ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 185–189

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Effect of the solvent and different crystal packing on the europium podand complex: tris(((2-hydroxy-3-methoxybenzyl)amino)ethylamine) tris(nitrato) europium(III)

F. Benetollo[a,*], G. Bombieri[b], G. Depaoli[c], V. Ferretti[d], M.R. Truter[e]

[a]*ICTIMA CNR, Corso Stati Uniti 4, 35127 Padova, Italy*
[b]*Istituto di Chimica Farmaceutica, Università di Milano, Viale Abruzzi 42, 20131 Milano, Italy*
[c]*Dipartimento di Chimica Inorganica Metallorganica e Analitica Università di Padova, Via Marzolo 1, 35131 Padova, Italy*
[d]*Dipartimento di Chimica, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy*
[e]*Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

Abstract

The title compound has been prepared and characterized by X-ray crystal structure determination. The X-ray studies demonstrated the presence of two crystal forms which differ in the solvent content. The coordination is as a tricapped trigonal prism, where each of bidentate nitrates is *trans* to the coordinated phenolic oxygen.

Keywords: Synthesis; Crystal structure; Europium; Podand

1. Introduction

The use of polydentate ligands for complexation with lanthanide ions has attracted our attention because of their possible application as luminescent probe (Eu, Tb) contrast agents (CA) for MRI (magnetic resonance imaging) (Gd). We have reported on the structures of Ln with DOTA (DOTA=1,4,7,10-tetraazacyclododecane *N*,*N*′,*N*″*N*‴-tetra-acetic acid). The series is not isostructural and depending on the ionic radii, different compounds can be obtained.

The metal is encapsulated by the ligand which provides eight donor sites (four O atoms and four N atoms) in a square antiprismatic geometry with a water molecule capping the oxygen plane for Eu [1,2], Gd [3,4], Ho [2], Lu [5], Ce [6] and Dy [6] while for lanthanum [7] a polymeric derivative has been detected the water is substituted by the oxygen of an adjacent carboxylic group; in Tm [6] the coordinated water is absent, and its coordination geometry is approximately square antiprismatic.

In this context we have prepared the complex of Eu with the ligand (tris-(((2-hydroxy-3-methoxybenzyl)amino)-ethyl)amine) (H_3L) known to form different types of complexes with lanthanides depending on the preparation conditions. Numerous studies on the subject made by Orvig and co-workers [8] demonstrated that monomeric neutral hepta-coordinated [GdL] species (I) and nine coordinated species of type $[LnH_3L(NO_3)_3]$ (Ln=Pr, Nd) (II) or hexacoordinated monomeric $Ln[H_3L]_2^{3+}$ charged species (Ln=Pr, Nd, Gd, Yb) (III) can be obtained (see Scheme 1), showing the importance of 3-methoxy groups on the phenyl rings for the coordination behaviour of this type of ligand versus the lanthanide ions.

We report the synthesis of the type (II) complex $Eu(H_3L)(NO_3)_3$ and the determination of its crystal structure in two different solvation forms.

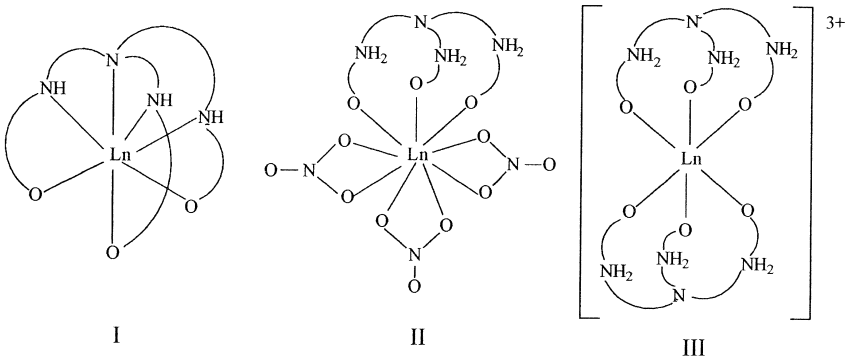
2. Experimental

2.1. Materials

$Eu(NO_3)_3 \cdot 6H_2O$, bis(2-aminoethyl)amine (tren), *o*-vanilin, methanol, tetrahydrofuran, acetonitrile, potassium borohydride were obtained from Aldrich and used without further purification.

