

Poly[aquaneodymium(III)- $\mu_5$ -2-oxido-5-sulfonatobenzoato]Xiao-Qin Wang, Jian Zhang, Zhao-Ji Li, Yi-Hang Wen,  
Jian-Kai Cheng and Yuan-Gen Yao\*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on  
the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002,  
People's Republic of China

Correspondence e-mail: yyg@ms.fjirm.ac.cn

Received 9 July 2004

Accepted 8 September 2004

Online 23 November 2004

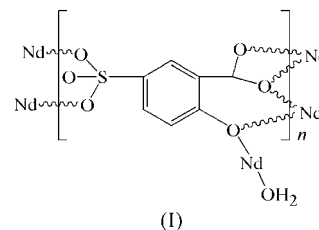
The title compound,  $[\text{Nd}(\text{C}_7\text{H}_3\text{O}_6\text{S})(\text{H}_2\text{O})]_n$  or  $[\text{Nd}(\text{SSA})(\text{H}_2\text{O})]_n$  ( $\text{H}_3\text{SSA}$  is 5-sulfosalicylic acid), was synthesized by the hydrothermal reaction of  $\text{Nd}_2\text{O}_3$  with  $\text{H}_3\text{SSA}$  in water. The compound forms a three-dimensional network in which the asymmetric unit contains one  $\text{Nd}^{\text{III}}$  atom, one SSA ligand and one coordinated water molecule. The central  $\text{Nd}^{\text{III}}$  ion is eight-coordinate, bonded to seven O atoms from five different SSA ligands [ $\text{Nd}-\text{O} = 2.405(4)-2.612(4) \text{ \AA}$ ] and one aqua O atom [ $\text{Nd}-\text{OW} = 2.441(4) \text{ \AA}$ ].

## Comment

Owing to the high coordination numbers of lanthanide ions and the inherent flexibility of their coordination geometries, much effort has been devoted to the study of novel lanthanide metal complexes. For instance, a two-dimensional brick-wall network complex,  $[\text{Tb}(\text{oba})(\text{Hoba})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  [Hoba is 4,4'-oxybis(benzoic acid); Liu *et al.*, 2002], and a series of three-dimensional hybrid coordination polymers,  $[\text{Ln}_2(\text{H}_2\text{O})_4\{(1,2\text{-BDC})_2(1,4\text{-BDC})\}]$  (BDC is benzenedicarboxylate; Thirumurugan & Natarajan, 2004), have recently been reported. The  $\text{H}_3\text{SSA}$  ligand has a strong coordination ability, as it possesses three different chelating groups ( $\text{SO}_3\text{H}$ ,  $\text{OH}$  and  $\text{COOH}$ ). It has been used extensively to construct metal-organic coordination polymers, such as a ladder-structure complex,  $[\text{Ba}_2(\text{SSA})_4(\text{H}_2\text{O})_{10}]$  (Ma *et al.*, 2003), and the two-dimensional complex  $[\text{Eu}(\text{SSA})_2(\text{H}_2\text{O})_5]_n$  (Starynowicz, 2000). However, much effort has been devoted to the investigation of transition metal-SSA coordination polymers, rather than the analogous compounds with lanthanide metals. Recently, we have become interested in the study of lanthanide metal complexes of multidentate ligands to assemble novel topological architectures. We report here the hydrothermal synthesis and crystal structure of the title compound,  $[\text{Nd}(\text{SSA})(\text{H}_2\text{O})]_n$ , (I).

The unit cell of (I) is composed of one  $\text{Nd}^{\text{III}}$  cation, one sulfosalicylate trianion and one water molecule. Each eight-

coordinate  $\text{Nd}^{\text{III}}$  ion is bonded to one water molecule, two sulfonate O atoms, three carboxylate O atoms and two hydroxy O atoms from five different SSA ligands in a dodecahedral geometry [ $\text{Nd}-\text{O} = 2.405(4)-2.612(4) \text{ \AA}$ ,  $\text{Nd}-\text{OW} = 2.441(4) \text{ \AA}$  and  $\text{O}-\text{Nd}-\text{O} = 50.86(13)-167.00(15)^\circ$ ].



