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## Key indicators

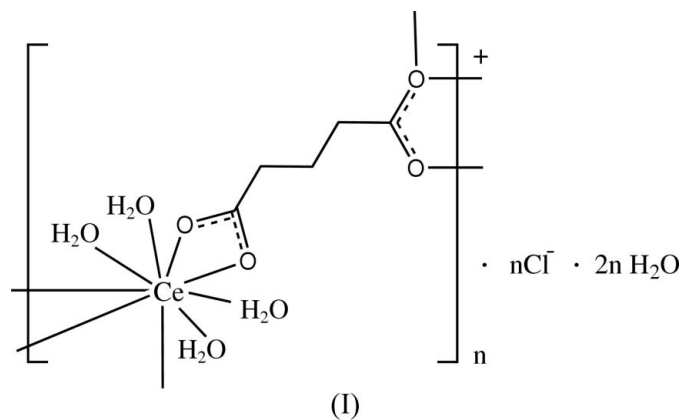
Single-crystal X-ray study  
 $T = 100$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.017  
 $wR$  factor = 0.034  
Data-to-parameter ratio = 24.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Poly[[tetraqua- $\mu_4$ -glutarato-cerium(III)] chloride dihydrate]

The title compound,  $\{[\text{Ce}(\text{C}_5\text{H}_6\text{O}_5)(\text{H}_2\text{O})_4]\text{Cl}\cdot 2\text{H}_2\text{O}\}_n$ , is a coordination polymer built up from binuclear units extending along [100] with the ligands as spacers. The complex polymers are held together by interlayer hydrogen bonds involving the counter-ion and the solvent water molecules embedded in the structure. The tetradentate glutarate dianion coordinates in a bridging–chelating mode, with one triply ligating O atom, and in a conventional carboxylate bridge to the water-coordinated  $\text{Ce}^{\text{III}}$  ion. In the centered cage assembly, two nine-coordinated  $\text{Ce}^{\text{III}}$  ions are linked through six oxo bridges.

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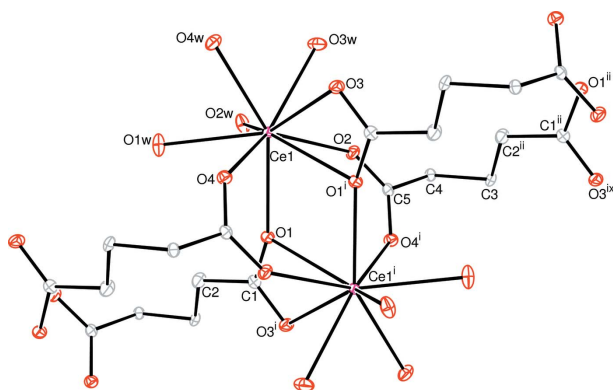
## Comment

The use of polycarboxylic acids as ambidentate and templating ligands has completely changed the field of zeolitic compounds, with a wide breadth of applications (Rao *et al.*, 2004; Rosi *et al.*, 2002; James, 2003). Extending our previous work on the self-assembly of polymeric networks from rare earths and  $\alpha,\omega$ -dicarboxylic acids (Rahahlia, 2003), we have obtained the title compound, (I), which is an ionic two-dimensional open framework compound.

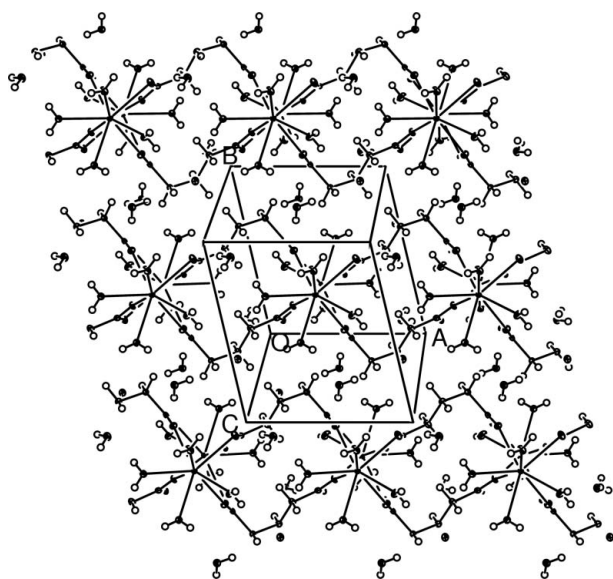


Six oxo-bridges link two Ce atoms and construct the basic entity, which extends along the  $a$  axis through the carbon backbone of the ligand and is interconnected along the  $c$  axis through an extensive hydrogen-bond scheme. Two  $\text{Ce}^{\text{III}}$  ions are linked through two  $\mu$ -1,1 and four  $\mu$ -1,3 oxo-bridges, forming a cage within which lies an inversion centre, with a distance between the two metals of 4.106 (2) Å (Fig. 1).

