Synthesis and Structure of the First Holmium and Erbium Diiodide Complexes of Composition $LLnI_2$ (Ln = Ho, Er)

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Dedicated to Professor M. Mikolajczyk on the occasion of his 65th birthday

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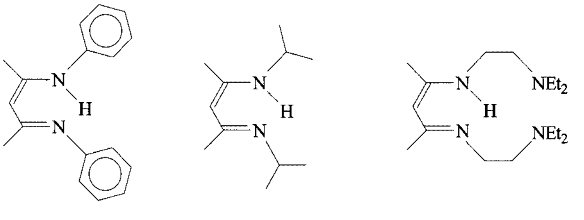
Two new diiodide complexes of stoichiometry $LLnI_2$ [Ln = Ho (**1**), Er (**2**)] with the β-diketiminato ligand 2-{[2-(diethylamino)ethyl]amino}-4-{[2-(diethylamino)ethyl]imino}pent-2-ene have been synthesized by the reaction of the lithium salt of the ligand with the corresponding triiodides. The complexes are thermally stable and soluble in common organic solvents. The X-ray structural and elemental analysis show that $LLnI_2$ is neutral, and as well free of solvent and lithium salt. The complexes adopt a pseudo-octahedral geometry with the two iodine atoms arranged in *trans* position to each other.

Introduction

Nitrogen-based ligands for preparing lanthanide complexes have been explored increasingly during the last decade.[1−6] Several samarium and gadolinium complexes of stoichiometry $(L1)GdBr_2$, $(L1)_3Ln$,[7] $(L2)_2LnBr$[8] (Ln = Sm, Gd) with different diimine ligands (Scheme 1) have been prepared by Magull et al. Recently, we reported the synthesis of β-diketiminato complexes of praseodymium $(L3)PrX_2$ (X = Cl, Br, BH_4).[9] All these compounds are thermally stable, monomeric in the solid state and soluble in common organic solvents.



Scheme 1. The proton-containing ligands L1, L2, and L3

Iodide complexes of lanthanides are less well known than the corresponding chloride derivatives, presumably due to the lower availability, higher instability, and higher price of the starting material LnI_3.[10,11] Several lanthanide iodide complexes of La^{III},[12] Ce^{III},[13,14] Sm^{III},[15,16,17] Yb^{III},[15,18,19] Lu^{III} [20] have been reported in the literature. The first erbium iodide complex Cp_2ErI was obtained by Maginn et al.[21] in 1963 and characterized by elemental analysis. So far only one iodide complex of erbium $[\{(Me_3Si)_2C_5H_3\}_2ErI](THF)$[20] has been structurally characterized. However, complexes of the lanthanides Tb to Ho are less well known and no reports on holmium iodide complexes can be found in the literature.

Organolanthanide iodide complexes have unique chemical properties due to the more labile Ln−I bond compared to the Ln−Cl ones. This allows metathesis reactions with iodine-containing derivatives. For instance, treatment of the iodide complex with $AgSbF_6$ produces the corresponding fluoride complex;[22] the reaction of $Cp''_2CeI{\cdot}2MeCN$ [$Cp'' = 1,3\text{-}C_5H_3(SiMe_3)_2$] with the silver(I) salt $AgBF_4$ in toluene gave the cationic complex in high yield.[12] Similar reactions with the closely related chlorides, however, result in complicated mixtures.[23]

Herein we report the synthesis and characterization of the first monomeric and solvent-free iodide complexes of stoichiometry $LLnI_2$ (Ln = Ho, Er) with the β-diketiminato ligand 2-{[2-(diethylamino)ethyl]amino}-4-{[2-(diethylamino)ethyl]imino}pent-2-ene (L3). The structural characterization of these complexes provides useful data in the rapidly growing field of organolanthanide chemistry. The synthetic methods used to obtain these complexes are also informative with respect to lanthanide halide chemistry. The latter species are important precursor for further reactions.

Results and Discussion

The lanthanide complexes **1** and **2** were prepared in a one-step synthesis from the corresponding THF adducts

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and stoichiometric amounts of the lithium salt of the ligand in THF followed by recrystallization from toluene (Scheme 2).

