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Preparation and Characterization of Lanthanide(III) Complexes with Polybenzimidazole Ligands. Crystal Structure of Bis[tris(*N*-methyl-1-benzimidazol-2-yl)-amine]lanthanum(III) Perchlorate Monoacetonitrile Solvate

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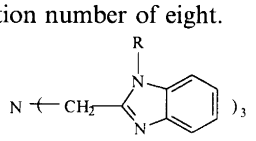
Complexes with the composition $[Ln(L^1)_2](ClO_4)_3 \cdot mCH_3CN \cdot nH_2O$ and $[Ln(L^2)_2](ClO_4)_3 \cdot mCH_3CN \cdot nH_2O$ (Ln = La, Sm, Eu, Tm; L^1 = tris(*N*-methyl-1-benzimidazol-2-yl)amine, L^2 = tris(*N*-ethyl-1-benzimidazol-2-yl)amine; *m n* = 0 or 1) have been characterized by infrared absorption spectroscopy (for the former) and elemental analysis. The X-ray crystal structure of the complex $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$ (La-**1**) has been determined. La-**1** crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 12.882(4)$, $b = 21.100(6)$, $c = 22.706(6)$ and $Z = 4$. The coordination geometry about the lanthanum(III) ion is best described as a slightly distorted triangulated dodecahedron comprising eight nitrogen atoms from two tetradentate ligands (L^1).

Lanthanides and their complexes are widely associated with their applications in chemistry, biochemistry, medicine and industry through their interesting properties (e.g. low toxicity, luminescence and powerful paramagnetism).[1] Although rare-earth metal cation complexes with anionic ligands containing oxygen as donor atoms have been the most studied,[2] more and more Ln^{III} complexes derived from nitrogen donors are being investigated and reported.[3–5] In this work we report the syntheses and characterization of lanthanide(III) complexes with the tripodal polybenzimidazole ligands tris(*N*-methyl-1-benzimidazol-2-yl)amine (L^1) and tris(*N*-ethyl-1-benzimidazol-2-yl)amine (L^2), having only nitrogens as coordinating centers and giving information on geometries with a coordination number of eight.



L^1: R = -CH_3 L^2: R = -CH_2CH_3

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Experimental

Materials. The ligands tris(*N*-methyl-1-benzimidazol-2-yl)amine (L^1) and tris(*N*-ethyl-1-benzimidazol-2-yl)amine (L^2) were synthesized by the methods described in Refs. 6 and 7. All other chemicals were commercially available and used without further purification. **Caution**: the perchlorate salts used in this study are potentially explosive and should be handled with care.

Preparation of complexes. The complexes were all synthesized in a similar way. A typical example is as follows: $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$ (La-**1**). To L^1 (100 mg, 0.22 mmol) dissolved in methanol (20 ml) was added $La(ClO_4)_3 \cdot H_2O$ (60 mg, 0.11 mmol) in methanol (5 ml) with stirring at room temperature, followed by precipitation of the complex as a white power. After having been stirred for several hours the white precipitate was filtered off and recrystallized by vapour diffusion of diethyl ether into a filtered acetonitrile solution of the complex. The other complexes $[Ln(L)_2](ClO_4)_3 \cdot mCH_3CN \cdot nH_2O$ (Ln = La, Sm, Eu, Tm; L = L^1, L^2; *m*, *n* = 0 or 1) were

Table 1. Analytical data for the complexes.

	Found (%)			Calculated (%)		
Complex	C	H	N	C	H	N
La-**1** $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$	48.68	4.13	15.04	48.83	4.17	15.25
La-**2** $[La(L^2)_2](ClO_4)_3 \cdot CH_3CN \cdot H_2O$	50.06	4.77	14.05	50.33	4.84	14.20
Sm-**1** $[Sm(L^1)_2](ClO_4)_3 \cdot CH_3CN \cdot H_2O$	47.71	4.16	14.97	47.81	4.23	14.93
Sm-**2** $[Sm(L^2)_2](ClO_4)_3 \cdot CH_3CN \cdot H_2O$	49.65	4.51	14.12	49.94	4.80	14.09
Eu-**1** $[Eu(L^1)_2](ClO_4)_3 \cdot CH_3CN \cdot H_2O$	47.64	4.02	15.10	47.75	4.22	14.92
Eu-**2** $[Eu(L^2)_2](ClO_4)_3 \cdot CH_3CN \cdot H_2O$	49.68	4.53	14.28	49.89	4.79	14.08
Tm-**1** $[Tm(L^1)_2](ClO_4)_3 \cdot CH_3CN$	47.90	4.02	15.18	47.79	4.08	14.93
Tm-**2** $[Tm(L^2)_2](ClO_4)_3$	49.51	4.59	13.52	49.68	4.58	13.52

obtained by a similar procedure. Analytical data for the isolated complexes are shown in Table 1.

