

**Tong-Ming Shang\* and Jian-Hua Sun**

Jiangsu Key Laboratory of Precious Metals Chemistry, Jiangsu Teachers University of Technology, Changzhou 213001, People's Republic of China

Correspondence e-mail: shangtm@jstu.edu.cn

**Key indicators**

Single-crystal X-ray study  
 T = 298 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.008 \text{ \AA}$   
 R factor = 0.038  
 wR factor = 0.094  
 Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

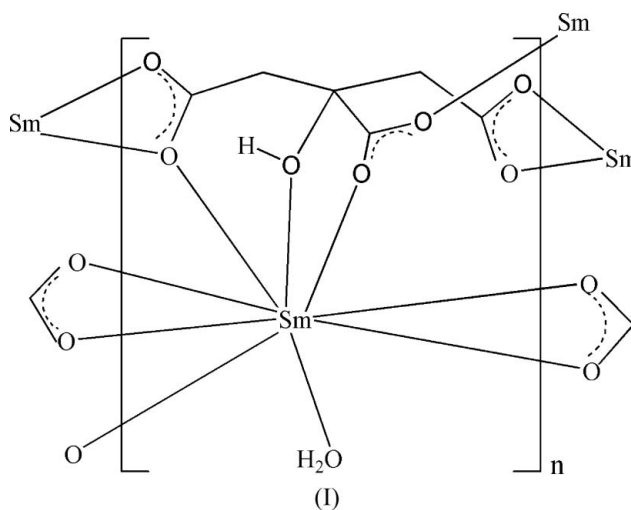
**Poly[[aquasamarium(III)]- $\mu_4$ -citrate- $\kappa^4\text{O}:\text{O}':\text{O}'':\text{O}'''$ ]**

Received 25 October 2006  
 Accepted 31 October 2006

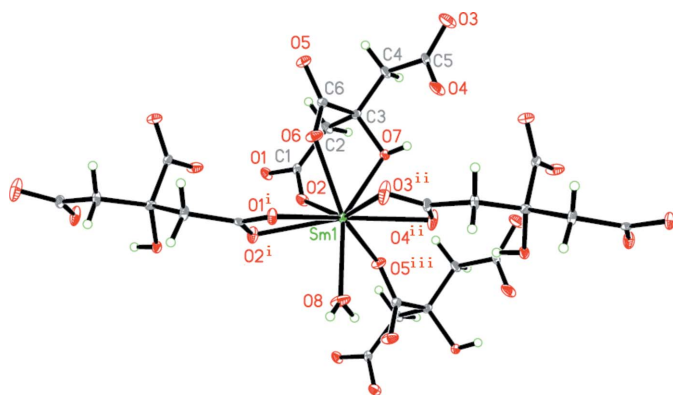
The title compound,  $[\text{Sm}(\text{C}_6\text{H}_5\text{O}_7)(\text{H}_2\text{O})]_n$ , was synthesized hydrothermally. Each  $\text{Sm}^{\text{III}}$  atom is coordinated by eight O atoms from four citrate trianions and one aqua O atom. Each citrate trianion functions as a  $\mu_4$ -bridging ligand, forming a layer structure. Neighbouring layers are held together by  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonding interactions, which generate a three-dimensional framework.

**Comment**

In recent years, the assembly of coordination polymers with citric acid and metal salts has attracted much attention owing to their intriguing architectures and potential applications in the field of materials chemistry (Asato *et al.*, 1991). Citric acid exists in human plasma at a concentration of 0.1 mM, which promotes metal ion solubilization and further contributes to their absorption by biological tissues (Martin *et al.*, 1986). Many coordination polymers with biologically relevant transition metal ions and citric acid have therefore been studied (Kotsakis *et al.*, 2003). Moreover, citric acid is an excellent polydentate ligand with abundant coordination modes, which has been extensively used in the construction of metal-organic frameworks with rare-earth metal ions for their potential applications as luminescent probes (Baggio *et al.*, 2004; Liu *et al.*, 2005). In order to further investigate the assembly of coordination polymers with rare-earth ions, we have studied the reaction of  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with citric acid and obtained the title compound, (I). We report here the crystal structure of (I).

