

**catena-Poly[[[diaqua[*trans*-3-(4-pyridyl)acrylato]samarium(III)]-di- $\mu$ -*trans*-3-(4-pyridyl)acrylato] dihydrate]**Yan-Jun Zhu,<sup>a</sup> Jin-Xiang Chen,<sup>a</sup> Wen-Hua Zhang,<sup>a</sup> Yong Zhang<sup>a</sup> and Jian-Ping Lang<sup>a,b\*</sup>

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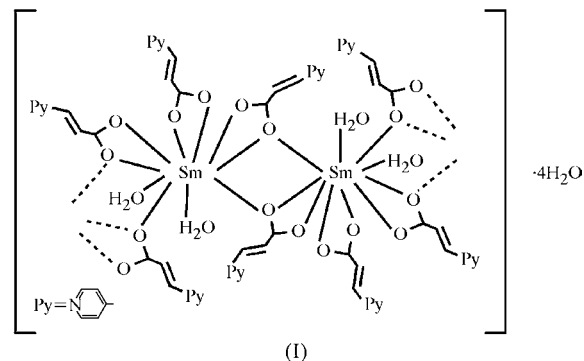
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In the title compound,  $\{[\text{Sm}(\text{4-pya})_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  [4-pya is *trans*-3-(4-pyridyl)acrylate,  $\text{C}_8\text{H}_6\text{NO}_2$ ], each  $\text{Sm}^{\text{III}}$  atom is ten-coordinated and has a bicapped square-antiprismatic coordination geometry. There is a crystallographic center of symmetry at the mid-point of the  $\text{Sm} \cdots \text{Sm}$  line within each  $[\text{Sm}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2$  dimer. Each dimer is interconnected by two pairs of bridging 4-pya ligands to form a one-dimensional chain. Neighboring chains are connected *via* hydrogen bonds to form a three-dimensional network.

**Comment**

Over the past few decades, there has been considerable interest in the coordination chemistry of lanthanide compounds because of their unique structures and their potential applications in advanced materials, such as Ln-doped semiconductors (Taniguchi & Takahei, 1993), and catalytic (Costes *et al.*, 1997; Bencini *et al.*, 1985), magnetic (Lisowski & Starynowicz, 1999), fluorescent (Alexander, 1995; Bermudez *et al.*, 2001) and non-linear optical materials (Reinhard & Gudel, 2002). As is well known, ligands containing a combination of N- and O-donor atoms are good building blocks for the formation of various lanthanide coordination compounds (Liang *et al.*, 2000; Pan *et al.*, 2000; Ma *et al.*, 1999; Costes *et al.*, 2002; Ouchi *et al.*, 1988; Kim *et al.*, 2004). *trans*-3-(4-Pyridyl)acrylic acid (4-Hpya) is one such interesting multifunctional ligand. Four coordination modes of 4-pya have been observed in the crystal structures of transition metal complexes of this ligand (Evans & Lin, 2001; Zhang *et al.*, 2000; Liu *et al.*, 2001). However, the chemistry of lanthanide complexes of 4-Hpya is less well studied (Zhou *et al.*, 2003). Owing to the large radii and the strong oxophilicity of  $\text{Ln}^{\text{III}}$  ions, we anticipated that coordination of 4-Hpya by  $\text{Ln}^{\text{III}}$  metals may lead to the formation of new compounds with

