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Frank T. Edelmann, Peter Dröse, Steffen Blaurock, Cristian G. Hrib. Effective Encapsulation of Europium(3+) by a Heptadentate Schiff-Base Ligand. Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie, 2010, 636 (8), pp.1431. 10.1002/zaac.201000141. hal-00552474

HAL Id: hal-00552474 https://hal.science/hal-00552474

Submitted on 6 Jan 2011

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Zeitschrift für Anorganische und Allgemeine Chemie

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Journal:	Zeitschrift für Anorganische und Allgemeine Chemie
Manuscript ID:	zaac.201000141.R1
Wiley - Manuscript type:	Communication
Date Submitted by the Author:	29-Apr-2010
Complete List of Authors:	Edelmann, Frank; Otto-von-Guericke-Universität Magdeburg, Lehrstuhl für Anorganische Chemie Dröse, Peter Blaurock, Steffen Hrib, Cristian G.
Keywords:	Europium , Schiff-base ligands , TRENDSAL ligand, Heptadentate ligands



SHORT COMMUNICATION

Effective Encapsulation of Europium(3+) by a Heptadentate Schiff-Base Ligand

ZAAC

Peter Dröse, Steffen Blaurock, Cristian G. Hrib and Frank T. Edelmann*

Dedicated to Professor Basil Kanellakopulos on the occasion of his 75th birthday

Keywords: Europium; Schiff-base ligands; TRENDSAL ligand; Heptadentate ligands

The bright yellow Schiff-base complex Eu(TRENDSAL) (1) $(\text{TRENDSAL} = \text{N}[\text{CH}_2\text{CH}_2\text{N}=\text{CH}(2-\text{OH}-3,5^{-t}\text{Bu}_2\text{C}_6\text{H}_2)]_3)$ was prepared in 71% yield by treatment of EuCl₃·6H₂O simultaneously with 3,5-di-tert-butylsalicylicaldehyde and tris(2-aminoethyl)amine in the presence of triethylamine. X-Rax crystal structure analyses of

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Magdeburg, Universitätsplatz 2, 39106 Magdeburg, Germany Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201000xxx or from the author.

Introduction

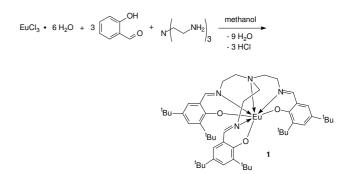
Macrocyclic Schiff-base ligands are of significant current interest as contrast media in magnetic resonance imaging [1,2] and as encapsulating ligands for radiopharmaceuticals [3]. Such ligands have become very popular due to their relatively straightforward synthesis as well as their multidentate nature which results in very high binding constants for many d- and f-block metals. In the coordination chemistry of lanthanids, steric saturation of the coordination sphere rather than electron-count is one of the guiding principles. Among the large number of ligand systems studied thus far in this respect, Schiff-base derivatives of the TREN moiety N(CH₂CH₂NH₂)₃ have been shown to be very effective, especially those derived from the reaction of salicylaldehyde derivatives with TREN. There have been a number of studies of the coordination unsubstituted chemistry of the parent ligand $N[CH_2CH_2N=CH(2-OHC_6H_4)]_3$ and its fully saturated analogue $N[CH_2CH_2NHCH_2(2-OHC_6H_4)]_3$ [4], including studies of their use as Tc-99 chelators in nuclear medicine [4b]. Orvig et al. have reported Ln derivatives of the saturated amino-phenol ligands N[CH2CH2NHCH2(2-OH-3- $R^{1}-5-R^{2}C_{6}H_{2}$]₃ ($R^{1} = H$, OMe; $R^{2} = H$, Cl, Br) [5,6], and mixed-metal and single-metal lanthanide derivatives of a range of Schiff-base ligands of the type N[CH₂CH₂N=CH(2- $OH-3-R^{1}-5-R^{2}C_{6}H_{2}$)]₃ have also been reported [6–14].

