DALTON

Metal template synthesis of lanthanide cryptates. Crystal structure of a dysprosium cryptate

Fernando Avecilla,[a] **Rufina Bastida,***[,b] **Andrés de Blas,**[a] **David E. Fenton,**[c] **Alejandro Macías,**[b] **Adolfo Rodríguez,**[b] **Teresa Rodríguez-Blas,**[a] **Santiago García-Granda**[d] **and Raul Corzo-Suárez**[d]

[a] *Departamento de Química Fundamental e Industrial, Universidad de La Coruña, Campus de la Zapateira s/n 15071 La Coruña, Spain*
[b] *Departamento de Química Inorgánica, Universidad de Santiago de Compostela, Avda. de las Ciencias s/n, 15706 Santiago de Compostela, Spain*
[c] *Department of Chemistry, The University, Sheffield S3 7HF, UK*
[d] *Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo, c/ Julián Clavería n°8, 33006 Oviedo, Spain*

Lanthanide(III) and yttrium(III) ions have been shown to behave as efficient metal templates in the synthesis of cryptates $[M_2L][NO_3]_6\cdot xH_2O\cdot y$solv (M = Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb) derived from the 2+3 condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-methylphenol. The complexes have been characterised by elemental analysis, molar conductivity, mass and IR spectroscopy and the yttrium complex was also characterised by NMR spectroscopy. The crystal structure of the dysprosium complex was determined.

Recently it has been reported that encapsulating ligands could enhance some interesting properties that make complexes of the lanthanide(III) ions valuable for the development of technological applications such as the selective extraction of metals, NMR image-contrast agents, fluoroimmunoassay and diagnostic agents.[1,2]

Although the ability of the lanthanide(III) metal ions to promote Schiff-base condensation of the appropriate diamine and dicarbonyl precursors, resulting in the formation of metal complexes of otherwise inaccessible macrocyclic ligands, is well established,[3–7] only one example where such ions might behave as templates for complexes with macrobicycles has been reported;[8] the yield, *ca.* 3%, was too low to consider that the lanthanide ion behaves as a true template.

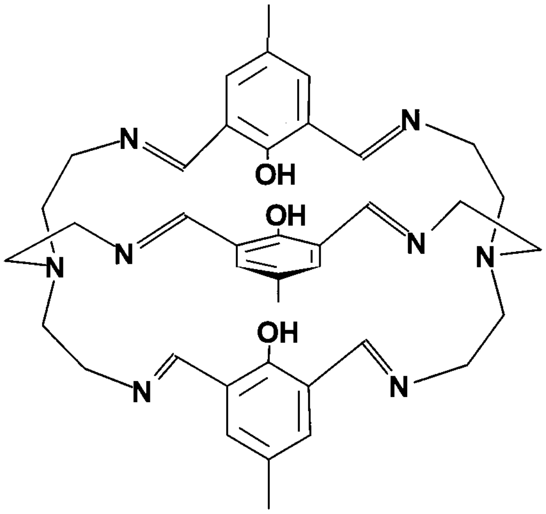
Many complexes of compound L have been reported, in particular, with sodium and transition metals.[9–13] When our work was in progress, the synthesis of mononuclear yttrium, gadolinium, europium and terbium complexes of L was reported by Nelson and co-workers.[14] They used a two-step procedure which includes the preparation of the sodium complex and then a transmetallation reaction in the presence of the corresponding metal perchlorate. Herein, we demonstrate the effectiveness of the yttrium(III) and lanthanide(III) nitrates (Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb) as templates in the synthesis of L.

Experimental

Measurements

Elemental analyses were carried out on a Carlo Erba EA 1108 elemental analyser. The IR spectra were recorded, as KBr discs, using a Perkin-Elmer 1330 spectrometer, proton NMR spectra on a Bruker AC 200 F spectrometer equipped with a Bruker B-VT-1000E variable-temperature unit and FAB mass spectra using a Fisons Quattro mass spectrometer with a caesium-ion gun and thioglycerol as matrix. Elemental analyses, proton NMR and mass spectra were obtained by Servicios Generales de Apoyo a la Investigación de la Universidad de A Coruña.

Conductivity measurements were carried out in *ca.* 10^{-3} mol dm^{-3} dimethylformamide solutions at 20 °C using a Crison Micro CM 2201 conductivimeter.