*Corresponding author. Tel.: +39-049-829-5611; fax: +39-049-870-2911.

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01131-8



Scheme 1.

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Geol FX90Q instrument.

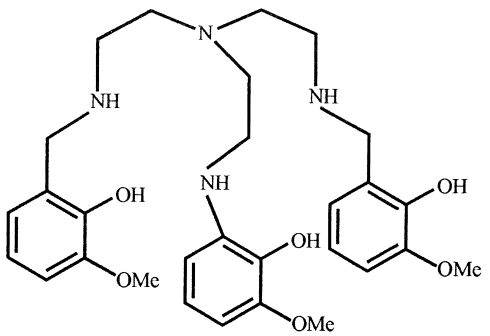
2.3. Ligand synthesis

The (tris(((2-hydroxy-3-methoxybenzyl)amino)ethyl)-amine) (H_3L) (see Scheme 2) was prepared according to the procedure reported in the literature [8]. The purity of the ligand was checked with ^{1}H NMR($CDCl_3$).

2.4. Synthesis of the europium complex

To a solution of $Eu(NO_3)_3 \cdot 6H_2O$ in methanol (50 ml) was added the ligand H_3L in tetrahydrofuran (20 ml) in the molar ratio 1/1. A precipitate formed immediately. The reaction mixture was stirred overnight. The precipitate was filtered off, washed with ethanol and acetonitrile and dried under vacuum. The pale yellow solid was suspended in acetonitrile in which it is almost insoluble. The mixture was gently heated and small portions of methanol added until the complete dissolution of the solid. The limpid solution was then left at room temperature in a closed vessel. After a week small, yellow-orange crystals separated suitable for the X-ray data collection.

Several experiments were done to check whether the $Eu(H_3L)(NO_3)_3$ crystalline complex could be converted to the $[Eu(H_3L)_2](NO_3)_3$ one, in the presence of NaOH. We followed the procedure described in Ref. [8]. A 2 N solution of NaOH was added dropwise to a suspension of $Eu(H_3L)(NO_3)_3$ in methanol. The solid redissolved to give a clear solution. After filtration an amorphous orange pale solid separated; it was unsuitable for an X ray diffraction study.



Scheme 2.

2.5. Crystal structure determination

2.5.1. X-ray data

Intensity data were collected on a Nonius Kappa CCD with monochromatic Mo Kα radiation for form **1** at room temperature (293 K) and for form **2** on a Siemens SMART CCD using monochromatic Mo Kα radiation at 293 and 100 K.

The structures were solved by the standard heavy atom method. Refinement was carried out by full-matrix least-squares; the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$. The H-atoms were placed in the observed positions except for the methyls introduced at calculated positions with fixed isotropic thermal parameters (1.2 $\mathbf{U}_{Eq.}$ of the parent carbon atom) the water protons were not introduced.

Structure refinement and final geometrical calculations were carried out with the SHELXL-93 [9] program, drawings were produced using ORTEP II [10].

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 149445 & 149446. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

In the bulk of the crystals two crystal forms are present. Their identity was discovered fortuitously by trying to collect data at room temperature and at 100 K on two different crystals.

Two different crystal cells were discovered hereinafter form **1** (which contains water and acetonitrile as solvent) and form **2** (which contains water as solvent). The crystal of form **2**, used for a quick data collection at 100 K, was also used for data collection at room temperature with longer exposure time in order to get better observations. In Table 1 the crystal data of the different forms are reported, and in Table 2 significant geometric parameters for the two forms.

The crystal structure of $Eu(H_3L)(NO_3)_3$ (form **1**) consists of discrete molecules (Fig. 1) packed in the monoclinic cell with water and acetonitrile.