As shown in Fig. 1, one carboxylate group, one hydroxy group and the  $\text{Nd}^{\text{III}}$  ion form a six-membered ring. The closest  $\text{Nd} \cdots \text{Nd}$  separation is  $3.983(5) \text{ \AA}$ , comparable with reported  $\text{Nd} \cdots \text{Nd}$  distances (Zhang *et al.*, 2003; Wan *et al.*, 2003; Legendziewicz *et al.*, 1999), indicating a lack of direct metal-metal interaction. Each pair of adjacent  $\text{Nd}^{\text{I}}$  and  $\text{Nd}^{\text{I}^{\text{v}}}$  atoms is bridged by a pair of hydroxy groups in a  $\mu_2$ -bridging coordination mode. Each pair of adjacent  $\text{Nd}^{\text{I}}$  and  $\text{Nd}^{\text{I}^{\text{v}}}$  atoms is bridged by a pair of carboxylate groups in a tridentate chelating-bridging coordination mode [symmetry codes: (i)  $-x, -y, -z$ ; (v)  $1+x, y, z$ ]. Adjacent atom pairs  $\text{Nd}^{\text{I}}/\text{Nd}^{\text{I}^{\text{v}}}$  and  $\text{Nd}^{\text{I}^{\text{v}}}/\text{Nd}^{\text{I}}$  [separations of  $3.983(5)$  and  $4.132(5) \text{ \AA}$ , respectively] are linked alternately into covalent chains running along the  $a$  axis. These one-dimensional covalent chains are further interconnected, *via* a pair of sulfonate groups in the bidentate bridging coordination mode, into two-dimensional covalent networks parallel to the  $ab$  plane. These two-dimensional layers are further integrated by SSA ligands into a three-dimensional framework, as shown in Fig. 2.

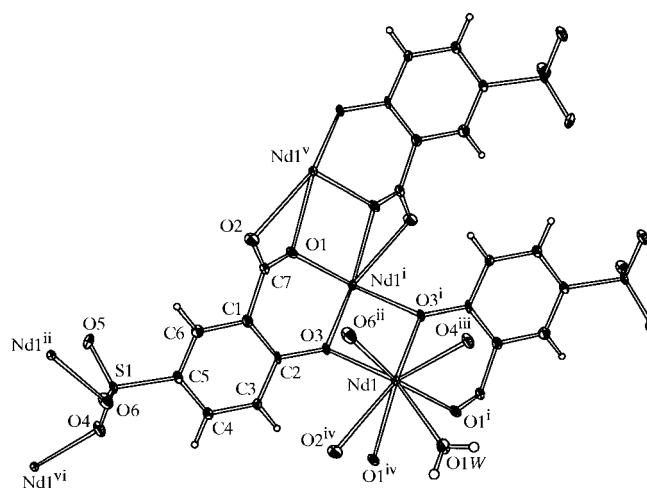
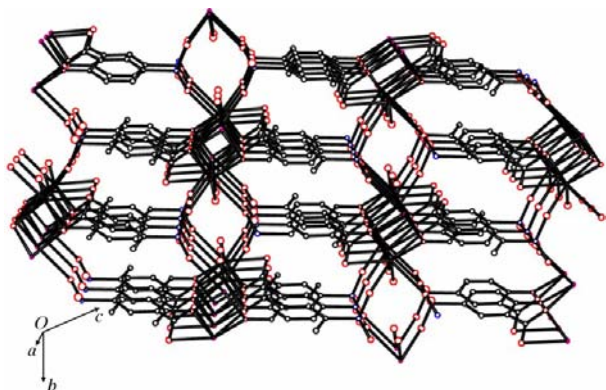


Figure 1

Part of the crystal structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, -y, -1-z$ ; (iii)  $x, 1+y, 1+z$ ; (iv)  $x-1, y, z$ ; (v)  $1+x, y, z$ ; (vi)  $x, y-1, z-1$ .]



