A Lanthanide-templated Schiff-base Condensation Reaction to give a Trinuclear Macrocyclic Complex†

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Template condensation of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in refluxing methanol in the presence of $Ln(NO_3)_3 \cdot xH_2O$ (Ln = La, Pr, Eu or Gd) gives $[Ln_3L^3(OH)_2(NO_3)_4] \cdot nH_2O$ (n = 4–7), where L^3 is a trianionic Schiff-base macrocyclic ligand formed from three diketone and three diamine units. Analogous reactions with $Ln(NCS)_3 \cdot xH_2O$ (Ln = La, Pr, Eu or Gd) as template give $[Ln_3L^3(OH)(NCS)_5] \cdot 7H_2O$, while $Ca(NO_3)_2 \cdot xH_2O$ gives $[CaL^2(NO_3)_2]$, where L^2 is a ring-contracted '2 + 2' Schiff-base macrocycle. The crystal structure of $[La_3L^3(OH)_2(NO_3)_4] \cdot 7H_2O$ has been determined [orthorhombic, space group *Pbca* (no. 61), a = 22.74(2), b = 21.130(5), c = 23.245(6) Å; R = 0.081, R' = 0.061]. An approximately equilateral triangle of La atoms (La $\cdots$ La $\approx$ 4 Å) is bridged by a μ_3-OH^- ligand and encapsulated by the (3 + 3) macrocycle.

Outside the areas of materials and electronics, the major actual (as opposed to potential) application of the lanthanides is the use of complexes of paramagnetic ions as shift reagents (especially Eu^{3+},$4f^6$) or relaxation agents (Gd^{3+},$4f^7$) in NMR spectroscopy and imaging.[1] For applications in medical NMR imaging or *in vivo* NMR spectroscopy it is necessary that the complex be stable under physiological conditions *i.e.* aqueous solutions at pH $\approx$7, and that potentially harmful free lanthanide ions are not present; the required stability is most likely to be achieved by using chelating or macrocyclic ligands. Template condensation reactions have been used to great effect in the synthesis of lanthanide complexes with macrocyclic Schiff-base ligands, and some of these have had the desirable properties of stability in aqueous solution *e.g.* **1**.[2] A Schiff-base condensation reaction has also yielded the first crystallographically characterised example of a complex where two Ln^{3+} ions are held in close proximity within a single macrocyclic ligand (**2**).[3] Complexes of this type offer a unique opportunity to investigate magnetic and electronic interactions between Ln^{3+} ions.

A report that template condensation of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in the presence of Ba^{2+} yielded a complex $[Ba(H_2L^1)][ClO_4]_2$[4] suggested that the large Ln^{3+} ions may also act as suitable templates for this condensation. Sakamoto[5] reported condensation of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in the presence of LnX_3 ($X = NO_3^-$, Ln = La or Pr; $X = SCN^-$, Ln = La, Pr, Nd, Sm or Eu), and characterised his complexes as $[Ln_2L^1]X_4$ on the basis of elemental analysis. Fenton *et al.*[6] independently reported the same condensation reaction with $La(NO_3)_3$ and used NMR spectroscopy and elemental analysis to characterise the major product as $[La_3L^3(NO_3)_6]$. In this paper we report our results in this area, including a single-crystal X-ray diffraction study showing that the product of this condensation is in fact $[La_3L^3(\mu_3\text{-}OH)(OH)(NO_3)_4] \cdot 7H_2O$, the first structurally characterised example of a trinuclear lanthanide Schiff-base complex.

Results and Discussion

Template Condensation of 2,6-*Diacetylpyridine with* 1,3-*Diamino-2-hydroxypropane in the Presence of Lanthanide Salts.*—Reaction of $La(NO_3)_3 \cdot xH_2O$ with 1 equivalent of each of 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane in refluxing methanol produced a fine pale yellow precipitate after *ca.* 1 h, and the reaction was complete after *ca.* 3 h. A similar reaction was observed with the nitrates of Pr, Eu and Gd, with the yield of product decreasing and the solubility in MeOH increasing for the heavier lanthanides. Lanthanide thiocyanates also gave rise to template condensation reaction, and elemental analysis (see Table 1) suggests that the products in this case were $[Ln_3L^3(OH)(NCS)_5] \cdot 7H_2O$. Only very small amounts of rather impure product were isolated for the chlorides, and no product at all for the perchlorates or acetates.