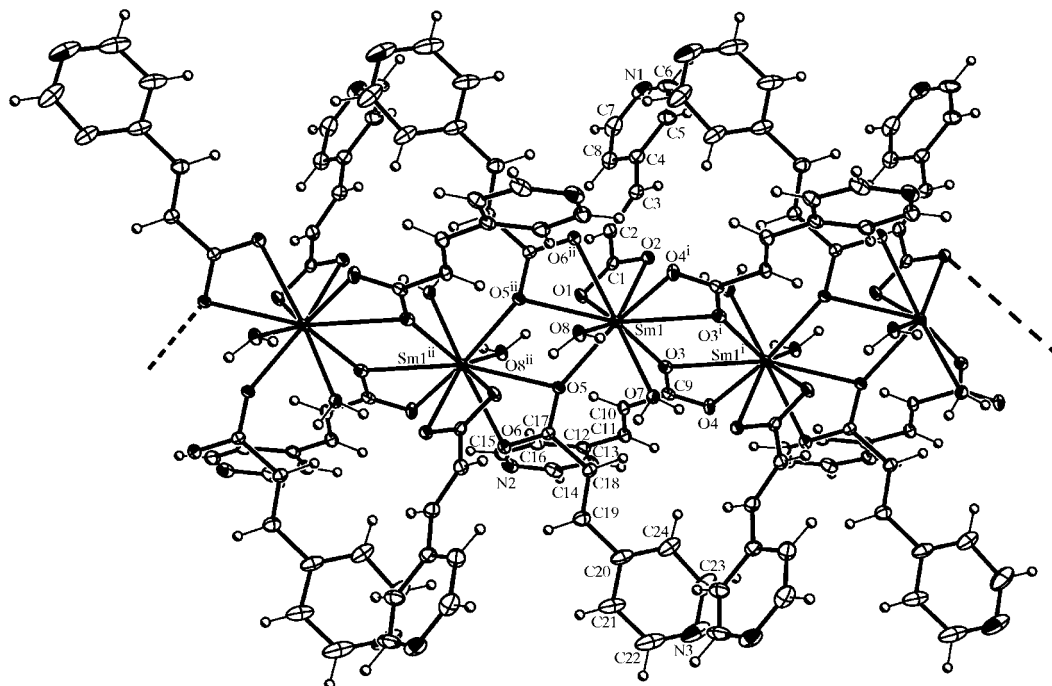
different coordination modes. We therefore carried out the reaction of  $\text{Sm}_2\text{O}_3$  with 4-Hpya by hydrothermal synthesis. We report here the crystal structure of the resulting complex, (I).



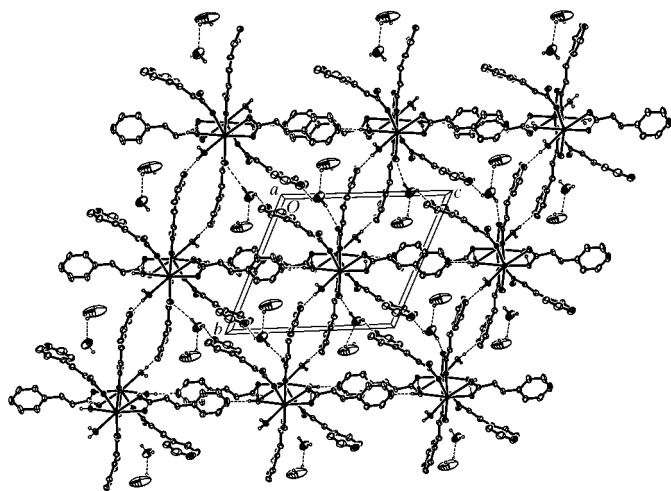
(I)

