Four Isotypic Highly Coordinated Lanthanide Complexes of the Tripodal Ligand Bis[(2-pyridyl)methyl][(1-methylimidazol-2-yl)methyl]amine

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

The Ln(III) complexes (Ln = Pr, Nd, Sm and Tb) of the tripodal ligand bis[(2-pyridyl)methyl][(1-methylimidazol-2-yl)methyl]amine (bpia) have been synthesized and characterized by single crystal X-ray structure determination as well as vibrational spectroscopy. The coordination spheres of the lanthanide cations are completed by three chelating nitrate anions yielding neutral complexes with a tenfold coordination of the metal ions. All four compounds are found to be isotypic, crystallizing in space group $P\bar{1}$ (No. 2) with Z = 2. On comparing the IR-spectra of the new complexes to the spectra of the free ligands a shift to higher wave numbers is observed for corresponding bands in both, bpia and nitrate ligands.

Key words: Crystal Structures, Tripodal Tetradentate Ligands, Rare Earth Metals, Imidazole

Introduction

Lanthanide(III) ion complexes have been studied widely for multiple reasons within the last years. The magnetic and spectroscopic properties of such compounds are of special interest to studies in biological systems [1] and possible physical applications. Such non-enzymatic reagents can efficiently promote the hydrolytic cleavage of phosphate esters (*e.g.* DNA or chemical toxins) [2 – 4]. The hydrolysis of phosphodiesters using small complex molecules is expected to have a fundamental impact on the development of artificial nucleases for use in biotechnology as well as for the detoxification of chemical weapons and insecticides [5].

The strong luminescence of Eu(III) and Tb(III) complexes [6 – 10] has been more closely investigated since this property may make these compounds useful as luminescent labels in fluoroimmunoassays [11 – 15]. Furthermore, the luminescence gives additional information on the site symmetry of the lanthanide cation. In this context, little work has been dedicated towards the variation of the ligand sphere of the lanthanide cores with a certain emphasis on aromatic nitrogen donors [16, 17]. Such aromatic ligands can act as chromophores which absorb energy and transfer it to the metal core [18]. Additionally, a protection of the
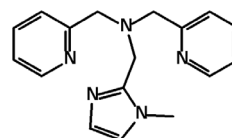

Fig. 1. Structure of the ligand bpia.

lanthanide ion from external interactions is desirable in order to avoid luminescence quenching. This protection can be achieved by binding as many ligands as possible to the metal core resulting in high coordination numbers.

Here we describe the syntheses and structural properties of the first rare earth complexes with the tripodal ligand bis[(2-pyridyl)methyl][(1-methylimidazol-2-yl)methyl]amine (bpia) (see Fig. 1) which was first synthesized by Buchanan *et al.* [19].

Experimental Section

General methods

All starting materials were obtained from commercial sources (Aldrich, Fluka) and were used without further purification. Elemental analyses were performed on a Heraeus CHN-O rapid analyzer at the Organisch-Chemisches Institut, University of Münster. From KBr pellets of the ligand and of the complexes IR spectra were obtained on a Bruker IFS 48

Table 1. Crystal data and structure refinement for **1**, **2**, **3**, and **4**.