Table 1 Analytical data (%) for $[Ln_3L^3]$ complexes (calculated values in parentheses)

Compound	C	H	N
$[La_3L^3(OH)_2(NO_3)_4] \cdot 4H_2O$	29.10 (30.45)	3.40 (3.70)	13.35 (12.85)
$[Pr_3L^3(OH)_2(NO_3)_4] \cdot 4H_2O$	28.40 (30.35)	3.30 (3.70)	12.95 (12.75)
$[Eu_3L^3(OH)_2(NO_3)_4] \cdot 4H_2O$	30.85 (29.65)	3.40 (3.05)	11.70 (12.50)
$[Gd_3L^3(OH)_2(NO_3)_4] \cdot 4H_2O$	30.00 (29.30)	3.55 (3.55)	12.25 (12.35)
$[La_3L^3(OH)(NCS)_5] \cdot 7H_2O$	32.35 (32.85)	3.40 (3.85)	12.95 (13.10)
$[Pr_3L^3(OH)(NCS)_5] \cdot 7H_2O$	32.75 (32.80)	3.45 (3.80)	13.10 (13.00)
$[Gd_3L^3(OH)(NCS)_5] \cdot 7H_2O$	32.95 (31.70)	3.20 (3.70)	12.20 (12.60)

Characterisation of the Lanthanide Products.—Infrared spectra showed a band at 1640 cm^{-1} due to ν(C=N) in all cases, and this, together with the absence of ν(N–H) and ν(C=O), confirmed that a Schiff-base macrocycle had been formed. Elemental analysis (see Table 1) was, however, unable to distinguish between Ln_2L^1 and Ln_3L^3, and mass spectra (see below) were not always straightforward. The lanthanum nitrate complex decomposed slowly in aqueous solution, precipitating $La(OH)_3$, but fortunately we were still able to obtain crystals from water which were suitable for X-ray diffraction. The gadolinium nitrate complex was far more stable in water, suggesting potential for use as an *in vivo* NMR relaxation agent.

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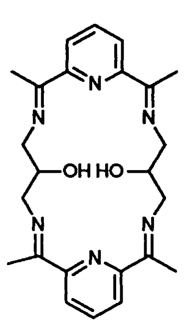
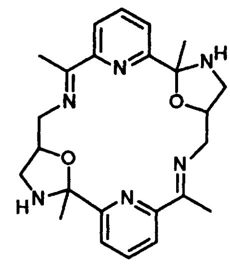
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

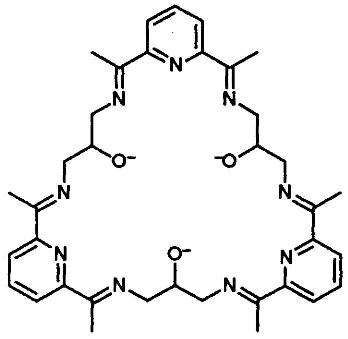
Non-SI unit employed: G = 10^{-4} T.



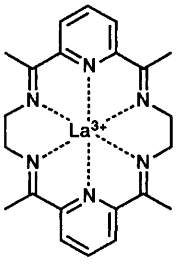
H_2L^1 (2+2)



L^2 (2+2)′



L^3 (3+3)



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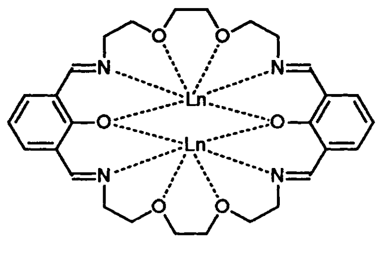

2

Elemental analysis, mass and IR spectra were indistinguishable for samples before and after recrystallisation from water, indicating that the OH groups are formed during the initial reaction in MeOH from water present in the reaction mixture. Elemental analyses are reported for powdered, vacuum-dried samples, and for nitrate complexes results indicate the presence of four H_2O molecules per macrocycle; in the X-ray structure determination seven H_2O molecules per macrocycle were located.

Description of Structure.—The structure is illustrated in Fig. 1; fractional atomic coordinates for the non-hydrogen atoms are given in Table 2. The La_3L^3 unit has approximate mirror-plane symmetry [through La(2)] and not the 3*m* symmetry that its constitution might allow. The three La atoms form an equilateral triangle of edge 4 Å. The 30-atom macrocyclic ring is made up of three planar seven-atom sections containing the pyridine rings and imine linkages; rotation about the CH_2–N and CH_2–$CH(O^-)$ single bonds provide flexibility in the macrocycle. The conformation around one of the $CH_2CH(O^-)CH_2$ chains is different from the other two (see Fig. 2).

