

A [Ce<sub>21</sub>] keplerate†Cite this: *Dalton Trans.*, 2017, **46**, 7677Angelos B. Canaj,<sup>a</sup> Milosz Siczek,<sup>b</sup> Tadeusz Lis,<sup>b</sup> Mark Murrie,<sup>c</sup> Euan K. Brechin<sup>\*d</sup> and Constantinos J. Milios<sup>id \*a</sup>Received 25th April 2017,  
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**The solvothermal reaction between Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 2-amino-isobutyric acid, 2-hydroxy-1-naphthaldehyde and 2-amino-2-methyl-1,3-propanediol in MeOH, in the presence of base, leads to the formation of a unique [Ce<sub>13</sub>Ce<sup>IV</sup><sub>8</sub>] keplerate cage.**

Keplerates are high symmetry polymetallic molecules that contain metal polyhedra that describe both Platonic and Archimedean solids, one inside the other, in a manner akin to Russian dolls.<sup>1</sup> They have been described widely in polyoxometalate chemistry, with perhaps the most celebrated example being the spherical {(Mo)Mo<sub>5</sub>}<sub>12</sub>M'<sub>30</sub> (M' = Fe<sup>III</sup>, Cr<sup>III</sup>, V<sup>IV</sup>) species whose corner-sharing M'<sub>3</sub> triangles (the M'<sub>30</sub> unit describes an icosidodecahedron) cause geometric spin frustration, analogous to that seen in planar Kagome lattices.<sup>2</sup> Such structures, which are often aesthetically very beautiful, are less well known in homometallic 3d, 4f and heterometallic 3d–4f cages,<sup>3–7</sup> and the d-block complexes that have been fully characterised have always shown magnetic behaviour different to that expected from theory, *i.e.* none have shown frustration effects. A recent study of a family Cu<sup>II</sup> keplerates has suggested this is due to structural disorder, even in systems where the apparent crystallographic symmetry is high.<sup>8</sup>

The diamagnetic Ce<sup>IV</sup> ion has been used both as an oxidising agent and as a template for the construction of high nuclearity Mn-based Single-Molecule Magnets (SMMs),<sup>9</sup> while the Ce<sup>III</sup> ion, which has no nuclear spin and possesses just one unpaired electron, has been investigated for both its potential Single-Ion Magnet (SIM) behaviour<sup>10–13</sup> and for addressing

multipolar exchange in f-electron molecules.<sup>14</sup> A review of the CSD reveals that only seventeen homometallic [Ce<sub>*n*</sub>] cages with a nuclearity larger than five have been published. Those with a nuclearity less than ten include two square-pyramidal [Ce<sub>5</sub>] complexes,<sup>15</sup> seven [Ce<sub>6</sub>] octahedra and trigonal antiprisms,<sup>16</sup> and four [Ce<sub>8</sub>]<sup>17</sup> compounds with topologies ranging from bicoronal trigonal prisms to ellipsoids. Species with nuclearities in double figures include a domed, body-centred pentagonal [Ce<sub>10</sub>] complex,<sup>18</sup> a pseudo-spherical [Ce<sub>13</sub>] lanthaball,<sup>19</sup> a spherical [Ce<sub>17</sub>] cage<sup>20</sup> and a [Ce<sub>22</sub>] species with a condensed metal–oxide core.<sup>18</sup> The latter is the largest homometallic cerium cage reported to date.