In this cage assembly, the  $\text{Ce}^{\text{III}}$  ion is nine-coordinate and binds to five O atoms from carboxylate ligands and four from water molecules. The corresponding coordination polyhedron is distorted, as a consequence of the bite angle which is very small (Table 1), and can be best described as a tricapped trigonal prism, atoms O1<sup>1</sup>, O1W and O3W being in the equa-



**Figure 1**  
A segment of the polymeric structure of (I), with 50% probability displacement ellipsoids. Solvent water molecules, the  $\text{Cl}^-$  anion and H atoms have been omitted for clarity. [Symmetry codes: (i)  $1-x, 1-y, 1-z$ ; (ii)  $-1+x, y, z$ ; (ix)  $-x, 1-y, 1-z$ .]



**Figure 2**  
A view of the packing of (I), viewed along the  $c$  axis.

torial capping positions [symmetry code: (i)  $-x+1, -y+1, -z+1$ ]. The tetradentate ligand exhibits two chelating modes. In the first, it is in a bridging-chelating mode, involving one triply ligating O atom, and in the second, it acts as a conventional carboxylate bridge. The average Ce—O(carboxylate) bond length of 2.535 (2) Å is consistent with the usual distances for a nine-coordinated  $\text{Ce}^{\text{III}}$  ion (Duan *et al.*, 2004) and is quite similar to the average Ce—O(aqua) bond length of 2.536 (2) Å. Within the ligand, other geometric parameters all lie in the expected ranges (Rao *et al.*, 2004). The *syn-anti* conformation of the ligand is illustrated by the  $\text{C2}^{\text{ii}}-\text{C3}-\text{C4}-\text{C5}$  [62.67 (18)°] and  $\text{C1}^{\text{ii}}-\text{C2}^{\text{ii}}-\text{C3}-\text{C4}$  [169.4 (2)°] torsion angles [symmetry code: (ii)  $-1+x, y, z$ ], which do not deviate significantly from the ideal values of 60° or 180°.

The connection of the basic binuclear units in two directions through the ligands as spacers, and *via* interlayer hydrogen

bonds, leads to the formation of channels surrounded by methylene groups, and hydrogen-bonded water molecules and  $\text{Cl}^-$  anions (Fig. 2). Strong hydrogen bonds are observed involving  $\text{Cl}^-$  anions and aqua ligands (O3W, O2W and O1W) as acceptors. Moreover, aqua ligands act as donors (O2W, O4W and O1W) to uncoordinated water molecules (O5W and O6W) and carboxylic O atoms (O4 and O3) as acceptors. In this complex scheme, a shorter hydrogen bond is observed between a coordinated water molecule (O4W) as donor and an uncoordinated one (O6W) as acceptor.

This study confirms that the infinite typical  $M-O-M$  subfeature distinguishing rare earth and alkaline earth dicarboxylates, cannot exist when an assembly cage is constructed around the metal.

## Experimental

Compound (I) was prepared by dissolving  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  (1 mmol) and glutaric acid (3 mmol) in deionized water (25 ml). Colourless crystals were obtained after several days, under ambient conditions.

### Crystal data

$[\text{Ce}(\text{C}_5\text{H}_6\text{O}_4)(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$   
 $M_r = 413.76$   
 Triclinic,  $P\bar{1}$   
 $a = 7.932$  (5) Å  
 $b = 8.803$  (5) Å  
 $c = 10.509$  (5) Å  
 $\alpha = 110.500$  (5)°  
 $\beta = 95.531$  (5)°  
 $\gamma = 103.439$  (5)°

$V = 655.7$  (6) Å<sup>3</sup>  
 $Z = 2$   
 $D_x = 2.096$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 3.71$  mm<sup>-1</sup>  
 $T = 100$  (2) K  
 Prism, colourless  
 0.60 × 0.30 × 0.20 mm

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (using intensity measurements) (DIFABS; Walker & Stuart, 1983)  
 $T_{\text{min}} = 0.254, T_{\text{max}} = 0.476$