L

Chemicals and starting materials

2,6-Diformyl-4-methylphenol was prepared according to the literature method.[15] Tris(2-aminoethyl)amine and the lanthanide(III) nitrates were from Aldrich and Alfa laboratories, used without further purification. Solvents were of reagent grade purified by the usual methods.

Preparations

Condensation between 2,6-diformyl-4-methylphenol and tris(2-aminoethyl)amine in absence of metal ions. Tris(2-aminoethyl)amine (1 mmol) was dissolved in acetonitrile (50 cm^3) and added dropwise to a stirred solution (200 cm^3) of 2,6-diformyl-4-methylphenol (1.5 mmol). The mixture was maintained at room temperature with stirring for 20 h. The yellow powder formed was filtered off, washed with acetonitrile and air dried (yield 0.238 g, 63.4%), m.p. 235–238 °C (decomp.) (Found: C, 66.2; H, 6.6; N, 16.1. $C_{39}H_{48}N_8O_3\cdot3H_2O\cdot0.5CH_3CN$ requires C, 66.3; H, 7.3; N, 16.4%). ν(C=N) 1635 cm^{-1}. δ_H(200 MHz, solvent $CDCl_3$, 298 K) 14.03 (3 H, br s, OH), 8.50 (6 H, br s, N=CH), 7.14 (6 H, br s, aryl H), 3.64 (12 H, br s, CH_2CH_2), 2.91 (12 H, br s, CH_2CH_2) and 1.60 (9 H, br s, CH_3). Low-temperature ^1H NMR (200 MHz, solvent $CDCl_3$, 203 K): δ 14.64 (s, OH), 13.97 (s, OH), 9.15 (s, N=CH), 8.87 (s, N=CH), 8.41 (s, N=CH), 7.97 (s, N=CH), 7.85 (s, N=CH), 7.79 (s, N=CH), 7.14 (d, $J = 7$, aryl H), 6.55 (d, $J = 7$ Hz, aryl H), 4.04–2.60 (m, CH_2CH_2), 2.29 (s, aryl CH_3), 2.18 (s, aryl CH_3) and 2.16 (s, aryl CH_3). FAB mass spectrum: *m/z* 677 (M^+) (calc. 676).

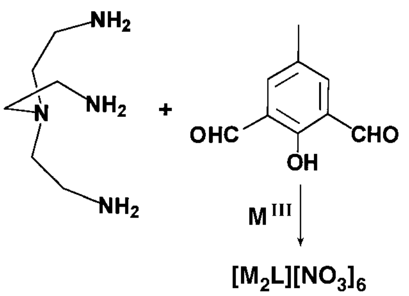
General procedure for the syntheses of lanthanide and yttrium complexes. 2,6-Diformyl-4-methylphenol (0.75 mmol) and $M(NO_3)_3\cdot xH_2O$ (0.5 mmol) were dissolved in hot absolute ethanol (35 cm^3). To this solution was added dropwise a tris(2-aminoethyl)amine solution (0.5 mmol) in absolute ethanol (25 cm^3) with constant stirring. After the addition was complete, the resulting solution was refluxed for *ca.* 24 h. The yellow powder precipitated was filtered off, washed with diethyl ether and air dried. The complexes of Y, Gd, Ho and Er were recovered from the resulting solution after evaporation and addition of diethyl ether. The complexes appear to be air stable, soluble in dimethyl sulfoxide, dimethylformamide, moderately soluble in water, acetonitrile, ethanol, methanol, and slightly soluble in chloroform and dichloromethane. The solutions remain unchanged for months.

Crystallography

Suitable single crystals of the complex $[DyL(NO_3)][Dy(NO_3)_5]\cdot 2MeCN$ were grown by slow evaporation of an acetonitrile solution of it.

Crystal data. $C_{39}H_{48}Dy_2N_{14}O_{21}\cdot 2C_2H_3N$, M_r = 1456.02, triclinic, space group $P1$, a = 12.947(9), b = 15.721(11), c = 16.60(2) Å, α = 97.08(7), β = 106.0(2), γ = 104.14(7)°, U = 3082(5) $Å^3$, Z = 2, D_c = 1.57 Mg m^{-3}, Mo-Kα radiation (graphite crystal monochromator, λ = 0.710 73 Å), μ = 2.487 mm^{-1}, $F(000)$ = 1448, T = 200(2) K.

