The First Crystal and Molecular Structure of Lanthanide Homodinuclear Macrocyclic Complexes showing Metal–Metal Pair Interactions.

Ishenkumba A. Kahwa,*[a] Susan Folkes,[a] David J. Williams,[b] Steven V. Ley,[b] Caroline A. O'Mahoney,[b] and Gary L. McPherson[c]

[a] *Chemistry Department, University of the West Indies, Mona, Kingston 7, Jamaica*
[b] *Chemistry Department, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.*
[c] *Chemistry Department, Tulane University, New Orleans, Louisiana 70118, U.S.A.*

Template condensation of 2,6-diformyl-*p*-cresol with 3,6-dioxa-1,8-octanediamine in the presence of lanthanide nitrates, yields homodinuclear macrocyclic complexes; solution of the structure of the gadolinium complex confirms encapsulation of a lanthanide cation pair in the macrocycle and luminescence of Eu^{3+} indicates Eu–Eu interactions.

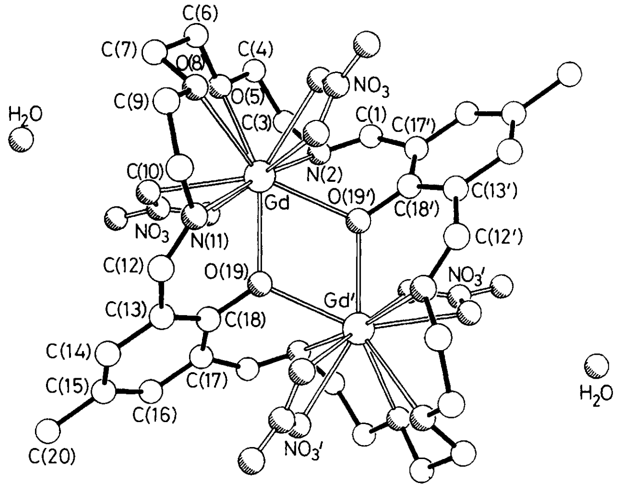


Figure 1. The molecular structure of $Gd_2(\mathbf{3})\cdot(NO_3)_4\cdot H_2O$. Macrocyclic torsion angles (°): O(19′)–C(18′)–C(17′)–C(1) 8, C(18′)–C(17′)–C(1)–N(2) 4, C(17′)–C(1)–N(2)–C(3) 162, C(1)–N(2)–C(3)–C(4) −93, N(2)–C(3)–C(4)–O(5) −55, C(3)–C(4)–O(5)–C(6) 167, C(4)–O(5)–C(6)–C(7) 179, O(5)–C(6)–C(7)–O(8) 61, C(6)–C(7)–O(8)–C(9) 177, C(7)–O(8)–C(9)–C(10) 155, O(8)–C(9)–C(10)–N(11) −46, C(9)–C(10)–N(11)–C(12) −117, C(10)–N(11)–C(12)–C(13) 169, N(11)–C(12)–C(13)–C(18) 17, C(12)–C(13)–C(18)–O(19) 9 (av. e.s.d. 2^0).

Synthesis and characterization of lanthanide (Ln) homodinuclear macrocyclic complexes is important for developing clear ideas about the nature and applications of lanthanide metal-metal interactions[1,2] in lasers,[3,4] phosphors[5—7] and characterization of complex biomolecules.[8,9] Lanthanide cross-relaxation processes[4,10,11] lead to energy up-conversion in lasers, efficient sensitized phosphors and determination of biomolecular metal-metal distances,[12] the depth of the active site from protein surfaces[13—15] and its local co-ordination symmetry.[8] Extractive metallurgy and n.m.r. tomography in which Gd^{3+} is a useful contrast enhancer,[16] should benefit from simultaneous scavenging or delivery of several lanthanide ions by a single chelate. The possibility that special imaging effects in n.m.r. tomography might be produced by tuning Ln–Ln or Ln–Ln′ electronic interactions with suitable polynucleating chelates is particularly exciting.