**Figure 2**  
The packing structure of (I), viewed along [100]. H atoms have been omitted for clarity.

It is worth noting that the 5-sulfosalicylic acid ligand is completely deprotonated in (I), behaving as a  $\mu_5$ -bridging ligand and linking five individual but symmetry-equivalent Nd atoms. In the three-dimensional framework, all the chelating units of SSA participate efficiently in the bonding to Nd atoms; the carboxylate group adopts a tridentate chelating-bridging mode connecting two Nd atoms, the hydroxy group acts as a  $\mu_2$ -bridge and the sulfonate group adopts a bidentate bridging mode bridging two Nd atoms.

**Experimental**

A mixture of  $\text{Nd}_2\text{O}_3$  (0.084 g, 0.25 mmol), 5-sulfosalicylic acid (0.110 g, 0.5 mmol) and NaOH (0.008 g, 0.2 mmol) in  $\text{H}_2\text{O}$  (16 ml) was sealed in a 25 ml Teflon-lined stainless steel vessel and heated to 433 K for 72 h. After the reaction, the vessel was cooled slowly to room temperature and purple crystals of (I) were obtained.

*Crystal data*

$[\text{Nd}(\text{C}_7\text{H}_3\text{O}_6\text{S})(\text{H}_2\text{O})]$	$Z = 2$
$M_r = 377.41$	$D_x = 2.737 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.0553(2) \text{ \AA}$	Cell parameters from 2164 reflections
$b = 8.2433(3) \text{ \AA}$	$\theta = 2.2\text{--}25.0^\circ$
$c = 9.96940(10) \text{ \AA}$	$\mu = 5.92 \text{ mm}^{-1}$
$\alpha = 111.733(2)^\circ$	$T = 293(2) \text{ K}$
$\beta = 94.984(2)^\circ$	Rhomboh, purple
$\gamma = 93.813(2)^\circ$	$0.30 \times 0.16 \times 0.12 \text{ mm}$
$V = 457.88(2) \text{ \AA}^3$	

*Data collection*

Siemens SMART CCD area-detector diffractometer	1621 independent reflections
$\varphi$ and $\omega$ scans	1538 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.334, T_{\text{max}} = 0.492$	$\theta_{\text{max}} = 25.0^\circ$
2425 measured reflections	$h = -7 \rightarrow 7$
	$k = -8 \rightarrow 9$
	$l = -11 \rightarrow 9$

*Refinement*

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 2.194P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.079$	$(\Delta\sigma)_{\text{max}} = 0.003$
$S = 1.08$	$\Delta\rho_{\text{max}} = 1.17 \text{ e \AA}^{-3}$
1595 reflections	$\Delta\rho_{\text{min}} = -1.30 \text{ e \AA}^{-3}$
151 parameters	
H atoms: see below	

**Table 1**

Selected geometric parameters ( $\text{\AA}, ^\circ$ ).