Solvothermal reaction of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (1 mmol) with 2-amino-isobutyric acid (Haib; 1 mmol), 2-hydroxy-1-naphthaldehyde (Hnaphth; 1 mmol) and 2-amino-2-methyl-1,3-propanediol (H<sub>2</sub>amp; 1 mmol) in MeOH, in the presence of base (NEt<sub>3</sub>) results in the formation of dark brown crystals of the complex [Ce<sup>IV</sup><sub>13</sub>Ce<sup>III</sup><sub>8</sub>O<sub>8</sub>(OH)<sub>27</sub>(L)<sub>12</sub>(NO<sub>3</sub>)<sub>9</sub>(H<sub>2</sub>O)<sub>4.6</sub>(MeOH)<sub>3</sub>]·9MeOH·4.2H<sub>2</sub>O (1·9MeOH·4.2H<sub>2</sub>O) in ~15% yield (see ESI,† L = the dianion of the Schiff-base between Hnaphth and Haib).‡ Complex 1 crystallises in the trigonal R<sub>3</sub> space group with Z = 1 in which Ce1 is at a site with  $\bar{3}$  symmetry and Ce5, O1, O4 W are at special positions with 3-fold symmetry. The metallic skeleton of 1 (Fig. 1) describes an outer [Ce<sup>III</sup><sub>8</sub>] cube (BVS: 2.92 and 2.66 for Ce4 and Ce5, respectively) encapsulating an inner [Ce<sup>IV</sup><sub>12</sub>] cuboctahedron (BVS: 3.98 and 3.73 for Ce2 and Ce3, respectively), which in turn encapsulates a single Ce<sup>IV</sup> ion (Ce1, BVS: 4.01). Both of the former units show little distortion from ideal polyhedra. The cube, comprising Ce4, Ce5 and symmetry equivalents (*s.e.*), and of approximate dimensions 7.3 × 7.3 × 7.4 Å, displays Ce...Ce...Ce angles varying between a minimum of 88.2(6)° and a maximum of 90.6(6)°. The Ce...Ce...Ce angles of the triangles within the cuboctahedron are in the range of 69.7(6) to 71.4(7)°, close to the expected 60° required for a perfect cuboctahedron.

By symmetry the central, eight coordinate Ce<sup>IV</sup> ion (Ce1) is in an ideal cube [CeO<sub>8</sub>] geometry, bonded to eight μ<sub>4</sub>-O<sup>2-</sup> ions with Ce–O in the 2.333(5) to 2.338(10) Å range, which also bond to the three Ce<sup>IV</sup> ions that make up the [Ce<sub>3</sub>] triangles of

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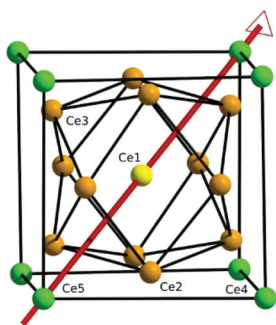


Fig. 1 The metallic skeleton of **1**. Colour code: Ce<sup>III</sup> = green, Ce<sup>IV</sup> = brown, central Ce<sup>IV</sup> = yellow. The red line indicates the 3-fold axis crossing Ce5, Ce1 and Ce5'.

the inner [Ce<sub>12</sub>] cuboctahedron. These Ce ions (Ce2, Ce3 and s.e.) are all eight coordinate and in square antiprismatic geometries ([CeO<sub>8</sub>]). Twenty four μ<sub>3</sub>-OH<sup>-</sup> ions (four on each face of the cube) link two Ce ions in the cuboctahedron to one Ce<sup>III</sup> ion in the cube. Ce4 (and s.e) is eight-coordinate adopting biaugmented trigonal prismatic geometry, while Ce5 (and s.e.) is six-coordinate and in distorted trigonal prismatic geometry. The nitrate anions are of two types: one chelating a Ce ion at the corner of the cube, and one μ-bridging between two Ce ions in the cuboctahedron, protruding out of the centre of the square face of the cube (Fig. 2). The L<sup>2-</sup> ligands (Fig. 3) are positioned along each edge of the cube, the deprotonated phenol moiety terminally bonded to (cube vertex) Ce4, and the carboxylate moiety bridging between Ce ions (Ce2, Ce3 and s.e.) in the cuboctahedron and Ce4'. Six L<sup>2-</sup> ligands are disordered over two equivalent positions and coordinate to Ce4 in two alternative ways (through carboxylate or phenolate oxygen atoms). It should also be mentioned that large accessible voids (~1000 Å<sup>3</sup>) are observed in the crystal structure.