Data collection and processing. Yellow unstable crystal, size 0.26 × 0.20 × 0.30 mm. Enraf-Nonius CAD-4 single-crystal diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections with θ between 5 and 10°. The space group was determined to be $P\bar{1}$ from the structure determination. The intensity data for 8564 reflections, *hkl* range (−14, −17, 0) to (13, 17, 18) and $0 < \theta < 23°$, were measured, using the ω–2θ scan technique and a variable scan rate with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 60 min. The final drift-correction factors were between 0.977 and 1.074. An all-reflections profile analysis was performed.[16] The structure was solved by Patterson methods using DIRDIF.[17] Isotropic least-squares refinement was made using SHELXL 93.[18] At this stage an empirical absorption correction was made using XABS 2:[19] minimum and maximum transmission correction factors 0.709 and 1.00. Hydrogen atoms were geometrically placed. During the final stages of the refinement on F^2 using SHELXL 93 the positional parameters and the anisotropic thermal parameters of the non-H atoms were refined (except for one carbon atom of the solvent acetonitrile molecules). The final conventional agreement factors were R = 0.068 and $wR2$ = 0.179 for the 5082 'observed' reflections $[I > 2\sigma(I)]$ and 732 variables. The function minimised was $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w = 1/[\sigma^2(F_o^2) + (0.0971P)^2 + 24.44P]$ with $\sigma(F_o^2)$ from counting statistics and $P = [\max(F_o^2,0) + 2F_c^2]/3$. The maximum shift/e.s.d. ratio in the last full-matrix least-squares cycle was 0.087. The final Fourier-difference map showed no peaks higher than 1.32 e $Å^{-3}$ nor deeper than −1.74 e $Å^{-3}$. Four peaks were deeper than −1.0 e $Å^{-3}$; the deepest were very close to atom Dy(2), and the rest near Dy(1). The eight peaks higher than 1.0 e $Å^{-3}$ were located near to both Dy atoms, and the rest (weaker than 1.1 e $Å^{-3}$) in the disordered solvent regions.



Scheme 1 M = Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb

The crystallographic plots were made by the EUCLID package.[20] Atomic scattering factors were taken from ref. 21. Geometrical calculations were made with PARST.[22] All calculations were made at the University of Oviedo at the Scientific Computer Centre on the X-ray group VAX computers.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/296.

Results and Discussion

Previous researchers have tried to prepare compound L in the absence of metal ions.[10,11] A complex mixture was obtained from which it was impossible to isolate, and characterise, L. We have carried out this experiment under very dilute conditions. Although the analysis of the yellow powder obtained is not good, the FAB mass spectrum shows a peak at *m/z* 677 corresponding to M^+ and the IR and NMR spectra are consistent with the formation of the compound. The absence of carbonyl and amine signals in the IR spectrum, together with the appearance of the imino signal, indicates that condensation and cyclisation have taken place. The ^1H NMR spectrum in $CDCl_3$ run at 298 K shows six broad singlets for OH (δ 14.03), N=CH (δ 8.50), aryl H (δ 7.14), CH_2CH_2 (δ 3.64 and 2.91) and aryl CH_3 (δ 1.60); when the spectrum was run at 203 K the signals were sharp, and two were obtained for OH, six for the azomethine hydrogens, two for the hydrogens of the aromatic ring, a complicated multiplet for the ethylene bridges and three singlets for the CH_3 groups. This behaviour confirms that we have prepared L, which undergoes, in solution, a fast conformational change at room temperature while at 203 K this change is slow on the NMR time-scale.

Reactions between 2,6-diformyl-4-methylphenol and tris(2-aminoethyl)amine in the presence of hydrated yttrium and lanthanide nitrates in a 3 : 2 : 2 mole ratio in absolute ethanol for *ca.* 24 h (Scheme 1) gave very good yields of analytically pure products $[M_2L][NO_3]_6\cdot xH_2O\cdot y$solv (M = Y, La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm or Yb) (Table 1). This reaction was also attempted with Sm and Lu but the elemental analyses are not consistent with this formula and they will be discussed elsewhere.