$$LnI_3(THF)_x + (L3)Li \xrightarrow[\text{2. toluene, -LiI}]{\text{1. THF, r.t.}} (L3)LnI_2 \qquad \begin{array}{ll} Ln = Ho & \mathbf{1} \\ = Er & \mathbf{2} \end{array}$$

$$L3{=}Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$$

Scheme 2. Preparation of the compounds **1** and **2**

The yield of the reaction of $LnI_3(THF)_x$ with (L3)Li in THF depends highly on the quality of the triiodide. The LnI_3 compounds can be obtained by a modified procedure[24] from Ln powder and iodine vapour followed by sublimation under vacuum. The high purity LnI_3 received from Aldrich in sealed ampoules under argon is also suitable for the experiment. The precursor LnI_3 can be dissolved by heating the reaction mixture for several hours. Compounds **1** and **2** are soluble in toluene, THF, acetonitrile, and dichloromethane. The ^1H NMR spectra of **1** and **2** in C_6D_6 and CD_2Cl_2, respectively, at room temperature show a set of broad resonances ($\Delta\nu_{1/2}$ ranges from 100 to 1000 Hz) with chemical shifts ranging from $\delta = 60$ to -80 ppm. Lowering of the temperature leads to more distinct resonances; however, the fine structure of the resonances could not be observed due to the paramagnetic nature of holmium and erbium.

The complexes $(L3)LnI_2$ are thermally stable, and their melting points are in the range 192−196 °C. Mass spectrometry and elemental analysis show that compounds **1** and **2** are monomeric, solvent-free and contain no lithium halides. The molecular ions of **1** and **2** in the EI mass spectra are weak. Both compounds exhibit two sets of strong signals in the EI-MS, which correspond to $[(L3)LnI]^+$ and $[M^+ - C_5H_{12}N]$ ions. The theoretical results of an isotope pattern calculation for $[(L3)LnI]^+$ and $[M^+ - C_5H_{12}N]$ are in good agreement with the experimental data. The relative intensities of these signals are nearly the same in both the spectra of **1** and **2** (3.2:1 and 2.9:1 respectively). Thus, in conclusion it is possible to use EI-MS analysis effectively for the characterization of these complexes.

X-ray Structural Analysis of $LLnI_2$

A summary of the crystallographic data and refinement parameters for the structures of **1** and **2** are given in Table 2. Selected bond lengths and angles are listed in Table 1.

Single crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution. $(L3)HoI_2$ crystallizes in the triclinic *P*$\bar{1}$ space group; while $(L3)ErI_2$ crystallizes in the monoclinic *C*2/*c* space group and has two symmetrically nonequivalent molecules in the unit cell. The X-ray structural analysis revealed that compounds **1** and **2** are monomeric in the solid state. The X-ray crystal structure of **1** resembles that of **2**, therefore only **1** is shown (Figure 1).

In both compounds the ligand coordinates to the metal center through the four nitrogen atoms. All four nitrogen atoms and the holmium or erbium atom are in the same plane. The iodine atoms in **1** and **2** are almost perpendicularly arranged within the equatorial plane, which is evident from the angles I(2)−Ho−I(1) [153.715(9)°] and

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**

Compound **1**			
Ho−N(1)	2.313(3)	N(1)−Ho−N(2)	79.51(10)
Ho−N(2)	2.314(3)	N(1)−Ho−N(3)	149.98(9)
Ho−N(3)	2.596(3)	N(2)−Ho−N(3)	70.70(9)
Ho−N(4)	2.617(3)	N(1)−Ho−N(4)	69.79(9)
Ho−I(2)	2.980(1)	N(2)−Ho−N(4)	149.22(9)
Ho−I(1)	3.058(1)	N(3)−Ho−N(4)	140.08(8)
		N(1)−Ho−I(2)	100.33(7)
		N(2)−Ho−I(2)	97.83(7)
		N(3)−Ho−I(2)	87.58(6)
		N(4)−Ho−I(2)	85.86(6)
		N(1)−Ho−I(1)	99.59(7)
		N(2)−Ho−I(1)	102.53(7)
		N(3)−Ho−I(1)	83.68(6)
		N(4)−Ho−I(1)	85.10(6)
		I(2)−Ho−I(1)	153.715(9)
Compound **2**			
Er−N(3)	2.300(5)	N(3)−Er−N(2)	80.87(19)
Er−N(2)	2.318(5)	N(3)−Er−N(4)	71.12(18)
Er−N(4)	2.595(6)	N(2)−Er−N(4)	151.73(19)
Er−N(1)	2.608(6)	N(3)−Er−N(1)	153.05(18)
Er−I(1)	2.962(1)	N(2)−Er−N(1)	72.41(19)
Er−I(2)	3.045(1)	N(4)−Er−N(1)	135.76(17)
		N(3)−Er−I(1)	97.72(14)
		N(2)−Er−I(1)	95.58(14)
		N(4)−Er−I(1)	84.70(13)
		N(1)−Er−I(1)	88.51(14)
		N(3)−Er−I(2)	97.96(14)
		N(2)−Er−I(2)	99.02(14)
		N(4)−Er−I(2)	88.78(13)
		N(1)−Er−I(2)	83.07(14)
		I(1)−Er−I(2)	160.050(16)