We have been synthesizing and studying the electronic properties of lanthanide homodinuclear macrocyclic complexes in order to determine the co-ordination characteristics essential for producing Ln–Ln and Ln–Ln′ coupling. We recently reported the syntheses,[17] hydrolytic,[18] magnetic and luminescence characteristics[19] of such complexes for a compartmental Schiff base ligand (**1**) which expressed recognition and high selectivity for a pair of lanthanide(III) cations. However, firm structural evidence for the dinuclearity of lanthanide complexes of chelating ligands (**1**) and (**2**)[20] and others[21,22] is lacking, although it is essential for understanding the nature of the metal-metal antiferromagnetic coupling and

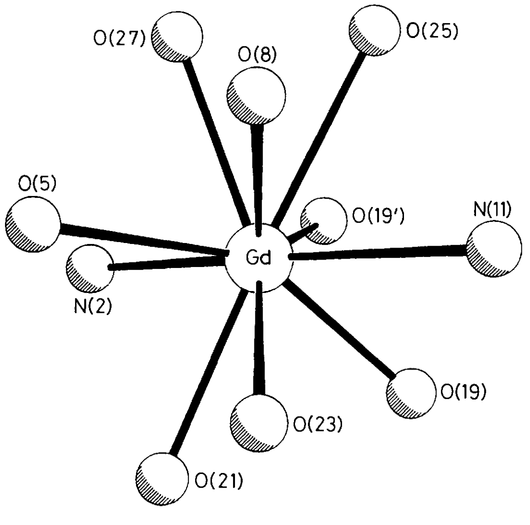


Figure 2. The co-ordination around each Gd atom. Bond lengths (Å): Gd–N(2) 2.46, Gd–O(5) 2.57, Gd–O(8) 2.68, Gd–N(11) 2.70, Gd–O(19) 2.34, Gd–O(21) 2.47, Gd–O(23) 2.52, Gd–O(25) 2.67, Gd–O(27) 2.51, Gd–O(19') 2.39 (av. e.s.d. 0.02 Å).

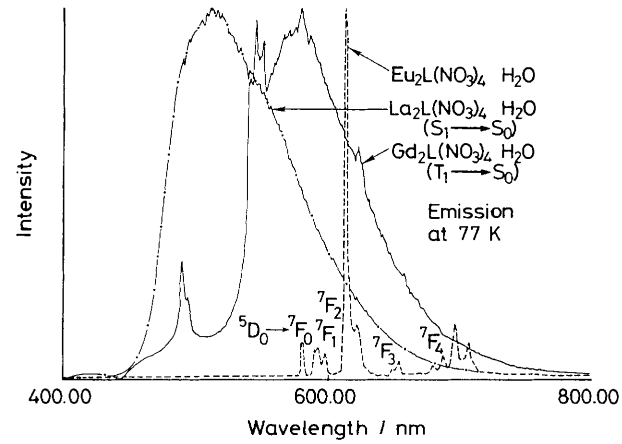
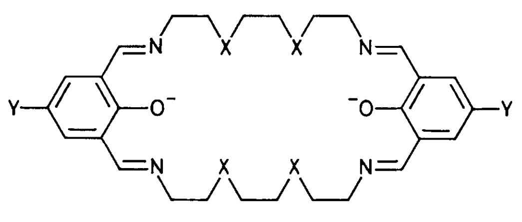


Figure 3. The 77 K luminescence spectra of complexes of L = (**3**) when excited at 370 nm. Sharp peaks of the Tb^{3+} impurity in 99.9% gadolinium nitrate are superimposed on the spectrum of the gadolinium complex. At Tb^{3+} levels higher than 1%, only strong Tb^{3+} luminescence is observed.



(**1**) X = NH, Y = Me
(**2**) X = O, Y = Cl
(**3**) X = O, Y = Me

energy transfer which we observed.[18] We have now solved the crystal structure of homodinuclear macrocyclic complexes of macrocycle (**3**) in which a Gd–Gd pair is indeed found within the macrocycle (Figure 1). Metal–metal interactions are expressed in a characteristic short decay time of the $^5D_0$ state of Eu–Eu pairs[18] (Figure 3).

The complexes $Ln_2\cdot(\mathbf{3})(NO_3)_4\cdot H_2O$ were prepared in 70—100% yield by a template procedure,[17] the yield dropping with decreasing cation size from La^{3+}—Tb^{3+}. The volume of methanol was 200 ml per mmol of Ln^{3+} and reactants were maintained at 50—60 °C without stirring.