Measurements. Microanalyses (C, H, N) were performed on a Carblo-Erba 1106 elemental analyzer. The IR spectra were recorded on a Nicolet-170SX FT-IR spectrophotometer as KBr discs in the range 4000–200 cm^{-1}.

X-Ray crystallographic data collection and structure determination. The single crystals of complex La-**1** were obtained by slow vapour diffusion of ether into acetonitrile solution of the complex. The data were collected on a Enraf-Nonius CAD4 diffractometer by the $\omega/2\theta$ scan mode with scan width $0.65+0.35 \tan\theta$, and a scan rate less than 5.49° min^{-1}, using graphite monochromated Mo-Kα ($\lambda=0.71073$ Å) radiation. Details of the data collection and processing are given in Table 2. Data were corrected for Lorentz and polarization effects. An absorption correction was applied using ψ-scan data.[8] The structure was solved by the heavy-atom method, followed by difference Fourier techniques. Refinement was carried out by full-matrix least-squares. All the hydrogen atoms were generated geometrically, but not refined. The final R-value was 0.060, and the R_w-value was 0.065 with $w=1/\sigma^2(F)$.

Table 2. Crystallographic data for $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$.

Empirical formula	$LaC_{56}H_{57}N_{15}Cl_3O_{12}$
Formula weight	1377.42
Temperature/K	296
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a/Å	12.882(4)
b/Å	21.100(6)
c/Å	22.706(6)
Volume/Å^3	6172(5)
Z	4
Density (calculated) /Mg m^{-3}	1.48
Absorption coefficient/cm^{-1}	8.93
F(000)	2808
Crystal size/mm	$0.55 \times 0.25 \times 0.30$
Index range	$0 \leqslant h \leqslant 15$; $-25 \leqslant k \leqslant 0$; $-27 \leqslant l \leqslant 0$
Reflections collected	6005
Independent reflections	6005
Observed reflections [$I>3\sigma(I)$]	4312
$R=\Sigma \|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.060
$R_w=[\Sigma w_i(\|F_{oi}\|-\|F_{ci}\|)^2/\Sigma w_i\|F_{oi}\|^2]^{1/2}$	0.065
Largest difference peak and hole/e Å^{-3}	1.20 and −1.13

Atomic scattering factors were taken from Ref. 9. All calculations were performed on a MICRO VAX 3100 computer using the TEXSAN program package. Atomic coordinates of non-hydrogen atoms are listed in Table 3, and selected bond lengths and angles in Table 4. Structure factors, thermal parameters, coordinates of hydrogen atoms and least-squares planes are available from the authors as supplementary material.

Results and discussion

Description of the structure. The structure of the complex $[La(L^1)_2](ClO_4)_2 \cdot CH_3CN$ consists of a $[La(L^1)_2]^{3+}$ cation, three non-coordinated perchlorate counter-anions and one acetonitrile solvent molecule. A perspective view of the $[La(L^1)_2]^{3+}$ cation, with the atom numbering scheme, is shown in Fig. 1, while the coordination polyhedron is shown in Fig. 2. In the complex cation $[La(L^1)_2]^{3+}$, eight nitrogen atoms originating from two L^1 ligands form a distorted dodecahedron around the lanthanum atom. It is interesting to see that this complex presents two kinds of La–N bond distances. The longer bond lengths are 2.73(1) and 2.77(1) Å for La–N1 and La–N8, respectively, which nitrogen atoms are from the tertiary amine. The shorter bond lengths range from 2.54(1) to 2.58(1) Å between the center La atom and N atoms from benzimidazole. The former values agree well with those observed in related systems such as $La(OAr)_3(NH_3)_4$ (Ar=2,6-*i*-$Pr_2C_6H_3$) (La–N= 2.748–2.84 Å)[10] and $[La(EDTA)(H_2O)_3]^-$ (La–N= 2.755 Å).[11] The latter is slightly shorter than those found in the complex $[LaFe(L^3)_3]^{5+}$ {where L^3=2-[6-(diethylcarbamoyl)pyridin-2-yl]-1,1′-dimethyl-2′-(5-methylpyridin-2-yl)-5,5′-methylenebis(1*H*-benzimidazole)} (La–N=2.68(2) Å).[5b] As shown above, the La–N-(benzimidazole) bond lengths are significantly shorter than the La–N(amine) bond lengths, due in part to the greater π-bonding ability of benzimidazole pendants compared to alkylamines of only σ-donors,[12] and in part to the geometric requirements of the tripodal ligand.