Each lanthanum is nine-co-ordinate, making five bonds to the macrocycle and four to O atoms of OH^-, NO_3^- or H_2O. All other bond lengths and angles are normal; selected interatomic distances are given in Table 3, in which short La–O distances suggest that O(7) and O(9) represent the OH^- ions. Other bond distances and angles are normal. Pairs of La_3L^3 are joined by two La–OH–La bridges to make a unit containing six lanthanum atoms lying across a crystallographic inversion centre (Fig. 3), with La(1)···La(3′) 4.62 Å and La(1)–O(9)–La(3′) 151°. There is an extended and intricate network of hydrogen bonding involving the non-macrocycle groups which links the OH^- and NO_3^- ions and lattice water molecules.

Mass Spectrometry of $[Ln_3L^3(OH)_2(NO_3)_4]$ *and* $[Ln_3L^3(OH)(NCS)_5]$.—Fast atom bombardment (FAB) mass spectra were run using 3-nitrobenzyl alcohol as the matrix, but in general the results were not straightforward. In all cases, except for $[Gd_3L^3(OH)_2(NO_3)_4]$, peaks were observed at *m/z* considerably greater than for the expected M^+; these probably occurred due to reaction with the matrix compound. Comparison of the spectrum for Ln = La (^{139}La, 100% abundant) with that for Ln = Pr (^{141}Pr, 100% abundant) (see Fig. 4) demonstrates the robustness of the Ln_3 unit: the major peaks in the spectrum of the Pr_3 complex occur at 6 *m/z* units higher than those for the La_3 complex. In both cases the base peak corresponds to $Ln_3O_4^+$ (*m/z* 481 for La, 487 for Pr). The spectrum of $[Gd_3L^3(OH)_2(NO_3)_4]$ is somewhat different in appearance; there is a major peak at *m/z* 1386 with the correct Gd_3 isotope pattern, corresponding to $[M - NO_3^-]$, and also a peak due to $Gd_3O_4^+$.

ESR Spectra.—Gadolinium(III) has a $4f^7$ electron configuration, giving rise to a ^8S ground state which is amenable to study by ESR spectroscopy at room temperature. The spectrum of a typical isolated Gd^{3+} ion in an ionic lattice shows the major resonance centred around $g = 2$. We have carried out detailed ESR studies of complexes of Gd^{3+} such as $[Gd(bipy)_2(NO_3)_3]$ (bipy = 2,2′-bipyridine)[7] and $[Gd(NCS)_6]^{3-}$,[8] and found their spectra to be as expected for Gd^{3+} in an ionic lattice. Magnetic interactions between neighbouring Gd^{3+} ions give rise to much more complex spectra; there have been detailed studies of Gd^{3+} pairs doped into a lanthanum ethyl sulfate host ($Gd^{3+} \cdots Gd^{3+}$ 7 Å) where the interaction is dipolar in origin,[9] and in a lanthanum chloride host ($Gd^{3+} \cdots Gd^{3+}$ 4.5 Å) where there is also exchange interaction.[10] In both these cases oriented single-crystal spectra show more resonances than in the single-ion case, and with a wider spectral spread, but the spectra are almost symmetrical about $g = 2$. There have so far been no ESR studies of larger clusters of Gd^{3+} ions.

The ESR spectrum of a pure solid sample of $[Gd_3L^3(OH)_2(NO_3)_4]$ showed a very broad (ΔH = 1900 G) featureless resonance centred at $g = 2.1$. A variety of magnetically dilute polycrystalline samples were then prepared. First, samples were prepared by carrying out the condensation reaction using mixed La–GdX_3 (La:Gd = 30:1, X = NCS or NO_3) starting material. The major Gd-containing product from this reaction would be expected, on statistical grounds, to be La_2GdL^3, doped into a diamagnetic La_3L^3 host. The spectrum of the solid produced when X = NCS is shown in Fig. 5. There is virtually no signal around $g = 2$; the major resonance is at $g = 5.9$. The spectrum of the sample where X = NO_3 is slightly more complex, showing major resonances at $g = 6.5$ and 4.1. A solid sample prepared by precipitation from a solution containing a mixture of $[La_3L^3(OH)_2(NO_3)_4]$ and $[Gd_3L^3(OH)_2(NO_3)_4]$ (this should give Gd_3 complex doped into La_3 complex) shows only a resonance at $g = 6$. The most notable feature of the spectra of magnetically dilute samples is the presence of very low-field resonances and the absence of resonances around $g = 2$, which probably reflects a larger than usual zero-field splitting for the Gd^{3+} ion. We cannot draw any conclusions about magnetic interactions between Gd^{3+} ions from these spectra of polycrystalline samples, however it is interesting that samples expected to contain Gd_3 complex and those expected to contain La_2Gd complex give essentially similar ESR spectra.

