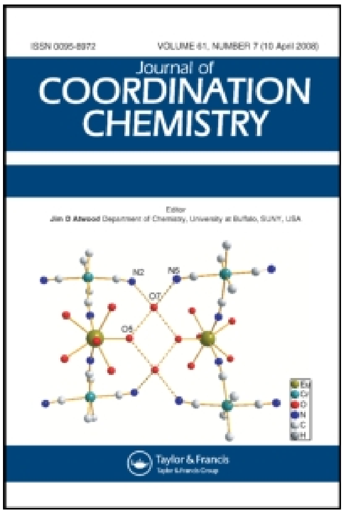

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A Novel, three-dimensional, Tetrachlorophthalato-bridged Samarium(III) complex $[Sm(tcph)_2(H_2O)_6]Hpip\cdot 5H_2O$

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A NOVEL, THREE-DIMENSIONAL, TETRACHLOROPHTHALATO-BRIDGED SAMARIUM(III) COMPLEX $[Sm(tcph)_2(H_2O)_6]Hpip \cdot 5H_2O$

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A novel, three-dimensional, tetrachlorophthalato-bridged samarium complex $[Sm(tcph)_2(H_2O)_6]Hpip \cdot 5H_2O$ (**1**) (tcph = tetrachlorophthalate dianion, pip = piperidine) has been synthesized and characterized by an X-ray structure determination. The title complex contains an unusual dimer formed by very short hydrogen bonds and gives a three-dimensional network by means of extensive hydrogen bonds. The fluorescence spectrum of **1** was measured.

Keywords: Samarium; Dimer; Hydrogen bond; Crystal structure

INTRODUCTION

Investigation of novel inorganic–organic hybrid framework assemblies represents one of the most active areas of material science and chemical research [1]. The intense interest in these materials is driven to a large extent by their interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, host–guest chemistry, ion exchange, catalysis, nonlinear optics, etc. [2]. Recently, the use of dicarboxylic acids linkers, forming extended metal ion structures, is of growing interest. Among the dicarboxylic acids, phthalic acid has been well studied in coordination polymers containing transition metals such as Cu, Mn, Co, and Zn, owing to the versatile bonding modes of phthalate dianions [3–14]. To our knowledge, very few lanthanide phthalato complexes have been reported and the samarium phthalato complex has not been reported to date. We used the tetrachlorophthalate dianion as a ligand and the title complex was obtained. The structure of **1** consists of the

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$[Sm(tcph)_2(H_2O)_6]^-$ anion, $(Hpip)^+$ cation and uncoordinated water molecules. Two adjacent mononuclear units are linked by short hydrogen bonds to form a dimer. A 3D network of **1** is constructed via a series of extensive O–H···O hydrogen bonds. Here we report the synthesis, crystal structure and fluorescence of **1**.

EXPERIMENTAL

Physical Measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 instrument. Infrared spectra using KBr pellets were recorded on a Shimadzu IR-408 spectrophotometer in the range 4000–600 cm^{-1} and fluorescence spectra were measured on an Acton Research SpectroPro-300i spectrophotometer with a xenon arc lamp as the light source.

Preparation of $[Sm(tcph)_2(H_2O)_6]Hpip \cdot 5H_2O$

An aqueous solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.088 g, 0.20 mmol) was added to an aqueous solution of tcph piperidinium salt (0.189 g, 0.20 mmol). The mixture was stirred at room temperature for half an hour. After filtration to remove any impurities, the solution was left undisturbed. Colourless crystals of **1** were obtained after several days. Yield, 40%. Anal. Calcd for $C_{21}H_{34}Cl_8NO_{19}Sm$ (%): C, 24.28; H, 3.27; N, 1.35. Found: C, 24.31; H, 3.29; N, 1.33. IR (KBr)/cm^{-1}: 3200 sh, 3100 sh, 1580 s, 1410 s, 1324 s, 910 m.

X-ray Crystallography

Suitable single crystals of **1** were selected and mounted on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) data collected by the ω–2θ scan technique at 293(2) K. Crystal data for **1**: $C_{21}H_{34}Cl_8NO_{19}Sm$, $M = 1038.44$, triclinic, $P_{\bar{1}}$, $a = 9.213(4)$, $b = 10.540(4)$, $c = 19.999(7)$ Å, $\alpha = 75.388(6)$, $\beta = 86.172(6)$, $\gamma = 85.376(7)^\circ$, $V = 1870.9(12)$ Å^3, $Z = 2$, $D_c = 1.843\ g\,cm^{-3}$, θ range $= 1.05$ to 25.00°, 9576 reflections collected, 6497 independent ($R(\text{int}) = 0.391$), 452 parameters, final R indices $[I > 2\sigma(I)]$, $R1 = 0.0443$, $wR2 = 0.0847$, GOF $= 0.970$. Unit-cell dimensions were obtained from least-squares refinements and the structure was solved by direct methods using SHELXS-97 [15]. Data were corrected for Lorentz and polarization effects. The metal atom in each complex was located in E-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. Final refinement was performed using SHELXL-97 [15] by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atom on F^2. The hydrogen atoms were added theoretically, riding on the atoms concerned and refined with fixed thermal factors.

