The Template Synthesis and Crystal and Molecular Structure of a Sexidentate Schiff-base Macrocyclic Complex of Samarium(III), $[Sm(C_{18}H_{18}N_6)(NO_3)(OH)(H_2O)]NO_3{\cdot}2MeOH$ †

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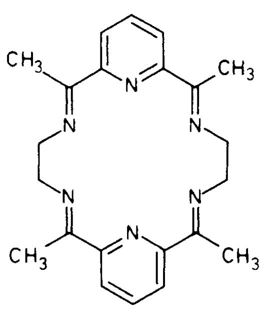
The template condensation of 2,6-pyridinedicarbaldehyde with ethylenediamine in the presence of $Sm(NO_3)_3$ gave a complex formulated as $[Sm(C_{18}H_{20}N_6O)(NO_3)_3]$. The complex was recrystallised from water and the *X*-ray crystal structure determined by the heavy-atom method and refined by least squares to a final *R* value of 0.073. The recrystallised compound can be formulated as the title complex. The Sm^{3+} cation is enclosed in the cyclic ligand and bonded to its six N atoms as well as to a bidentate NO_3^- anion, to one OH^- anion, and to a water molecule. Some O · · · O contact distances can be ascribed to hydrogen bonds; the clathrate solvent molecules are disordered.

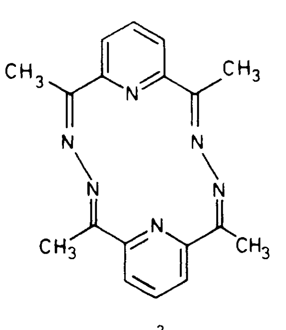
Recent reports have described the template synthesis of lanthanide complexes of the 18-membered hexa-aza-macrocycle L^1 where complexes were obtained only with lanthanum(III) nitrate and perchlorate, and cerium(III) nitrate.[1,2] The heavier lanthanide cations (Tb, Dy, Ho, Er, Tm, Yb, and Lu) were found to be effective as templating agents in the synthesis of complexes of the 14-membered quadridentate hexa-aza-macrocycle L^2.[3] We have found that all of the lanthanide ions (La $\longrightarrow$ Lu, except Pm) to be effective as template ions in the synthesis of macrocyclic complexes derived from 2,6-pyridinedicarbaldehyde and ethylenediamine.[4] This paper reports the crystal and molecular structure of a samarium(III) complex prepared by this route.‡

Experimental

The samarium(III) complex was prepared by refluxing together in methanol (30 cm³) for 3 h, samarium(III) nitrate, 2,6-pyridinedicarbaldehyde, and ethylenediamine in the mol ratio 1 : 2 : 2. The fine powdery product was filtered off, washed with methanol and dried under vacuum (Found: C, 33.0; H, 2.95; N, 19.35. $C_{18}H_{18}N_6Sm{\cdot}H_2O$ requires C, 32.25; H, 2.95; N, 18.9%). The bulk sample was recrystallised from water to give colourless well formed crystals which from the structural analysis were of the compound $[Sm(C_{18}H_{18}N_6)(NO_3)(OH)(H_2O)]NO_3{\cdot}2MeOH$.



L^1



L^2

X-Ray Crystallography.—A crystal of approximate dimensions 0.1 × 0.2 × 0.1 mm was selected for the measurement of intensities. Data collection was made on a Philips diffractometer with a graphite monochromator and Mo-K_α radiation. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings.

Crystal data. $C_{20}H_{29}N_8O_{10}Sm$, M = 691.4, Triclinic, space group $P\bar{1}$, a = 16.02(1), b = 9.64(1), c = 8.29(1) Å, α = 91.06(3), β = 95.26(3), γ = 92.18(3)°, U = 1 273 Å³, Z = 2, D_c = 1.67 g cm⁻³, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 23.9 cm⁻¹.

Intensities were measured by the θ—2θ method, with a scan speed of 2° min⁻¹ between 2 and 25°, yielding 3 957 independent reflections, 3 289 of which were significantly above background $I > 3\sigma(I)$. After subtracting the background, the data were corrected for Lorentz–polarization factors and for absorption.[5] Two standard reflections measured periodically were constant within counting statistics.

