

## [Sm(NO<sub>3</sub>)<sub>3</sub>(TPTZ)(H<sub>2</sub>O)]·2H<sub>2</sub>O [TPTZ is 2,4,6-tris(2-pyridyl)-1,3,5-triazine]

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The title compound, aquatris(nitrato)[2,4,6-tris(2-pyridyl)-1,3,5-triazine]samarium dihydrate, [Sm(NO<sub>3</sub>)<sub>3</sub>(C<sub>18</sub>H<sub>12</sub>N<sub>6</sub>)(H<sub>2</sub>O)]·2H<sub>2</sub>O, was prepared from Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 2,4,6-tris(2-pyridyl)-1,3,5-triazine. The metal atom is ten-coordinate being bonded to the terdentate TPTZ ligand, three bidentate nitrates and a water molecule.

### Comment

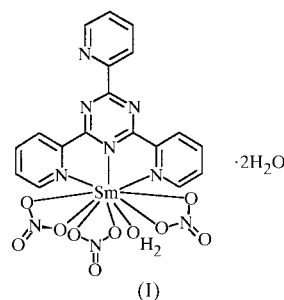
There is much current interest in the use of tridentate ligands such as 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ), and terpyridine and its derivatives, for the extraction and separation of metal ions (Chan *et al.*, 1996; Byers *et al.*, 1996). These ligands are being used in the nuclear industry as solvent extraction reagents since they are able to separate trivalent actinides An<sup>III</sup> in preference to lanthanides Ln<sup>III</sup> from nitric acid media in synergistic combination with a weak acid such as 2-bromodecanoic acid. The ligands have been found to form 1:1 complexes with lanthanides in the presence of nitric acid in which they act as an approximately planar tridentate ligand (Chan *et al.*, 1996) and this is likely to be the mode in which they separate the metal ions.

The inclusion of 2-bromopropionic acid in the complex preparation was an attempt to better replicate the conditions under which the liquid–liquid extraction experiments take place as it closely resembles the most often used synergist, 2-bromodecanoic acid. In the liquid–liquid extraction process, the ligand and synergist in hydrogenated tetrapropene are used to extract the metal ions from nitric acid media. We have shown previously that a mixture of 2-bromodecanoic acid, samarium nitrate and terpyridine (terpy) can result in the protonation of terpyridine and the formation of an ion pair of formula [(H<sub>2</sub>terpy)(NO<sub>3</sub>)]<sup>+</sup>[Sm(terpy)(NO<sub>3</sub>)<sub>4</sub>]<sup>-</sup> in which the diprotonated terpy is not coordinated to the Sm<sup>III</sup> ion (Drew, Hudson, Iveson, Russell, Liljenzin *et al.*, 1998).

The extraction performance of terpyridine has indeed been found to decrease at higher nitric acid concentrations because

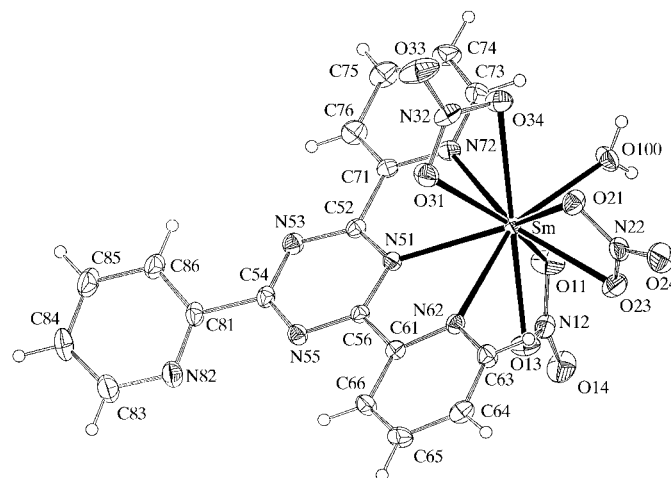
it becomes diprotonated, cannot coordinate to the metal and also has increased solubility in the aqueous phase (Hågstrom *et al.*, 1999). However, in the presence of 2-bromopropionic acid, none of the heterocyclic N atoms in TPTZ were protonated, a fact which presumably reflects the lower basicity of the TPTZ N atoms compared with those in terpyridine.

The structure of the title compound, (I), is shown in Fig. 1 and is the first to be determined of a lanthanide(III) nitrate/TPTZ complex. The metal atom is ten-coordinate, being bonded to three N atoms from the TPTZ ligand, three nitrate anions and one water molecule. In addition, there are two water molecules in the asymmetric unit. The bond to the water molecule is by far the shortest at 2.420 (4) Å compared to 2.492 (4)–2.615 (4) Å for the Sm–O(nitrate) bonds. The Sm–N51 bond to the central N atom of the ligand is, at 2.571 (4) Å, significantly shorter than the other two bonds from the metal to the ligand, *viz.* 2.644 (5) and 2.631 (4) Å.



The angles subtended by the pyridine rings at the central triazine ring are 6.3 (2) and 4.9 (2)° for the coordinated rings and 17.5 (2)° for the uncoordinated ring. The metal atom is 0.05 Å from the plane of the central triazine ring.

The structure of the TPTZ ligand has been published previously (Drew, Hudson, Iveson, Russell & Madic, 1998). Other high coordinate related structures containing this ligand include [Ce(TPTZ)(NO<sub>3</sub>)<sub>4</sub>] (Chan *et al.*, 1996), in which the metal is 11-coordinate being bound to the terdentate TPTZ



**Figure 1**

The structure of the title compound with ellipsoids scaled to 25% probability. H atoms are included with small arbitrary radii.

and four bidentate nitrates, [Eu(TPTZ)Cl<sub>3</sub>(HOME)<sub>2</sub>] (Wietzke *et al.*, 1999), in which the metal is eight-coordinate being bonded to the terdentate ligand, three chlorides and two solvent methanols, and [Pr(TPTZ)(OAc)<sub>3</sub>]<sub>2</sub>, a centrosymmetric dimer in which the metal is ten-coordinate being bonded to the terdentate ligand and three acetates, one of which bridges to the other metal (Wietzke *et al.*, 1999).

