

catena-Poly[[pentaquaathulium(III)]- μ -5-sulfonatobenzene-1,3-dicarboxylato] 4,4'-bipyridyl 1.5-solvate hemihydrate]

 Yu-Ling Wang,^a Qing-Yan Liu^{a,b*} and Li Xu^b

^aCollege of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang, Jiangxi 330022, People's Republic of China, and ^bState 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: qyliuchemistry@gmail.com

Received 8 April 2007

Accepted 7 May 2007

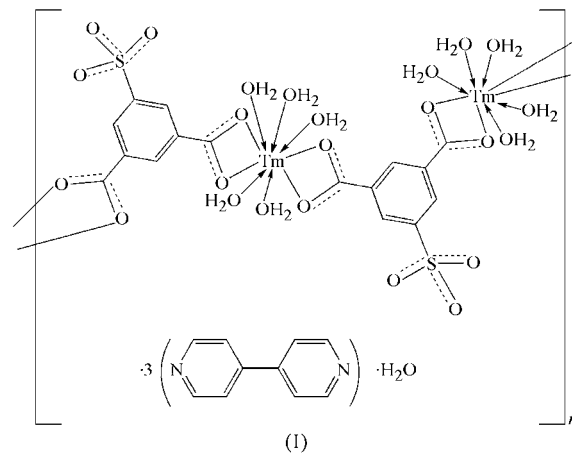
Online 14 June 2007

The crystal structure of the title compound, $\{[\text{Tm}(\text{C}_8\text{H}_3\text{O}_7\text{S})\cdot(\text{H}_2\text{O})_5]\cdot 1.5\text{C}_{10}\text{H}_8\text{N}_2\cdot 0.5\text{H}_2\text{O}\}_n$, is built up from two $[\text{Tm}(\text{SIP})(\text{H}_2\text{O})_5]$ molecules (SIP^{3-} is 5-sulfonatobenzene-1,3-dicarboxylate), three 4,4'-bipyridyl (bpy) molecules and one solvent water molecule. One of the bpy molecules and the solvent water molecule are located on an inversion centre and a twofold rotation axis, respectively. The Tm^{III} ion coordination is composed of four carboxylate O atoms from two trianionic SIP^{3-} ligands and five coordinated water molecules. The Tm^{3+} ions are linked by the SIP^{3-} ligands to form a one-dimensional zigzag chain propagating along the c axis. The chains are linked by interchain $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds to generate a two-dimensional layered structure. The bpy molecules are not involved in coordination but are linked by $\text{O}\cdots\text{H}\cdots\text{N}$ hydrogen bonds to form two-dimensional layers. The two-dimensional layers are further bridged by the bpy molecules as pillars and the solvent water molecules through hydrogen bonds, giving a three-dimensional supramolecular structure. π - π stacking interactions between the parallel aromatic rings, arranged in an offset fashion with a face-to-face distance of 3.566 (1) Å, are observed in the crystal packing.

Comment

Crystal engineering and supramolecular chemistry have been the most active areas of materials research in recent years owing to the intriguing structural topologies examined and potential applications in host-guest chemistry, catalysis and electrical conductivity (Biradha & Zaworotko, 1998; Yaghi *et al.*, 1995; Conn & Rebek, 1997). The key to successful construction of supramolecular architectures is the control and manipulation of coordination bonds and noncovalent interactions by careful selection of the coordination geometry of the metal centres and organic ligands containing appro-

priate functional groups (such as carboxylic acid and pyridine; Tong *et al.*, 1999; Dong *et al.*, 2000). Among the linker molecules, carboxylic acids such as acetic acid, succinic acid and



benzene-1,3,5-tricarboxylic acid have been studied extensively because of their versatile coordination modes (Saalfrank *et al.*, 2001; Bowden *et al.*, 2003; Yaghi *et al.*, 1997). We recently investigated the influence of changing of one of the carboxylate groups of benzene-1,3,5-tricarboxylic acid for a sulfonate group by using 5-sulfoisophthalic acid with the goal of obtaining materials with desirable properties. The sulfonate group has one more O atom than the carboxylate group and thus can provide three potential hydrogen-bond acceptors