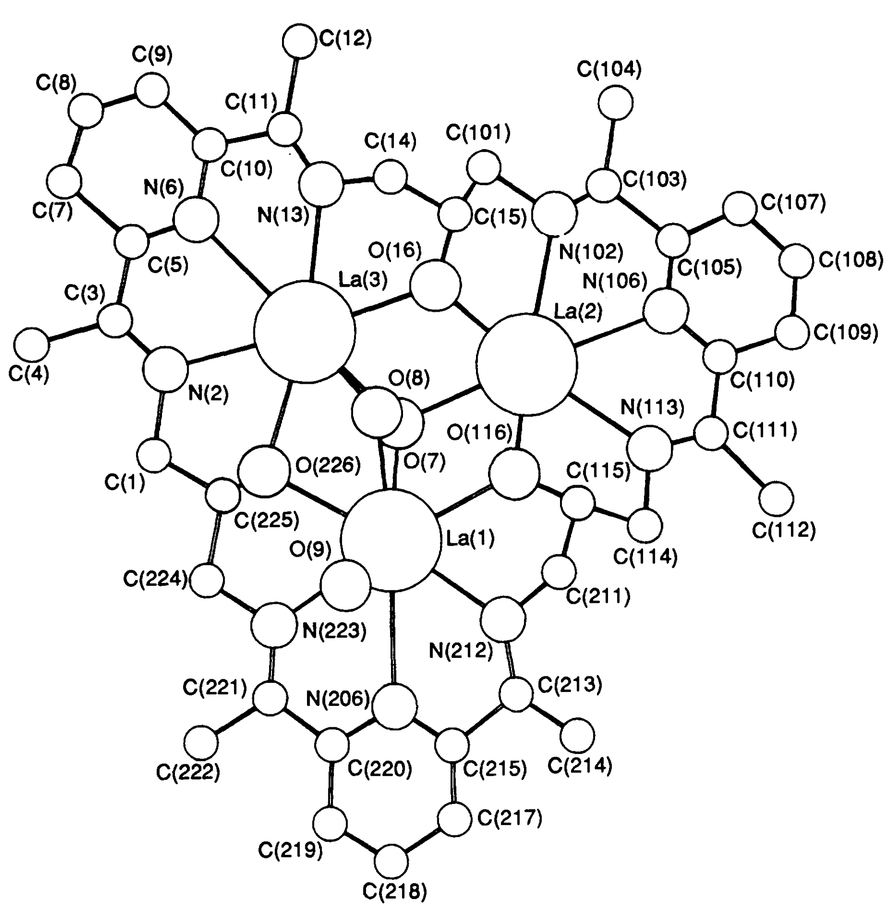

Fig. 1 The structure of the La_3L^3 complex, omitting some H_2O molecules and NO_3^- groups for clarity

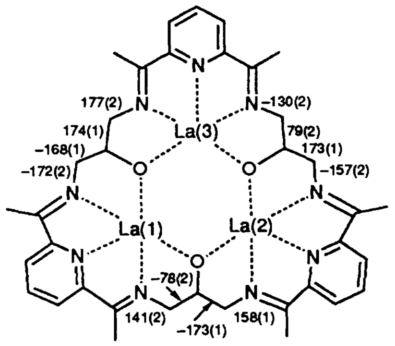

Fig. 2 Torsion angles (°) about bonds in the flexible parts of the macrocycle. The approximate mirror plane, normal to the La_3 ring, passes through La(2) and bisects La(1) $\cdots$ La(3)

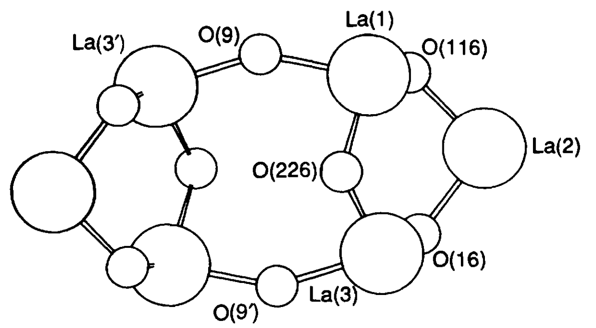

Fig. 3 Linkage of two La_3 units, across a crystallographic inversion centre, by La–OH–La bridges