The di-tert-butyl substituted analogue N[CH₂CH₂N=CH- $(2-OH-3,5-^{t}Bu_{2}C_{6}H_{2})]_{3}$ (= TRENDSAL) was previously employed for the rare earth elements Gd, Sm, and Nd as well as indium, leading in all cases to the formation of the solvates $1 \cdot DME$ (DME = 1,2-dimethoxyethane) and 1. MeCN demonstrated the tight encapsulation of the Eu³⁺ ion, allowing not even the "slim" acetonitrile to enter the coordination sphere of europium.

mononuclear complexes [15]. This very bulky tripodal ligand is generally assumed to encapsulate even the largest lanthanide ions and thereby prevent solvation of the resulting complexes. We report here a positive proof of this assumption by showing that in the newly synthesized europium(III) complex Eu(TRENDSAL) (1) not even the "slim" ligand acetonitrile is able to enter the coordination sphere of the tightly encapsulated Eu^{3+} ion.

Results and Discussion

Previously reported synthetic routes to lanthanide TRENDSAL complexes involved either treatment of the lanthanide silylamide precursors Ln[N(SiMe₃)₂]₃ with the free ligand [15a] or, in the case of Gd, reaction of the ligand with $Gd(NO_3)_3$ ·6H₂O in the presence of NaOH. [15b] The first method requires the preparation of the Ln[N(SiMe₃)₂]₃ precursors, while the latter reaction suffers from fairly low yields (<50%). We prepared the hitherto unknown europium(III) complex Eu(TRENDSAL) (1) by a simple one-pot reaction as illustrated in Scheme 1 via treatment of europium(III)-trichloride hexahydrate with 3,5-di-tertbutylsalicylicaldehyde and tris(2-aminoethyl)amine in a molar ratio of 1:3:1. The reaction was carried out in refluxing methanol using triethylamine as HCl-scavenger.



Scheme 1. Synthesis of Eu(TRENDSAL) (1).

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Soxhlet extration of the crude product with toluene afforded the desired unsolvated product as a bright yellow, crystalline solid in 71% yield.Spectroscopic characterization of unsolvated **1** was straightforward. A mass spectrum showed the molecular ion at m/z 944.7 with 90% relative intensity. Despite the paramagnetic nature of the cerium(3+) ion a meaningful ¹H NMR spectrum could be obtained. Although spread out over a range of *ca*. 60 ppm, all signals could be unambiguously assigned.

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In order to test the possibility (or impossibility) of adduct formation with donor solvents, compound 1 was recrystallized either from DME (= 1,2-dimethoxyethane) or acetonitrile. In both cases, bright yellow single crystals were obtained which were structurally characterized by X-ray diffraction. Crystallization from DME afforded the DME solvate 1.DME. Crystal data and structure refinement details are listed in Table 1, and selected bond lengths and angles for 1.DME are summarized in Table 2. As expected, the DME is not coordinated to europium but intercalated in the crystal lattice. The molecular structure of Eu(TRENDSAL) in 1. DME is depicted in Figure 1. The overall coordination geometry around the central europium(3+) ion can be best described as distorted capped octahedral with TRENDSAL acting as triply deprotonated heptadentate ligand. It is easily recognized how the very bulky TRENDSAL ligand wraps around the central Eu(3+) ion. The six tert-butyl substituents in the periphery of the ligand largely add to the effective shielding of the europium. The Eu-O distances are 2.211(2), 2.213(2), and 2.222(2) Å, which compares favorably with the Sm-O bond lengths of 2.218(3), 2.222(4), and 2.232(4) Å in Sm(TRENDSAL) as well as the Nd-O distances of 2.241(6), 2.242(6), and 2.248(4) in Nd(TRENDSAL). [15a] Typical for complexes of this kind is the presence of two types of Ln-N distances. In 1. DME the average Eu-N distance to the three imine nitrogens is 2.526(2) Å, while a significantly longer Eu-N bond length of 2.793(2) Å is found for the interaction with the apical amine nitrogen. For comparison, in Sm(TRENDSAL) the corresponding Sm-N distances are 2.556(3) Å (average for imine nitrogens) and 2.818(4) Å (apical). [15a]

Figure 1. Molecular structure of Eu(TRENDSAL) in 1. DME.