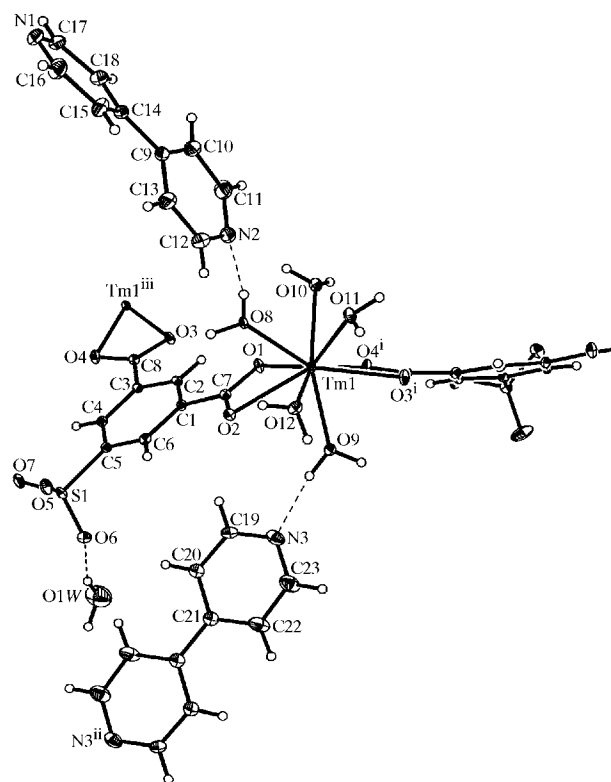


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $x, -y, z + \frac{1}{2}$; (ii) $-x - 1, -y + 1, -z$; (iii) $x, -y, z - \frac{1}{2}$.]

(Evans *et al.*, 1999). The combination of the 5-sulfoisophthalic acid ligand with metal ions produced several complexes with diverse structural topologies (Liu & Xu, 2005*a*, 2006). The hydrothermal reaction of Tm_2O_3 , 5-sulfoisophthalic acid monosodium salt (NaH_2SIP) and 4,4'-bipyridyl (bpy) yields the title complex, (I). We present its structure here.

The asymmetric unit of (I) consists of a $[\text{Tm}(\text{SIP})(\text{H}_2\text{O})_5]$ molecule, one and a half bpy molecules, and one-half of a solvent water molecule. One of the bpy molecules and the solvent water molecule are located on an inversion centre and a twofold rotation axis, respectively. As depicted in Fig. 1, the Tm atom is nine-coordinated by four carboxylate O atoms from two SIP^{3-} ligands and five O atoms from coordinated water molecules. The Tm–O bond lengths range from 2.292 (2) to 2.507 (2) Å, with an average value of 2.393 Å, and the O–Tm–O bond angles range from 53.03 (6) to 146.00 (7)° (Table 1). The bond dimensions involving Tm are normal and are comparable to the values in related thulium(III) complexes (Liu & Xu, 2005*b*). Each SIP^{3-} anion bridges two neighbouring Tm^{3+} ions through its two chelating carboxylate groups (Fig. 1). The sulfonate group is uncoordinated and engaged in hydrogen bonding with the coordinated water molecules. The three identical S–O bond distances

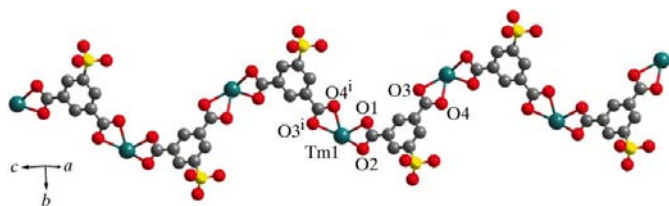


Figure 2
A view of the $[\text{Tm}(\text{SIP})(\text{H}_2\text{O})_5]_2$ zigzag chain. [Symmetry code: (i) $x, -y, z + \frac{1}{2}$]