Solution of the structure was achieved by the heavy-atom method through Patterson and Fourier maps. Refinement of scale-factor, positional and thermal parameters converged to give a final agreement index *R* of 0.073, when the largest parameter shift in the last cycle was *ca.* 0.2σ. The structure was refined by full-matrix least squares, minimizing the function $\Sigma w\Delta F^2$ with w = 1. There are two independent molecules of clathrate MeOH which, from inspection of the Fourier-difference maps, are evidently disordered. The carbon atoms lie on inversion centres at $\frac{1}{2},0,\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ respectively

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† Aqua(3,6,14,17,23,24-hexa-azatricyclo[17,3,1,1^{8,12}]tetracosa-1(23),2,6,8,10,12(24),13,17,19,21-decaene)(hydroxo)(nitrato)-samarium(III) nitrate–methanol (1/2).

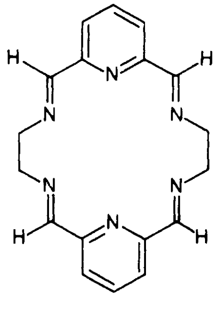
Supplementary data available (No. SUP 23791, 19 pp.): temperature factors, non-bonded contact distances, angles within the macrocyclic ligand, observed and calculated structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ Ca^{2+}, Sr^{2+}, and Ba^{2+}, but not Mg^{2+}, have been found to be effective in the template synthesis of L^1 (S. M. Nelson, *Pure Appl. Chem.*, 1980, **52**, 2461). Although the ions La^{3+} (1.061 Å) to Nd^{3+} (0.995 Å) have comparable ionic radii to Ca^{2+} (0.99 Å), the lanthanide contraction diminishes the radii across the series and it would appear that at Sm^{3+} (0.964 Å) the radius is small enough to begin to lose its ' best-fit ' situation for L^3 which would have a similar cavity size to L^1.

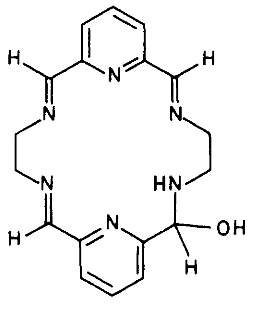
Table 1. Atomic co-ordinates with e.s.d.s

Atom	*x*	*y*	*z*
Sm	0.242 2(1)	0.216 3(1)	0.164 6(1)
N(1)	0.322 2(12)	−0.020 7(19)	0.154 5(21)
N(2)	0.328 5(11)	0.160 5(21)	−0.083 9(23)
N(3)	0.289 5(11)	0.426 0(21)	−0.007 7(23)
N(4)	0.148 9(9)	0.437 3(19)	0.142 9(21)
N(5)	0.104 5(11)	0.220 5(20)	0.312 6(24)
N(6)	0.229 2(8)	0.042 4(16)	0.397 5(19)
N(7)	0.115 5(7)	0.073 6(14)	−0.067 8(16)
N(8)	0.819 4(12)	0.385 4(21)	0.400 8(20)
O(1)	0.150 9(7)	0.013 2(12)	0.054 2(14)
O(2)	0.139 2(7)	0.199 1(12)	−0.083 7(13)
O(3)	0.062 0(7)	0.012 6(14)	−0.160 8(15)
O(4)	0.397 3(7)	0.245 1(13)	0.245 4(14)
O(5)	0.271 5(7)	0.366 5(12)	0.407 4(13)
O(6)	0.856 2(11)	0.287 4(18)	0.361 6(25)
O(7)	0.850 9(10)	0.502 3(19)	0.417 4(22)
O(8)	0.743 2(10)	0.368 8(18)	0.408 8(24)
O(9) *	0.509 0(13)	0.069 5(22)	0.342 2(26)
O(10) *	0.496 2(14)	0.465 6(23)	0.324 8(27)
C(1)	0.319 3(12)	−0.110 6(21)	0.277 7(25)
C(2)	0.637 2(13)	0.232 8(22)	0.719 0(26)
C(3)	0.590 1(14)	0.263 1(24)	0.846 2(28)
C(4)	0.588 1(14)	0.173 1(24)	0.974 6(27)
C(5)	0.631 7(12)	0.051 8(20)	0.969 7(24)
C(6)	0.370 5(12)	0.052 9(21)	0.903 0(24)
C(7)	0.338 8(13)	0.271 2(22)	0.794 7(26)
C(8)	0.359 9(13)	0.406 8(21)	0.890 7(25)
C(9)	0.247 2(12)	0.534 6(20)	−0.024 9(23)
C(10)	0.171 6(12)	0.548 4(20)	0.061 8(23)
C(11)	0.128 1(14)	0.673 7(24)	0.051 0(28)
C(12)	0.057 1(15)	0.677 7(25)	0.131 6(29)
C(13)	0.030 1(14)	0.564 0(23)	0.217 2(28)
C(14)	0.078 3(12)	0.442 0(20)	0.223 6(24)
C(15)	0.057 5(12)	0.322 1(21)	0.312 5(24)
C(16)	0.085 2(12)	0.100 5(20)	0.415 9(24)
C(17)	0.165 9(12)	0.069 8(20)	0.516 1(24)
C(18)	0.264 6(12)	−0.073 3(20)	0.404 5(24)
C(19)	0.5000	0.0000	0.5000
C(20)	0.5000	0.5000	0.5000