Magnetic Susceptibility.—Magnetic susceptibilities were measured at 297 K for $[Gd_3L^3(OH)_2(NO_3)_4]\cdot 4H_2O$ and for $[Pr_3L^3(OH)(NCS)_5]\cdot 7H_2O$. For the praseodymium complex $\mu = 3.43$ per metal ion, which is just within the normal range for Pr^{3+}; the gadolinium complex had $\mu = 6.85$, which is significantly less than the spin-only value of 7.94 normally seen for complexes of Gd^{3+}. The magnetic susceptibility has not been measured for any other trilanthanide complexes, however a weak antiferromagnetic coupling has been reported for a Pr_2 macrocyclic complex.[11]

Template Condensations with $Ca(NO_3)_2\cdot xH_2O$.—Ionic radius is an important factor governing the course of a template condensation reaction, and Ca^{2+} (nine-co-ordinate radius = 1.32 Å) has been found to react in a similar way to La^{3+} (nine-co-ordinate radius = 1.35 Å) and Pr^{3+} (nine-co-ordinate radius = 1.32 Å) in the condensation of 2,6-diacetylpyridine with ethane-1,2-diamine, which gives a '2 + 2' complex with Ca^{2+} (ref. 12) as well as with La^{3+} or Pr^{3+}.[2] With this in mind we carried out the reaction of $Ca(NO_3)_3\cdot xH_2O$ with 1 equivalent of each of 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane in refluxing methanol. After *ca*. 3.5 h a white microcrystalline solid was obtained. The yield based on calcium was much improved when the reacting ratio was 1:2:2. Analytical and spectroscopic data (see Table 4) show that the product is $[CaL^2(NO_3)_2]$ where the ligand L^2 has the ring-contracted structure found in the analogous lead complex.[4] The FAB mass spectrum run in 3-nitrobenzyl alcohol–dimethyl sulfoxide shows a peak at *m*/*z* 536.1903, corresponding to $[M - NO_3^-]$.

Experimental

Proton NMR spectra were recorded on a Bruker AX 200 spectrometer, mass spectra on a VG 7070 spectrometer, and

Table 2 Fractional coordinates of non-hydrogen atoms of $[Ln_3L^3(OH)_2(NO_3)_4]\cdot 7H_2O$ with standard deviations

