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[11,23-Dimethyl-15,19-diaza-3,7-diazonia-tricyclo[19.3.1.1^{9,13}]tetracosa-1(25),2,7,9,11,-13(26),14,19,21,23-decaene-25,26-diolato-$\kappa^4N^{15},N^{19},O,O'$]tris(nitrato-$\kappa^2O,O'$)samarium(III)

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Key indicators

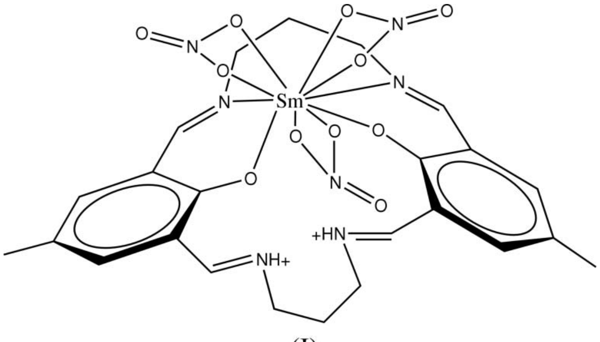
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.070
wR factor = 0.079
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, [$Sm(NO_3)_3(C_{24}H_{28}N_4O_2)$], the Sm atom has tenfold coordination, built up from two imino N atoms, two deprotonated phenolic O atoms and three bidentate nitrate groups. The Sm ion is incorporated in an out-of-plane position relative to the macrocyclic ligand, which adopts a folded conformation.

Comment

Compartmental macrocyclic ligands derived from the Schiff base condensation of 2,6-diformyl-4-methylphenol have received much attention since their metal complexes have provided particular supramolecular systems with various architectures and dimensions for exploring new functional materials (Alexander, 1995). As part of an investigation of the structures of such lanthanide compounds, the title mononuclear Sm^{III} complex, (I), is reported here (Fig. 1).



(I)

The organic ligand acts as a tetradentate *N*,*N*,*O*,*O*-chelate binding to a single Sm^{III} atom which is overall ten-coordinate. Related ligands have already been shown to coordinate metal ions in a mononuclear fashion (Drew *et al.*, 1994), using a coordination mode which involves proton transfer to the uncoordinated imino nitrogen. In turn, these NH groups in (I) participate in bifurcated intramolecular N—H···(O,O) bonds (Table 2). The other 'chamber' of the ligand is thus not involved in coordination to the metal. The out-of-plane position of the Sm ion is probably due to a mismatch between the size of the macrocyclic cavities and the radius of the metal ion.

Three nitrate groups acting as bidentate ligands complete the coordination of samarium. In this compound the macrocyclic ligand is considerably bent with the two phenol groups forming a dihedral angle of 98.60 (5)°. A similar value of 115.9° has already been observed in a related nickel complex (Starynowicz & Lisowski, 1999). However this folding of the ligand is less pronounced than in the protonated free ligand where the two phenol rings are almost parallel (Atkins *et al.*,

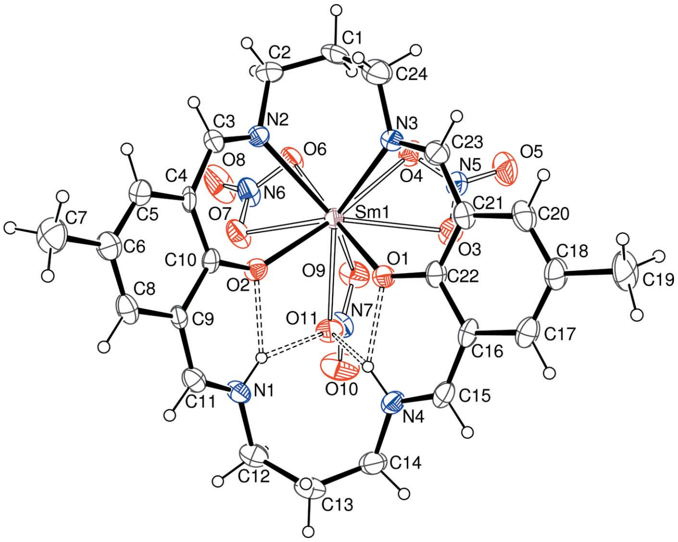


Figure 1
View of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). The hydrogen bonds are indicated by dashed lines.

1993). The bond lengths involving the metal ion in (I) are comparable to the corresponding values observed in a similar Sm^{III} complex (Spodine *et al.*, 2000).

Experimental

1,3-Diaminopropane (2.4 mmol, 178 mg) dissolved in methanol (10 ml) was added dropwise with stirring to a methanol solution (10 ml) of samarium nitrate hexahydrate (2.4 mmol 1.06 g) and 2,6 diformyl-4-methylphenol (2.4 mmol, 400 mg); the yellow solution so obtained was refluxed for 12 h. After keeping the resulting solution in air for 1 d, colourless single crystals of (I) suitable for X-ray analysis were obtained.

Crystal data

$[Sm(NO_3)_3(C_{24}H_{28}N_4O_2)]$
$M_r = 740.93$
Monoclinic, $P2_1/c$
$a = 15.7532$ (13) Å
$b = 9.7237$ (5) Å
$c = 19.1342$ (15) Å
$\beta = 104.457$ (12)°
$V = 2838.1$ (4) Å^3
$Z = 4$
$D_x = 1.734$ Mg m^{-3}
Ag $K\alpha$ radiation
Cell parameters from 987 reflections
$\theta = 3.0$–$17.0°$
$\mu = 1.15$ mm^{-1}
$T = 293$ K
Prism, colourless
0.20 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: none
30402 measured reflections
6093 independent reflections
4029 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.082$
$\theta_{\rm max} = 20.5°$
$h = -19 \rightarrow 19$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.079$
$S = 1.61$
4029 reflections
388 parameters
H-atom parameters constrained
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 1.71$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.71$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Sm1—O1	2.335 (5)	Sm1—O7	2.604 (6)
Sm1—O2	2.346 (5)	Sm1—O9	2.641 (7)
Sm1—O3	2.628 (6)	Sm1—O11	2.552 (6)
Sm1—O4	2.616 (6)	Sm1—N2	2.598 (7)
Sm1—O6	2.563 (5)	Sm1—N3	2.634 (7)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H12···O2	0.95	1.90	2.619 (6)	131
N1—H12···O11	0.95	2.26	3.082 (10)	145
N4—H19···O1	0.95	1.94	2.655 (6)	130
N4—H19···O11	0.95	2.34	3.063 (10)	132

The H atoms were placed in idealized locations (C—H = 0.95 Å and N—H = 0.95 Å) and refined as riding, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(carrier). The highest difference peak is 0.12 Å from atom Sm1 and the deepest hole is 1.39 Å from O11..

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *KappaCCD Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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