	[Pr(bpia)(NO$_3$)$_3$] (**1**)	[Nd(bpia)(NO$_3$)$_3$] (**2**)	[Sm(bpia)(NO$_3$)$_3$] (**3**)	[Tb(bpia)(NO$_3$)$_3$] (**4**)
Empirical formula	C$_{17}$H$_{19}$N$_8$O$_9$Pr	C$_{17}$H$_{19}$N$_8$NdO$_9$	C$_{17}$H$_{19}$N$_8$O$_9$Sm	C$_{17}$H$_{19}$N$_8$O$_9$Tb
Formula weight, g/mol	620.31	623.64	629.75	638.32
Crystal color and shape	light green cubes	violet cubes	yellow cubes	yellow plates
Crystal system		triclinic		
Space group		$P\bar{1}$ (No. 2)		
Unit cell dimensions				
a	8.463(2) Å	8.424(2) Å	8.459(2) Å	8.408(2) Å
b	12.046(2) Å	12.013(2) Å	12.082(2) Å	12.057(2) Å
c	12.078(2) Å	12.013(2) Å	12.103(2) Å	12.093(2) Å
α	89.85(3)°	89.97(3)°	90.00(3)°	89.81(3)°
β	72.22(3)°	72.32(3)°	72.42(3)°	72.63(3)°
γ	85.28(3)°	85.25(3)°	85.40(3)°	85.47(3)°
Volume, Å^3	1168.2(4)	1153.9(4)	1175.0(4)	1166.1(4)
Formula units/cell	2	2	2	2
D$_c$, g/cm^3	1.764	1.795	1.780	1.818
Diffractometer (wavelength, Å)		Siemens P3 (Mo-K$_\alpha$, λ = 0.71073, Graphite monochromator)		
Temperature, K		293(2)		
Absorption coefficient, mm^{-1}	2.150	2.315	2.563	3.097
Data collection range	4.84° < 2θ < 54.00° (+h, ±k, ±l)	4.86° < 2θ < 54.00° (−h, ±k, ±l)	4.82° < 2θ < 53.98° (+h, ±k, ±l)	4.84° < 2θ < 53.98° (+h, ±k, ±l)
Reflections collected	5460	5384	5482	5418
Independent reflections	5108 [R(int) = 0.0309]	5033 [R(int) = 0.0252]	5130 [R(int) = 0.0170]	5068 [R(int) = 0.0345]
Observed reflections [$I > 2\sigma(I)$]	3982	4156	4752	4384
Program for structure solution		Patterson, SHELXS-97 [22]		
Program for structure refinement		SHELXL-97, Full matrix on F^2 [22]		
Goodness-of-fit on F^2	1.025	0.956	1.157	1.107
Final R values ($I > 2\sigma(I)$)	$R1$ = 0.0452, $wR2$ = 0.0827[a]	$R1$ = 0.0397, $wR2$ = 0.0929[b]	$R1$ = 0.0311, $wR2$ = 0.0727[c]	$R1$ = 0.0666, $wR2$ = 0.1588[d]
Final R value (all data)	$R1$ = 0.0699, $wR2$ = 0.0907[a]	$R1$ = 0.0498, $wR2$ = 0.0958[b]	$R1$ = 0.0355, $wR2$ = 0.0747[c]	$R1$ = 0.0808, $wR2$ = 0.1752[d]
$(\Delta/\rho)_{max}$; $(\Delta/\rho)_{min}$, e$^-$ Å^{-3}	0.963; −0.918	1.528; −1.532	0.980; −0.919	2.474; −3.311

$w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2)/3$; [a] x = 0.0357, y = 0; [b] x = 0.0594, y = 0; [c] x = 0.0315, y = 1.3983; [d] x = 0.0929, y = 8.9804.

spectrometer (4000−400 cm^{-1}). The ligand bpia was synthesized following a procedure described elsewhere [20, 21].

*Syntheses of the complexes with the general formula [Ln(bpia)(NO$_3$)$_3$] (Ln = Pr (**1**), Nd (**2**), Sm (**3**), Tb (**4**))*

The complexes were obtained from lanthanide nitrate and the ligand in water following similar synthetic routes. To a solution of 0.12 mmol of Ln(NO$_3$)$_3$ · 6H$_2$O (51 mg for **1**, 52 mg for **2**, 53 mg for **3**) or 0.24 mmol (104 mg) of Tb(NO$_3$)$_3$ · 5H$_2$O for **4** in 5 ml of water was added a solution (water/methanol = 5/2) of 34 mg (0.12 mmol) of bpia for **1**−**3** and 68 mg (0.24 mmol) of bpia for **4**, respectively. The reaction mixture was stirred for 3 h at ambient temperature. Single crystals suitable for X-ray diffraction were obtained upon slow evaporation of the solvent after sev-