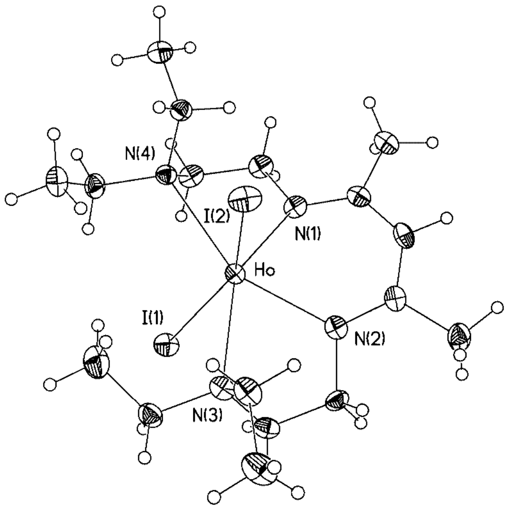

Figure 1. ORTEP drawing (50% thermal probability ellipsoids) of the crystal structure of **1** with atomic numbering scheme

I(1)−Er(1)−I(2) [160.050(16)°] (Table 1). Moreover, each iodine atom is tilted slightly toward the pendant arm. It should be pointed out that the angles between the iodine atoms in **1** and **2** are naturally larger than those between the halogen atoms in $(L3)PrX_2$ (X = Cl, Br) [Cl(2)−Pr−Cl(1) = 136.42(3)°; Br(1)−Pr−Br(2) = 137.080(12)°][9] due to the larger diameter of the praseodymium atom and the smaller ones of chlorine and bromine. For both complexes the metal atoms lie slightly out of the plane of the diimine ligand framework. The coordination number at the holmium and erbium atoms in **1** and **2** is six and the geometry around the metal atom is pseudo-octahedral.

The Ln−N bond lengths of the pendant arm are longer than those of the backbone, as for the distances in the praseodymium complex $(L3)PrX_2$ (X = Cl, Br),[9] due to the coordinative and covalent character involved in different bonding modes. The Er−I bond length is similar to those found in the literature (Er−I: 2.931 Å).[20]

Conclusions

We have reported the synthesis and characterization of two new diiodide complexes of stoichiometry $(L3)LnI_2$. These compounds are easily available when a β-diketiminato-based ligand and holmium or erbium triiodides are used. The X-ray structural and elemental analysis show that $(L3)LnI_2$ is neutral, and free of solvent and lithium salt. The complexes are thermally stable, soluble in common organic solvents and could be used as versatile starting material for studying the chemistry of water- and oxygen-free lanthanide compounds.

Experimental Section

General Remarks: All operations were performed using standard Schlenk line and dry box techniques under purified nitrogen or argon. High-purity water-free holmium and erbium triiodides were

Table 2. Crystallographic data of the X-ray diffraction studies of **1** and **2**

	1	**2**
Empirical formula	$C_{17}H_{35}HoI_2N_4$	$C_{34}H_{70}Er_2I_4N_8$
M_r	714.22	1433.10
Temperature [K]	133(2)	133(2)
Radiation used (λ [Å])	Mo-K_α (0.71073)	Mo-K_α (0.71073)
Crystal description	yellow block	yellow block
Crystal size [mm]	0.5 × 0.6 × 1.1	0.6 × 0.8 × 1.1
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å]	8.6723(10)	18.757(4)
b [Å]	11.6655(14)	14.450(3)
c [Å]	12.1951(14)	34.233(7)
α [°]	82.839(9)	90
β [°]	73.226(9)	95.37(3)
γ [°]	79.433(9)	90
V [Å^3]	1157.8(2)	9238(3)
Z,	2	8
F (000)	676	5424
$\rho_{calcd.}$ [g·cm^{-3}]	2.049	2.061
μ [mm^{-1}]	6.090	6.314
Total reflections	17725	25044
Unique reflections	3634	7600
R(int)	0.0879	0.1355
Scan range Θ [°]	1.78 to 24.00	1.78 to 24.98
Completeness to Θ_{max} [%]	100.0	93.8
Index ranges	$-9 \le h \le 9$	$-22 \le h \le 22$
	$-13 \le k \le 13$	$-17 \le k \le 17$
	$-13 \le l \le 13$	$-40 \le l \le 40$
Data/restrains/parameters	3634/0/223	7600/0/433
$R1$,[a] [b] $wR2$ [$I > 2\sigma(I)$][c]	0.0192, 0.0468	0.0390, 0.1003
$R1$,[a] [d] $wR2$ (all data)[c] [d]	0.0216, 0.0476	0.0449, 0.1041
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2 [e]	1.018	1.077
Max./min. electr. dens. [e·Å^{-3}]	1.088, −0.804	2.112, −1.514

