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Note

The synthesis and crystal structure of a cerium(III) complex of 2,6-bis[2-formylphenoxymethyl]pyridine

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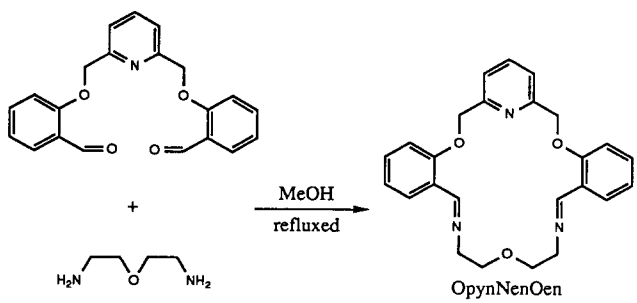
Abstract

The synthesis and X-ray crystal structure of a ten-coordinate cerium(III) nitrate complex of 2,6-bis[2-formylphenoxymethyl]-pyridine is reported.

Keywords: Crystal structures; Cerium complexes; Macrocyclic ligand complexes

1. Introduction

Eighteen-membered pyridinyl-derived N_3O_3-Schiff base macrocycles have been prepared by lanthanide-templated cyclocondensation reactions [1]. The synthesis of the 20-membered macrocycle OpynNenOen, derived from bis(2-aminoethyl)ether and 2,6-bis[2-formylphenoxymethyl]pyridine (Opyn), has been achieved both by non-template (Scheme 1) and templated reactions involving barium and lead(II) [2]. In contrast the application of template methodology to this reaction using hydrated lanthanide nitrates in methanol was found to be unsuccessful in promoting the cyclocondensation and generally yielded intractable materials. This may be related to the smaller radius of the cerium cation (1.39 Å) compared with the radii of lead(II) (1.54 Å) and barium (1.66 Å) [3].



Scheme 1.

2. Results and discussion

The reaction of cerium(III) nitrate with the macrocycle OpynNenOen in a 1:1 ratio in methanol yielded a crystalline product. There was an absence of bands characteristic of imine groups from the starting material in the IR spectrum of this product (4000–600 cm^{-1}; KBr disc) but strong absorptions at 1659 and 1655 cm^{-1}, indicating the presence of carbonyl groups, were present. In addition there are bands at 3445, 1639 and 834 cm^{-1} suggestive of water molecules coordinated to the metal. The FAB mass spectrum of the complex gave a parent peak at 611 a.m.u. corresponding to $[Ce(Opyn)(NO_3)_2]^+$ with a further peak at 348 a.m.u. corresponding to $[(Opyn)H]^+$, reinforcing the suggestion of an acyclic ligand. The above information together with microanalytical data led to the formulation of the product as $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$ which had been formed by a retro-Schiff base reaction, the water being provided either from the solvent methanol or from the hydrated cerium salt, with accompanying cerium(III) complexation (Scheme 2). The ^1H NMR spectra for

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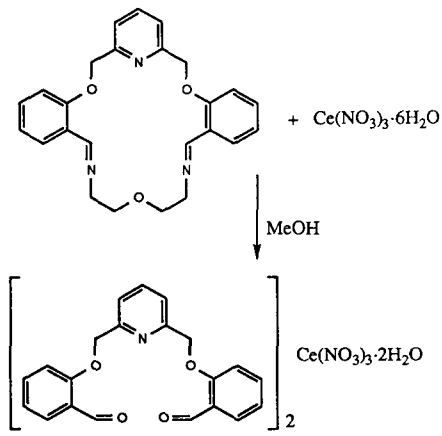
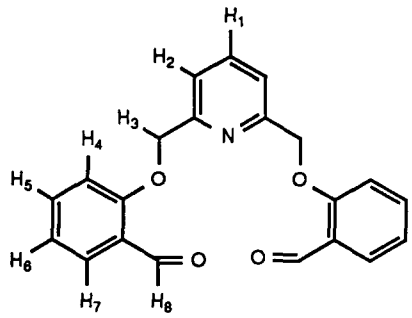


Scheme 2.

Table 1
^{1}H NMR data (ppm) for the ligand (Opyn) and the complex $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$



	Ligand signal	Complex signal
H_1	7.81m, 3H	7.93t, 1H
H_2	7.81	7.79d, 2H
H_3	5.34s, 4H	5.37s, 4H
H_4	7.21d, 2H	7.22d, 2H
H_6	7.08t, 2H	7.10t, 2H
H_5	7.60m, 4H	7.62m, 4H
H_7	7.60	7.62
H_8	10.55s, 2H	10.52s, 2H

the free ligand (Opyn) and the complex $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$ are very similar (Table 1) suggesting that the two-fold symmetry of the ligand is retained in solution.