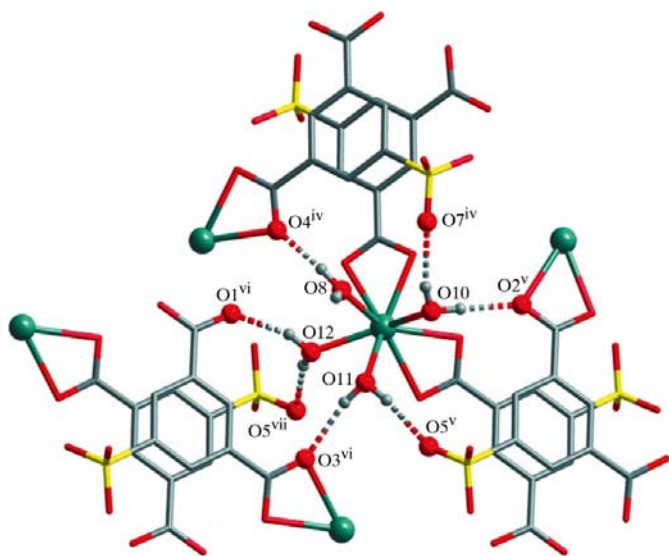


Figure 3
A perspective view of the hydrogen bonds between the chains. Dashed lines indicate hydrogen bonds. [Symmetry codes: (iv) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z$; (v) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, -y + 1, z + \frac{1}{2}$]

(Table 1) suggest that strong conjugation of the sulfonate group is predominant in this structure. The Tm ions are linked by the SIP^{3-} ligands to produce a one-dimensional zigzag chain propagating along the crystallographic c axis, as shown in Fig. 2. The chain is repeated by translation about every 17.4 Å along the c direction, comparable with the length of the c axis. The chains are linked by interchain hydrogen bonds between (i) coordinated water molecules and carboxylate O atoms and (ii) coordinated water molecules and sulfonate O

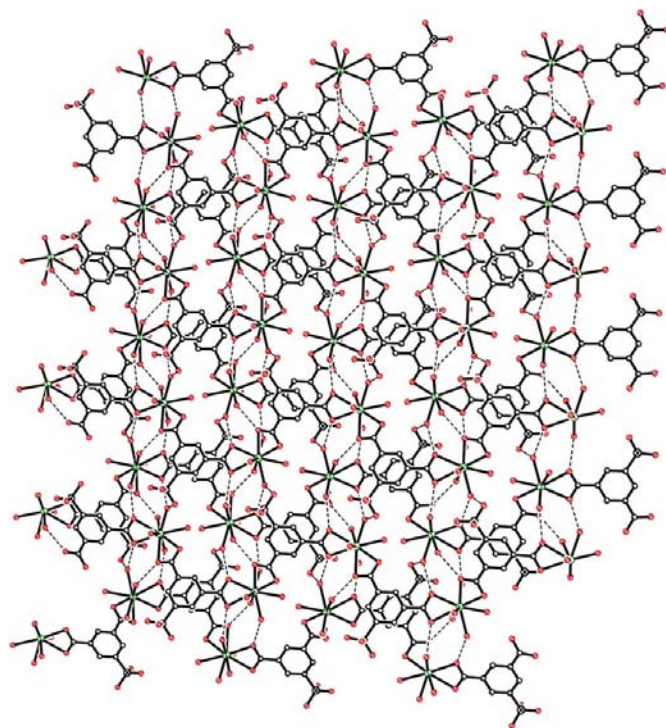


Figure 4
A perspective view of the two-dimensional layered structure. Dashed lines between the O atoms indicate hydrogen bonds.