eral days. **1**: 56 mg; 76%; m.p. > 350 °C; C$_{17}$H$_{19}$N$_8$O$_9$Pr (620.31 g mol^{-1}): calcd. C 32.92, H 3.09, N 18.06; found C 32.81, H 3.14, N 18.24. **2**: 44 mg; 59%; m.p. > 350 °C; C$_{17}$H$_{19}$N$_8$O$_9$Nd (623.64 g mol^{-1}): calcd. C 32.74, H 3.07, N 17.97; found C 32.68, H 3.16; N 18.21. **3**: 39 mg; 51%; m.p. 346 °C; C$_{17}$H$_{19}$N$_8$O$_9$Sm (629.75 g mol^{-1}): calcd. C 32.42, H 3.04, N 17.79; found C 32.18, H 2.94, N 17.44. **4**: 133 mg; 87%; m.p. 333 °C; C$_{17}$H$_{19}$N$_8$O$_9$Tb (638.32 g mol^{-1}): calcd. C 31.99, H 3.00, N 17.55; found C 31.90, H 3.03, N 17.98.

Single crystal structure analysis

The unit cell data and diffraction intensities of the complexes were collected on a Siemens P3 four-circle diffractometer at 293 K with graphite monochromated Mo-K$_\alpha$ ra-

Table 2. Selected bond lengths [Å] in **1**, **2**, **3**, and **4**.

	1	2	3	4
Ln(1)-N(1)	2.693(5)	2.673(4)	2.669(3)	2.635(7)
Ln(1)-N(2)	2.716(4)	2.692(4)	2.693(3)	2.663(7)
Ln(1)-N(3)	2.691(4)	2.680(4)	2.674(3)	2.651(9)
Ln(1)-N(4)	2.550(4)	2.530(4)	2.529(3)	2.480(8)
Ln(1)-O(1)	2.574(4)	2.546(4)	2.537(3)	2.497(8)
Ln(1)-O(2)	2.655(4)	2.638(4)	2.635(3)	2.603(9)
Ln(1)-N(6)	3.050(5)	3.015(5)	3.015(4)	2.995(10)
Ln(1)-O(4)	2.583(4)	2.569(4)	2.562(3)	2.529(8)
Ln(1)-O(5)	2.529(4)	2.510(4)	2.498(3)	2.466(7)
Ln(1)-N(7)	2.981(6)	2.964(5)	2.962(4)	2.911(9)
Ln(1)-O(7)	2.569(4)	2.544(4)	2.538(3)	2.502(8)
Ln(1)-O(8)	2.583(4)	2.557(4)	2.555(3)	2.526(8)
Ln(1)-N(8)	3.002(5)	2.976(5)	2.974(4)	2.935(8)

Table 3. Angles [°] between selected atoms in **1**, **2**, **3**, and **4**.

	1	2	3	4
N(1)-Ln(1)-N(2)	61.2(2)	61.3(2)	61.7(2)	61.5(2)
N(1)-Ln(1)-N(3)	98.3(2)	98.6(2)	98.8(2)	99.7(3)
N(1)-Ln(1)-N(4)	98.3(2)	98.6(2)	99.3(2)	99.7(3)
N(1)-Ln(1)-N(6)	73.3(2)	73.3(2)	72.7(2)	72.4(3)
N(1)-Ln(1)-N(7)	95.4(2)	95.2(2)	95.1(2)	94.8(3)
N(1)-Ln(1)-N(8)	166.2(2)	166.0(2)	165.8(2)	165.4(3)
N(2)-Ln(1)-N(3)	62.2(2)	62.5(2)	63.0(2)	63.9(2)
N(2)-Ln(1)-N(4)	63.0(2)	63.4(2)	63.8(2)	64.3(2)
N(2)-Ln(1)-N(6)	120.4(2)	120.5(2)	120.5(2)	120.0(3)
N(2)-Ln(1)-N(7)	123.4(2)	123.1(2)	123.5(2)	123.4(2)
N(2)-Ln(1)-N(8)	118.5(2)	118.5(2)	118.7(1)	119.1(2)
N(3)-Ln(1)-N(4)	103.2(2)	103.6(2)	104.2(2)	104.4(3)
N(3)-Ln(1)-N(6)	90.8(2)	90.8(2)	90.6(2)	90.3(3)
N(3)-Ln(1)-N(7)	166.1(2)	165.9(2)	166.0(2)	165.5(3)
N(3)-Ln(1)-N(8)	71.4(2)	71.0(2)	70.9(2)	69.9(3)
N(4)-Ln(1)-N(6)	164.7(2)	164.6(2)	164.3(2)	164.5(3)
N(4)-Ln(1)-N(7)	72.0(2)	71.5(2)	71.6(2)	71.6(3)
N(4)-Ln(1)-N(8)	93.1(2)	93.1(2)	92.8(2)	93.0(3)
N(6)-Ln(1)-N(7)	95.8(2)	95.9(2)	95.3(2)	95.3(3)
N(6)-Ln(1)-N(8)	97.3(2)	97.0(2)	97.1(2)	96.8(3)
N(7)-Ln(1)-N(8)	95.6(2)	95.9(2)	95.7(2)	96.1(3)