21564 measured reflections  
 3827 independent reflections  
 3561 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 30.0^\circ$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.017$   
 $wR(F^2) = 0.034$   
 $S = 1.05$   
 3827 reflections  
 154 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 0.3197P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.83$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.99$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|                           |              |                             |             |
|---------------------------|--------------|-----------------------------|-------------|
| O1—Ce1                    | 2.4572 (15)  | O1W—Ce1                     | 2.5687 (18) |
| O1—Ce1 <sup>i</sup>       | 2.6061 (16)  | O2W—Ce1                     | 2.5314 (16) |
| O2—Ce1                    | 2.4945 (16)  | O3W—Ce1                     | 2.5198 (16) |
| O3—Ce1                    | 2.6273 (18)  | O4W—Ce1                     | 2.5246 (15) |
| O4—Ce1                    | 2.4910 (16)  |                             |             |
| O1 <sup>i</sup> —Ce1—O3   | 49.75 (4)    |                             |             |
| Ce1—O2—C5—C4              | -179.16 (12) | Ce1 <sup>i</sup> —O1—Ce1—O4 | -74.83 (5)  |
| C5—C4—C3—C2 <sup>ii</sup> | -62.67 (18)  | Ce1 <sup>i</sup> —O1—Ce1—O2 | 71.50 (6)   |

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $x-1, y, z$ .

**Table 2**  
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$                        | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| O1W—H11 $\cdots$ O6W <sup>i</sup>    | 0.78  | 2.02        | 2.797 (3)   | 173           |
| O1W—H12 $\cdots$ Cl1 <sup>iii</sup>  | 0.78  | 2.55        | 3.321 (3)   | 169           |
| O2W—H21 $\cdots$ O5W <sup>j</sup>    | 0.84  | 2.13        | 2.795 (3)   | 135           |
| O2W—H22 $\cdots$ Cl1 <sup>iii</sup>  | 0.74  | 2.46        | 3.179 (2)   | 167           |
| O3W—H31 $\cdots$ Cl1 <sup>iv</sup>   | 0.81  | 2.33        | 3.125 (2)   | 172           |
| O3W—H32 $\cdots$ Cl1 <sup>i</sup>    | 0.81  | 2.46        | 3.207 (3)   | 155           |
| O4W—H41 $\cdots$ O5W <sup>v</sup>    | 0.77  | 2.03        | 2.783 (3)   | 167           |
| O4W—H42 $\cdots$ O6W <sup>vi</sup>   | 0.87  | 1.93        | 2.801 (3)   | 175           |
| O5W—H51 $\cdots$ Cl1                 | 0.77  | 2.52        | 3.296 (3)   | 176           |
| O5W—H52 $\cdots$ O4 <sup>vii</sup>   | 0.79  | 2.01        | 2.801 (3)   | 175           |
| O6W—H61 $\cdots$ Cl1 <sup>viii</sup> | 0.76  | 2.48        | 3.229 (2)   | 171           |
| O6W—H62 $\cdots$ O3 <sup>ix</sup>    | 0.76  | 2.04        | 2.788 (3)   | 171           |

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (iii)  $-x+2, -y+1, -z+1$ ; (iv)  $x-1, y, z-1$ ; (v)  $x, y, z-1$ ; (vi)  $x, y-1, z-1$ ; (vii)  $-x+1, -y, -z+1$ ; (viii)  $-x+1, -y+1, -z+2$ ; (ix)  $-x, -y+1, -z+1$ .

Water H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . Methylene H atoms were placed in geometrically idealized positions, with  $C-H = 0.97 \text{ \AA}$ , and refined in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The highest electron-density peak in the final difference Fourier map is  $0.65 \text{ \AA}$  from atom H21.

Data collection: *DENZO* (Otwinowski & Minor, 1997); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

- Duan, L.-M., Xu, J.-Q., Xie, F.-T., Liu, Y.-B. & Ding, H. (2004). *Inorg. Chem. Commun.* **7**, 216–219.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- James, S. L. (2003). *Chem. Soc. Rev.* **32**, 276–288.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Rahahlia, N. (2003). MSc Dissertation, Annaba University, Algeria.
- Rao, C. N. R., Natarajan, S. & Vaidyanathan, R. (2004). *Angew. Chem. Int. Ed.* **43**, 1466–1496.
- Rosi, N. L., Eddaoudi, M., Kim, J., O’Keeffe, M. & Yaghi, O. M. (2002). *CrystEngComm*, **4**, 68, 401–404.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.