

Trinitrato [*N,N,N'*-tris(2,3-dimethoxybenzamido)triethylamine]-neodymium(III). Synthesis, crystal structure and luminescence of a Nd complex containing tripodal amide ligands

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A neodymium complex containing tripodal amide ligands has been synthesised and X-ray analysis has revealed the polymeric nature of the complex in the solid state.

Lanthanide(III) cations have found wide application as potential luminescent biomedical diagnostic and therapeutic agents (Eu, Tb),¹ contrast agents for magnetic resonance imaging (Gd),² catalysts in RNA hydrolysis³ and in fluorescence imaging.⁴ The application of lanthanide complexes depends on both the metal ion and type of ligand. The luminescence properties of Nd³⁺ complexes have been intensively investigated as they offer opportunities to develop new materials suitable for optical amplifiers operating at 1.3 μm .⁵ This window is important for telecommunications systems. It has been shown that effective sensitization of the Nd³⁺ emission can be achieved by incorporation of organic ligands like deuterated hexafluoroacetylacetonate anion,⁶ fluorescein-bearing calix[4]arene cages,⁷ and phenolic cryptand.⁸ In this context, we were interested in using multidentate tripodal ligands containing the amide functionality to complex with Nd³⁺ and investigate their luminescence behaviour.

The reaction of hydrated neodymium nitrate with *N,N,N'*-tris(2,3-dimethoxybenzamido)triethylamine,⁹ **L**, in a 1 : 1, ratio in acetonitrile afforded complex **1** in satisfactory yield. Single crystals of **1** suitable for X-ray analysis were obtained from the slow evaporation of an acetonitrile solution at room temperature for a few days. The coordination geometry of the metal centre in **1** can be described as a tri-capped trigonal prism and its perspective drawing, together with some selected bond parameters, is shown in Fig. 1. This analysis also revealed the polymeric nature of **1** in the solid state. Each Nd³⁺ is coordinated by three amide carbonyl groups from three different tripodal ligands and doubly coordinated to three nitrate ions. This coordination leads to considerable weakening of the C–O bond strength (ν_{CO} , 1599 cm^{-1}) as evident from the solid state (KBr disc) IR spectroscopic measurement. The central amino N atom of the tripod ligand is found to coincide with the crystallographic three-fold rotation symmetry axis. This novel structural arrangement has never before been observed for lanthanide complexes with tripodal ligands. Normally, all three arms tend to wrap around a single metal centre to give a thermodynamically favourable product.¹⁰ This salient observation may be attributed to the acetonitrile solvent molecule that is situated on the three-fold crystallographic axis in such a way as to interact with all three NH groups of the tripodal ligand.

The photophysical properties of complex **1** have been studied at low (10 K) and room (290 K) temperature; the photoluminescence spectrum is shown in Fig. 2. Nd³⁺ ions were

excited by means of an argon laser with the 512 nm line and recorded on a double grating monochromator with a cooled photomultiplier tube. Complex **1** shows structured emission peaks at 880, 1060 and 1350 nm, which are assigned as $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$ and $^4\text{I}_{13/2}$, respectively. The narrow structure is rather similar to that observed for the luminescence of Nd : YAG. Further investigations into this type of polymeric lanthanide-based materials are in progress.

Experimental

Synthesis

Nd(NO₃)₃ · 6H₂O (47 mmol) and *N,N,N'*-tris(2,3-dimethoxybenzamido)triethylamine (47 mmol) were dissolved in acetonitrile (25 ml). The mixture was allowed to reflux for 2 days and the product of 1 : 1 metal-to-ligand ratio as evidenced from elemental analysis was obtained. (Yield 30%). Crystals were obtained by slow evaporation of an acetonitrile solution. Anal. **1**: Found: C, 41.8; H, 4.8; N, 11.4. Calc for C₃₅H₄₅N₈O₁₈Nd: C, 41.6; H, 4.5; N, 11.1%. IR (KBr, cm^{-1}):