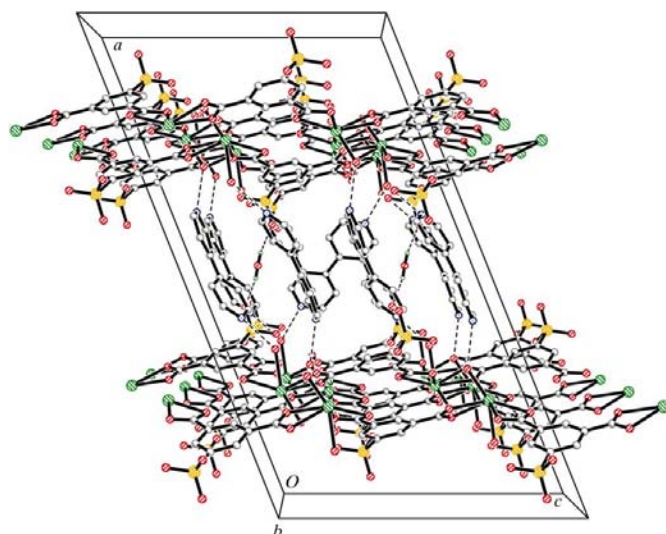


Figure 5
A view of the packing for (I) (viewed down the c axis), showing the bpy pillars between the layers. Some atoms have been omitted for clarity.

atoms, with O··O distances of 2.695 (2)–3.038 (3) Å (Table 2), to generate a two-dimensional layered structure (Figs. 3 and 4). π – π stacking interactions between the parallel benzene rings, arranged in an offset fashion with a face-to-face distance of 3.566 (1) Å and a centroid-to-centroid distance of 3.677 (2) Å, are observed within the two-dimensional layer.

The bpy molecules are not involved in coordination but link the chains through hydrogen bonds between coordinated water molecules and pyridyl N atoms, as depicted in Fig. 5. It is interesting that the bpy molecules exhibit two types of conformations with the two pyridyl rings coplanar and twisted with a dihedral angle of 26.2 (2)°. The two-dimensional layers are further linked by the bpy molecules as pillars through O–H··N hydrogen bonds (Table 2) to produce a three-dimensional supramolecular framework structure as illustrated in Fig. 5. The solvent water molecule is located in the space between the two-dimensional layers and stabilized by hydrogen bonding with the sulfonate group, with an O··O distance of 2.785 (3) Å. The extensive hydrogen bonds and π – π stacking interactions are responsible for the three-dimensional supramolecular framework structure.

Experimental

The title compound was synthesized by a hydrothermal method under autogenous pressure. A mixture of Tm₂O₃ (38.6 mg, 0.1 mmol), NaH₂SIP (28.6 mg, 0.1 mmol), bpy (23.4 mg, 1.5 mmol) and distilled water (15 ml) was stirred under ambient conditions. The final mixture was sealed in a 25 ml Teflon-lined steel autoclave, heated at 438 K for five days and then cooled to room temperature. Colourless prism-like crystals of (I) were obtained, recovered by filtration, washed with distilled water and dried in air (yield 56%). Analysis calculated for C₄₆H₅₂N₆O₂₅S₂Tm₂: C 37.04, H 3.52, N 5.64%; found: C 36.99, H 3.50, N 5.61%.