The *X*-ray analysis† (Figure 1) shows the complex to have a propeller conformation with approximate non-crystallographic D_2 symmetry, there being a crystallographic 2-fold axis passing through the centre, and normal to the mean plane, of the macrocycle. Both gadolinium atoms lie within the macrocycle and are bridged by the two phenolate oxygen atoms. Each gadolinium atom is ten co-ordinate, being bound to two nitrogen and two oxygen atoms of the macrocycle, four nitrate oxygens and two phenolate oxygen atoms (Figure 2). The co-ordination geometry is a distorted bi-capped dodecahedral with N(11), O(19), O(21), O(23), N(2), O(19'), O(25), and O(27) forming the vertices with capping by O(5) and O(8). The Gd–X co-ordination distances are in the range 2.34—2.69 Å, the shortest contacts being to the phenolate oxygens. The Gd_2O_2 ring is slightly folded (by 9°) about the O(19)–O(19') direction. The Gd–Gd' and O(19)–O(19') distances are 3.97 and 2.55 Å respectively; this Gd–Gd' distance is comparable to that found in other complexes containing Ln_2O_2 rings.[28] The phenyl rings are rotated by *ca.* 60° in opposite senses out of the Gd_2O_2 plane. The two partial occupancy included water molecules are not co-ordinated to either gadolinium atom but lie within hydrogen bonding distance (3.00 Å) of nitrate oxygen atoms.

The ^{13}C cross polarisation magic angle spinning (CPMAS) n.m.r. spectra of the ligand in diamagnetic $La_2\cdot(\mathbf{3})(NO_3)_4\cdot H_2O$ is simple showing peaks at δ 19.01 (Me), 60.21 (=N–CH_2), 70.76 (–OCH_2), a triplet at 125.76, 126.50 and 127.27 (non-phenolic aromatic quaternary), 140.25 (aromatic non-quatenary), 158.22 (phenolic), and 168.80 (imine). The spectrum of the complex $La_2\cdot(\mathbf{1})(NO_3)_4$ contained broad peaks due to the nitrogen nuclear quadrupole moment and features a doublet at δ 19.54 and 21.35 (Me), 51.69 (CH_2NHCH_2), 62.54 (=NCH_2), 127.42 (non-phenolic aromatic quatenary), 138.65 (aromatic non-quatenary), 158.24 (phenolic), and 167.38 (imine). The spectrum of the orange complex $La_2\cdot(\mathbf{1})(NO_3)_2(OH)_2$ is similar but the peaks are broader. Whereas the splittings in the spectra are probably due to differences in the ligand conformations, the close similarities in chemical shifts indicate that ligands (**1**) and (**3**)[17—19,29] co-ordinate to lanthanum in the same way. The spectra of the paramagnetic complexes are complicated and are being studied in detail because of their important implications to the use of Gd^{3+} as a contrast enhancement agent; modulation of the electronic properties of the lanthanide ions could produce special imaging effects important to n.m.r. tomography.

The complexes $Ln_2\cdot(\mathbf{3})(NO_3)_4$ exhibit either ligand fluorescence for Ln = La, or phosphoresence for Ln = Gd (1200 μs)

---

† *Crystal data* for: $Gd_2C_{30}H_{38}N_4O_6(NO_3)_4\cdot H_2O$, monoclinic, space group *C*2, $a = 17.396(5)$, $b = 11.554(3)$, $c = 11.814(4)$ Å, $\beta = 117.73(2)°$, $U = 2102$ Å^3, $Z = 2$ (the molecule is disposed about a 2-fold axis), $M = 1130.2$, $D_c = 1.79$ g cm^{-3}, $\mu(\text{Cu-}K_\alpha) = 221$ cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite-monochromated Cu-K_α radiation using ω-scans. The structure was solved by the heavy-atom method and refined anisotropically[32] using absorption corrected data to give $R = 0.068$, $R_w = 0.066$ for 1354 independent observed relections [$|F_0| > 3\sigma(|F_0|)$, $\theta < 58°$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

and ligand sensitized Ln^{3+} luminescence for Ln = Eu (300 μs) and Ln = Tb (Figure 3). Europium(III) luminescence originates from the $^5D_0$ state to the ^7F_J Stark levels;[30,31] the short luminescence lifetime of the $^5D_0$ state is typical for Eu–Eu pairs.[18] Terbium luminescence originates from the $^5D_4$ state to ^7F_J Stark levels and is efficiently sensitized by the blue shoulder of the ligand triplet state (Figure 3).