All the complexes have been characterised by elemental analysis (C, N, H), molar conductance, mass and IR spectroscopy. Suitable single crystals for X-ray diffraction were grown by slow evaporation of an acetonitrile solution of the dysprosium complex. The analytical and conductivity data are presented in Table 1. The molar conductance data in dimethylformamide are in the range reported for 3:1 electrolytes in this solvent.[23] If we compare this result with the crystal structure of the dysprosium complex it is clear that, in solution, two nitrate ions have been displaced by solvent molecules, otherwise this complex would behave as a 1:1 electrolyte.

Table 1 Analytical data, yields and molar conductances (in dimethylformamide) for the complexes $[M_2L][NO_3]_6 \cdot xH_2O \cdot yEt_2O$

			Analysis (%)*				
M	*x*	*y*	C	N	H	Yield (%)	Λ_m/Ω^{-1} cm^2 mol^{-1}
Y	2	2(EtOH)	38.3 (38.1)	14.8 (14.5)	4.6 (4.8)	25	183.5
La	4	—	33.4 (33.5)	13.3 (14.0)	3.9 (4.1)	87	213.8
Ce	4	—	33.6 (33.4)	13.8 (14.0)	4.0 (4.0)	79	230.7
Pr	4	—	33.7 (33.4)	13.7 (14.0)	4.2 (4.0)	50	209.3
Nd	4	—	33.1 (33.2)	13.9 (13.9)	4.1 (4.0)	78	212.3
Eu	6	—	32.7 (32.1)	13.1 (13.4)	4.1 (4.1)	47	205.4
Gd	4	0.5	33.8 (33.4)	13.3 (13.3)	4.1 (4.2)	40	
Tb	1	1.5	36.1 (36.1)	13.4 (13.1)	4.3 (4.3)	73	203.8
Dy	8	—	30.9 (30.9)	13.0 (12.9)	4.1 (4.3)	35	208.9
Ho	4	0.5	33.1 (33.1)	13.1 (13.2)	4.2 (4.1)	55	214.1
Er	4	1	33.4 (33.8)	12.9 (12.8)	4.3 (4.4)	40	205.5
Tm	8	—	30.2 (30.6)	12.2 (12.8)	3.9 (4.2)	30	223.8
Yb	6	—	31.5 (31.2)	12.4 (13.1)	4.0 (4.0)	30	208.3

* Required values in parentheses

Table 2 Infrared data (cm^{-1}) for the complexes $[M_2L][NO_3]_6 \cdot xH_2O \cdot yEt_2O$

M	ν(C=N)	$\nu(NO_3)$
Y	1651	1488, 1299, 1350
La	1652	1483, 1447, 1319
Ce	1649	1479, 1451, 1300
Pr	1645	1481, 1449, 1296
Nd	1649	1481, 1451, 1304
Eu	1650	1483, 1450, 1300
Gd	1649	1483, 1450, 1300
Tb	1649	1483, 1451, 1300
Dy	1650	1482, 1450, 1300
Ho	1648	1483, 1450, 1301
Er	1649	1484, 1453, 1301
Tm	1649	1487, 1453, 1303
Yb	1657	1483, 1450, 1294

Table 3 The FAB mass spectral data for the complexes $[M_2L][NO_3]_6 \cdot xH_2O \cdot yEt_2O$

M	Peak (*m/z*)	Assignment	% Base peak
Y	764	$[Y(L-2H)]^+$	89.05
	975	$[Y_2(L-3H)(NO_3)_2]^+$	100
La	813	$[La(L-2H)]^+$	35
Ce	814	$[Ce(L-2H)]^+$	82.67
	1077	$[Ce_2(L-3H)(NO_3)_2]^+$	10
Pr	815	$[Pr(L-2H)]^+$	80.25
	1079	$[Pr_2(L-3H)(NO_3)_2]^+$	18.44
Nd	818	$[Nd(L-2H)]^+$	59.64
	1085	$[Nd_2(L-3H)(NO_3)_2]^+$	<10
Eu	826	$[Eu(L-2H)]^+$	100
	977	$[Eu_2(L-3H)]^+$	6.04
	1039	$[Eu_2(L-3H)(NO_3)]^+$	8.17
	1101	$[Eu_2(L-3H)(NO_3)_2]^+$	<5
Gd	832	$[Gd(L-2H)]^+$	89.44
	1111	$[Gd_2(L-3H)(NO_3)_2]^+$	22
Tb	833	$[Tb(L-2H)]^+$	100
	1115	$[Tb_2(L-3H)(NO_3)_2]^+$	6.31
Dy	837	$[Dy(L-2H)]^+$	47
	1122	$[Dy_2(L-3H)(NO_3)_2]^+$	<5
Ho	839	$[Ho(L-2H)]^+$	100
	1127	$[Ho_2(L-3H)(NO_3)_2]^+$	89
Er	841	$[Er(L-2H)]^+$	65.59
	1131	$[Er_2(L-3H)(NO_3)_2]^+$	29
Tm	843	$[Tm(L-2H)]^+$	21.68
	1135	$[Tm_2(L-3H)(NO_3)_2]^+$	<5
Yb	848	$[Yb(L-2H)]^+$	10.46