A packing diagram (Figure 2) clearly shows that the DME solvent is just intercalated in the crystal structure as solvent of crystallization without any interaction with the europium. While this was not unexpected, we then investigated the

crystallization of **1** from acetonitrile. It is well established from early work by Kanellakopulos *et al.* that the small, "slim" acetonitrile ligand is able to add to even fairly crowded lanthanide complexes such as the tris(cyclopentadienyls) [16] as well as the tris(amidinates). [17]

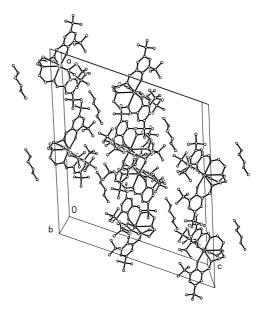


Figure 2. Unit cell of 1. DME showing the intercalated solvent of crystallization.

Crystallization of unsolvated 1 from acetonitrile afforded the solvate 1·MeCN in the form of air-stable, bright yellow crystals. Once again, the X-ray study revealed the formation of a solvate with acetonitrile molecules intercalated in the crystal lattice of Eu(TRENDSAL) (Figure 3). This finding can be seen as a positive proof for the very effective encapsulation of the central europium(3+) ion by the bulky heptadentate TRENDSAL ligand. Clearly not even the "slim" acetonitrile ligand is able to enter the completely shielded coordination sphere of europium.

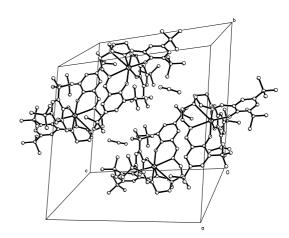


Figure 3. Unit cell of 1. MeCN showing the intercalated solvent of crystallization.

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The solvate $1 \cdot \text{MeCN}$ crystallizes in the triclinic space group P-1 with two independent molecules in the asymmetric unit (Table 1). As can been seen from Table 2, bond lengths and angles in the Eu(TRENDSAL) molecule in $1 \cdot \text{MeCN}$ do not differ significantly from those in $1 \cdot \text{DME}$. Apparently not even a labile complex exists in acetonitrile solution, as a ¹H NMR spectrum of **1** in CD₃CN showed no measurable paramagnetic shift of the solvent resonances.

Conclusions

The new Schiff-base complex Eu(TRENDSAL) (1) was prepared in 71% yield in a straightforward manner by treatment of EuCl₃·6H₂O simultaneously with 3,5-di-*tert*butylsalicylicaldehyde and tris(2-aminoethyl)amine in the presence of triethylamine. Single crystal X-ray diffraction studies of the solvates 1·DME and 1·MeCN showed that encapsulation of the central Eu³⁺ ion by the bulky heptadentate TRENDSAL ligand is so effective that not even the small, "slim" acetonitrile ligand is able to enter the coordination sphere of europium.

Experimental Section

All starting materials were obtained from commercial sources and used as received. The ¹H NMR spectrum was recorded in THF- d_8 solution on a Bruker DPX 400 spectrometer at 25 °C. Chemical shifts were referenced to TMS. Microanalysis was performed using a Leco CHNS 923 apparatus. The intensity data of **1**·MeCN and **1**·DME were collected on a Stoe IPDS 2T diffractometer with MoK_a radiation. The data were collected with the Stoe XAREA [18] program using ω -scans. Space groups were determined with XRED32 [18] program. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97. [18]