* The population parameters of O(9) and O(10) are 0.45 and 0.38 respectively (see text).



L^3



L^4

and the corresponding oxygen atoms are statistically distributed on symmetric positions around these centres. Scattering factors for Sm were from ref. 6, and those for C, N, and O from ref. 7. The samarium scattering factor was corrected for anomalous dispersion with constant average values $\Delta f' = -0.533$ and $\Delta f'' = 3.442$ for the real and imaginary components. All calculations were done using the *X*-RAY program system.[8] Final atomic co-ordinates are listed in Table 1; distances and angles are in Table 2 and Figure 3.

Results and Discussion

A series of lanthanide complexes were prepared by the template condensation of 2,6-pyridinedicarbaldehyde and ethylenediamine in the presence of lanthanide nitrates. It was expected that all of the complexes were of the hexa-azamacrocyclic ligand L^3, but the i.r. spectra for the heavier lanthanide (Nd ⟶ Lu, except Eu and Pm) complexes showed different and unexpected spectra when compared with those for the lighter lanthanide (La ⟶ Pr and Eu) complexes. The spectra exhibited a complete absence of bands corresponding to either carbonyl or primary amine groups in both cases, but for the former group a distinctive sharp band at *ca.* 3 220 cm^{-1} characteristic of a secondary amine group was present as well as imine bands. The addition of a water molecule across the imine double bond would lead to the formation of a carbinolamine species, L^4, and the occurrence of such an addition is supported by ^{13}C and ^1H n.m.r. spectral data.[9] The samarium(III) complex recovered from the template experiment has present a band at 3 210 cm^{-1}, but when the bulk sample is recrystallised from water it was noted that some changes had occurred in the i.r. spectrum; the sharp band at 3 210 cm^{-1} had disappeared and a new sharp band was present at 3 560 cm^{-1}. This band could be assigned to a Sm–OH group. The intensity of the band *ca.* 1 380 cm^{-1} assigned to the $-NO_3$ group was increased, and the band at 1 080 cm^{-1} also associated with $-NO_3$ had vanished. In order to determine the nature of the product an *X*-ray crystal structure determination was undertaken.

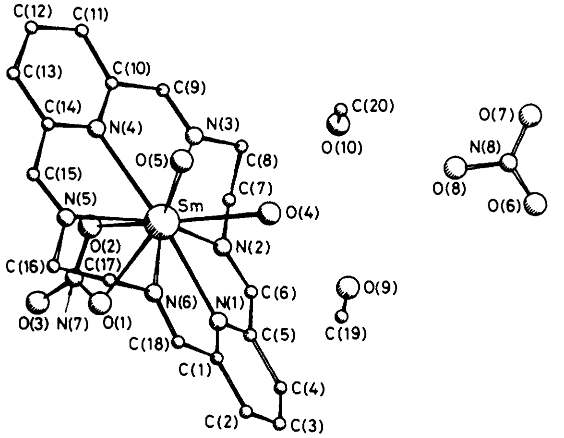


Figure 1. Crystal structure of $[Sm(C_{18}H_{18}N_6)(NO_3)(OH)(H_2O)]NO_3 \cdot 2MeOH$

The *X*-ray crystal structure consists of discrete complex $[Sm(C_{18}H_{18}N_6)(NO_3)(OH)(H_2O)]^+$ cations, NO_3^- anions, and clathrate MeOH molecules, as shown in Figure 1. The Sm^{3+} ion is ten-co-ordinate being directly bonded to the heteroatoms of the sexidentate ligand, to one chelating nitrate group, to the oxygen atoms of the OH^- ion and of one H_2O molecule.