The structure of **1** is similar to those seen in the [Cu<sub>12</sub>Mg<sub>8</sub>] (and analogous) species reported in ref. 8, and somewhat resemble a family of pentadecanuclear [Ln<sub>15</sub>] clusters whose structures can be described as five vertex-sharing cubane-like [Ln<sub>4</sub>(μ<sub>3</sub>-OH)<sub>4</sub>]<sup>8+</sup> units,<sup>21</sup> and an octadecanuclear [Cu<sub>12</sub>Eu<sub>6</sub>] cluster also possessing a keplerate-like structure.<sup>22</sup>

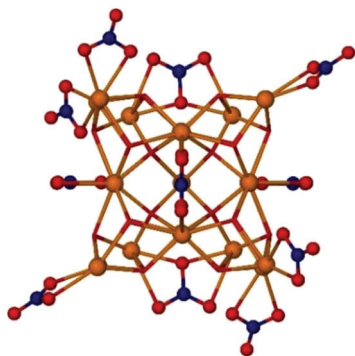


Fig. 2 The bonding modes of the nitrates present in **1**. Colour code: Ce = brown, N = blue, O = red.

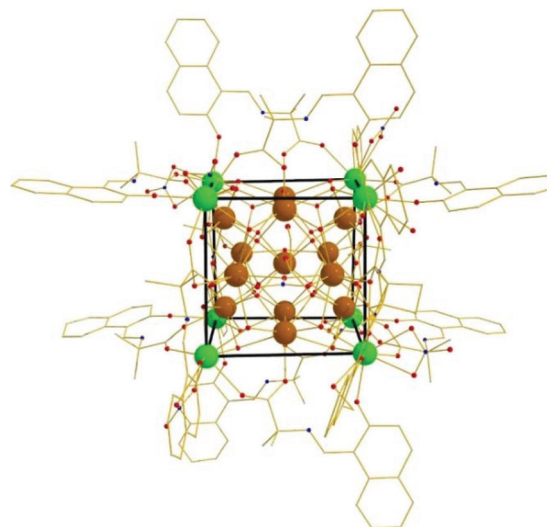


Fig. 3 The crystal structure of **1**. Colour code: Ce<sup>III</sup> = green, Ce<sup>IV</sup> = brown, N = blue, O = red, C = gold. H-atoms omitted for clarity.

Dc magnetic susceptibility measurements were performed on **1** in the 2–300 K temperature range under an applied magnetic field of 0.1 T, and the results are plotted as  $\chi_M T$  vs.  $T$  in Fig. 4 (top), with the isothermal magnetisation ( $M$  vs.  $H$ ) curves shown in the inset. The room temperature  $\chi_M T$  value of 6.46 cm<sup>3</sup> mol<sup>-1</sup> K is very close to the theoretical value of 6.43 cm<sup>3</sup> mol<sup>-1</sup> K expected for eight Ce<sup>III</sup> ions (<sup>2</sup>F<sub>5/2</sub>,  $g_J = 6/7$ ). Upon cooling, the  $\chi_M T$  product decreases steadily, reaching 3.34 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. Given that the Ce<sup>III</sup>...Ce<sup>III</sup> separation is over 7 Å, this decrease is consistent with the depopulation of ligand-field sublevels.<sup>11,23</sup> In terms of such large “metal-oxide”-like species, magnetic data have been only reported for the [Ce<sub>13</sub>] ‘lanthaball’ where some Ce...Ce distances are much

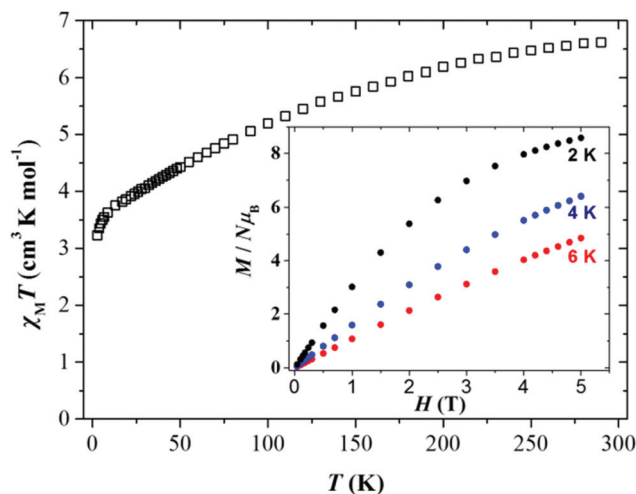


Fig. 4 Plot of  $\chi_M T$  vs.  $T$  for **1** in the 2–300 K temperature range, under an applied field of 0.1 T (top). Inset:  $M$  vs.  $H$  for **1** in the 0–5 T and 2.0–6.0 K field and temperature ranges.