Crystal data

[Tm(C₈H₇O₇S)(H₂O)₅]₂·1.5C₁₀H₈N₂·0.5H₂O
M_r = 745.46
 Monoclinic, C2/c
a = 30.516 (5) Å
b = 10.8142 (16) Å
c = 17.350 (3) Å
 β = 111.795 (2)°
V = 5316.4 (15) Å³
Z = 8
 Mo K α radiation
 μ = 3.49 mm⁻¹
T = 130 K
 0.33 × 0.30 × 0.08 mm

Data collection

Rigaku Mercury70 diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku & Molecular Structure Corporation, 2000)
T_{min} = 0.328, *T_{max}* = 0.762
 20149 measured reflections
 6071 independent reflections
 5742 reflections with *I* > 2 σ (*I*)
R_{int} = 0.029

Refinement

R[*F*² > 2 σ (*F*²)] = 0.023
wR(*F*²) = 0.051
S = 1.00
 6071 reflections
 403 parameters
 12 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max}$ = 0.91 e Å⁻³
 $\Delta\rho_{\min}$ = -0.87 e Å⁻³

Aromatic H atoms were placed in calculated positions and treated using a riding-model approximation [C–H = 0.93 Å and *U_{iso}*(H) = 1.2*U_{eq}*(C)]. H atoms bonded to O atoms were visible in a difference map and were refined with a DFIX (*SHELXL97*; Sheldrick, 1997a)

Table 1

Selected geometric parameters (Å, °).

Tm1–O8	2.2919 (18)	Tm1–O3 ⁱ	2.4366 (17)
Tm1–O12	2.3124 (18)	Tm1–O11	2.4517 (19)
Tm1–O9	2.314 (2)	Tm1–O2	2.5073 (17)
Tm1–O1	2.3994 (17)	S1–O6	1.434 (2)
Tm1–O10	2.4027 (19)	S1–O7	1.451 (2)
Tm1–O4 ⁱ	2.4249 (18)	S1–O5	1.473 (2)
O8–Tm1–O12	75.67 (7)	O1–Tm1–O3 ⁱ	126.69 (6)
O8–Tm1–O9	136.62 (6)	O10–Tm1–O3 ⁱ	93.56 (6)
O12–Tm1–O9	75.56 (7)	O4 ⁱ –Tm1–O3 ⁱ	53.59 (6)
O8–Tm1–O1	82.78 (6)	O8–Tm1–O11	74.11 (6)
O12–Tm1–O1	128.08 (6)	O12–Tm1–O11	71.68 (7)
O9–Tm1–O1	90.18 (7)	O9–Tm1–O11	124.97 (7)
O8–Tm1–O10	72.19 (6)	O1–Tm1–O11	144.62 (7)
O12–Tm1–O10	137.67 (7)	O10–Tm1–O11	73.54 (7)
O9–Tm1–O10	146.00 (7)	O4 ⁱ –Tm1–O11	109.21 (6)
O1–Tm1–O10	74.08 (6)	O3 ⁱ –Tm1–O11	69.35 (6)
O8–Tm1–O4 ⁱ	141.33 (6)	O8–Tm1–O2	71.07 (6)
O12–Tm1–O4 ⁱ	142.85 (6)	O12–Tm1–O2	75.27 (6)
O9–Tm1–O4 ⁱ	74.53 (7)	O9–Tm1–O2	70.66 (6)
O1–Tm1–O4 ⁱ	73.48 (6)	O1–Tm1–O2	53.03 (6)
O10–Tm1–O4 ⁱ	72.17 (6)	O10–Tm1–O2	117.76 (6)
O8–Tm1–O3 ⁱ	143.25 (6)	O4 ⁱ –Tm1–O2	114.11 (6)
O12–Tm1–O3 ⁱ	96.07 (6)	O3 ⁱ –Tm1–O2	142.31 (6)
O9–Tm1–O3 ⁱ	71.65 (7)	O11–Tm1–O2	136.63 (6)