The acyclic nature of the complex was confirmed by X-ray structure analysis. The molecular structure is illustrated in Fig. 1 with bonds and angles presented in Table 2. The cerium is ten-coordinated, the bonding being provided by oxygen atoms from three symmetrically bidentate nitrate anions together with two oxygen atoms from the water molecules and one carbonyl oxygen from each Opyn ligand. The second carbonyl oxygen atom in each ligand molecule is not coordinated. All the bond lengths were significantly shorter than the sum of the van der Waals radius of oxygen and ten-

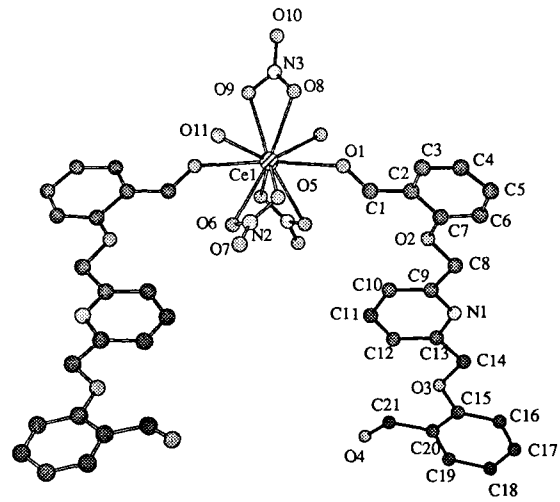


Fig. 1. The crystal structure of $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$ showing one component of the disordered nitrate.

coordinate Ce(III) (2.790 Å). Although structurally characterized ten-coordinate lanthanide complexes are well known, structural information for tri(bidentate nitrato)lanthanide complexes with an additional four monodentate oxygen ligands is limited [4]. In the structures of $Ln(NO_3)_3 \cdot 4dmso$ the average Ln–O distances to the dmso are shorter than those to the nitrate anions, La (2.475 versus 2.653 Å) and Nd (2.385 versus 2.661 Å) [5]. In $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$ the bond lengths for $Ce–O_{carbonyl}$ are longer (2.614(9) Å) than those for $Ce–O_{water}$ and $Ce–O_{NO_3}$ for which the average value is 2.538(10) Å.

The coordinated water molecules are involved in hydrogen bonding with a pyridyl nitrogen, and with the non-coordinated benzaldehyde oxygen atoms of different symmetry related molecules O(11)...N(1)[a] 2.856 Å, O(11)...O(4)[b] 2.832 Å; with symmetry operations: [a] $x, -y, 0.5+z$; [b] $0.5+x, -0.5-y, 0.5+z$). Inversion related pairs of N...O hydrogen bonds link molecules in chains parallel to the crystallographic c-axis: inversion related pairs of O...O hydrogen bonds cross-link these chains to form a three-dimensional network.

3. Experimental

3.1. Reaction of OpynNenOen with cerium(III) nitrate

A solution of OpynNenOen [2] (1 mmol) and cerium(III) nitrate (1 mmol) in methanol (100 cm^3) was refluxed for ~2 h then allowed to cool to room temperature. It was left to stand undisturbed in order to slowly remove the solvent. The product was recrystallized from acetonitrile to give crystals suitable for X-ray analysis. The crystalline product, $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$, was isolated in 19% yield. *Anal.* Found: C, 47.93; H, 3.54; N, 6.64. Calc. for

Table 2
Selected bond lengths (Å) and angles (°) for $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$