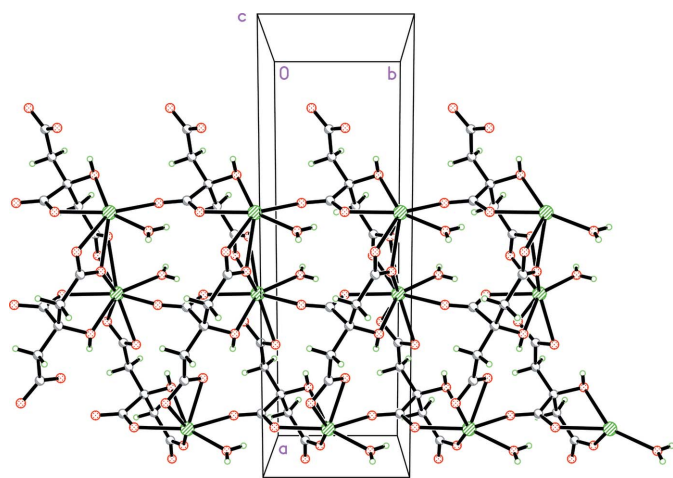


In (I), each  $\text{Sm}^{\text{III}}$  atom is coordinated by eight O atoms from four citrate trianions and one aqua O atom (Fig. 1). The  $\text{Sm}-$



**Figure 1**

The local coordination environment of the Sm<sup>III</sup> ion in (I). Displacement ellipsoids are drawn at the 30% probability level. The atom-numbering scheme of the asymmetric unit is shown, together with some symmetry-equivalent atoms. [Symmetry codes: (i)  $1 - x, y, \frac{3}{2} - z$ ; (ii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ; (iii)  $x, 1 + y, z$ .]



**Figure 2**

The two-dimensional network structure of (I).

O bond lengths range from 2.371 (4) to 2.628 (4) Å (Table 1). The three carboxylate groups of each ligand are all deprotonated and adopt different coordination modes. Each citrate trianion act as a  $\mu_4$ -bridging ligand linking four adjacent Sm<sup>III</sup> cations to form a tetranuclear subunit; the shortest and longest bridged Sm $\cdots$ Sm distances are 4.1846 (7) and 7.4403 (7) Å, respectively. The tetranuclear units are further linked into a layered structure parallel to the *ab* plane (Fig. 2). Intermolecular O—H $\cdots$ O hydrogen bonds between the layers generate a three-dimensional framework (Table 2).

## Experimental

Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (44.5 mg, 0.1 mmol) and citric acid (19.2 mg, 0.1 mmol) were dissolved in deionized water (10 ml). The solution was placed in a Teflon-lined stainless steel bomb (25 ml). The bomb was heated at 393 K for 3 d and then slowly cooled to room temperature. Colourless block-shaped crystals for X-ray analysis were obtained in about 78% yield.

## Crystal data

[Sm(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)(H<sub>2</sub>O)]  
 $M_r = 357.47$   
 Monoclinic,  $C2/c$   
 $a = 19.2938$  (19) Å  
 $b = 6.1520$  (6) Å  
 $c = 15.6816$  (15) Å  
 $\beta = 103.682$  (1)°  
 $V = 1808.5$  (3) Å<sup>3</sup>

$Z = 8$   
 $D_x = 2.626$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 6.52$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 Block, colourless  
 $0.16 \times 0.15 \times 0.15$  mm

## Data collection

Bruker SMART APEX CCD  
 diffractometer  
 $\omega$  and  $\varphi$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2002)  
 $T_{\min} = 0.365$ ,  $T_{\max} = 0.372$

4745 measured reflections  
 1792 independent reflections  
 1597 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.134$   
 $\theta_{\text{max}} = 26.0^\circ$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.094$   
 $S = 1.05$   
 1792 reflections  
 137 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.95$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -3.24$  e Å<sup>-3</sup>  
 Extinction correction: SHELXL97  
 Extinction coefficient: 0.00159 (17)

**Table 1**

Selected geometric parameters (Å, °).