shorter (4–5 Å) and the data are consistent with very weak to zero intramolecular Ce<sup>III</sup>...Ce<sup>III</sup> interactions.<sup>19</sup>

Even assuming that the Ce<sup>III</sup>...Ce<sup>III</sup> interactions in **1** are vanishingly small, in order to model the  $\chi_{MT}$  vs.  $T$  data, we would need two sets of crystal field parameters (for Ce4 and Ce5, where the local symmetry is approximately  $C_{2v}$  and  $D_{3h}$ , respectively). The magnetisation isotherms (Fig. 4, inset) do not reach the value expected if each Ce<sup>III</sup> ion has an  $m_j = 5/2$  ground state ( $M/N\mu_B = 17.1$ ). Analysis is further complicated by the fact that both ions are in low symmetry coordination environments (SHAPE parameters of 3.58 and 4.62, for Ce4 and Ce5, respectively), which will cause mixing of the different  $m_j$  states and hence, it is likely that the ground state of each Ce<sup>III</sup> ion is not a pure  $m_j$  state. *Ab initio* computational studies could provide insight here.<sup>10</sup>

We also investigated the dynamic magnetic behaviour of **1** in zero and applied dc fields, as some Ce<sup>III</sup> single-ion complexes have been shown to show slow magnetic relaxation (Fig. S1†). However, no temperature or frequency dependent out-of-phase susceptibility signals were observed, ruling out the possibility of Single-Molecule Magnet behaviour. Ce<sup>III</sup> is an oblate ion<sup>24</sup> and ideally an axial crystal field is required to stabilise  $m_j = \pm 5/2$  as the ground state for each ion. We ascribe the lack of slow relaxation of the magnetisation to the non-axial coordination environments at Ce4 and Ce5, which could promote stabilisation of smaller  $m_j$  states such as  $m_j = \pm 3/2$  or  $m_j = \pm 1/2$  that would lower or destroy the spin-reversal barrier. In addition, the low symmetry coordination environment at each Ce<sup>III</sup> ion could introduce significant transverse anisotropy, leading to efficient quantum tunnelling.

In summary, we have reported the synthesis of a very rare example of a cerium complex adopting a keplerate “Russian doll” structure, consisting of a cube encapsulating a cuboctahedron encapsulating a single cerium ion. This [Ce<sub>21</sub>] species is the second largest molecular cerium cluster reported to date, smaller only than the [Ce<sub>22</sub>] cage reported by Kögerler and co-workers in 2012. Cerium is very much an underused element in molecule-based magnetism despite having a long history in the chemistry and physics of solid-state permanent magnets. The realization that the cores of these molecular species are simple metal oxides conforming to Archimedean and Platonic solids, with building blocks analogous to those seen in POM chemistry, would suggest that extremely large homo- and heterovalent cerium-based “molecular metal oxides” possessing unusual magnetic behaviours are yet to be discovered, which is a tantalizing prospect.

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## Notes and references

† Crystal data for **1**: C<sub>192</sub>H<sub>248.60</sub>Ce<sub>21</sub>N<sub>21</sub>O<sub>118.80</sub>,  $M = 7694.02$ , trigonal, space group  $R\bar{3}$ ,  $a = 20.830(5)$  Å,  $\alpha = 106.55(3)^\circ$ ,  $V = 7617(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 100$  K,  $R_1(I > 2\sigma) =$

0.068 and  $wR_2(\text{all data}) = 0.198$  for 35 039 reflections collected, 8254 observed reflections ( $I > 2\sigma(I)$ ) of 14 429 ( $R_{\text{int}} = 0.054$ ) unique reflections, GOF = 1.11. CCDC reference number: 1545734.

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