The coordination geometry around the metal ion is a tricapped trigonal prism, where the phenoxy O atoms O(1), O(2), O(3) and three oxygens of the nitrate O(7), O(10), O(13) form a distorted trigonal prism and O(8), O(11), O(14) are in the capping positions (Fig. 2).

The ligand is zwitterionic and three protons bridge the NH_2^+ and O^- atoms of the adjacent phenoxy moieties. The three endo-oriented H atoms form bifurcated hydrogen bonds of different strength with the phenolate oxygen atoms (see Table 3); while two of the exooriented hydrogens form intermolecular hydrogen bonds with the clathrate water and with the CH_3CN solvent moiety.

In half the molecules the arms of the ligand (amine phenol) form a left-handed screw and the nitrate ions form right-handed screw about the metal, in the other half of the molecules the ligand arms are right- and the nitrates left-handed. This type of conformation is quite analogous to that reported for the Gd complex [tris(3-aza-4-methylhept-4-ene-6-on-1-yl)amine]$(NO_3)_3$ [11].

The chelate nitrates are rather asymmetric with a range Eu–$O(NO)_3$ from 2.521(3) to 2.633(3) Å. The lone pair of

Table 2
Selected bond lengths (Å) and angles (°) for $[Eu(H_3L)(NO_3)_3]\cdot(CH_3CN)(H_2O)$ (**1**) and $[Eu(H_3L)(NO_3)_3]\cdot(H_2O)_3$ (**2**)

Compound	**1**	**2**
Eu–O(1)	2.278(3)	2.248(5)
Eu–O(2)	2.303(2)	2.282(6)
Eu–O(3)	2.250(2)	2.249(5)
Eu–O(7)	2.581(3)	2.584(6)
Eu–O(8)	2.624(3)	2.619(6)
Eu–O(10)	2.535(3)	2.518(7)
Eu–O(11)	2.633(3)	2.650(6)
Eu–O(13)	2.521(3)	2.578(6)
Eu–O(14)	2.601(3)	2.565(6)
O(1)–Eu–O(2)	81.14(8)	81.5(2)
O(1)–Eu–O(3)	83.04(9)	83.8(2)
O(2)–Eu–O(3)	80.52(8)	80.2(2)
O(1)–Eu–O(8)	83.49(8)	87.1(2)
O(1)–Eu–O(7)	84.31(9)	91.3(2)
O(2)–Eu–O(10)	89.42(8)	93.5(2)
O(2)–Eu–O(11)	84.33(9)	84.5(2)
O(3)–Eu–O(11)	76.16(9)	73.5(2)
O(3)–Eu–O(13)	90.51(9)	84.6(2)
O(13)–Eu–O(14)	49.69(9)	49.1(2)
O(10)–Eu–O(11)	49.04(9)	48.6(2)
O(7)–Eu–O(8)	48.61(8)	48.7(2)

Table 1
Crystal data

	1 (293 K)	**2** (293 K)
Compound	$[Eu(H_3L)(NO_3)_3]\cdot(CH_3CN)(H_2O)$	$[Eu(H_3L)(NO_3)_3]\cdot(H_2O)_3$
Formula	$C_{32}H_{47}N_8O_{16}Eu$	$C_{30}H_{48}N_7O_{18}Eu$
Mol wt	951.74	946.71
Color/shape	Yellow/needles	Yellow/needles
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.8538(3)	12.353(2)[a] [12.291(2)]
b (Å)	15.8325(4)	15.600(2) [15.492(2)]
c (Å)	19.5377(5)	20.072(2) [19.967(2)]
β (°)	90.369(1)	95.760(5) [95.145(8)]
V (Å^3)	3976.0(2)	3848.6(7)
Z	4	4
D_c (g cm^{-3})	1.590	1.634
$F(000)$	1944	1936
θ_{max} (°)	34	27
Radiation (λ, Å)	Mo Kα(0.71069)	Mo Kα (0.71069)
μ (cm^{-1})	16.57	17.15
T (K)	293	293
No. reflections collected	56 317	16 966
No. unique	14 841	7378
No. observed [$I=2.5\sigma(I)$]	7574	5962
Weighting scheme w	$1/[\sigma^2(F_o^2)+(0.0270P)^2]$[b]	$1/[\sigma^2(F_o^2)+31.4P]$[b]
$R=\Sigma[\lvert F_o\rvert-\lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.034	0.060
R_w (on F^2)	0.080	0.138
GOF	0.911	1.392