The IR spectra of the products (Table 2) show a band at *ca.* 1650 cm^{-1} attributable to ν(C=N). In the region 1500–1300 cm^{-1} all the spectra exhibit at least three bands at *ca.*1480, 1450 and 1300 cm^{-1} due to the presence of bi- and mono-dentate nitrates. When the spectra are recorded as KBr discs, one very intense band at 1385 cm^{-1}, characteristic of ionic nitrate, is observed; in Fluorolube this band disappears indicating that bromide ion can displace a co-ordinated nitrate.

The FAB mass spectra of the complexes are summarised in Table 3. All the spectra exhibit an intense peak corresponding to $[M(L-2H)]^+$, confirming the presence of the macrobicyclic complex. In those cases where the lanthanide cations are polyisotopic, the calculated and observed isotopic patterns were identical. With the exception of lanthanum and ytterbium, another medium-intensity peak due to $[M_2(L-3H)(NO_3)_2]^+$ can also be observed. For related compounds this latter peak has been attributed to the presence of ion pairs between the complex anion and the complex cation in the thioglycerol solution,[13] but it can also be considered that the deprotonated ligand formed during the ionisation process can accommodate another metal ion inside its cavity. It is interesting that it is not possible to find any peak due to L + 1, which confirms the high kinetic complex stability of the species and shows that only when the cryptand breaks can the metal exit from the cavity.

Crystals of composition $[DyL(NO_3)][Dy(NO_3)_5] \cdot 2MeCN$ were grown by slow evaporation of a MeCN solution. They contain two different structural units, the anion $[Dy(NO_3)_5]^{2-}$ and the cation $[DyL(NO_3)]^{2+}$. In the former (Fig. 1) the Dy^{III} is 10-co-ordinated, being bonded to five bidentate nitrate ions. The oxygens define a distorted bicapped dodecahedron very similar to that reported[24] for $[Ce(NO_3)_5]^{2-}$, and the average Dy–O distance is 2.43 Å.

The structure of $[DyL(NO_3)]^{2+}$ is shown in Fig. 2. The metal ion is placed asymmetrically at one end of the cavity, and is eight-co-ordinated, being bonded to three imino-nitrogen atoms, three phenolic oxygens and one of the bridgehead nitrogen atoms. The eighth position is occupied by one oxygen of a monodentate nitrate ion. The co-ordination distance is 2.438(12) for the nitrate oxygen and in the range 2.253–2.321 Å for the phenolic oxygens, 2.47–2.51 Å for the azomethine nitrogens, and 2.678(12) Å for the bridgehead nitrogen atom (Table 4). This shows the weak interaction between the Dy^{III} and the amine nitrogen in contrast with the strong interaction with the imino nitrogen and phenolic oxygen. The co-ordination polyhedron can best be described as a distorted dodecahedron.

It is also interesting that the cryptand adopts a conformation that resembles a triple helix, twisting around the axis that passes through both amine nitrogens, the angles between the planes defined by the phenolic rings being 89.2, 91.2 and 111.0°. The distance between the bridgehead nitrogens is 8.361 Å, very similar to that reported for $[CdL][ClO_4]_2$ (8.20–8.41 Å) and shorter than that of $[Cd_2(L-3H)]ClO_4$ (9.01 Å).[10] This shows how L can expand or contract the hole to fit the metal size or to accommodate two metal ions.