Nd1—O1 <sup>i</sup>	2.405 (4)	Nd1—O4 <sup>iii</sup>	2.481 (4)
Nd1—O3	2.407 (4)	Nd1—O1 <sup>iv</sup>	2.488 (4)
Nd1—O3 <sup>i</sup>	2.431 (4)	Nd1—O2 <sup>iv</sup>	2.612 (4)
Nd1—O1W	2.441 (4)	Nd1—Nd1 <sup>i</sup>	3.9835 (5)
Nd1—O6 <sup>ii</sup>	2.453 (4)		
O1 <sup>i</sup> —Nd1—O3	108.83 (14)	O1W—Nd1—O1 <sup>iv</sup>	74.32 (16)
O1 <sup>i</sup> —Nd1—O3 <sup>i</sup>	70.46 (13)	O6 <sup>ii</sup> —Nd1—O1 <sup>iv</sup>	127.74 (14)
O3—Nd1—O3 <sup>i</sup>	69.15 (14)	O4 <sup>iii</sup> —Nd1—O1 <sup>iv</sup>	140.28 (15)
O1 <sup>i</sup> —Nd1—O1W	74.01 (17)	O1 <sup>i</sup> —Nd1—O2 <sup>iv</sup>	111.66 (13)
O3—Nd1—O1W	154.36 (15)	O3—Nd1—O2 <sup>iv</sup>	86.44 (14)
O3 <sup>i</sup> —Nd1—O1W	132.59 (15)	O3 <sup>i</sup> —Nd1—O2 <sup>iv</sup>	154.09 (14)
O1 <sup>i</sup> —Nd1—O6 <sup>ii</sup>	167.00 (15)	O1W—Nd1—O2 <sup>iv</sup>	69.45 (15)
O3—Nd1—O6 <sup>ii</sup>	78.23 (15)	O6 <sup>ii</sup> —Nd1—O2 <sup>iv</sup>	79.14 (14)
O3 <sup>i</sup> —Nd1—O6 <sup>ii</sup>	103.20 (15)	O4 <sup>iii</sup> —Nd1—O2 <sup>iv</sup>	128.60 (14)
O1W—Nd1—O6 <sup>ii</sup>	104.56 (18)	O1 <sup>iv</sup> —Nd1—O2 <sup>iv</sup>	50.86 (13)
O1 <sup>i</sup> —Nd1—O4 <sup>iii</sup>	87.13 (14)	O1 <sup>i</sup> —Nd1—C7 <sup>iv</sup>	87.63 (14)
O3—Nd1—O4 <sup>iii</sup>	133.73 (14)	O3—Nd1—C7 <sup>iv</sup>	87.01 (14)
O3 <sup>i</sup> —Nd1—O4 <sup>iii</sup>	76.71 (14)	O3 <sup>i</sup> —Nd1—C7 <sup>iv</sup>	139.00 (15)
O1W—Nd1—O4 <sup>iii</sup>	71.10 (16)	O1W—Nd1—C7 <sup>iv</sup>	67.48 (16)
O6 <sup>ii</sup> —Nd1—O4 <sup>iii</sup>	80.28 (15)	O6 <sup>ii</sup> —Nd1—C7 <sup>iv</sup>	103.88 (15)
O1 <sup>i</sup> —Nd1—O1 <sup>iv</sup>	64.78 (15)	O4 <sup>iii</sup> —Nd1—C7 <sup>iv</sup>	138.08 (16)
O3—Nd1—O1 <sup>iv</sup>	83.85 (14)	O1 <sup>iv</sup> —Nd1—C7 <sup>iv</sup>	25.89 (15)
O3 <sup>i</sup> —Nd1—O1 <sup>iv</sup>	115.38 (13)	O2 <sup>iv</sup> —Nd1—C7 <sup>iv</sup>	25.17 (15)

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

H atoms bonded to C atoms were positioned geometrically ( $\text{C—H} = 0.93 \text{ \AA}$ ) and allowed to ride on their parent C atoms before the final refinement cycle, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The water H atoms were located in difference maps, with  $\text{O—H}$  distances restrained to  $0.82(2) \text{ \AA}$ , and refined as riding, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: XPREP in SHELXTL (Siemens, 1994); program(s) used to solve structure: SHELXTL; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

This work was supported financially by the State Key Basic Research and Development Plan of China (grant No. 001CB108906), the National Natural Science Foundation of China (grant No. 20173063) and the Natural Science Foundation of Fujian Province (grant No. E0020001).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1019). Services for accessing these data are described at the back of the journal.

**References**

Legendziewicz, J., Keller, B., Turowska-Tyrk, I. & Wojciechowski, W. (1999). *New J. Chem.* **23**, 1097–1103.  
 Liu, G. F., Qiao, Z. P., Wang, H. Z., Chen, X. M. & Yang, G. (2002). *New J. Chem.* **26**, 791–795.  
 Ma, J. F., Yang, J., Li, L., Zheng, G. L. & Liu, J. F. (2003). *Inorg. Chem. Commun.* **6**, 581–583.  
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.  
 Siemens (1994). *SAINTE* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1996). *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Starynowicz, P. (2000). *J. Alloys Compd.* **305**, 117–120.  
 Thirumurugan, A. & Natarajan, S. (2004). *Eur. J. Inorg. Chem.* pp. 762–770.  
 Wan, Y. H., Jin, L. P. & Wang, K. Z. (2003). *J. Mol. Struct.* **649**, 85–93.  
 Zhang, L. P., Wan, Y. H. & Jin, L. P. (2003). *Polyhedron*, **22**, 981–987.