[a] The corresponding values at 100 K are reported in square brackets.
[b] $P=\max(F_o^2-F_c^2)^{2/3}$.

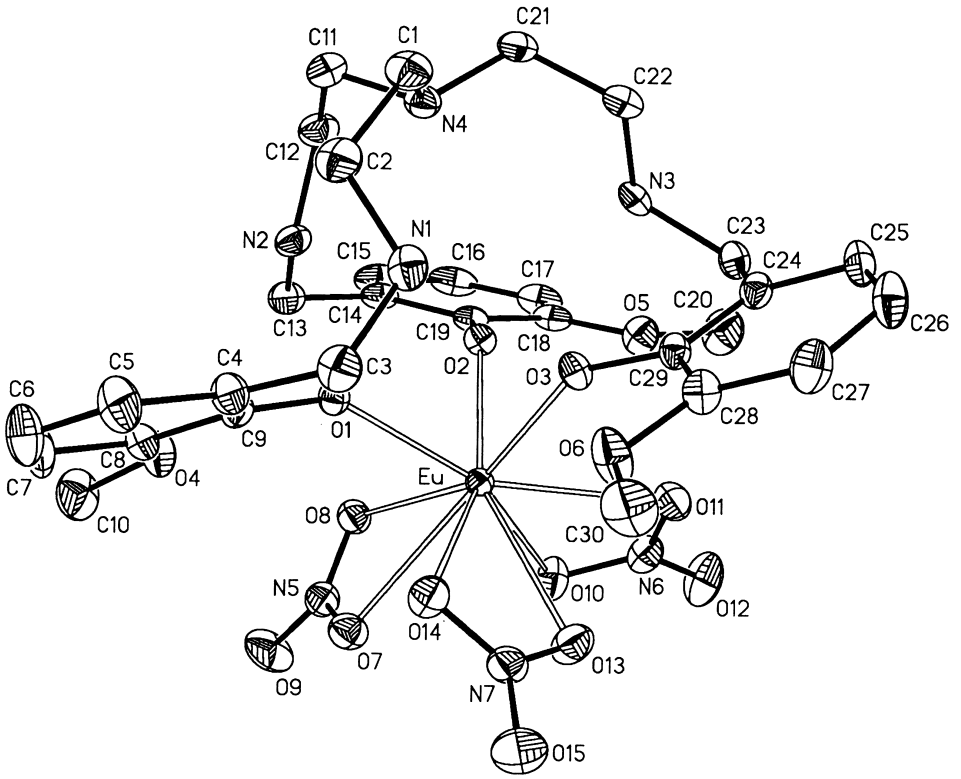


Fig. 1. One molecule of $[Eu(H_3L)(NO_3)_3]$ showing the designations of the atoms. The vibration ellipsoids are those of form **1** at 40% confidence level.

the tertiary nitrogen atom is pointing in the direction of Eu atom as found in the compound previously quoted.