Sm1—O6	2.371 (4)	Sm1—O4 <sup>ii</sup>	2.481 (5)
Sm1—O8	2.375 (4)	Sm1—O2 <sup>iii</sup>	2.529 (4)
Sm1—O5 <sup>i</sup>	2.409 (4)	Sm1—O7	2.547 (4)
Sm1—O2	2.413 (4)	Sm1—O1 <sup>iii</sup>	2.628 (4)
Sm1—O3 <sup>ii</sup>	2.476 (5)		
O6—Sm1—O8	145.32 (15)	O2—Sm1—O2 <sup>iii</sup>	61.20 (17)
O6—Sm1—O5 <sup>i</sup>	137.52 (15)	O3 <sup>ii</sup> —Sm1—O2 <sup>iii</sup>	121.53 (15)
O8—Sm1—O5 <sup>i</sup>	76.10 (15)	O4 <sup>ii</sup> —Sm1—O2 <sup>iii</sup>	164.34 (15)
O6—Sm1—O2	75.85 (16)	O6—Sm1—O7	64.62 (13)
O8—Sm1—O2	118.60 (16)	O8—Sm1—O7	148.94 (14)
O5 <sup>i</sup> —Sm1—O2	72.24 (15)	O5 <sup>i</sup> —Sm1—O7	77.39 (13)
O6—Sm1—O3 <sup>ii</sup>	77.51 (17)	O2—Sm1—O7	67.08 (14)
O8—Sm1—O3 <sup>ii</sup>	87.71 (19)	O3 <sup>ii</sup> —Sm1—O7	95.04 (16)
O5 <sup>i</sup> —Sm1—O3 <sup>ii</sup>	126.10 (16)	O4 <sup>ii</sup> —Sm1—O7	72.09 (15)
O2—Sm1—O3 <sup>ii</sup>	152.44 (17)	O2 <sup>iii</sup> —Sm1—O7	123.55 (14)
O6—Sm1—O4 <sup>ii</sup>	108.11 (16)	O6—Sm1—O1 <sup>iii</sup>	70.24 (14)
O8—Sm1—O4 <sup>ii</sup>	85.76 (17)	O8—Sm1—O1 <sup>iii</sup>	75.39 (13)
O5 <sup>i</sup> —Sm1—O4 <sup>ii</sup>	75.40 (15)	O5 <sup>i</sup> —Sm1—O1 <sup>iii</sup>	145.34 (14)
O2—Sm1—O4 <sup>ii</sup>	132.09 (16)	O2—Sm1—O1 <sup>iii</sup>	105.22 (14)
O3 <sup>ii</sup> —Sm1—O4 <sup>ii</sup>	52.06 (15)	O3 <sup>ii</sup> —Sm1—O1 <sup>iii</sup>	71.81 (14)
O6—Sm1—O2 <sup>iii</sup>	81.91 (15)	O4 <sup>ii</sup> —Sm1—O1 <sup>iii</sup>	121.32 (14)
O8—Sm1—O2 <sup>iii</sup>	79.47 (16)	O2 <sup>iii</sup> —Sm1—O1 <sup>iii</sup>	49.72 (13)
O5 <sup>i</sup> —Sm1—O2 <sup>iii</sup>	105.68 (15)	O7—Sm1—O1 <sup>iii</sup>	134.75 (13)

Symmetry codes: (i)  $x, y + 1, z$ ; (ii)  $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (iii)  $-x + 1, y, -z + \frac{3}{2}$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O8—H8B $\cdots$ O1 <sup>iv</sup>	0.82	1.88	2.692 (6)	170
O8—H8A $\cdots$ O6 <sup>i</sup>	0.82	1.85	2.652 (6)	165
O7—H7 $\cdots$ O4	0.82	1.92	2.618 (6)	142

Symmetry codes: (i)  $x, y + 1, z$ ; (iv)  $x, -y + 2, z - \frac{1}{2}$ .

The H atoms of the water molecule were located in a difference Fourier map. They were initially refined with an O—H distance

restraint of 0.82 (1) Å and later allowed to ride on the O atom with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The remaining H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of  $\text{Csp}^3\text{-H} = 0.97$  Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , and  $\text{O-H} = 0.82$  Å, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . The highest peak is located 0.83 Å from atom Sm1 and the deepest hole 0.03 Å from the same atom. The poor crystal quality may be the reason for the high  $R_{\text{int}}$  value.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2002); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of the Education Department of Jiangsu Province (grant

No. 05 KJB150023), and the Natural Science Foundation of Jiangsu Teachers University of Technology.

### References

- Asato, E., Driessen, W. L., Graaff, R. A. G., Hulsbergen, F. B. & Reedijk, J. (1991). *Inorg. Chem.* **30**, 4210–4218.
- Baggio, R. & Perec, M. (2004). *Inorg. Chem.* **43**, 6965–6968.
- Bruker (2002). *SADABS* (Version 2.03), *SAINTE* (Version 6.02), *SMART* (Version 5.62) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.
- Kotsakis, N., Raptopoulou, C. P., Tangoulis, V., Terzis, J., Giapintzakis, J., Jakusch, T., Kiss, T. & Salifoglou, A. (2003). *Inorg. Chem.* **42**, 22–31.
- Liu, S.-G., Liu, W., Zuo, J.-L., Li, Y.-Z. & You, X.-Z. (2005). *Inorg. Chem. Commun.* **8**, 328–330.
- Martin, R. B. (1986). *Inorg. Biochem.* **28**, 181–187.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.