Table 3. Atomic coordinates for $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$.

Atom	*x*	*y*	*z*	B_{eq} [a]/Å^2
La	0.37271(6)	0.19965(3)	0.21650(3)	2.36(2)
Cl(1)	−0.1346(4)	0.2692(2)	0.1778(2)	5.6(2)
Cl(2)	0.2273(5)	0.4652(3)	0.3407(4)	8.0(3)
Cl(3)	0.0357(6)	0.1077(3)	0.4090(2)	7.1(3)
O(1)	−0.139(1)	0.2585(7)	0.2364(6)	8.6(9)
O(2)	−0.116(2)	0.2101(9)	0.1512(6)	12(1)
O(3)	−0.054(1)	0.3122(8)	0.1713(8)	10(1)
O(4)	−0.226(1)	0.294(1)	0.1556(9)	11(1)
O(5)	0.131(2)	0.4385(8)	0.328(1)	14(1)
O(6)	0.226(2)	0.514(1)	0.376(1)	15(2)
O(7)	0.264(2)	0.495(2)	0.288(1)	22(3)
O(8)	0.297(2)	0.419(1)	0.348(1)	18(2)
O(9)	0.010(3)	0.060(1)	0.3683(9)	19(2)
O(10)	−0.000(2)	0.162(1)	0.391(1)	19(2)
O(11)	−0.033(4)	0.089(2)	0.450(1)	30(4)
O(12)	0.121(2)	0.108(1)	0.428(1)	19(2)
N(1)	0.194(1)	0.2491(6)	0.2618(5)	3.4(6)
N(2)	0.189(1)	0.3664(6)	0.1416(6)	4.4(7)
N(3)	0.2598(9)	0.2709(6)	0.1501(5)	3.2(6)
N(4)	0.0804(8)	0.0875(6)	0.2391(5)	3.8(6)
N(5)	0.243(1)	0.1207(5)	0.2586(5)	3.3(6)
N(6)	0.345(1)	0.2810(6)	0.4015(5)	4.2(7)
N(7)	0.3885(9)	0.2730(5)	0.3060(4)	3.0(5)
N(8)	0.555(1)	0.1495(5)	0.1712(5)	2.9(5)
N(9)	0.6534(8)	0.1369(5)	0.3246(6)	3.5(6)
N(10)	0.4959(8)	0.1383(5)	0.2859(5)	3.2(5)
N(11)	0.399(1)	0.0187(5)	0.1076(6)	3.8(6)
N(12)	0.360(1)	0.1179(5)	0.1330(5)	3.4(5)
N(13)	0.5765(8)	0.3020(7)	0.0871(5)	3.4(5)
N(14)	0.505(1)	0.2770(5)	0.1749(6)	3.2(6)
N(15)	0.458(3)	0.115(2)	−0.0079(9)	14(2)
C(1)	0.338(2)	0.066(1)	−0.083(1)	10(2)
C(2)	0.404(2)	0.096(1)	−0.040(1)	8(2)
C(11)	0.175(1)	0.3125(6)	0.2405(7)	3.7(7)
C(12)	0.206(1)	0.3155(8)	0.1753(7)	3.9(8)
C(13)	0.237(1)	0.3546(8)	0.0865(8)	4.7(9)
C(14)	0.242(2)	0.3899(9)	0.0352(9)	6(1)
C(15)	0.299(2)	0.364(1)	−0.009(1)	8(1)
C(16)	0.345(1)	0.303(1)	−0.0043(7)	6(1)
C(17)	0.337(1)	0.2683(8)	0.0472(7)	4.6(8)
C(18)	0.278(1)	0.2958(8)	0.0930(6)	3.5(7)
C(19)	0.129(2)	0.4234(7)	0.1563(8)	5.9(9)
C(21)	0.108(1)	0.2043(5)	0.2416(7)	4.5(7)
C(22)	0.142(1)	0.1374(8)	0.2483(5)	3.2(7)
C(23)	0.143(1)	0.0335(6)	0.2413(6)	3.7(7)
C(24)	0.117(1)	−0.0297(7)	0.2328(7)	4.6(8)
C(25)	0.198(1)	−0.0727(7)	0.2404(8)	5(1)
C(26)	0.296(2)	−0.0522(8)	0.2549(8)	6(1)
C(27)	0.323(1)	0.0114(7)	0.2613(7)	4.9(8)
C(28)	0.240(1)	0.0545(6)	0.2533(6)	3.5(7)
C(29)	−0.029(1)	0.0877(8)	0.2265(9)	6(1)
C(31)	0.203(1)	0.2517(8)	0.3294(6)	4.2(8)
C(32)	0.313(1)	0.2713(6)	0.3452(6)	3.0(6)
C(33)	0.452(1)	0.2902(7)	0.3979(6)	3.5(7)
C(34)	0.526(2)	0.300(1)	0.4422(7)	5(1)
C(35)	0.623(2)	0.3054(8)	0.4249(8)	6(1)
C(36)	0.651(1)	0.3016(9)	0.3678(8)	6(1)
C(37)	0.581(1)	0.2931(7)	0.3230(7)	3.8(7)
C(38)	0.480(1)	0.2860(7)	0.3392(6)	3.6(7)
C(39)	0.281(2)	0.2793(8)	0.4530(8)	6(1)
C(41)	0.639(1)	0.163(1)	0.2167(8)	6.5(9)
C(42)	0.595(1)	0.1416(6)	0.2756(6)	2.7(6)
C(43)	0.588(1)	0.1304(7)	0.3705(7)	4.0(8)
C(44)	0.606(2)	0.1238(8)	0.4327(7)	6(1)
C(45)	0.518(2)	0.1204(9)	0.4681(8)	7(1)
C(46)	0.418(2)	0.1193(8)	0.443(1)	6(1)