Complex (I) crystallizes in the space group  $P\bar{1}$ , and the asymmetric unit contains one-half of an  $[\text{Sm}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2$  dimer and two solvent water molecules. Complex (I) has a one-dimensional chain structure extending along the *a* axis (Fig. 1). Each repeating  $[\text{Sm}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2$  dimer within the chain is interconnected by four tridentate bridging 4-pya anions. There is a crystallographic center of symmetry at the mid-point of the  $\text{Sm}1 \cdots \text{Sm}1^i$  line within the dimer [symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ]. The  $\text{Sm}1$  center coordinates to eight O atoms of 4-pya ligands and two water O atoms, forming a bicapped square-antiprismatic coordination geometry. The  $\text{Sm} \cdots \text{Sm}$  contact within the dimer is 4.303 (1) Å, shorter than the  $\text{Sm} \cdots \text{Sm}$  separation [4.468 (1) Å] between dimers. Both  $\text{Sm} \cdots \text{Sm}$  contacts are too long to include metal–metal interactions. In the dimer, the 4-pya ligand exhibits two coordination modes. In neither of the two modes does the N atom of the pyridyl group bond to Sm. In one mode, the 4-pya ligand chelates the  $\text{Sm}^{\text{III}}$  center *via* atoms O1 and O2 to form a four-membered  $\text{SmO}_2\text{C}$  ring. In the other mode, 4-pya acts as a tridentate ligand, chelating the  $\text{Sm}1$  ion *via* atoms O3<sup>i</sup> and O4<sup>i</sup>, and bridging the  $\text{Sm}1^i$  ion *via* atom O3<sup>i</sup>. Because of the existence of the different coordination modes of 4-pya, the  $\text{Sm}1-\text{O}$  bond distances range from 2.404 (2) to 2.712 (2) Å (Table 1). The  $\text{Sm}1-\text{O}1$  bond length is comparable to that of the  $\text{Sm}1-\text{O}2$  bond, implying that atoms O1 and O2 of this 4-pya ligand are almost symmetrically bound to atom  $\text{Sm}1$ . However, the 4-pya ligand containing atoms O3<sup>i</sup> and O4<sup>i</sup> binds to  $\text{Sm}1$  in an unsymmetric way, as the  $\text{Sm}1-\text{O}3^i$  bond is 0.24 (2) Å longer than the  $\text{Sm}1-\text{O}4^i$  bond. It is noted that the  $\text{Sm}1-\text{O}3^i$  bond is the longest among all the  $\text{Sm}1-\text{O}$  bonds. This may be ascribed to the fact that atom O3<sup>i</sup> binds strongly to atom  $\text{Sm}1^i$  of the same dimer, with an  $\text{Sm}1^i-\text{O}3^i$  distance of 2.488 (2) Å. Interestingly, the structure of (I) differs from that reported for the lanthanide–3-pya complex  $[\text{La}(\text{C}_8\text{H}_6\text{NO}_2)_3]_n$  [3-pya is *trans*-3-(3-pyridyl)acrylate; Zhou *et al.*, 2003]. Each  $\text{La}^{\text{III}}$  ion in the latter complex is eight-coordinated with seven O atoms and one N atom from the 3-pya ligand, forming a two-dimensional network.

In the unit cell of (I), the coordinated water molecules interact with the O atoms of the 4-pya ligands to form intramolecular hydrogen bonds ( $\text{O}8-\text{H}27 \cdots \text{O}1$  and  $\text{O}7-\text{H}25 \cdots \text{O}2$ ; Table 2). Furthermore, one of the free water molecules


**Figure 1**

An ORTEP (Johnson, 1976) view of the dimeric unit and the atom labeling for (I). Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + 2, -y + 1, -z + 1$ .]


**Figure 2**

A packing diagram (looking down the  $a$  axis) for (I), showing the three-dimensional network formed by hydrogen bonds (dashed lines) between the polymeric chains.

and the coordinated water molecules interact with the O and N atoms of the 4-pya ligands of adjacent chains to afford intermolecular hydrogen bonds, thereby forming a three-dimensional hydrogen-bonded network (Fig. 2).

## Experimental

4-Hpya was prepared as reported previously (Alcalde *et al.*, 1992). Other reagents were obtained from commercial sources and used as received. A mixture of  $\text{Sm}_2\text{O}_3$  (0.06 g, 0.17 mmol), 4-Hpya (0.15 g, 1 mmol) and water (10 ml) was heated in a stainless steel reactor with a Teflon liner at 413 K for 4 d and then cooled slowly to room

temperature. The resulting colorless crystals were collected by filtration, washed with ethanol and then air-dried (yield 8%, 0.018 g). The crystal used for the structure determination was obtained directly from the above preparation. Analysis found: C 43.59, H 3.86, N 6.38%; calculated for  $\text{C}_{48}\text{H}_{52}\text{N}_6\text{O}_{20}\text{Sm}_2$ : C 43.23, H 3.93, N 6.30%. IR (KBr,  $\text{cm}^{-1}$ ): 3238 (*m*), 3045 (*m*), 1646 (*s*), 1601 (*s*), 1544 (*s*), 1404 (*s*), 1253 (*m*), 990 (*m*), 822 (*m*), 744 (*m*), 590 (*m*).