The short Gd–O (phenolate) and C–O (phenolate) bonds reflect covalency in the Ln–phenolate bond[19] which may facilitate a super-exchange Ln–Ln interaction in the lanthanide pairs. Detailed work on the Ln–Ln interactions is in progress.

We thank the U.W.I. Postgraduate and Research Publications Committee and The British Council for financial support, Dr. C. Groombridge (Royal Holloway) for help with the CPMAS n.m.r. experiments and Texaco Chemical Co. for a gift of 3,6-dioxa-1,8-octanediamine.

Received, 14th April 1989; Com. 9/01542F

References

1 S. H. Schugar, E. I. Solomon, W. L. Cleveland, and L. Goodman, *J. Am. Chem. Soc.*, 1975, **97**, 6442.
2 F. Varsanyi and G. H. Dieke, *Phys. Rev. Lett.*, 1961, **7**, 442.
3 L. F. Johnson and H. J. Guggeinheim, *Appl. Phys. Lett.*, 1971, **19**, 44.
4 S. A. Pollack and D. B. Chang, *J. Appl. Phys.*, 1988, **64**, 2885.
5 H. S. Killian, F. P. Van Herwijnen, and G. Blasse, *J. Solid State Chem.*, 1988, **74**, 39.
6 G. Blasse and G. Bril, *Phillips Tech. Rev.*, 1970, **31**, 303.
7 G. Blasse *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 143.
8 W. D. Horrocks and M. Albin, *Prog. Inorg. Chem.*, 1984, **31**, 1.
9 F. S. Richardson, *Chem. Rev.*, 1982, **82**, 541.
10 L. F. Johnson, J. E. Geusic, and Z. G. Van Uitert, *Appl. Phys. Lett.*, 1966, **8**, 200.
11 A. Lezama, M. Oria, and C. B. De Aranjo, *Phys. Rev. B*, 1986, **33**, 4493.
12 S. M. Yeh and C. F. Mears, *Biochemistry*, 1980, **19**, 5057.
13 C. F. Mears and L. S. Rice, *Biochemistry*, 1981, **20**, 610.
14 C. F. Mears, M. S. Yeh, and L. Stryer, *J. Am. Chem. Soc.*, 1981, **103**, 1607.
15 W. W. Harrocks, Jr., and D. R. Sudnick, *Acc. Chem. Res.*, 1981, **14**, 384.
16 R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901.
17 I. A. Kahwa, J. Selbin, T. C-Y. Hsieh, and R. A. Laine, *Inorg. Chim. Acta*, 1986, **118**, 179.
18 I. A. Kahwa, J. Selbin, C. J. O'Connor, J. W. Foise, and G. L. McPherson, *Inorg. Chim. Acta*, 1988, **148**, 265.
19 I. A. Kahwa, F. R. Fronczeck, and J. Selbin, *Inorg. Chim. Acta*, 1988, **148**, 273; 1987, **126**, 227.
20 E. Bullita, U. Cassellato, F. Guerriero, and P. A. Vigato, *Inorg. Chim. Acta*, 1987, **139**, 59.
21 S. Sakamoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1546.
22 O. P. Pandey, *Polyhedron*, 1987, **6**, 1021.
23 G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.
24 C. C. Hinkley, *J. Am. Chem. Soc.*, 1969, **91**, 5160.
25 B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**,49.
26 A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, 1973, **73**, 553.
27 B. M. Alsaadi, F. J. C. Rossotti, and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, 1980, 597.
28 J. W. More, M. D. Glick, and W. A. Baker, Jr., *J. Am. Chem. Soc.*, 1970, **94**, 1858.
29 J-C. G. Bunzil, E. Moret, U. Cassellato, P. Guerriero, and P. A. Vigato, *Inorg. Chim. Acta*, 1988, **150**, 133.
30 J. H. Forsberg, *Coord. Chem. Rev.*, 1973, **10**, 195.
31 S. P. Sinha and E. Butter, *Mol. Phys.*, 1969, **16**, 285.
32 G. M. Sheldrick, SHELXTL, 'An integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data,' University of Göttingen, F.R.G., Rev. 4.1, 1983.