The co-ordination polyhedron (Figure 2) can be described as an irregular antiprism capped on its ' square ' faces by the N(1) and N(4) atoms. The best plane through atoms O(1), O(4), N(2), and N(6), which comprise one face of the antiprism, makes a dihedral angle of 6.7° with the best plane through atoms O(2), O(5), N(3), and N(5), which make up the other face. The Sm–N(' pyridinic ') bond lengths [2.66(1) and 2.65(1) Å] are significantly longer than the Sm–N(imine) ones (mean 2.62 Å) and all the Sm–N distances are significantly shorter than those found in a related cryptate complex of samarium, $[Sm_2(C_{18}H_{36}O_6N_2)(NO_3)_6]\cdot H_2O$,[10] in which the nitrogen atoms are sp^3 hybridized. The metal–ligand bond distances are also a little shorter than those found in $[La(L^1)(NO_3)_3]$ where La–O(nitrato) = 2.68—2.76 Å. The differences may be due in part to the different co-ordination number in the complexes (10 in the case of Sm and 12 in the case of La) as well as to the diminished radius of the central metal ion. The Sm–O(nitrato) bonds are in the normal range and agree well with those found in other samarium complexes.[10,11] A remarkable difference is found between the Sm–OH and Sm–OH_2 bond distances.

The N atoms of the multidentate ligand (Figure 3) are sp^2 hybridized: N(1) and N(4) contribute to the electronic mesomeric effect of the aromatic rings (C–N = 1.33 and 1.36 Å) whereas each of the chain N atoms makes with the C atoms a single (C–N = 1.48 and 1.50 Å) and a double bond (C=N = 1.26 and 1.27 Å). As a consequence the Sm–N(1)–C and Sm–N(4)–C angles are all comparable (120 and 122°) whereas the Sm–N=C angles (122 and 124°) are systematically larger than Sm–N–C (118°). As expected, in the chelated nitrate the N–O bonds in the side towards Sm^{3+} are longer by *ca.* 0.05 Å than that on the free side; on the contrary, the N–O bond lengths and angles are of the same order in the NO_3^- anion.

Among the several O · · · O contact distances, the O(4) · · ·

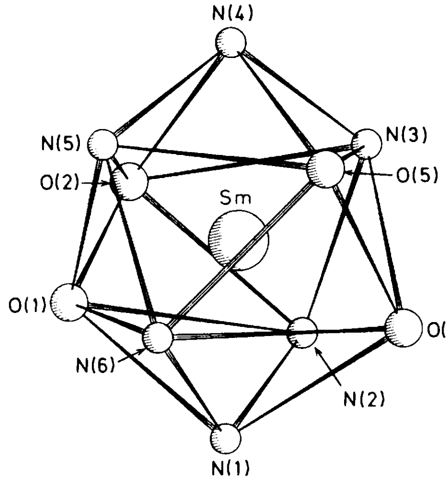


Figure 2. Co-ordination polyhedron around Sm^{3+}

Table 2. Bond distances (Å) and angles (°)

(*a*) Distances

(*i*) Metal co-ordination sphere

Sm–N(1)	2.66(1)	Sm–O(1)	2.51(1)
Sm–N(2)	2.64(1)	Sm–O(2)	2.52(1)
Sm–N(3)	2.62(1)	Sm–O(4)	2.52(1)
Sm–N(4)	2.65(1)	Sm–O(5)	2.46(1)
Sm–N(5)	2.62(1)		
Sm–N(6)	2.60(1)		

(*ii*) Nitrates

N(7)–O(1)	1.28(2)	N(8)–O(6)	1.19(3)
N(7)–O(2)	1.27(2)	N(8)–O(7)	1.22(2)
N(7)–O(3)	1.22(2)	N(8)–O(8)	1.23(2)

(*b*) Angles

(*i*) Metal co-ordination sphere

O(1)–Sm–O(2)	50.6(4)	N(4)–Sm–O(2)	69.1(3)
O(4)–Sm–O(5)	68.5(4)	N(4)–Sm–O(5)	69.6(3)
N(2)–Sm–N(3)	62.5(5)	N(4)–Sm–N(3)	61.1(4)
N(5)–Sm–N(6)	63.2(5)	N(4)–Sm–N(5)	60.4(5)
N(1)–Sm–O(1)	66.1(3)	O(1)–Sm–N(5)	73.3(3)
N(1)–Sm–O(4)	66.6(3)	O(5)–Sm–N(6)	77.6(3)
N(1)–Sm–N(2)	60.4(5)	O(4)–Sm–N(3)	76.4(3)
N(1)–Sm–N(6)	61.4(5)	O(2)–Sm–N(2)	73.0(3)