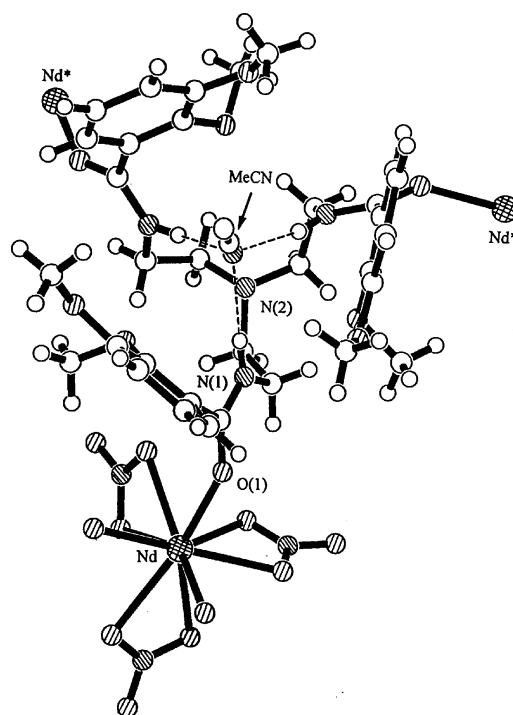


Fig. 1 Perspective view of complex **1** in the solid state. Selected bond lengths (Å): Nd–O(1) 2.40(1), Nd...Nd* 10.991(1).

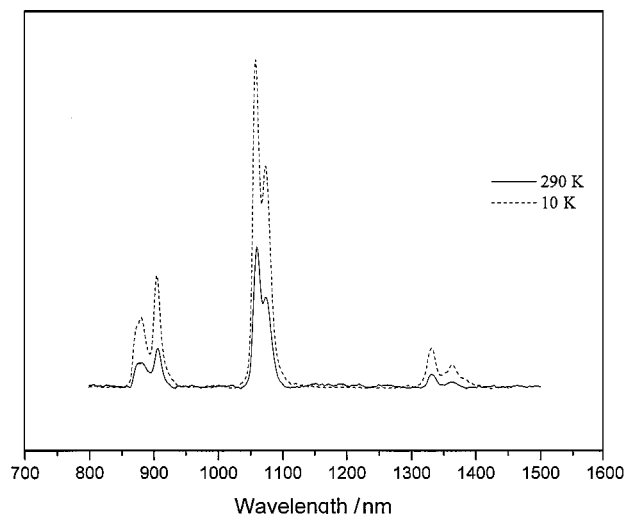


Fig. 2 Photoluminescence spectra of complex **1** at 10 K (---) and 290 K (—) in the solid state.

3358, 1599, 1576, 1475, 1458, 1385, 1304, 1265, 1070, 995, 752. FAB MS: m/z 907 $[M - NO_3]^+$, 844 $[M - 2 NO_3]^+$, 781 $[M - 3 NO_3]^+$.

Crystallography

Single crystals of complex **1** suitable for X-ray crystallographic studies were mounted in glass capillaries. Diffraction data were collected at room temperature on a Bruker AXS SMART CCD diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). Crystal data for $C_{35}H_{45}N_8O_{18}Nd$, **1**: $M = 1010.02$, primitive trigonal, $a = 10.993(1)$, $c = 21.554(2)$ Å, $U = 2255.7(3)$ Å³, $T = 298$ K, space group $P3c1$ (no. 158), $Z = 2$, $\mu(\text{Mo-K}\alpha) = 12.29$ cm⁻¹, 6553 reflections measured, 1965 unique ($R_{\text{int}} = 0.056$), 1158 observed reflections [$I > 1.5\sigma(I)$] were used in all calculations. The structure was solved by direct methods (SIR92) and expanded using Fourier techniques, it was refined by full-matrix least-squares analysis on F to $R = 0.042$, $R_w = 0.044$

and a goodness-of-fit 1.24. The absolute configuration of the structure has been determined by refining the Flack parameter [0.007(1)].

CCDC reference number 440/228. See <http://www.rsc.org/suppdata/nj/b0/b006976k/> for crystallographic files in .cif format.

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