Table 3. (Continued.)

Atom	x	y	z	B_{eq}[a]/Å^2
C(47)	0.396(1)	0.1246(7)	0.3844(7)	4.5(8)
C(48)	0.486(1)	0.1308(7)	0.3472(7)	3.4(7)
C(49)	0.766(1)	0.138(1)	0.327(1)	8(1)
C(51)	0.540(1)	0.0827(7)	0.1540(6)	3.5(7)
C(52)	0.432(1)	0.0752(7)	0.1305(6)	3.7(7)
C(53)	0.295(1)	0.0268(7)	0.0945(7)	4.5(8)
C(54)	0.220(2)	−0.0140(9)	0.0709(8)	6(1)
C(55)	0.121(2)	0.009(1)	0.0654(8)	7(1)
C(56)	0.099(2)	0.073(1)	0.0804(7)	6(1)
C(57)	0.173(1)	0.1133(9)	0.1022(7)	4.9(8)
C(58)	0.270(1)	0.0874(7)	0.1099(6)	3.3(7)
C(59)	0.463(2)	−0.0369(9)	0.100(1)	8(1)
C(61)	0.585(1)	0.1878(6)	0.1180(6)	3.1(6)
C(62)	0.557(1)	0.2572(7)	0.1275(6)	3.3(7)
C(63)	0.535(1)	0.3575(7)	0.1096(6)	3.1(7)
C(64)	0.532(1)	0.4173(7)	0.0855(8)	5(1)
C(65)	0.480(2)	0.4647(8)	0.1187(8)	5(1)
C(66)	0.435(1)	0.4489(8)	0.1726(7)	4.5(8)
C(67)	0.440(1)	0.3874(7)	0.1949(6)	3.6(7)
C(68)	0.490(1)	0.3423(7)	0.1637(6)	2.4(6)
C(69)	0.627(2)	0.2932(8)	0.0304(6)	5.4(8)

[a] $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 4. Selected bond lengths (in Å) and angles (in °) for $[La(L^1)_2](ClO_4)_3 \cdot CH_3CN$.

La–N(1)	2.73(1)	La–N(8)	2.77(1)
La–N(3)	2.58(1)	La–N(10)	2.58(1)
La–N(5)	2.54(1)	La–N(12)	2.57(1)
La–N(7)	2.56(1)	La–N(14)	2.54(1)
N(1)–La–N(8)	179.6(4)	N(12)–La–N(7)	174.9(3)
N(3)–La–N(10)	174.3(4)	N(14)–La–N(5)	178.9(4)
N(1)–La–N(3)	61.5(4)	N(8)–La–N(10)	61.0(4)
N(1)–La–N(5)	63.6(4)	N(8)–La–N(12)	61.5(4)
N(1)–La–N(7)	62.4(4)	N(8)–La–N(14)	62.6(4)
N(1)–La–N(10)	118.6(3)	N(8)–La–N(3)	118.9(4)
N(1)–La–N(14)	117.4(4)	N(8)–La–N(5)	116.4(3)
N(1)–La–N(12)	118.9(4)	N(8)–La–N(7)	117.3(3)
N(3)–La–N(5)	103.4(4)	N(10)–La–N(14)	97.9(4)
N(3)–La–N(7)	99.0(4)	N(10)–La–N(12)	98.7(4)
N(3)–La–N(14)	77.6(4)	N(10)–La–N(5)	81.1(3)
N(3)–La–N(12)	85.7(4)	N(10)–La–N(7)	76.7(3)
N(5)–La–N(7)	98.6(4)	N(14)–La–N(12)	101.5(4)
N(5)–La–N(12)	78.3(4)	N(14)–La–N(7)	81.6(4)