(*ii*) Nitrates

O(1)–N(7)–O(2)	115(1)	O(6)–N(8)–O(7)	123(2)
O(1)–N(7)–O(3)	121(1)	O(6)–N(8)–O(8)	117(2)
O(2)–N(7)–O(3)	123(1)	O(7)–N(8)–O(8)	119(2)

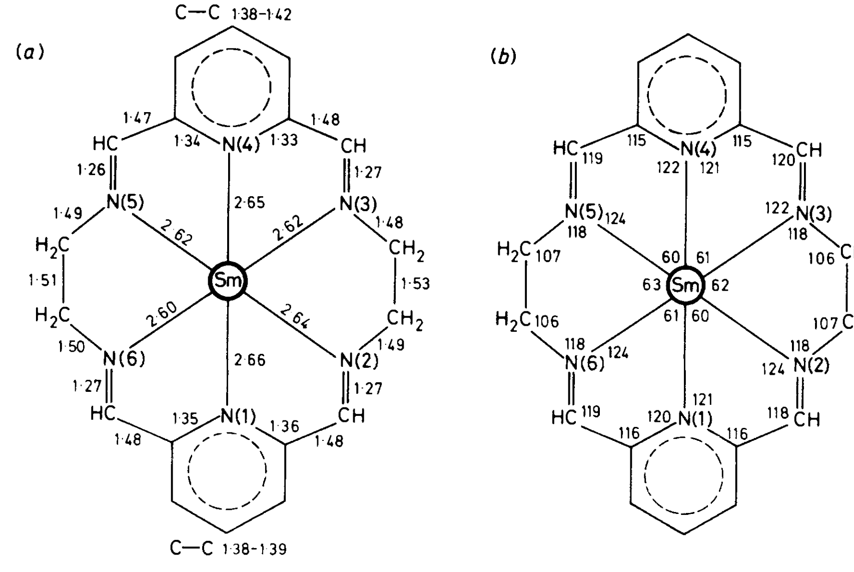


Figure 3. (*a*) Bond lengths (Å) and (*b*) bond angles (°) in the bonded ligand (angles in the ' pyridine ' rings have normal values)

O(5) distance of 2.80 Å between the hydroxo and water oxygen atoms and the O(5) ··· O distances to the non-co-ordinated nitrate ion could be reasonably ascribed to hydrogen bonding.

From the results of the structure determination it is apparent that during recrystallization of the bulk sample which, unless dried efficiently, must contain trapped methanol there is a modification of the macrocycle so that the tetra-imino-form, L^3, is recovered. It is possible that whereas for the lighter, and larger radius lanthanides this is the preferred product on a cavity-fit basis, for the heavier, and smaller radius lanthanides the ligand readily adds water to gain flexibility to enable complexation to occur. Such addition of solvent molecules (H_2O or ROH) is known to occur in order to release strain in macrocyclic ligands and so to produce a more flexible species.[12] The condensation of primary amines with carbonyl groups is presumed to proceed *via* carbinolamine intermediates [13] and a second possibility therefore is that the bulk samarium(III) product isolated is a complex of the carbinolamine precursor of the tetraimine macrocycle.

There is also a hydrolysis of $Sm(NO_3)_3$ to $Sm(OH)(NO_3)_2$. If on dissolution in water a dissociation of the complex occurs to give free ligand and aquated Sm^{3+}, then it is plausible that the reaction sequence (1) and (2) occurs.[14]

$$SmL(NO_3)_3 \xrightarrow{H_2O} [Sm(H_2O)_n]^{3+} + L + 3NO_3^- \quad (1)$$

$$[Sm(H_2O)_n]^{3+} \rightleftharpoons [Sm(OH)(H_2O)_{n-1}]^{2+} + H_3O^+ \quad (2)$$

It is not obvious why the $[Sm(OH)(NO_3)(H_2O)]^{2+}$ unit should be stabilized by the macrocycle.

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