Symmetry code: (i) *x*, -*y*, *z* + ½.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O1W–H1W···O6	0.92 (5)	1.90 (5)	2.785 (3)	161 (5)
O8–H8A···O4 ^{ix}	0.89 (1)	1.804 (11)	2.695 (2)	175 (3)
O8–H8B···N2	0.89 (1)	1.841 (13)	2.713 (3)	166 (3)
O9–H9A···N3	0.89 (3)	1.94 (3)	2.811 (3)	167 (3)
O9–H9B···N1 ^x	0.90 (3)	1.88 (3)	2.764 (3)	168 (3)
O10–H10B···O7 ^{ix}	0.89 (3)	2.17 (3)	3.038 (3)	166 (3)
O10–H10C···O2 ^v	0.89 (1)	1.845 (11)	2.730 (2)	172 (3)
O11–H11B···O5 ^v	0.89 (1)	2.068 (11)	2.954 (3)	173 (3)
O11–H11B···O5A ^v	0.89 (1)	2.116 (18)	2.974 (7)	161 (3)
O11–H11C···O3 ^{vi}	0.89 (3)	2.13 (3)	3.001 (3)	169 (3)
O12–H12B···O5 ^{viii}	0.89 (3)	1.868 (15)	2.723 (4)	161 (3)
O12–H12C···O1 ^{vi}	0.88 (3)	1.991 (15)	2.839 (3)	161 (3)

Symmetry codes: (v) -*x* - ½, *y* - ½, -*z* + ½; (vi) -*x* - ½, *y* + ½, -*z* + ½; (vii) *x*, -*y* + 1, *z* + ½; (ix) -*x* - ½, -*y* + ½, -*z*; (x) *x* - ½, *y* - ½, *z*.

restraint [O–H = 0.90 (1) Å] and with *U_{iso}*(H) values set at 1.5*U_{eq}*(O). Atom O5 of the sulfonate group was found to be disordered and was modelled over two sets of positions using restraints on the anisotropic displacement parameters. The major and minor disorder components have refined occupancies of 78.6 (7) and 21.4 (7)%, respectively. The atoms of the terminal pyridyl ring and the sulfonate group have larger displacement parameters because of their freedom of libration.

Data collection: *CrystalClear* (Rigaku & Molecular Structure Corporation, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Education Department of Jiangxi Province (grant No. 2007–125) and the initial fund for Doctor from Jiangxi Normal University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3091). Services for accessing these data are described at the back of the journal.

References

- Biradha, K. & Zaworotko, M. J. (1998). *J. Am. Chem. Soc.* **120**, 6431–6432.
- Bowden, T. A., Milton, H. L., Slawin, A. M. Z. & Lightfoot, P. (2003). *Dalton Trans.* pp. 936–939.
- Brandenburg, K. (2005). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.
- Conn, M. M. & Rebek, J. Jr (1997). *Chem. Rev.* **97**, 1647–1668.
- Dong, Y. B., Smith, M. D., Layland, R. C. & zur Loye, H.-C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 775–780.
- Evans, C. C., Sukarto, L. & Ward, M. D. (1999). *J. Am. Chem. Soc.* **121**, 320–325.
- Liu, Q. Y. & Xu, L. (2005a). *CrystEngComm*, **7**, 87–89.
- Liu, Q. Y. & Xu, L. (2005b). *Eur. J. Inorg. Chem.* pp. 3458–3466.
- Liu, Q. Y. & Xu, L. (2006). *Eur. J. Inorg. Chem.* pp. 1620–1628.
- Rigaku & Molecular Structure Corporation (2000). *CrystalClear*. Version 1.3. Rigaku Corporation, Tokyo, Japan, and MSC, The Woodlands, Texas, USA.
- Saalfrank, R. W., Bernt, I. & Hampel, F. (2001). *Chem. Eur. J.* **7**, 2770–2774.
- Sheldrick, G. M. (1997a). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Tong, M. L., Lee, H. Y., Chen, X. M., Huang, R. B. & Mak, T. C. W. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3657–3659.
- Yaghi, O. M., Davis, C. E., Li, G. M. & Li, H. L. (1997). *J. Am. Chem. Soc.* **119**, 2861–2868.
- Yaghi, O. M., Li, G. M. & Li, H. L. (1995). *Nature (London)*, **378**, 703–706.