Electronic Supplementary Material (ESI) for Dalton Transactions

SUPPLEMENTARY INFORMATION

Tetradecanuclear polycarbonatolanthanoid clusters: diverse coordination modes of carbonate providing access to novel core geometries

*Anthony S. R. Chesman, David R. Turner, Boujemaa Moubaraki, Keith S. Murray, Glen B. Deacon and Stuart R. Batten**

[*] Dr. A. S. R. Chesman, Dr. D. R. Turner, Dr. B. Moubaraki, Prof. K. S. Murray, Prof. G. B. Deacon, Prof. S. R. Batten
School of Chemistry
Monash University
Wellington Rd, Clayton, VIC 3800, Australia
Fax: (+61) 03 9905 4597
E-mail: stuart.batten@sci.monash.edu.au
Homepage: www.chem.monash.edu.au/staff/sbatten/index.html

Supplementary Structural Information

The μ_3-hydroxide ligand bridges three lanthanoid atoms. Each of the lanthanoid atoms has a bidentate chelation from one, and a monodentate coordination from another, of three unique carbonate ligands displaying a μ_5-η^2(O,O′):η^1(O):η^1(O′):η^1(O″):η^1(O″) coordination mode (Scheme 1, Fig. S1a). These three μ_5-carbonate ligands bridge to another six lanthanoid atoms, which are also coordinated by three unique carbonate ligands displaying a μ_4-η^2(O,O′):η^2(O′,O″):η^1(O):η^1(O″) coordination mode (Fig. S1b). The [$Ln_{10}(CO_3)_6$(OH)] core moiety is completed by an additional lanthanoid atom which is coordinated by the three aforementioned μ_4 carbonate ligands (Fig. S1c).