Table 4 Bond lengths (Å) and angles (°) for the dysprosium complex

Dy(1)–O(4)	2.253(11)	Dy(2)–O(75)	2.40(2)
Dy(1)–O(6)	2.320(11)	Dy(2)–O(20)	2.42(2)
Dy(1)–O(3)	2.321(11)	Dy(2)–O(10)	2.42(2)
Dy(1)–O(5)	2.438(12)	Dy(2)–O(41)	2.43(2)
Dy(1)–N(27)	2.470(12)	Dy(2)–O(22)	2.430(12)
Dy(1)–N(9)	2.51(2)	Dy(2)–O(14)	2.44(2)
Dy(1)–N(32)	2.51(2)	Dy(2)–O(16)	2.44(2)
Dy(1)–N(8)	2.678(12)	Dy(2)–O(26)	2.45(2)
Dy(2)–O(18)	2.36(2)	Dy(2)–O(33)	2.471(13)
O(6)–Dy(1)–N(32)	132.5(4)	O(3)–Dy(1)–N(8)	123.9(4)
O(6)–Dy(1)–N(27)	72.5(4)	O(3)–Dy(1)–O(6)	69.7(4)
O(6)–Dy(1)–N(9)	139.9(4)	O(3)–Dy(1)–O(5)	142.7(4)
O(6)–Dy(1)–N(8)	135.6(4)	O(3)–Dy(1)–O(4)	78.2(4)
O(5)–Dy(1)–O(6)	75.9(4)	O(5)–Dy(1)–N(27)	71.6(4)
O(4)–Dy(1)–N(32)	72.7(4)	O(5)–Dy(1)–N(9)	139.4(4)
O(4)–Dy(1)–N(27)	157.2(4)	N(27)–Dy(1)–N(9)	98.0(4)
O(4)–Dy(1)–N(9)	90.4(4)	O(5)–Dy(1)–N(32)	74.3(4)
O(4)–Dy(1)–N(8)	134.6(4)	N(27)–Dy(1)–N(32)	129.1(5)
O(4)–Dy(1)–O(6)	87.4(4)	N(9)–Dy(1)–N(32)	84.2(5)
O(4)–Dy(1)–O(5)	114.5(4)	O(5)–Dy(1)–N(8)	73.4(4)
O(3)–Dy(1)–N(32)	141.2(4)	N(27)–Dy(1)–N(8)	67.9(4)
O(3)–Dy(1)–N(27)	84.6(4)	N(9)–Dy(1)–N(8)	66.6(4)
O(3)–Dy(1)–N(9)	70.6(4)	N(32)–Dy(1)–N(8)	66.7(5)

Table 5 Possible hydrogen bonds

Donor–H/Å	Donor···Acceptor/Å	H···Acceptor/Å	Donor–H···Acceptor/°
O(3)–H(3) 0.820(18)	O(3)···N(19) 2.625(19)	H(3)···N(19) 1.889(19)	O(3)–H(3)···N(19) 148.8(15)
O(4)–H(4) 0.820(13)	O(4)···N(25) 2.647(16)	H(4)···N(25) 1.895(15)	O(4)–H(4)···N(25) 152.0(14)
O(6)–H(6) 0.820(15)	O(6)···N(13) 2.643(19)	H(6)···N(13) 1.906(19)	O(6)–H(6)···N(13) 149.1(14)