RESULTS AND DISCUSSION

Structure Description

The structure of **1** consists of the $[Sm(tcph)_2(H_2O)_6]^-$ anion, $(Hpip)^+$ cation and uncoordinated H_2O. Selected bond lengths and angles are presented in Table I. The anion

TABLE I Selected distances (Å) and angles (°) in **1**

Sm(1)–O(1)	2.409(4)	Sm(1)–O(14)	2.469(4)
Sm(1)–O(11)	2.422(4)	Sm(1)–O(10)	2.472(4)
Sm(1)–O(12)	2.432(5)	Sm(1)–O(5)	2.472(4)
Sm(1)–O(13)	2.446(4)	Sm(1)–O(6)	2.670(4)
Sm(1)–O(9)	2.453(4)	O(1)–C(7)	1.245(6)
O(2)–C(7)	1.249(6)	Cl(1)–C(2)	1.724(5)
O(1)–Sm(1)–O(11)	123.86(17)	O(11)–Sm(1)–O(9)	73.87(19)
O(1)–Sm(1)–O(12)	141.57(15)	O(12)–Sm(1)–O(9)	142.87(16)
O(11)–Sm(1)–O(12)	71.5(2)	O(13)–Sm(1)–O(9)	145.04(14)
O(1)–Sm(1)–O(13)	74.29(14)	O(1)–Sm(1)–O(14)	73.14(14)
O(11)–Sm(1)–O(13)	132.41(17)	O(11)–Sm(1)–O(14)	69.94(15)
O(12)–Sm(1)–O(13)	71.45(15)	O(12)–Sm(1)–O(14)	82.35(17)
O(1)–Sm(1)–O(9)	71.14(14)	O(13)–Sm(1)–O(14)	76.51(15)
O(12)–Sm(1)–O(10)	77.10(17)	O(9)–Sm(1)–O(14)	98.04(17)
O(13)–Sm(1)–O(10)	130.31(15)	O(1)–Sm(1)–O(10)	140.33(15)
O(9)–Sm(1)–O(10)	77.32(16)	O(11)–Sm(1)–O(10)	66.67(15)
O(14)–Sm(1)–O(10)	135.92(14)	O(10)–Sm(1)–O(5)	74.19(14)
O(1)–Sm(1)–O(5)	74.40(13)	O(1)–Sm(1)–O(6)	107.49(13)
O(11)–Sm(1)–O(5)	133.47(16)	O(11)–Sm(1)–O(6)	127.89(16)
O(12)–Sm(1)–O(5)	123.30(16)	O(12)–Sm(1)–O(6)	73.93(16)
O(13)–Sm(1)–O(5)	92.11(14)	O(14)–Sm(1)–O(5)	147.41(14)
O(9)–Sm(1)–O(5)	73.88(15)	C(7)–O(1)–Sm(1)	139.7(4)
O(1)–C(7)–O(2)	126.3(5)	C(15)–O(5)–Sm(1)	98.5(3)
O(5)–C(15)–O(6)	122.3(5)	C(15)–O(6)–Sm(1)	89.0(3)

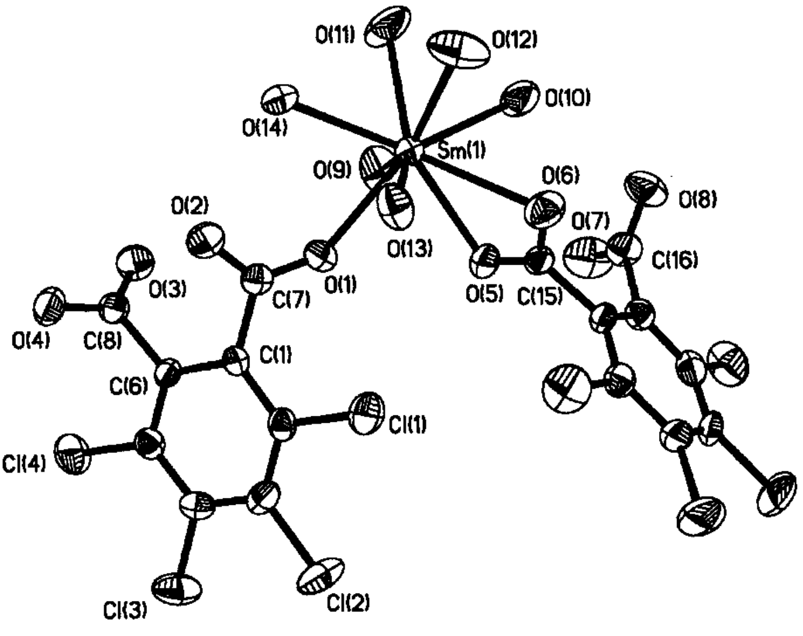

FIGURE 1 An ORTEP view of the $[Sm(tcph)_2(H_2O)_6]^+$ anion with atom numbering scheme. H atoms have been omitted for clarity. The displacement ellipsoids are drawn at 30% probability level.

