NJC
Letter

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

Winnie Po-Wan Lai[a] **and Wing-Tak Wong***[a,b]

[a] *Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China. E-mail: wtwong@hkucc.hku.hk; Fax +852 2547 2933*
[b] *PKU-HKU Joint Laboratory on Rare Earth Materials and Bioinorganic Chemistry, Peking University, Beijing, 100871, P. R. China*

Received (in Montpellier, France) 28th August 2000, Accepted 4th October 2000
First published as an Advance Article on the web 15th November 2000

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 hydrolysis[3] and in fluorescence imaging.[4] The application of lanthanide complexes depends on both the metal ion and type of ligand. The luminescence properties of Nd^{3+} 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 Nd^{3+} 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 Nd^{3+} 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 Nd^{3+} 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. Nd^{3+} 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 $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$, 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

$Nd(NO_3)_3 \cdot 6H_2O$ (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 $C_{35}H_{45}N_8O_{18}Nd$: C, 41.6; H, 4.5; N, 11.1%. IR (KBr, cm^{-1}):

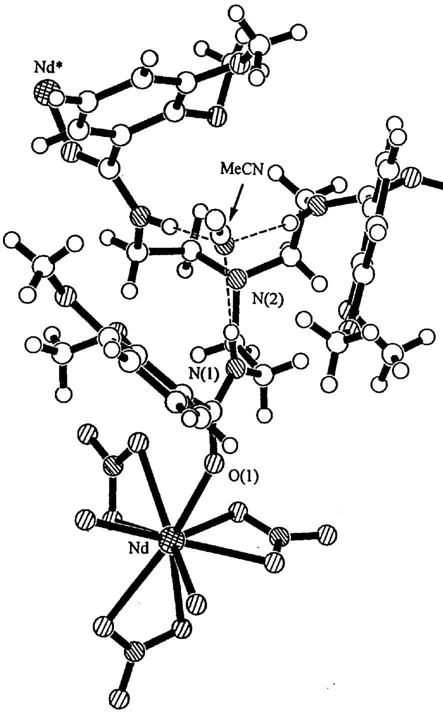

Fig. 1 Perspective view of complex **1** in the solid state. Selected bond lengths (Å): Nd–O(1) 2.40(1), Nd···Nd* 10.991(1).

DOI: 10.1039/b006976k

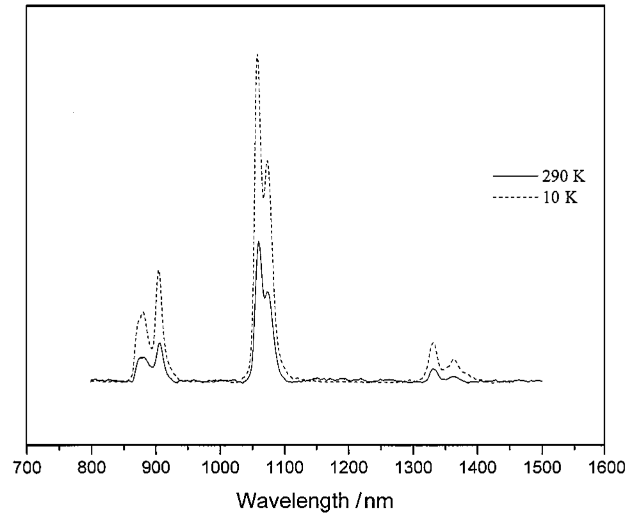

Fig. 2 Photoluminescence spectra of complex **1** at 10 K (– – –) and 290 K (——) in the solid state.

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-Kα 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, $U = 2255.7(3)$ Å^3, $T = 298$ K, space group $P3c1$ (no. 158), $Z = 2$, μ(Mo-Kα) = 12.29 cm^{-1}, 6553 reflections measured, 1965 unique ($R_{int} = 0.056$), 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.

Acknowledgements

We gratefully acknowledge financial support from the Hong Kong Research Grants Council and the University of Hong Kong. W. P.-W. L. acknowledges the receipt of a postgraduate studentship administered by the University of Hong Kong.

Notes and references

1 L. Thunus and R. Lejeune, *Coord. Chem. Rev.*, 1999, **184**, 125.

2 C. F. G. C. Geraldes, A. D. Sherry, E. Lazar, A. Miseta, P. Boguer, E. Berenyi, B. Sumegi, G. E. Kiefer, K. McMillan, F. Maton and R. N. Muller, *Magn. Reson. Med.*, 1993, **30**, 696; V. Alexander, *Chem. Rev.*, 1995, **95**, 273; M. Botta, *Eur. J. Inorg. Chem.*, 2000, 399.

3 T. Bruice, A. Tsubouchi, R. Dempey and L. Olson, *J. Am. Chem. Soc.*, 1996, **118**, 9867.

4 I. Hemmila, *Applications of Fluorescence in Immunoassays*, Wiley, New York, 1991.

5 R. J. Mears and S. R. Bater, *Opt. Quantum Electron*, 1992, **24**, 517; A. Beeloy and S. Faulkner, *Chem. Phys. Lett.*, 1997, **266**, 116; M. H. V. Werbs, J. W. Hofsbraat, F. A. J. Geurts and J. W. Verhoeven, *Chem. Phys. Lett.*, 1997, **276**, 196; M. P. O. Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruël, J. W. Hofsbraat, F. A. J. Geurts and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2141; S. Yangida, Y. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima and T. Yamanaka, *Coord. Chem. Rev.*, 1998, **171**, 461; Y. Wada, T. Okubo, M. Ryo, T. Nalcazawa and S. Yanagida, *J. Am. Chem. Soc.*, 2000, **122**, 8583.

6 Y. Hasegawa, K. Murakoshi, Y. Wada, S. Yanagida, J.-H. Kim, N. Nakashima and T. Yamanaka, *Chem. Phys. Lett.*, 1996, **248**, 8.

7 M. P. O. Wolbers, F. C. J. M. van Veggel, F. G. A. Peters, E. S. E. van Beelen, J. W. Hofstraat, F. A. J. Geurts and D. N. Reinhoudt, *Chem. Eur. J.*, 1998, **4**, 772.

8 C. Platas, F. Avecilla, A. de Blas, T. Rodriguez-Blas, C. F. G. C. Geraldes, E. Toth, A. E. Merbach and J.-C. G. Bunzli, *J. Chem. Soc., Dalton Trans.*, 2000, 611.

9 S. J. Rodgers, C. W. Lee, C. Y. Ng and K. N. Raymond, *Inorg. Chem.*, 1987, **26**, 1622.

10 P. Caravan, T. Hedlund, S. Liu, S. Sjoberg and C. Orvig, *J. Am. Chem. Soc.*, 1995, **117**, 11230; C. D. Sun and W. T. Wong, *Inorg. Chim. Acta*, 1997, **255**, 355; C. Y. Su, B. S. Kang, Q. C. Yang and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 2000, 1857.