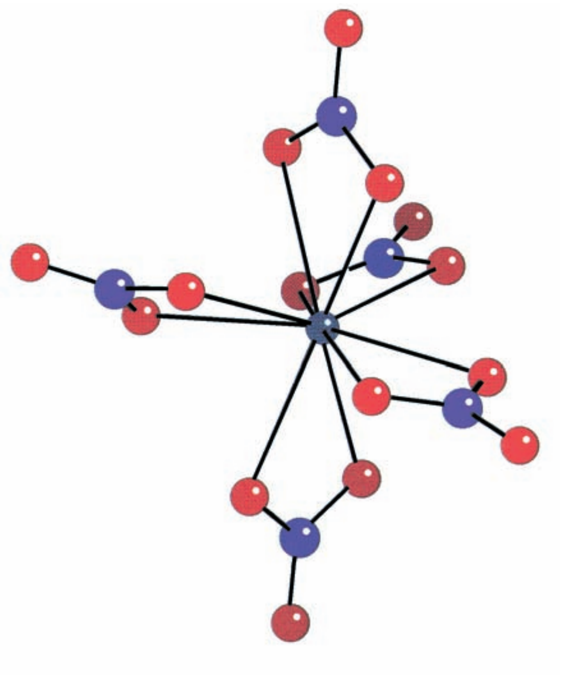


Fig. 1 Crystal structure of the Dy complex anion

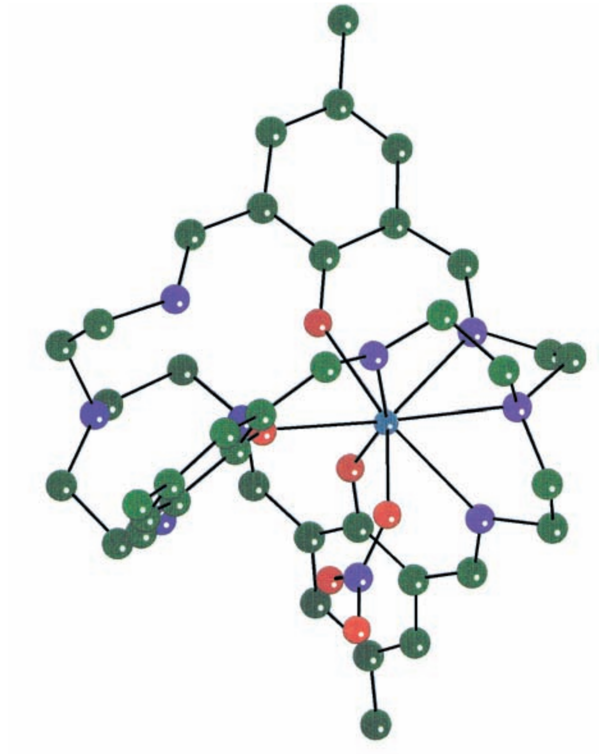


Fig. 2 Crystal structure of the Dy complex cation. Hydrogen atoms have been omitted for simplicity

Nelson and co-workers[10,14] have shown the possibility of a proton transfer from the phenol to the unco-ordinated imino nitrogen when the metal is Zn^{2+}, Cd^{2+}or Pb^{2+}, Y^{3+} and Sc^{3+}. We have investigated this possibility and tried to find the position of these hydrogens but due to the crystal instability the H atom positions are not reliable. For hydrogens in geometric positions (Table 5) the distances O (donor)···N (acceptor) are in the range 2.625–2.647 Å, larger than those reported for the complex of Cd (2.59–2.62),[10] although the charge (+3) is larger on the metal. This agrees with the Dy–O distances observed, only one of which is short enough [2.253(11) Å] to consider that the proton transfer from the co-ordinated phenoxy oxygen has occurred, while the other two are too long (2.32 Å).

In order to confirm whether the proton transfer has occurred, Nelson and co-workers[10] have used the NMR spectra of the diamagnetic complexes. Nevertheless, it must be remembered that in solution the hydrogen bond should be in dynamic equilibrium and be affected by many factors like temperature, concentration, solvent nature, pH, *etc*. The situation for any proton is different, even for the three protons in every molecule. Moreover no distinct region on the δ scale can be assigned to the resonances of exchangeable protons since the position of these signals is strongly dependent upon the medium and temperature.[25] Finally it must be stated that the system in solution can be different from the solid state.