Similar examples were also found in the transition-metal complexes with such ligands.[13,14]

The atoms defining the planes are given in parentheses: P_1 (N5, N14, N7, N12), P_2 (N5, N14, N3, N10), P_3 (N5, N14, N1, N8), P_4 (N7, N12, N3, N10), P_5 (N7, N12, N1, N8) and P_6 (N3, N10, N1, N8). The displacements of the La atom from those planes are only 0.0594, 0.0372, 0.0104, 0.0167, 0.0599 and 0.0688 Å, respectively. There are six types of different dihedral angles between these planes: P_3–P_5 119.42° (about 120°); P_3–P_6 59.09 and P_5–P_6 60.33° (about 60°); P_1–P_4 51.30, P_4–P_5 50.49 and P_3–P_6 50.84° (average 50.88°); P_1–P_3 77.46,P_2–P_3 77.91 and P_1–P_2 78.80° (average 78.06°); P_1–P_6 88.93, P_2–P_5 89.08 and P_3–P_4 89.77° (about 90°) ; P_1–P_5 127.95,

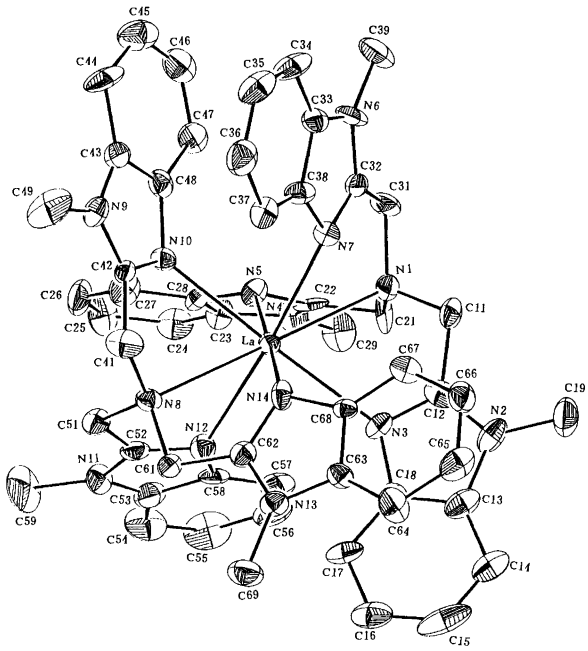

Fig. 1. Structure of the cation of $[La(L^1)_2]^{3+}$.

P_2–P_6 128.75 and P_2–P_4 130.10° (average 128.93°). The angles N1–La–N8 179.6, N12–La–N7 174.9, N3–La–N10 174.3 and N14–La–N5 178.9° are close to 180°. The coordination polyhedron (LaN8 core) has nearly perfect C_i symmetry; the distortion is mainly reflected in two elongated vertices (N1, N8).

Infrared spectra. The strong features at 1475 and 1439 cm^{-1} for L^1, assignable to the stretching mode for –C=N–C=C– of benzimidazole rings of the free ligand,[15]

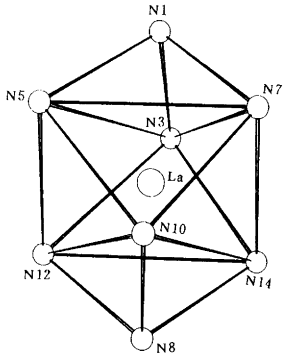

Fig. 2. Coordination polyhedron of the cation of $[La(L^1)_2]^{3+}$.

are all shifted to higher frequencies by 14–16 cm^{-1} in their complexes of La-**1** (1489 and 1453 cm^{-1}), Sm-**1** (1490 and 1454 cm^{-1}), Eu-**1** (1490 and 1455 cm^{-1}) and **Tm-1** (1491 and 1456 cm^{-1}). This indicates that all the benzimidazole rings in L^1 coordinate to the Ln center, as observed in the crystallographic results already presented. The perchlorate anions in the complexes all show symmetric vibrations (1083 and 622 cm^{-1} for La-**1**, 1086 and 623 cm^{-1} for Sm-**1**, 1088 and 623 cm^{-1} for Eu-**1**, 1090 and 624 cm^{-1} for **Tm-1**), typical of an uncoordinated ionic perchlorate group.[16] The close similarity of these complexes suggests a similar coordination environment around the metal.

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