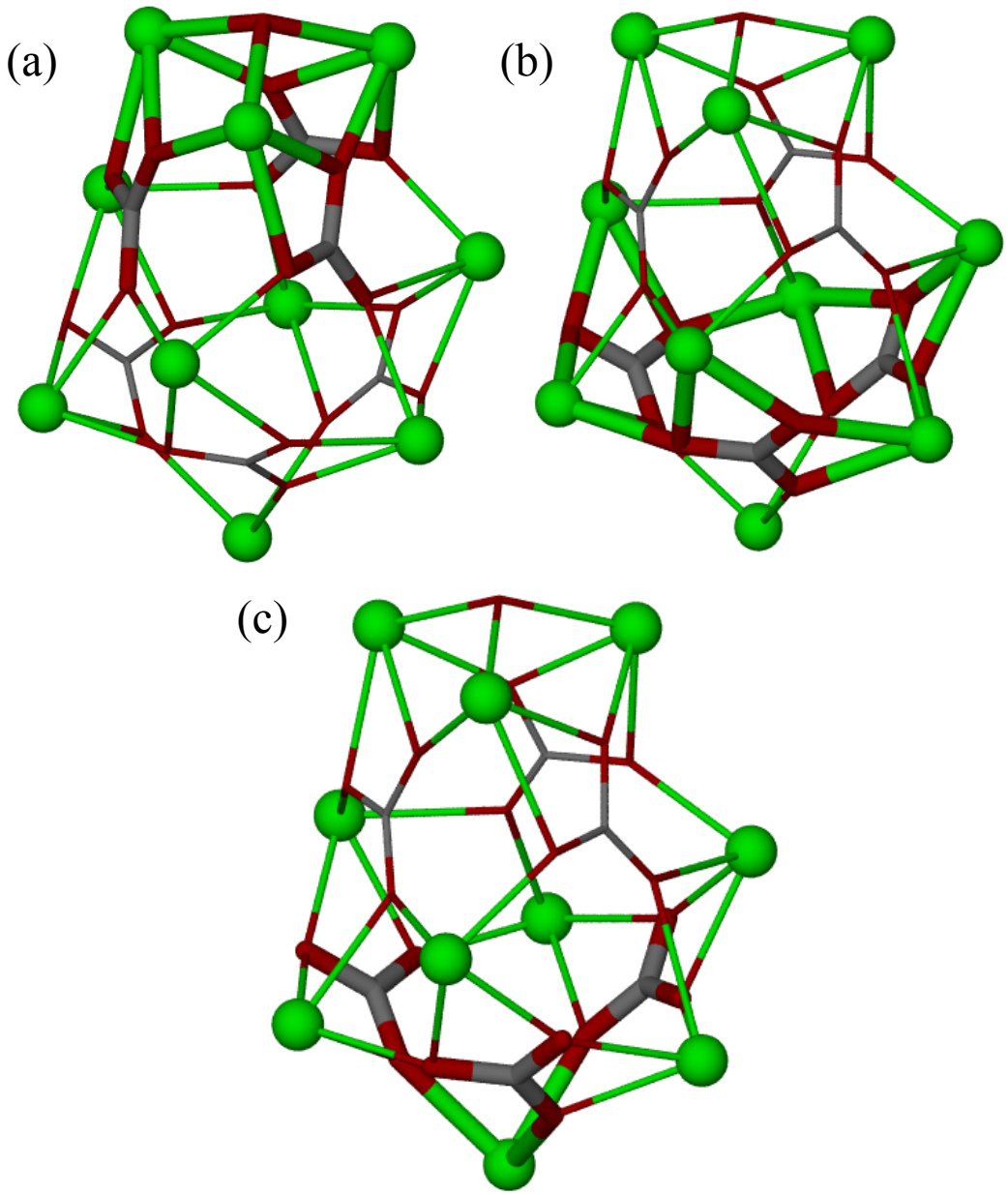

Fig. S1 The [$Gd_{10}(CO_3)_6$(OH)] core moiety from the crystal structure of **1**·$28H_2O$. Key bonds highlighted for emphasis.

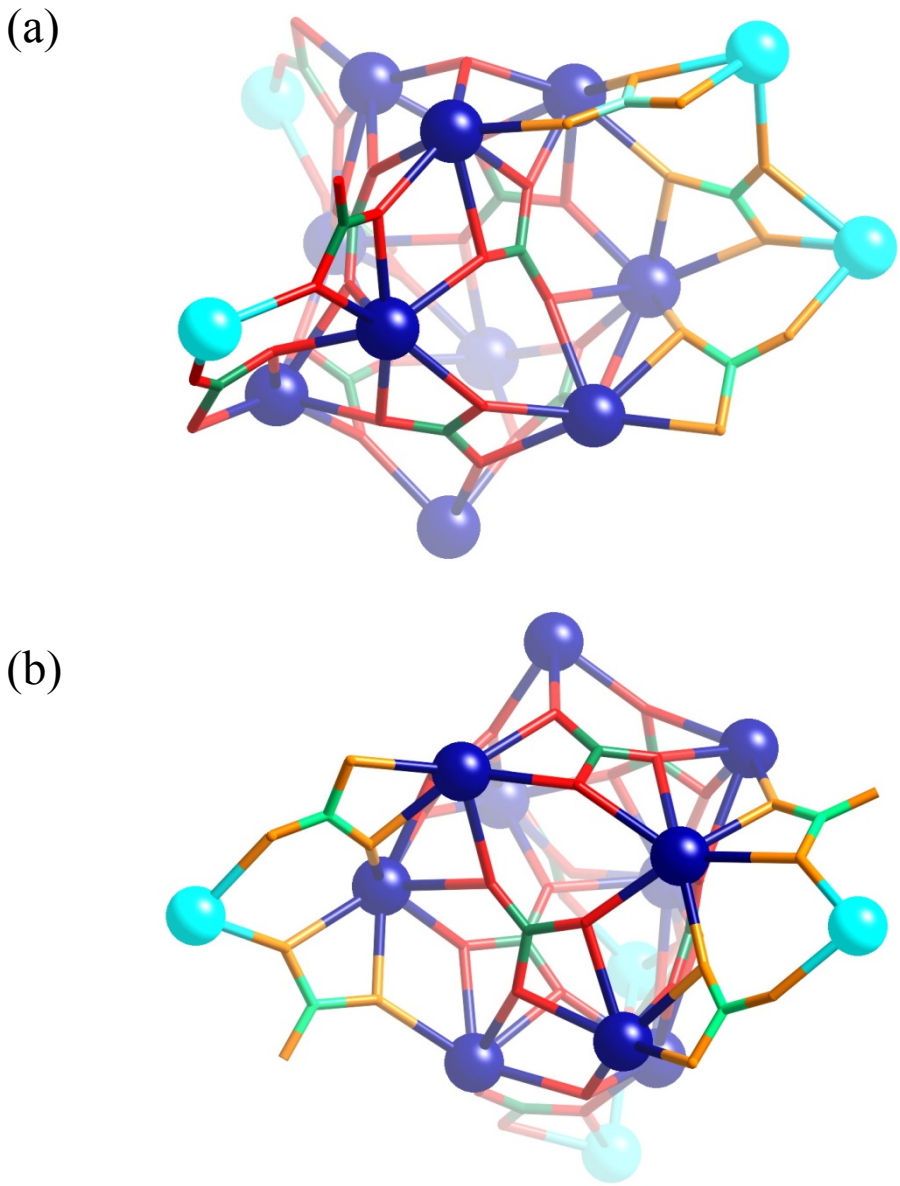

Fig. S2 The four additional gadolinium atoms which attach to the periphery of the $[Gd_{10}(CO_3)_6(OH)]$ moiety to form the $[Gd_{14}(CO_3)_{13}(OH)]$ core, from the crystal structure of **1**·$26H_2O$. Peripheral Gd and key carbonate ligands highlighted for emphasis.