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Denotes the value of the residual considering only the reflections with $I > 2\sigma(I)$. [c] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)/3$. [d] Denotes the value of the residual considering all reflections. [e] $S = [\Sigma[w(F_o^2 - F_c^2)^2]/[(n - p)^{1/2}]]$, n: number of data, p: parameters used.

purchased from Aldrich in ampoules sealed under argon. Compound (L3)H [L3 = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$] was prepared by known literature methods.[9,25,26] The purity of (L3)H was checked by elemental analysis, and ^1H and ^{13}C NMR spectroscopy. Toluene and THF were dried with Na/benzophenone and distilled under nitrogen prior to use; C_6D_6 was dried with Na and degassed; CD_2Cl_2 was dried with CaH_2 and degassed. ^1H NMR spectra were recorded using a Bruker AM 200 spectrometer. Chemical shifts are reported in δ units downfield from Me_4Si with the solvent as the reference signal. Mass spectra were recorded using a Finnigan MAT 8230 instrument, and elemental analysis were carried out at the Analytical Laboratories of the Institute of Inorganic Chemistry at the University of Göttingen. Melting points were determined in sealed capillary tubes under nitrogen and are not corrected.

Synthesis of Complexes 1 and 2. (L3)HoI$_2$: The methods for the preparation of **1** and **2** are the same, therefore only the method for (L3)HoI$_2$ is described. Compound (L3)H (0.6 g, 0.64 mL, 2.0 mmol) was added to dry THF (30 mL) in a 50-mL Schlenk flask. The mixture was cooled to −78 °C and a solution of MeLi in Et_2O (1.26 mL, 1.6 M, 2.0 mmol) was added dropwise. The solution was stirred for 1 h at −78 °C, allowed to warm to room temperature, and then stirred at room temp. until methane evolution had ceased. This solution was added dropwise to a suspension of HoI_3 (1.09 g, 2.0 mmol) in THF (30 mL) at room temp. in a 100-mL Schlenk flask. Then the reaction mixture was heated until all the precipitate dissolved. THF was removed under vacuum, and the residue was extracted with 60 mL of toluene. The yellow toluene solution was allowed to stand overnight at room temperature, when a white powder (LiI) separated from a clear yellow solution. The solution was filtered and concentrated to 20 mL. The resulting solution was left undisturbed overnight. Finally, yellow crystals formed, which were separated by filtration, washed with pentane (10 mL), and dried in vacuo. The next portions of crystals was obtained from the toluene solution. Yield of **1** 1.10 g (75%). M.p. 194−196 °C. $C_{17}H_{35}HoI_2N_4$ (714.22): calcd. C 28.58, H 4.90, I 35.59, N 7.85; found C 28.50, H 4.93, I 35.71, N 7.75. EI-MS: m/z (%) = 714 (1) [M^+], 628 (27) [$M^+ - C_5H_{12}N$], 587 (86) [(L3)HoI$^+$], 557 (2) [$M^+ - C_{10}H_{24}N$], 536 (3) [$M^+ - C_{12}H_{18}N_2$], 495 (2) [(L3)HoI$^+ - C_5H_{12}N$], 419 (3) [HoI_2^+], 296 (2) [(L3)$^+$], 210 (7) [(L3)$^+ - C_5H_{12}N$], 100 (11) [$C_6H_{14}N$], 86 (100) [$C_5H_{12}N$]. **LErI$_2$:** Yield of **2** 1.10 g (75%). M.p. 192−194 °C. $C_{17}H_{35}ErI_2N_4$ (716.55): calcd. C 28.49, H 4.89, I 35.48, N 7.82; found C 28.50, H 4.92, I 35.44, N 7.85. EI-MS: m/z (%) = 715 (1) [M^+], 629 (4.6) [$M^+ - C_5H_{12}N$], 588 (15) [(L3)ErI$^+$], 558 (2) [$M^+ - C_{10}H_{24}N$], 537 (2) [$M^+ - C_{12}H_{18}N_2$], 499 (2) [(L3)ErI$^+ - C_5H_{12}N$], 296 (5) [(L3)$^+$], 210 (5) [(L3)$^+ - C_5H_{12}N$], 100 (12) [$C_6H_{14}N$], 86 (100) [$C_5H_{12}N$].

X-ray Crystallographic Study: Crystal data and experimental conditions are listed in Table 2. Selected bond lengths and bond angles with standard deviations in parentheses are presented in Table 1. Intensity data for the crystal structures of **1** and **2** were collected with a Stoe image plate IPDS II-system. All structures were solved by direct methods (SHELXS-97) and refined against F^2 using SHELXL-97.[27] The heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to U_{iso} of the parent atoms. CCDC-187724 (**1**) and -187725 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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