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
La(1)	0.0781(1)	0.4230(1)	0.4208(1)	C(225)	−0.0469(7)	0.4654(7)	0.3612(8)
La(2)	0.1886(1)	0.5651(1)	0.3699(1)	O(7)	0.0848(5)	0.5220(5)	0.3558(4)
La(3)	0.0159(1)	0.5989(1)	0.4041(1)	O(8)	0.0698(4)	0.5275(4)	0.4876(4)
C(1)	−0.1067(8)	0.5030(8)	0.3545(9)	O(9)	0.0412(5)	0.3865(5)	0.5116(5)
C(3)	−0.1314(8)	0.6108(8)	0.3512(7)	O(10)	0.0303(5)	0.6480(5)	0.3017(5)
C(4)	−0.1951(7)	0.5922(8)	0.3402(7)	O(11)	0.1053(5)	0.3776(5)	0.3211(5)
C(5)	−0.1210(8)	0.6784(8)	0.3614(8)	O(12)	0.1558(5)	0.6141(6)	0.2688(6)
C(7)	−0.1606(8)	0.7262(8)	0.3462(8)	O(13)	0.1966(6)	0.7089(6)	0.1973(6)
C(8)	−0.1479(8)	0.7915(9)	0.3525(8)	O(14)	0.2066(8)	0.8383(8)	0.1648(8)
C(9)	−0.0934(8)	0.8037(9)	0.3763(8)	O(15)	0.0396(12)	0.4947(11)	0.2291(12)
C(10)	−0.0545(7)	0.7556(8)	0.3903(7)	O(16)	0.1198(5)	0.6335(5)	0.4158(5)
C(11)	0.0036(9)	0.7690(9)	0.4206(9)	O(116)	0.1734(5)	0.4741(5)	0.4309(5)
C(12)	0.0173(8)	0.8398(7)	0.4306(8)	O(226)	−0.0191(5)	0.4847(4)	0.4148(5)
C(14)	0.0894(7)	0.7284(7)	0.4658(7)	N(2)	−0.0914(6)	0.5721(7)	0.3580(6)
C(15)	0.1383(8)	0.6923(8)	0.4354(8)	N(6)	−0.0684(7)	0.6951(6)	0.3819(7)
C(101)	0.1618(7)	0.7268(7)	0.3859(7)	N(13)	0.0354(7)	0.7223(7)	0.4349(7)
C(103)	0.2551(9)	0.7123(9)	0.3357(8)	N(102)	0.2152(7)	0.6908(6)	0.3640(7)
C(104)	0.2642(9)	0.7795(8)	0.3208(8)	N(106)	0.2978(6)	0.6058(7)	0.3379(6)
C(105)	0.3028(8)	0.6676(8)	0.3199(8)	N(113)	0.2838(7)	0.4900(7)	0.3814(7)
C(107)	0.3570(8)	0.6852(9)	0.2951(8)	N(206)	0.0767(7)	0.2868(6)	0.4225(7)
C(108)	0.3988(9)	0.6425(9)	0.2869(8)	N(212)	0.1666(6)	0.3524(6)	0.4677(6)
C(109)	0.3941(8)	0.5819(9)	0.3026(7)	N(223)	−0.0150(6)	0.3551(6)	0.3816(6)
C(110)	0.3434(8)	0.5647(9)	0.3292(8)	N(1N1)	0.2284(8)	0.5969(8)	0.5207(8)
C(111)	0.3312(9)	0.5022(9)	0.3516(9)	O(1N1)	0.2456(5)	0.5999(5)	0.4654(5)
C(112)	0.3752(9)	0.4503(9)	0.3485(9)	O(2N1)	0.1770(6)	0.5824(7)	0.5330(6)
C(114)	0.2668(9)	0.4313(9)	0.4113(8)	O(3N1)	0.2668(7)	0.6126(7)	0.5556(7)
C(115)	0.2229(8)	0.4484(8)	0.4571(8)	N(1N2)	0.2233(11)	0.4585(11)	0.2550(11)
C(220)	0.0272(8)	0.2559(8)	0.4023(8)	O(1N2)	0.1923(10)	0.4839(10)	0.2868(10)
C(211)	0.2073(7)	0.3947(8)	0.4958(7)	O(2N2)	0.2034(9)	0.4042(10)	0.2381(9)
C(213)	0.1690(8)	0.2935(9)	0.4727(8)	O(3N2)	0.2756(8)	0.4593(8)	0.2454(9)
C(214)	0.2208(8)	0.2567(9)	0.5001(8)	N(1N3)	0.0016(10)	0.3122(11)	0.2321(11)
C(215)	0.1229(9)	0.2569(9)	0.4450(8)	O(1N3)	0.0368(7)	0.2803(8)	0.2573(8)
C(217)	0.1190(9)	0.1895(9)	0.4516(8)	O(2N3)	−0.0425(8)	0.2853(8)	0.2094(8)
C(218)	0.0687(9)	0.1585(9)	0.4309(8)	O(3N3)	−0.0050(7)	0.3682(8)	0.2326(8)
C(219)	0.0243(9)	0.1899(9)	0.4056(8)	N(1N4)	0.1439(14)	0.6225(15)	0.0718(11)
C(221)	−0.0189(8)	0.2950(8)	0.3804(8)	O(1N4)	0.1821(11)	0.6629(12)	0.0843(11)
C(222)	−0.0780(8)	0.2615(8)	0.3614(8)	O(2N4)	0.1189(17)	0.6002(19)	0.1111(14)
C(224)	−0.0643(7)	0.3940(7)	0.3638(8)	O(3N4)	0.1307(10)	0.6211(11)	0.0239(9)

Table 3 Selected interatomic distances (Å)

(*a*) Lanthanum–macrocycle					
La(1)–O(116)	2.431(12)	La(2)–O(16)	2.383(12)	La(3)–O(16)	2.489(12)
La(1)–O(226)	2.571(12)	La(2)–O(116)	2.413(12)	La(3)–O(226)	2.552(12)
La(1)–N(206)	2.880(16)	La(2)–N(102)	2.728(16)	La(3)–N(2)	2.725(15)
La(1)–N(212)	2.732(15)	La(2)–N(106)	2.732(15)	La(3)–N(6)	2.843(16)
La(1)–N(223)	2.716(15)	La(2)–N(113)	2.697(16)	La(3)–N(13)	2.741(16)
(*b*) Lanthanum–oxygen of H_2O, OH^- or NO_3^-					
La(1)–O(7)	2.583(12)	La(2)–O(7)	2.551(12)	La(3)–O(7)	2.519(12)
La(1)–O(8)	2.706(11)	La(2)–O(12)	2.673(14)	La(3)–O(8)	2.745(11)
La(1)–O(9)	2.399(11)	La(2)–O(1N1)	2.676(13)	La(3)–O(9′)*	2.371(12)
La(1)–O(11)	2.583(13)	La(2)–O(1N2)	2.583(23)	La(3)–O(10)	2.619(13)

* O(9′) is at $-x, 1 - y, 1 - z$.