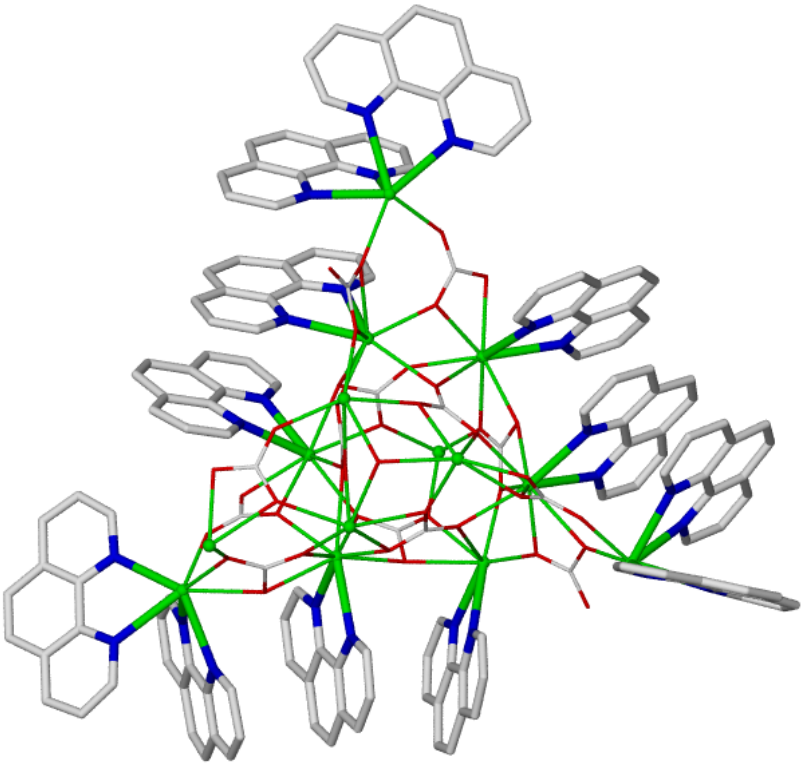

Fig. S3 Three sets of four π-stacking phen ligands on the surface of the $[Gd_{14}(CO_3)_{13}]$ moiety from the crystal structure of **1**. Aqua, nitrate and ccnm ligands omitted for clarity. Key bonds highlighted for emphasis.

Table S1 Metal/ligand connectivity

Atom	Connected ligands [and atoms]
Ln(1)	5 CO_3 [O(1)], [O(4)], [O(7), O(8)], [O(10)], [O(13), O(14)]; 1 phen [N(29), N(30)]
Ln(2)	5 CO_3 [O(6)], [O(23), O(24)], [O(25)], [O(38)]; 1 H_2O [O(44)]; 1 OH [O(43)]; 1 phen [N(31), N(32)]
Ln(3)	5 CO_3 [O(5)], [O(16), O(17)], [O(23)], [O(25), O(26)], [O(28)]; 1 phen [N(33), N(34)]
Ln(4)	3 CO3 [O(3)], [O(4), O(6)], [O(10), O(11)]; 1 ccnm [O(50), O(51)]; 1 H_2O [O(45)]; 1 OH [O(43)]
Ln(5)	4 CO_3 [O(5)], [O(8), O(9)], [O(16)], [O(28), O(29)]; 1 ccnm [O(52)]; 1 phen [N(35), N(36)]
Ln(6)	4 CO_3 [O(17), O(18)], [O(21)], [O(22)], [O(31), O32)]; 1 ccnm [O(56)]; 1 phen [N(37), N(38)]
Ln(7)	3 CO_3 [O(9)], [O(18)], [O(19)]; 3 ccnm [N(5), O(53)], [N(8), O(55)], [N(11), O(57)]
Ln(8)	5 CO_3 [O(2)], [O(20), O(21)], [O(22)], [O(32)], [O(34), O(35)]; 1 phen [N(39), N(40)]
Ln(9)	4 CO_3 [O(1)], [O(7)], [O(13)], [O(19), O(20)]; 1 ccnm [O(54)]; 1 H_2O [O(46)]; 1 phen [N(41),N(42)]
Ln(10)	4 CO_3 [O(2), O(3)], [O(24)], [O(35)], [O(37)]; 2 ccnm [N(14), O(59)], [O(60)]; 1 OH [O(43)]
Ln(11)	2 CO_3 [O(12)], [O(14)]; 1 ccnm [N(20), O(62)]; 1 H_2O [O(47)]; 2 phen [N(43), N(44)], [N(45), N(46)]
Ln(12)†	2 CO_3 [O(30)], [O(26)]; 1 H_2O [O(48)]; 2 phen [N(47), N(48)], [N(49), N(50)]
Ln(13)	2 CO_3 [O(33)], [O(34), O(36)]; 2 ccnm [O(64)], [O(66)]; 2 phen [N(51), N(52)], [N(53), N(54)]
Ln(14)	2 CO_3 [O(36)], [O(37), O(38)]; 3 ccnm [O(58)], [N(23), O(65)], [N(26), O(67)]; 1 H_2O [O(49)]

† In **1** a NO_3 ligand [O(40), O(41)] coordinates to Gd(12), in **2** a ccnm ligand [N(58), O(68)] coordinates to Dy(12)