Preparation Eu(TRENDSAL) (1): To a stirred solution of 2.93 g (8 mmol) europium(III) chloride hexahydrate in methanol (100 ml) were added 5.60 g (24 mmol) 3,5-di-tert-butylsalicylicaldehyde in methanol (80 ml) and 2.43 g (24 mmol) triethylamine in 80 ml of the same solvent. The yellow mixture was stirred under reflux for 1 h. A solution of 1.30 g (8.9 mmol, slight excess) of tris(2aminoethyl)amine in methanol (80 ml) was added dropwise over a period of 30 min to the boiling reaction mixture, followed by refluxing for another 24 h. The solvent was completely removed under reduced pressure using a rotary evaporator (300 mbar, 40 °C) and desired Eu(TRENDSAL) (1) was purified by Soxhlet extraction of the remaining solid with 180 ml of toluene. The clear, yellow extract was concentrated in vacuo to a volume of 50 ml and cooled 5 °C for 24 h to afford 5.33 g (71%) of 1 as bright yellow crystals. Solvated crystals suitable for X-ray diffraction were obtained by recrystallization from either DME or acetonitrile. M.p. 234 °C (dec). IR (KBr pellet): v_{max} 2954 (vs), 2905 (st), 2865 (m), 1619 (vs, C=N), 1548 (m), 1533 (st), 1460 (st), 1435 (st), 1412 (st), 1391 (st), 1361 (m), 1334 (st), 1325 (st), 1275 (m), 1257 (st), 1166 (st), 836 (m), 744 (st) cm⁻¹. ¹H NMR (400MHz, THF-d₈): δ = -29.78 (s, 3H, N=CH), -0.68 (s, 3H, Ar-H), -0.28 (s, 27H, ^tBu), 3.23 (s, 3H, Ar-H), 3.39 (s, 3H, CH₂), 7.82 (s, 27H, ^tBu), 11.52 (s br, 3H, CH₂), 16.74 (s, 3H, CH₂), 28.88 (s br, 3H, CH₂). EI-MS: m/z 944.7 (90, [M]⁺), 929.7 (20, [M - CH₃]⁺), 219.1 (100, [CH(2-OH- $3,5^{-t}Bu_2C_6H_2)]^+).$

Supporting Information (see footnote on the first page of this article): ORTEP drawings and X-ray structural data as well as complete CIF files for **1·DME** and **1·MeCN**. **Table 1.** Crystallographic Data for **1·MeCN** and **1·DME**.

	1.DME	1·MeCN	
Empirical formula	$C_{53}H_{83}EuN_4O_4$	C53H78EuN5O3	
<i>a</i> (Å)	27.648(6)	16.3739(2)	
<i>b</i> (Å)	16.227(3)	17.8199(2)	
<i>c</i> (Å)	24.817(5)	20.7191(3)	
α (°)	90	93.0927(11)	
β (°)	111.71(3)	109.0384(11)	
γ (°)	90	112.2090(11)	
$V(Å^3)$	10344(4)	5181.13(13)	
Ζ	8	4	
Formula weight	992.19	985.16	
Space group	C2/c	P-1	
<i>T</i> (°C)	-140	-100	
λ (Å)	0.71073	0.71073	
$D_{calcd} (g cm^{-3})$	1.274	1.263	
μ (mm ⁻¹)	1.258	1.255	
Independent reflections	12770	27967	
Parameters	578	1156	
Largest diff. peak	2.421	0.897	
R(Fo or Fo ²)	0.0395	0.0486	
R_w (Fo or Fo ²)	0.0955	0.0708	

Table 2. Bond lengths [Å] and angles [°] for 1.DME.

Eu-O(1)	2.211(2)	Eu-N(2)	2.531(2)
Eu-O(2)	2.213(2)	Eu-N(1)	2.793(2)
Eu-O(3)	2.222(2)	N(2)-C(7)	1.287(4)
Eu-N(4)	2.516(2)	N(3)-C(8)	1.290(4)
Eu-N(3)	2.530(2)	N(4)-C(9)	1.283(4)
O(1)-Eu-O(2)	95.08(8)	O(2)-Eu-N(2)	164.97(8)
O(1)-Eu-O(3)	96.13(8)	O(3)-Eu-N(2)	91.64(8)
O(2)-Eu-O(3)	94.61(8)	N(4)-Eu-N(2)	105.23(8)
O(1)-Eu-N(4)	166.90(8)	N(3)-Eu-N(2)	103.56(8)
O(2)-Eu-N(4)	89.73(8)	O(1)-Eu-N(1)	120.75(7)
O(3)-Eu-N(4)	71.30(8)	O(2)-Eu-N(1)	121.34(8)
O(1)-Eu-N(3)	89.53(8)	O(3)-Eu-N(1)	122.23(7)
O(2)-Eu-N(3)	70.78(7)	N(4)-Eu-N(1)	65.92(7)
O(3)-Eu-N(3)	164.79(8)	N(3)-Eu-N(1)	65.37(7)
N(4)-Eu-N(3)	103.56(8)	N(2)-Eu-N(1)	65.49(8)
O(1)-Eu-N(2)	70.64(8)		