ESR spectra on a Bruker ER200D spectrometer. Elemental analyses were carried out by Mr. S. Apter of this department.

Preparations.—$[La_3L^3(OH)_2(NO_3)_4]\cdot nH_2O$. The salt $La(NO_3)_3\cdot xH_2O$ (6.22 mmol) was dissolved in MeOH (25 cm^3) and this solution was added to a solution of 2,6-diacetylpyridine (1.019 g, 6.02 mmol) and 1,3-diamino-2-hydroxypropane (0.533 g, 6.14 mmol) in MeOH (25 cm^3). The mixture was stirred and heated under reflux for 3 h. The resulting pale yellow microcrystalline precipitate was filtered off, washed (cold MeOH) and dried *in vacuo*. Yield = 5.29 g (60%). Products were normally analytically pure as isolated by this method, but further purification could be achieved by Soxhlet extraction of the crude product with MeOH.

A similar method was adopted for complexes of other lanthanides with yields of 40 (Pr), 25 (Eu) and 18% (Gd). Solubility in MeOH increased markedly for the heavier lanthanides.

$[La_3L^3(OH)(NCS)_5]\cdot 7H_2O$. The preparation of these complexes was carried out in a similar manner to that above, using methanolic solutions of $Ln(NCS)_3\cdot xH_2O$. Yields were 40 (La), 48 (Pr), 23 (Eu) and 20% (Gd).

Crystallisation for X-ray diffraction. A sample of the crude product was dissolved in the minimum volume of warm water. The resulting solution was filtered to remove a small quantity of fine white solid and the filtrate left overnight at room temperature. Clear pale yellow-orange tablets were formed.

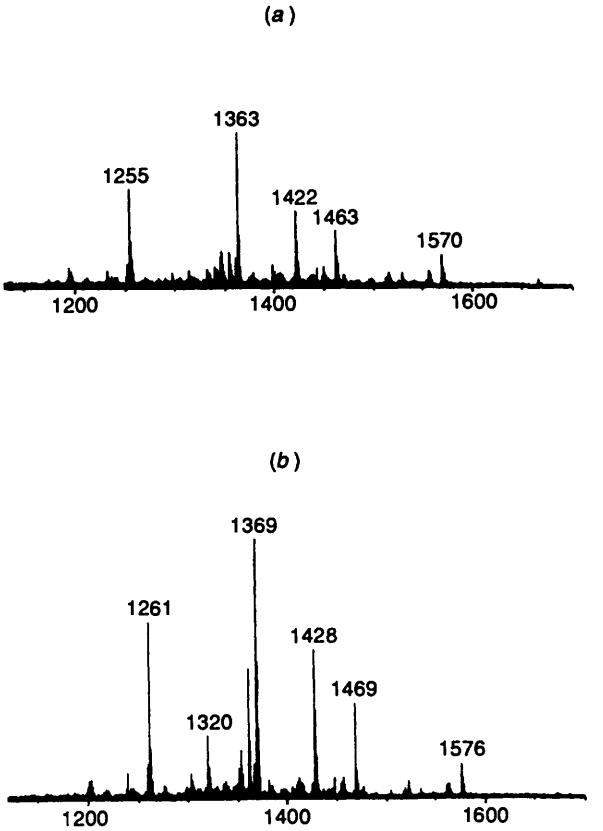

Fig. 4 The FAB mass spectra of $[Ln_3L^3(OH)(NCS)_5]$ [Ln = La (*a*) or Pr (*b*)]