The M–N bond lengths in the present structure are, as expected, shorter than the Ce–N and Pr–N distances [2.720 (8), 2.673 (7), 2.733 (7); 2.674 (6), 2.687 (7), 2.717 (6) Å] and comparable with the Eu–N distances [2.646 (6), 2.555 (5), 2.646 (6) Å] in the above TPTZ structures.

It is noteworthy that in TPTZ metal complexes, the unbonded pyridine N atoms form hydrogen bonds with solvent molecules. Thus, in the above Eu and Pr structures, solvent methanol forms a bifurcated hydrogen bond to N82 and N55 (using the numbering scheme in the present structure), while in the present structure, the water molecule O300 forms a single hydrogen bond to N82 at 2.801 (6) Å.

There is an extensive hydrogen-bond pattern in the crystal involving the three water molecules (see Table 1).

## Experimental

The title compound was prepared by initially adding Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0711 g, 0.16 mmol) in CH<sub>3</sub>CN (10 ml) dropwise to a stirred solution containing TPTZ (0.05 g, 16 mmol) in CH<sub>3</sub>CN (10 ml). After stirring for a few minutes, 2-bromopropionic acid (0.024 g, 0.16 mmol) was added and the solution was stirred for a further 30 min. It did not prove necessary to separate out the acid and suitable crystals were obtained after three weeks at room temperature.

### Crystal data

[Sm(NO <sub>3</sub> ) <sub>3</sub> (C <sub>18</sub> H <sub>12</sub> N <sub>6</sub> )(H <sub>2</sub> O)]·2H <sub>2</sub> O	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 702.76	<i>D<sub>x</sub></i> = 1.866 Mg m <sup>-3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 9.592 (12) Å	Cell parameters from 4276 reflections
<i>b</i> = 11.989 (14) Å	<i>θ</i> = 1.97–25.99°
<i>c</i> = 12.574 (14) Å	<i>μ</i> = 2.428 mm <sup>-1</sup>
<i>α</i> = 115.219 (10)°	<i>T</i> = 293 (2) K
<i>β</i> = 102.680 (10)°	Needle, colourless
<i>γ</i> = 94.734 (10)°	0.30 × 0.10 × 0.10 mm
<i>V</i> = 1251 (3) Å <sup>3</sup>	

### Data collection

Marresearch Image Plate	4275 independent reflections
95 frames at 2° intervals, counting time 2 min	4052 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)	<i>θ</i> <sub>max</sub> = 25.97°
<i>T</i> <sub>min</sub> = 0.473, <i>T</i> <sub>max</sub> = 0.784	<i>h</i> = 0 → 11
4275 measured reflections	<i>k</i> = -14 → 14
	<i>l</i> = -15 → 14
	Intensity decay: none

**Table 1**

Selected hydrogen-bond geometry (Å).

O100...O200 <sup>i</sup>	2.676 (6)	O300...O200	2.791 (7)
O100...O21 <sup>ii</sup>	2.838 (5)	O300...O33 <sup>iii</sup>	2.944 (6)
O300...O200	2.791 (7)		

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

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 1.8862P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.094$	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
<i>S</i> = 1.087	$\Delta\rho_{max} = 0.92 \text{ e \AA}^{-3}$
4275 reflections	$\Delta\rho_{min} = -0.96 \text{ e \AA}^{-3}$
380 parameters	Extinction correction: SHELXL93 (Sheldrick, 1993)
H atoms: see below	

H atoms bonded to C atoms were introduced in calculated positions. H atoms bonded to the water ligand were located from a difference Fourier map, but those on the free water molecules were not located and not included. All H atoms were refined with displacement parameters fixed at values of 1.2 times that of the atom to which they were bonded.

Data collection: XDS (Kabsch, 1988); cell refinement: XDS; data reduction: XDS; program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL93 (Sheldrick, 1993); molecular graphics: PLATON (Spek, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1386). Services for accessing these data are described at the back of the journal.

## References

- Byers, P., Chan, G. Y. S., Drew, M. G. B. & Hudson, M. J. (1996). *Polyhedron*, **15**, 2845–2849.
- Chan, G. Y. S., Drew, M. G. B., Hudson, M. J., Isaacs, N. S. & Byers, P. (1996). *Polyhedron*, **15**, 3385–3398.
- Drew, M. G. B., Hudson, M. J., Iveson, P. B., Russell, M. L., Liljenzin, J. O., Skålberg, M., Spjuth, L. & Madic, C. (1998). *J. Chem. Soc. Dalton Trans.* pp. 2973–2982.
- Drew, M. G. B., Hudson, M. J., Iveson, P. B., Russell, M. L. & Madic, C. (1998). *Acta Cryst.* **C54**, 985–987.
- Hågstrom, I., Spjuth, L., Enarsson, A., Liljenzin, J. O., Skålberg, M., Hudson, M. J., Iveson, P. B., Madic, C., Cordier, P. Y., Hill, C. & Francois, N. (1999). *Solv. Extract. Ion Exch.* **17**, 221–228.
- Kabsch, W. (1988). *J. Appl. Cryst.* **21**, 916–932.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). SHELXL93. University of Göttingen, Germany.
- Spek, A. L. (1994). PLATON. University of Utrecht, The Netherlands.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
- Wietzke, R., Mazzanti, M., Latour, J. M. & Pecaut, J. (1999). *Inorg. Chem.* **38**, 3581–3585.