diation ($\lambda = 0.71073$ Å) using the ω-scan technique. The complete data collection parameters and details of the structure solutions and refinements are given in Table 1. The four structures were solved by Patterson syntheses and refined in full matrix least-squares analyses on F^2 using the programs SHELXS 97 and SHELXL 97 [22]. In final cycles all non-hydrogen atoms were refined anisotropically with ligand hydrogen riding on ideal positions. The isotropic displacement parameters for the ligand's methyl group were refined with 1.5 times and for all other hydrogen atoms with 1.2 times the U_{eq} value of the bonding atoms. Selected bond lengths and angles are detailed in Tables 2 and 3. As a representative of the four isostructural compounds the ellipsoid plot and the unit cell of [Pr(bpia)(NO₃)₃] (**1**) are presented in Fig. 2 and 3. Atomic coordinates, displacement parameters, and all bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of the data can be obtained free of charge on application to The Di-
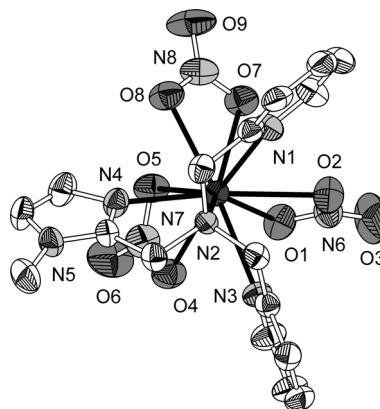
Fig. 2. Ellipsoid plot of [Pr(bpia)(NO₃)₃] (**1**) (50% probability); hydrogen atoms omitted for clarity.
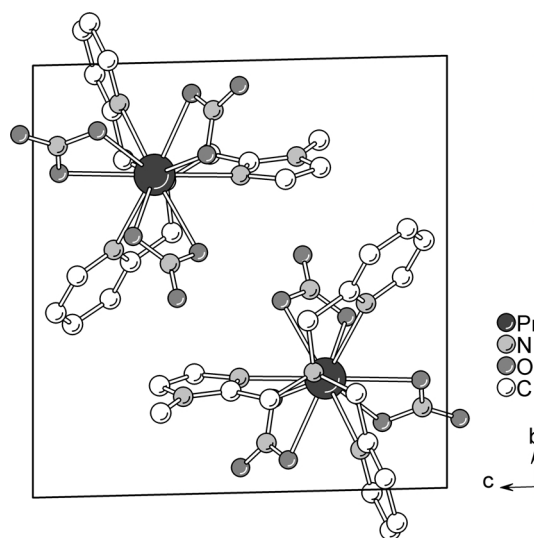
Fig. 3. Unit cell of [Pr(bpia)(NO₃)₃] (**1**); hydrogen atoms omitted for clarity.

rector, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, on full quoting the journal citation and deposition number CCDC 227379 (**1**), CCDC 227378 (**2**), CCDC 227380 (**3**), CCDC 227381 (**4**).