The NMR spectrum of the yttrium complex in CD_3CN shows one very broad signal for OH at δ 12.93, two signals for the azomethine hydrogens [δ 8.47 (d), $J = 15$ Hz; 8.29 (s)] together with signals due to the aromatic hydrogens [δ 7.64 (d), $J = 3$, 7.46 (d), $J = 3$ Hz], ethylene bridges [δ 3.90–2.77 (m)] and the methyl groups [δ 2.31 (s)]. The most interesting feature in order to decide whether the proton transfer has occurred is that two signals can be observed for the imino hydrogens, a singlet and a doublet. A correlation spectroscopy (COSY) experiment was performed but it was not helpful in deciding whether the doublet was coupled with the signal at δ 12.93 due to the broad nature of the OH signal and low solubility. More information was obtained from a selective spin-decoupling experiment. This showed that the broad signal at δ 12.93 and the doublet at δ 8.47 are coupled. This fact together with the broad nature of the first signal indicates that in acetonitrile solution, at 298 K, proton transfer has occurred and the hydrogen bond can be described as $O\cdots HN^+$. At low temperature the situation is slightly different: the NMR spectrum shows three signals for OH (or NH^+) protons, and a complicated signal for the azomethine hydrogens, which means that the three protons involved in the hydrogen bonds are not equivalent and neither are the six CH=N protons. Unfortunately at the freezing temperature of acetonitrile the spectrum is not completely resolved and it is not possible to decide whether one, two, three or none of the protons was transferred from the phenolic oxygen to the imino nitrogen under these conditions. Some authors have reported the same behaviour[10] and consider that this is due to conformational mobility. Nevertheless, it may be also due to changes in the equilibrium. It can also be asked whether the doublet observed at room temperature means that the three imino nitrogens are protonated, or if in the NMR resolution time we can only see an average of the three signals. On the other hand, in D_2O at room temperature, the spectrum does not show the signals for the OH protons and those due to the azomethine protons appear as two singlets (δ 8.46, 8.16).

Acknowledgements

We thank Xunta de Galicia (XUGA 20903B94) and Universidad de la Coruña for financial support.

References

1 N. Sabbatini, M. Guardigli and J. M. Lehn, *Coord Chem. Rev.*, 1993, **123**, 201.
2 V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
3 D. E. Fenton and P. A. Vigato, *Chem. Soc. Rev.*, 1988, **17**, 69.
4 R. Bandín, R. Bastida, A. de Blas, P. Castro, D. E. Fenton, A. Macías, A. Rodríguez and T. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1994, 1185.
5 P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17.
6 R. Bastida, A. de Blas, P. Castro, D. E. Fenton, A. Macías, R. Rial, A. Rodríguez and T. Rodriguez-Blas, *J. Chem. Soc., Dalton Trans.*, 1996, 1493.
7 H. Adams, R. Bastida, A. de Blas, M. Carnota, D. E. Fenton, A. Macías, A. Rodríguez and T. Rodríguez-Blas, *Polyhedron*, 1997, **16**, 567.
8 H. Smith, Z. E. Reyes, Ch. Lee and K. N. Raymond, *Inorg. Chem.*, 1988, **27**, 4154.
9 M. D. Timken, W. A. Marrit, D. N. Hendrickson, R. A. Gagné and E. Sinn, *Inorg. Chem.*, 1987, **24**, 4202.
10 M. G. B. Drew, O. W. Howarth, G. G. Morgan and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1994, 3149.
11 P. Chakraborty and S. K. Chandra, *Polyhedron*, 1994, **13**, 683.
12 M. G. B. Drew, C. J. Harding, V. McKee, G. G. Morgan and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 1035.
13 K. Zhou, S. Gou, Z. Wang and Z. Yuang, *Polyhedron*, 1995, **14**, 3505.
14 M. G. B. Drew, O. W. Howarth, C. J. Harding, N. Martin and J. Nelson, *J. Chem. Soc., Chem. Commun.*, 1995, 903.
15 S. Taniguchi, *Chem. Soc. Jpn.*, 1984, **57**, 2683.
16 D. F. Grant and E. J. Gabe, *J. Appl. Crystallogr.*, 1978, **11**, 114; M. S. Lehman and F. K. Larsen, *Acta Crystallogr., Sect A*, 1974, **30**, 580.
17 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, *DIRDIF user's guide*, Technical report, Crystallography Laboratory, University of Nijmegen, 1992.
18 G. M Sheldrick, SHELXL 93, in *Crystallographic Computing 6*, eds. H. D. Flack, P. Parkanyi and K. Simon, Oxford University Press, 1993.
19 S. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53.
20 A. L. Spek, The EUCLID package, in *Computational Crystallography*, ed D. Sayre, Oxford, Clarendon Press, 1982, p. 528.
21 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham (present distributor, Kluwer Academic Publishers, Dordrecht), 1974, vol. 4.
22 M. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
23 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
24 A. R. Al-Karaghouli and J. S. Wood, *Chem. Commun.*, 1970, 135.
25 H. Günter, *NMR Spectroscopy. An introduction*, Wiley, New York, 1980.

Received 27*th September* 1996; *Paper* 6/06626G