Bond lengths			
Ce(1)–O(1)	2.614(9)	Ce(1)–O(5)	2.547(10)
Ce(1)–O(6)	2.577(10)	Ce(1)–O(11)	2.534(8)
Ce(1)–O(8)	2.512(10)	Ce(1)–O(9)	2.520(10)
O(11)...N(1) [a]	2.856	H(O11B)...N(1) [a]	1.853
O(11)...O(4) [b]	2.832	H(O11A)...(O4) [b]	1.832
Bond angles			
O(1)–Ce(1)–O(5)	63.1(3)	O(1)–Ce(1)–O(6)	103.6(3)
O(5)–Ce(1)–O(6)	48.5(3)	O(1)–Ce(1)–O(11)	112.8(3)
O(5)–Ce(1)–O(11)	68.9(3)	O(6)–Ce(1)–O(11)	72.7(3)
O(1)–Ce(1)–O(8)	70.9(4)	O(5)–Ce(1)–O(8)	92.9(4)
O(6)–Ce(1)–O(8)	132.9(3)	O(11)–Ce(1)–O(8)	67.7(3)
O(1)–Ce(1)–O(9)	116.1(4)	O(5)–Ce(1)–O(9)	130.1(3)
O(6)–Ce(1)–O(9)	131.5(4)	O(11)–Ce(1)–O(9)	67.0(3)
O(8)–Ce(1)–O(9)	49.2(2)	O(1)–Ce(1)–O(1A)	173.3(4)
O(5)–Ce(1)–O(1A)	113.6(3)	O(6)–Ce(1)–O(1A)	70.9(3)
O(11)–Ce(1)–O(1A)	69.6(3)	O(8)–Ce(1)–O(1A)	115.5(4)
O(9)–Ce(1)–O(1A)	70.6(4)	O(1)–Ce(1)–O(5A)	113.6(3)
O(5)–Ce(1)–O(5A)	125.4(5)	O(6)–Ce(1)–O(5A)	86.2(3)
O(11)–Ce(1)–O(5A)	132.3(3)	O(8)–Ce(1)–O(5A)	139.9(3)
O(9)–Ce(1)–O(5A)	101.4(4)	O(5)–Ce(1)–O(6A)	86.2(3)
O(1)–Ce(1)–O(6A)	70.9(3)	O(11)–Ce(1)–O(6A)	147.0(3)
O(6)–Ce(1)–O(6A)	74.6(5)	O(9)–Ce(1)–O(6A)	143.1(3)
O(8)–Ce(1)–O(6A)	137.4(4)	O(5)–Ce(1)–O(11A)	132.3(3)
O(1)–Ce(1)–O(11A)	69.6(3)	O(11)–Ce(1)–O(11A)	140.2(5)
O(6)–Ce(1)–O(11A)	147.0(3)	O(9)–Ce(1)–O(11A)	76.4(3)
O(8)–Ce(1)–O(11A)	76.9(3)	Ce(1)–O(1)–C(1)	127.6(8)

Symmetry related atoms by the following operations: [a] $x, -y, 0.5+z$; [b] $0.5+x, -0.5-y, 0.5+z$.

$C_{42}H_{34}N_5O_{17}Ce \cdot 2H_2O$: C, 47.73; H, 3.62; N, 6.63%. The ^1H NMR spectral data (250 MHz; CD_3CN) for the complex $[Ce(Opyn)_2](NO_3)_3 \cdot 2H_2O$ together with that of the free Opyn ligand are shown in Table 1.

3.2. Crystal structure

Crystal data for $Ce(C_{21}H_{17}NO_4)_2(NO_3)_3 \cdot 2H_2O$: $M = 1056.85$, crystallized from acetonitrile as clear prisms, crystal dimensions $0.40 \times 0.32 \times 0.18$ mm; monoclinic, $a = 20.708(8)$, $b = 9.212(5)$, $c = 22.722(9)$ Å, $\beta = 103.81(3)°$, $U = 4209(3)$ Å^3, $Z = 4$, $D_c = 1.67$ g cm^{-3}, space group $C2/c$ (C_{2h}^6, No. 15), Mo Kα radiation ($\lambda = 0.71069$ Å), μ (Mo Kα) = 11.82 cm^{-1}, $F(000) = 2140$.

Three dimensional, room temperature X-ray data were collected in the range $3.5 < 2\theta < 50.0°$ on a Nicolet R3 diffractometer by the ω-scan method. The 2470 independent reflections (of 4107 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarization effects, and for absorption by analysis of nine azimuthal scans (minimum and maximum transmission coefficients of 0.427 and 0.509). The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least-squares methods. One nitrate was found to be disordered across the C_2 axis, and the anion was modelled with 50% occupancies for nitrogen and three oxygens. Hydrogen atoms were included in calculated positions, or along intermolecular hydrogen bonds, and refined in riding mode. Refinement converged at a final $R = 0.0898$ ($R_w = 0.0794$, 295 parameters, mean and maximum δ/σ 0.003, 0.015), with allowance for the thermal anisotropy of all non-hydrogen atoms, with the exception of the atoms of the half occupancy nitrate. Minimum and maximum final electron density: -2.58 and $+2.92$ e Å^{-3} close to the cerium atom. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.00050F^2]$ was used in the latter stages of refinement. Complex scattering factors were taken from Ref. [6] and from the program package SHELXTL [7] as implemented on a Data General DG30 computer.

4. Supplementary material

Tables of bond lengths and angles, anisotropic thermal vibrational parameters and atomic coordinates, all with e.s.d.s, hydrogen atom position parameters, observed structure amplitudes and calculated structure factors are available from the authors on request.

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