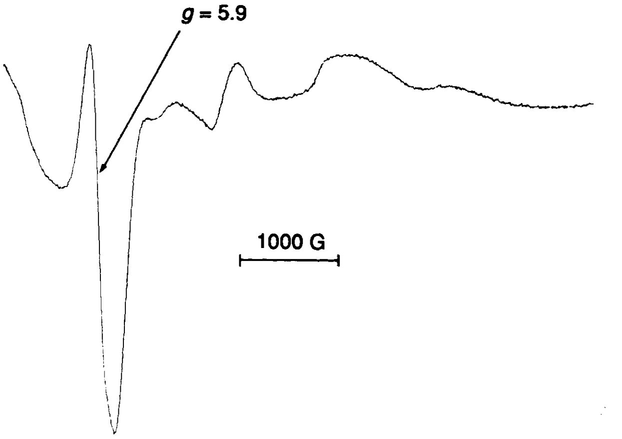

Fig. 5 The X-band ESR spectrum of polycrystalline $[(La,Gd)_3L^3(OH)(NCS)_5]$

Table 4 Analytical and spectroscopic data for $[CaL^2(NO_3)_2]$

	C	H	N
Found	48.15	5.05	18.65
Calc.	(48.15)	(5.05)	(18.70)
IR(Nujol) (cm^{-1})	3303 ν(N–H) 1647 ν(C=N)		
^1H NMR $[(CD_3)_2SO]$ (δ)	1.91 (s, CH_3) 2.45 (s, CH_3)		
FAB mass spectrum (*m*/*z*)	536.1903		
Calc. for $[M - NO_3^-]$	536.1934		

$[CaL^2(NO_3)_2]$. A solution of $Ca(NO_3)_2 \cdot xH_2O$ (1.50 mmol), 2,6-diacetylpyridine (0.487 g, 2.99 mmol) and 1,3-diamino-2-hydroxypropane (0.269 g, 2.99 mmol) in MeOH (20 cm^3) was heated under reflux for 3.5 h. After this time a considerable amount of white microcrystalline precipitate had formed. The reaction mixture was cooled to −15 °C overnight to complete precipitation. The product was filtered off, washed (cold MeOH) and dried *in vacuo*. Yield = 0.374 g (42%).

Structure Determination of $[La_3L^3(OH)_2(NO_3)_4]\cdot 7H_2O$.—*Crystal data*. $C_{36}H_{58}La_3N_{13}O_{24}$, $M = 1473.51$, $T_{meas} = 26$ °C, orthorhombic, space group *Pbca* (no. 61), $a = 22.74(2)$, $b = 21.130(5)$, $c = 23.245(6)$ Å, $U = 11\,169.1$ Å^3 (by least-squares refinement on diffractometer angles for 20 centred reflections, $12 < 2\theta < 17°$, $\lambda = 0.710\,69$ Å), $D_m = 1.72$ g cm^{-3}, $Z = 8$, $D_c = 1.75$ g cm^{-3}, $F(000) = 5824$. Yellow-orange, air- and moisture-stable tablets. Crystal dimensions 0.28 × 0.23 × 0.11 mm, μ(Mo-Kα) = 23.77 cm^{-1}.

Data collection and processing. Stoe Stadi 2 diffractometer, ω scans, graphite-monochromated Mo-Kα radiation; 6354 reflections measured (*h* 0–20, *k* 0–22, *l* 0–18; spindle along a $2\theta_{max} = 46.08°$), 5614 unique [absorption correction by DIFABS[13] after structure solution (maximum, minimum transmission factors 0.78, 0.60)], giving 4491 with $I > 4\sigma(I)$. Three standard reflections measured per layer, no significant variation.

Structure analysis and refinement. Direct methods (SHELXS 86[14]). Full-matrix least-squares refinement (SHELX 76[15]) with 18 atoms anisotropic and hydrogens of the macrocycle in calculated positions with one, overall, U_{iso} (= 0.05 Å^2). Four NO_3^- groups identified with some difficulty; these groups were constrained to have N–O 1.22(8) Å and O–N–O 120(8)°. Hydrogen atoms of OH^- and OH_2 not located. Weights, $w = 1/[\sigma^2(F_o)]$ with $\sigma(F_o)$ from counting statistics. Final *R* and *R'* values were 0.0814 and 0.0613. Neutral atom scattering factors for C, N, O and H are inlaid in SHELX 76; the value for La was from Cromer and Waber.[16] Values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[17] Other programs used are in refs. 18 and 19.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to the SERC for a studentship (to I. D.), to Johnson Matthey plc for a gift of lanthanide oxides, and to Drs. P. Thornton (magnetic susceptibility measurements) and A. Oduwole (ESR spectra) of Queen Mary and Westfield College London.

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Received 2nd *October* 1992; *Paper* 2/05302K