectra and reinforced the conclusion that the observed redox activity arises solely from the V<sub>12</sub>-cage and is unmodified by the lanthanide ion. In addition, the voltammograms of both **1** and **2** remained consistent as the scan rate was increased, though a discernible increase in the peak to peak separation of each redox wave was observed.

Furthermore, as in the case of many vanadium-containing POMs,<sup>16</sup> compounds **1**–**5** are photosensitive and a solid sample will spontaneously undergo reduction if left under sunlight, as indicated by a gradual colour change from orange to dark green. To quantify this effect we directly reduced a small powdered sample of **1** using UV irradiation over several days, occasionally agitating the sample to ensure homogeneity, in order to yield the reduced species **1'** as a dark green powder. Bulk electrolysis of **1'** conducted at +1.0 V found that the cluster had been reduced by 4 electrons (found:  $4.0 \pm 0.3 e^-$ ), indicating that the V<sub>12</sub>-cage can support a mixed-valence configuration in the solid state upon direct photoreduction.

In summary, we have successfully isolated a new series of lanthanide-substituted dodecavanadate clusters, (TBA)<sub>2</sub>[Ln(V<sub>12</sub>O<sub>32</sub>(Cl))(H<sub>2</sub>O)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (where Ln = Gd, Tb, Dy, Ho and Er), via a facile synthetic procedure, revealing an unprecedented new type of heteropolyvanadate structural motif. We believe that these compounds present an exciting new potential building block in polyoxovanadate chemistry, and through functionalisation of the lanthanide ion via ligand exchange or further heteroatom substitution at the open end of the V<sub>12</sub>-cage, it may be possible to isolate new species with potentially interesting magnetic, luminescent or electronic properties that we hope to exploit in future work.

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## Notes and references

† Crystallographic data for compound **1**: C<sub>44</sub>H<sub>94</sub>ClGdN<sub>8</sub>O<sub>32</sub>V<sub>12</sub>, M<sub>r</sub> = 2083.3 g mol<sup>-1</sup>; orange block crystal; orthorhombic, space group P2<sub>1</sub>2<sub>1</sub>2,  $a = 15.6592(14)$ ,  $b = 25.175(2)$ ,  $c = 10.2383(9)$ ,  $V = 4036.1(6) \text{ \AA}^3$ ,  $Z = 2$ . Full details on the crystallography and structural refinement of **1** may be obtained from CSD quoting CCDC 913544.

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