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[Eu(1)-O(1)	2.1901(17)	Eu(2)-O(13)	2.2114(17)
	Eu(1)-O(2)	2.2212(16)	Eu(2)-O(11)	2.2151(17)
	Eu(1)-O(3)	2.2219(17)	Eu(2)-O(12)	2.2172(16)
	Eu(1)-N(3)	2.513(2)	Eu(2)-N(14)	2.507(2)
	Eu(1)-N(4)	2.526(2)	Eu(2)-N(13)	2.5194(19)
	Eu(1)-N(2)	2.543(2)	Eu(2)-N(12)	2.534(2)
	Eu(1)-N(1)	2.789(2)	Eu(2)-N(11)	2.806(2)
	N(2)-C(7)	1.284(3)	N(12)-C(107)	1.280(3)
	N(3)-C(8)	1.282(3)	N(13)-C(108)	1.279(3)
	N(4)-C(9)	1.280(3)	N(14)-C(109)	1.281(3)
	O(1)-Eu(1)-O(2)	95.57(6)	O(13)-Eu(2)-O(11)	99.12(6)
	O(1)-Eu(1)-O(3)	92.85(7)	O(13)-Eu(2)-O(12)	94.14(7)
	O(2)-Eu(1)-O(3)	94.91(6)	O(11)-Eu(2)-O(12)	96.65(6)
	O(1)-Eu(1)-N(3)	91.44(7)	O(13)-Eu(2)-N(14)	71.56(6)
	O(2)-Eu(1)-N(3)	70.90(6)	O(11)-Eu(2)-N(14)	169.72(7)
	O(3)-Eu(1)-N(3)	165.52(7)	O(12)-Eu(2)-N(14)	88.51(7)
	O(1)-Eu(1)-N(4)	162.66(7)	O(13)-Eu(2)-N(13)	164.13(7)
	O(2)-Eu(1)-N(4)	91.49(7)	O(11)-Eu(2)-N(13)	87.39(7)
	O(3)-Eu(1)-N(4)	70.74(7)	O(12)-Eu(2)-N(13)	70.63(6)
	N(3)-Eu(1)-N(4)	105.84(7)	N(14)-Eu(2)-N(13)	102.73(7)
	O(1)-Eu(1)-N(2)	70.35(6)	O(13)-Eu(2)-N(12)	91.61(7)
	O(2)-Eu(1)-N(2)	165.02(7)	O(11)-Eu(2)-N(12)	70.79(6)
	O(3)-Eu(1)-N(2)	90.99(7)	O(12)-Eu(2)-N(12)	166.90(7)
	N(3)-Eu(1)-N(2)	103.47(6)	N(14)-Eu(2)-N(12)	104.48(7)
	N(4)-Eu(1)-N(2)	103.47(7)	N(13)-Eu(2)-N(12)	104.22(7)
	O(1)-Eu(1)-N(1)	122.28(7)	O(13)-Eu(2)-N(11)	122.41(6)
	O(2)-Eu(1)-N(1)	121.47(6)	O(11)-Eu(2)-N(11)	118.33(7)
	O(3)-Eu(1)-N(1)	122.43(7)	O(12)-Eu(2)-N(11)	120.48(6)
	N(3)-Eu(1)-N(1)	65.82(6)	N(14)-Eu(2)-N(11)	65.62(6)
	N(4)-Eu(1)-N(1)	65.83(7)	N(13)-Eu(2)-N(11)	65.18(6)
	N(2)-Eu(1)-N(1)	65.52(6)	N(12)-Eu(2)-N(11)	65.20(6)

Acknowledgement

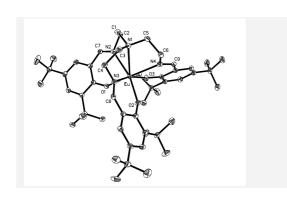
P. D. thanks the government of Sachsen-Anhalt for a Ph.D. scholarship (Graduiertenförderung). Financial support by the Ottovon-Guericke-Universität Magdeburg is also gratefully acknowledged.

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- Received: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

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