## Crystal data

$[\text{Sm}(\text{C}_8\text{H}_6\text{NO}_2)_3(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$   
 $M_r = 666.83$   
 Triclinic,  $P\bar{1}$   
 $a = 8.2459$  (8) Å  
 $b = 12.6631$  (15) Å  
 $c = 14.3286$  (16) Å  
 $\alpha = 111.782$  (2)°  
 $\beta = 98.825$  (2)°  
 $\gamma = 100.605$  (2)°  
 $V = 1324.7$  (3) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.672$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 5348 reflections  
 $\theta = 3.1$ – $25.3$ °  
 $\mu = 2.28$  mm<sup>-1</sup>  
 $T = 193$  (2) K  
 Block, colorless  
 0.35 × 0.15 × 0.10 mm

## Data collection

Rigaku Mercury diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Jacobson, 1998)  
 $T_{\min} = 0.678$ ,  $T_{\max} = 0.796$   
 13165 measured reflections  
 4840 independent reflections  
 4571 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 25.4$ °  
 $h = -9 \rightarrow 9$   
 $k = -12 \rightarrow 15$   
 $l = -17 \rightarrow 17$   
 720 standard reflections  
 every 6 reflections  
 intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.064$   
 $S = 1.18$   
 4840 reflections  
 338 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0293P)^2 + 0.9553P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.011$   
 $\Delta\rho_{\text{max}} = 0.95$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.70$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Sm1—O5	2.404 (2)	Sm1—O8	2.508 (2)
Sm1—O7	2.457 (2)	Sm1—O6 <sup>ii</sup>	2.519 (2)
Sm1—O4 <sup>i</sup>	2.471 (2)	Sm1—O1	2.557 (2)
Sm1—O3	2.488 (2)	Sm1—O5 <sup>ii</sup>	2.659 (2)
Sm1—O2	2.499 (2)	Sm1—O3 <sup>i</sup>	2.712 (2)
O5—Sm1—O7	77.38 (7)	O4 <sup>i</sup> —Sm1—O3	111.35 (7)
O5—Sm1—O4 <sup>i</sup>	154.64 (8)	O5—Sm1—O8	83.36 (7)
O7—Sm1—O4 <sup>i</sup>	83.76 (8)	O5—Sm1—O1	75.81 (7)
O5—Sm1—O3	79.83 (7)	O1—Sm1—O5 <sup>ii</sup>	67.31 (7)
O7—Sm1—O3	74.40 (7)		

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+2, -y+1, -z+1$ .**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H25 <sup>i</sup> ···O2 <sup>i</sup>	0.85 (2)	1.83 (2)	2.675 (3)	171 (3)
O7—H26 <sup>i</sup> ···N1 <sup>iii</sup>	0.85 (2)	2.04 (2)	2.870 (4)	166 (3)
O8—H27 <sup>i</sup> ···O1 <sup>ii</sup>	0.84 (3)	1.93 (3)	2.741 (3)	162 (3)
O8—H28 <sup>i</sup> ···N2 <sup>iv</sup>	0.84 (4)	2.05 (4)	2.883 (4)	177 (3)
O9—H29 <sup>i</sup> ···O4 <sup>v</sup>	0.85 (3)	2.17 (2)	2.997 (4)	163 (6)
O9—H30 <sup>i</sup> ···N3 <sup>vi</sup>	0.85 (5)	2.22 (4)	2.913 (6)	138 (5)

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

The positions of the H atoms of the water molecules were located in difference Fourier maps and were then refined with restraints on the O—H and H···H distances [O—H = 0.85(10) Å and H···H = 1.39(10) Å]; the water H-atom isotropic displacement parameters were set at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . All other H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrystalClear* (Rigaku/MSC, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1225). Services for accessing these data are described at the back of the journal.

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