The form **2** differs from **1** in the presence of three water molecules per complex unit, instead of one water and one acetonitrile. This produces some difference in the conformation of the flexible part of the ligand: mainly in the C(14)–C(13)–N(2)–C(12)–C(11)–N(4) chain with torsion around C(13)–N(2) of 60.1(5)° in **1** compared to 53.7(9)° in **2**, around N(2)–C(12) −179.0(3)° in **1** and −174.1(8)° in **2** and 69.6(5)° in **1** versus 66.6(9)° in **2** for C(11)–C(12). In addition the torsion angle N(4)–C(21)–C(22)–N(3) is 77.0(5)° in **1** and 83(1)° in **2**. This may be related to the more extensive H-bonding interaction in form **2**, O(17)···O(18) is 2.87(1) (the water protons were not detected) and each water molecule H-bonds to a nitrate

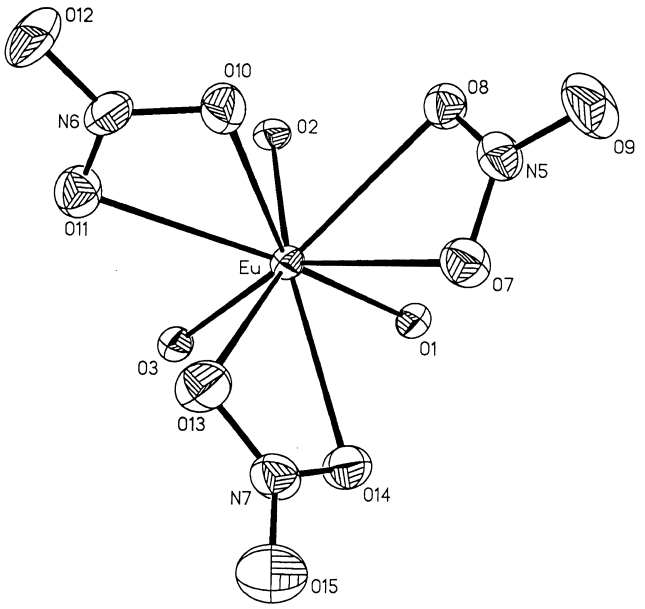


Fig. 2. Coordination about the Eu(III) ion in form **1**.

Table 3
Significant hydrogen bond interactions

Donor		Acceptor	H→Acceptor (Å)		Angle (°)
Form **1**					
N(1)	2.855(4)	O(1)	H(11)	2.37(4)	119(3)
N(1)	2.943(5)	O(3)	H(11)	2.24(4)	144(4)
N(1)	2.81(1)	$O(16)_w$	H(1)	2.01(4)	146(4)
N(2)	2.869(4)	O(1)	H(21)	2.05(7)	157(6)
N(2)	2.775(4)	O(2)	H(21)	2.39(7)	107(5)
N(2)	2.913(6)	$N(8)_{(CH3CN)}$	H(2)	1.94(8)	148(4)
N(3)	2.855(4)	O(2)	H(3)	2.18(3)	152(3)
N(3)	2.874(4)	O(3)	H(3)	2.40(3)	123(3)
Form **2**					
N(1)	2.876(10)	O(1)	H(11)	2.42(6)	124(6)
N(1)	3.009(9)	O(3)	H(11)	2.44(4)	139(6)
N(1)	2.859(10)	$O(16)_w$	H(1)	1.77(9)	153(6)
N(2)	2.92(1)	O(1)	H(21)	2.30(8)	138(7)
N(2)	2.893(9)	O(2)	H(21)	2.32(8)	132(7)
N(2)	2.88(1)	$O(17)_w$	H(2)	1.88(9)	161(8)
N(3)	2.860(9)	O(2)	H(3)	1.98(9)	153(8)
N(3)	2.820(9)	O(3)	H(3)	2.25(9)	118(7)

oxygen atom (O(13)···O(17) 3.00(1) Å, O(10)···O(18) 3.02(1) Å and O(14)···O(16) 2.82(3) Å) (see Table 3). The effect is to make the volume occupied per non-hydrogen atom 1.7% less in form **2** than in form **1**.

A comparison of the Eu–O bond distances in the two forms does not show significant differences.

The crystal structure of Eu (type II) confirms that proposed by Orvig and co-workers [11] on the basis of spectral and analytical data for Pr and Nd ($Ln(H_3L)(NO_3)_3$) while for Gd and Yb isolated under similar conditions they have obtained type III complexes ($Ln(H_3L)_2(NO_3)_3$).