Results and Discussion

The ligand bpia was prepared following literature procedures [20, 21]. Single crystals of the complexes precipitated from solutions of equimolar amounts of the ligand and Ln(III) nitrate in a mixture of water and methanol (water/methanol = 5/2). The ligand bpia provides an exclusively nitrogen containing donor set de-

Table 4. Selected vibrational modes (in cm^{-1}) in the IR region and their assignment for **1** to **4** and the free ligand bpia.

1	2	3	4	bpia	Assignment
1605	1606	1606	1606	1589 (vs)	$\delta_{aromat.}$
1572	1572	1572	1573	1566 (vs)	$\delta_{aromat.}$
1488	1472	1504	1473	1472 (s)	$\delta_{aromat.}$
1384	1384	1384	1384	1380 – 1350*	v (N-O) nitrate

* Vibrations of nitrate anions as given in [27].

rived from two pyridine moieties, one methylimidazol arm and the central tertiary amine.

*The crystal structures of the complexes with the general formula [Ln(bpia)(NO$_3$)$_3$] (Ln = Pr (**1**), Nd (**2**), Sm (**3**), Tb(**4**))*

The four isotypic compounds crystallize in the triclinic space group $P\bar{1}$ (No. 2) with two complex molecules per unit cell. The coordination of three nitrate anions to the metal yields neutral complexes. The structure refinements converged to $R_1 = 0.0452$ (**1**), $R_1 = 0.0397$ (**2**), $R_1 = 0.0311$, and $R_1 = 0.0666$ (**4**). The lattice constants of the four unit cells vary only slightly (Table 1).

The rare earth ions are surrounded by an N$_4$O$_6$ donor set. This coordination sphere derives from the tripodal ligand bpia and four $\eta_{1,3}$ bound nitrate ions. Accordingly, the lanthanide ions exibit a tenfold coordination, a rare but not unusual array for rare earth complexes. The nitrate oxygen atoms show bond lengths of 2.529(4) to 2.655(4) Å for **1**, 2.510(4) to 2.638(4) Å for **2**, 2.498(3) to 2.635(3) Å for **3**, and 2.466(7) to 2.603(9) Å for **4**. These distances are comparable to those published for other La, Eu and Tb-complexes [16, 23 – 25]. As a result of the decreasing ionic radii among lanthanide group metals the Ln-O bond lengths become continuously shorter from **1** – **4**. Due to the bidentate binding of the three nitrate counter ions relative short Ln-N(NO$_3$) distances are observed. The N-O bond lengths of the coordinating oxygen donor atoms differ only slightly. As a result of electrostatic effects the negatively charged mesomeric part of the nitrate molecules is directed towards the

metal cation. The shortest N-O bond length is found for the non-coordinating O-atom. Accordingly, it can clearly be distinguished between N-O bonds with double bond character and N-O bonds with a lower bond order. Similar to the bonding conditions discussed in reference [15], bpia forms strong bonds to the rare earth atoms. Especially the coordinating distance of the imidazole donor moiety is relative small. This is a result of the higher Lewis basicity compared to the pyridine moieties.

Since bpia forms exclusively five membered chelate rings with a coordinated metal ion, the cis angles of the ligand are small. Therefore, the coordination sphere of the metal ion can be filled up with three chelating nitrate ligands. This constellation of ligands yields complexes with a high shielding of the metal ion.

IR-Spectroscopy

Infrared vibrational spectroscopy was performed in the region from 4000 to 400 cm^{-1} on all four complexes and the ligand. In these spectra characteristic bands for aromatic and aliphatic groups of the C-H-N scaffold are found. Some of the most intense vibrational features can be assigned to aromatic C=N and C=C ligand vibrations (Table 4). A shift to higher wavenumbers is found upon comparison of corresponding bands in the spectra of the free and the coordinated ligand. This shift demonstrates that ligation causes an increase in the force constants of the ligand. A similar shift is found for the characteristic N-O band of the nitrate ligands compared to those reported for nitrate ions in the literature [27].

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