unit is shown in Fig. 1. Sm(1) is surrounded by nine oxygen atoms, three from two carboxylate groups of two tcph ligands and the others from six coordinating water molecules. One tetrachlorophthalate ligand behaves as 1,3 chelating, while the other is coordinated to the same metal atom by one of the oxygen atoms of its

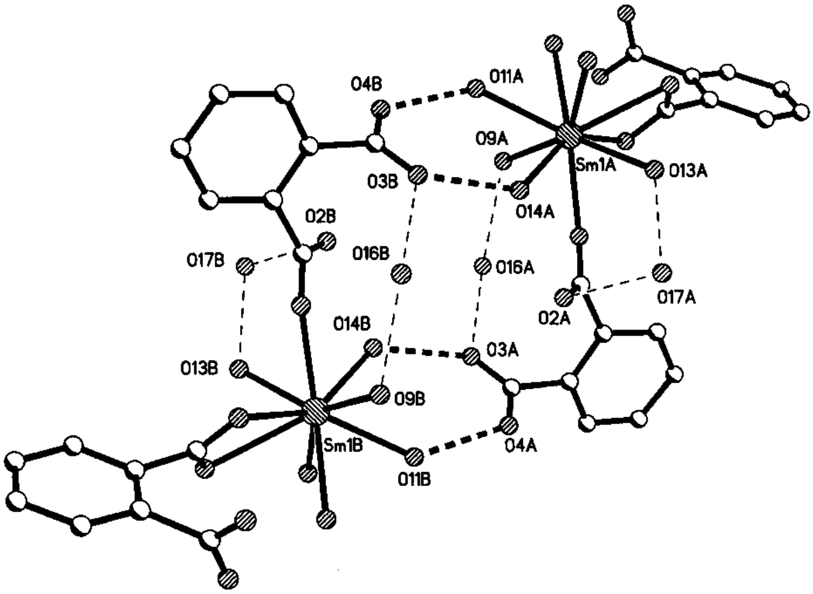

FIGURE 2 Fragment of the crystal structure of Complex **1** showing the dimeric unit formed by hydrogen bonds. H atoms have been omitted for clarity.

TABLE II Hydrogen bonds in **1**

D–H···A	*d(D–H)* (Å)	*d(H···A)* (Å)	*d(D···A)* (Å)	∠*DHA*(°)
O(11A)–H(11B)···O(4B)	0.852	1.765	2.616	177.1
O(14A)–H(14B)···O(3B)	0.849	1.929	2.774	173.2
O(14B)–H(14D)···O(3A)	0.849	1.929	2.774	173.2
O(11B)–H(11D)···O(4A)	0.852	1.765	2.616	177.1
O(9A)–H(9BA)···O(16A)	0.851	2.264	2.713	113.1
O(17B)–H(17C)···O(2B)	0.851	1.956	2.784	163.7
O(16A)–H(16B)···O(6AB)	0.864	2.055	2.801	144.0

carboxylate groups in the anion. Sm–O distances range from 2.409(4) to 2.670(4) Å and resemble those in $[Eu_2(BDC)_3(H_2O)]_n$ [16]. It is interesting that two adjacent $[Sm(tcph)_2(H_2O)_6]^+$ anions are linked by four short hydrogen bonds between uncoordinated carboxylate oxygen atoms and coordinated water molecules [O(4B)···O(11A), O(11B)···O(4A) = 2.616 Å, O(3B)···O(14A), O(14B)···O(3A) = 2.774 Å], which results in two rings. In addition, short hydrogen bonds (O···O distances range from 2.713 to 2.855 Å) also exist within the anion. The oxygen atoms from lattice water [O(16A), O(16B)] act as acceptors and the coordinated water molecules as donors [*d*(O···O) = 2.713, 2.748 Å and angles ∠(O–H···O) = 113.1, 166.9°] as do carboxylate oxygen atoms [*d*(O···O) = 2.784, 2.801 Å and angles ∠(O–H···O) = 144.0, 163.7°]. Thus neighbouring mononuclear structural units form an unusual dimer by means of short hydrogen bonds (Fig. 2). The Sm···Sm distance is 6.476 Å. Hydrogen bonding distances and angles are presented in Table II. For clarity the conventional description of hydrogen bonding structural parameters has been adopted: D···A indicates the distance between a donor D atom and acceptor A atom, H···A the distance between a donor hydrogen atom bound to D and acceptor, while ∠DHA indicates the angle. There are many hydrogen bonds, owing to the presence of fully deprotonated carboxylate groups and a significant number of water molecules.

Fluorescence

Both Complex **1** and $Sm(NO_3)_3 \cdot 6H_2O$ exhibit fluorescent bands attributable to the $^4G_{5/2} \rightarrow {}^6H_J$ transitions in the range 550–750 nm. It is found that the intensity of the transitions in **1** is slightly stronger than in $Sm(NO_3)_3 \cdot 6H_2O$. This may be attributed to the coordination environment and site symmetry of Sm [17].

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Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-215640. Copies of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax (44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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