Then the change in the structure is at the Gd where the substitution of the three nitro groups with the polydentate ligand results in the formation of the cationic complexes $Ln(H_3L)_2^{3+}$ with a reduction in the coordination number from nine to six. According to Orvig and co-workers [11] the reduction of the ionic radius of Gd (0.94 Å for six coordination and 1.05 Å for nine, versus 0.95 and 1.07 Å, respectively, for Eu [12]) causes crowding between the three methoxy groups and the three bidentate nitrate anions, therefore the coordination of the second tridentate H_3L ligand becomes favourable and the six coordinate complexes are formed.

Even though the importance of the size of the ions is remarkable, other relevant factors must be considered for the formation of a particular derivative, starting from the types of the neutral and charged ligands to the nature and amount of the solvent used in the synthetic procedure as in the recent report by Drew et al. [13] on the crystal structures of the complete series of lanthanide nitrates with the terdentate ligand 4-amino-bis(2,6-(2-pyridil)-1,3,5-triazine. Five structural types have been detected with the nitrate anions behaving from chelating to monodentate and with different amounts of coordinated waters. The systematic survey of the crystal structures by White and co-workers [14,15] of the complete series of lanthanides with a particular ligand is also very enlightening.

Concluding, it is not so easy to establish a priori the behaviour of a particular ligand with the whole series of lanthanides considering the nature mainly ionic of the bonds to the metal ion, and the role that could be played by non-covalent secondary interactions like hydrogen-bonding and steric repulsion.

Acknowledgements

We acknowledge the help of Professor Elisabetta Foresti, University of Bologna, in the data collection on the SMART diffractometer.

References

[1] M.R. Spirlet, J. Rebizant, J.F. Desreux, M.F. Loncin, Inorg. Chem. 23 (1984) 359.
[2] F. Benetollo, G. Bombieri, S. Aime, M. Botta, Acta Crystallogr. C55 (1999) 353.
[3] J.P. Dubost, M. Leger, M.I. Langlois, D. Meyer, M.C.R. Schaefer, Sci. Paris Ser. 2 (312) (1991) 349.
[4] C.A. Chang, I.C. Francesconi, M.F. Malley, K. Kumar, J.Z. Gougoutas, M.F. Tweedle, D.W. Lee, L. Wilson, Inorg. Chem. 32 (1993) 3501.
[5] S. Aime, A. Barge, M. Botta, M. Fasano, J.D. Ayala, G. Bombieri, Inorg. Chim. Acta 246 (1996) 423.
[6] G. Bombieri, F. Benetollo, S. Aime, M. Botta, L. Calabi, presented at the Glasgow (1999) Meeting XVIII IUCr Congress, p. 410.
[7] S. Aime, A. Barge, F. Benetollo, G. Bombieri, M. Botta, F. Uggeri, Inorg. Chem 36 (1997) 4287.
[8] S. Liu, L.W. Yang, S.J. Rettig, C. Orvig, Inorg. Chem. 32 (1993) 2773.
[9] G.M. Sheldrick, 'SHELXL93', Programm for the Refinement of Crystal Structures, University of Göttingen, Germany.
[10] C.K. Johnson, 'ORTEP II' report ORNL-5138, Oak Ridge National Laboratory, TN, USA, 1976.
[11] A. Smith, S.J. Rettig, C. Orvig, Inorg. Chem. 27 (1988) 3929.
[12] R.D. Shannon, Acta Crystallogr. A32 (1976) 751.
[13] M.G.B. Drew, M.J. Hudson, P.B. Iveson, C. Madic, M.L. Russell, J. Chem. Soc., Dalton Trans. (2000) 2711 and Refs. therein.
[14] C.J. Kepert, Wei-Min Lu, B.W. Skelton, A.H. White, Aust. J. Chem. 47 (1994) 365.
[15] L.I. Semenova, A.H. White, Aust. J. Chem. 52 (1999) 507, and Refs. therein.