

Preliminary communication

Organometallic compounds of the lanthanides. CIII <sup>☆</sup>.

Mixed sandwich complexes of the 4f elements: synthesis and crystal structure of

( $\eta^8$ -cyclooctatetraenyl)( $\eta^5$ -2,5-di-tert.-butylpyrrolyl) samarium, -thulium, and -lutetium

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Abstract

$[(\eta^8\text{-C}_8\text{H}_8)\text{Ln}(\mu\text{-Cl})(\text{THF})_2]$  (Ln = Sm, Tm, Lu) reacts with  $\text{Na}[\text{pyr}^*]$  ( $\text{pyr}^* = \text{NC}_4\text{H}_2^1\text{Bu}_2\text{-2,5}$ ) to form  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ln}(\eta^5\text{-pyr}^*)(\text{THF})_x]$  (Ln = Sm **1**, x = 1; Ln = Tm **2**, Lu **3**, x = 0). The novel sandwich compounds have been characterized by C, H, N analysis, mass spectrometry and NMR spectroscopy. Additionally, an X-ray structural analysis of **1** was performed. The crystals of **1** are monoclinic, space group  $\text{P2}_1/c$  with  $a = 11.131(2)$  Å,  $b = 20.023(3)$  Å,  $c = 20.118(5)$  Å,  $\beta = 91.16(2)^\circ$ ,  $V = 4482.8(14)$  Å<sup>3</sup> and  $Z = 4$ . The final refinement resulted in  $R1 = 3.09\%$  ( $I > 2\sigma(I)$ ).

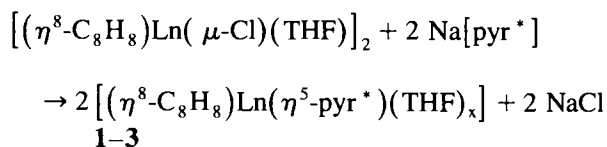
**Keywords:** Samarium; Thulium; Lutetium; Mixed sandwich complexes

1. Introduction

In recent years we have been interested in organolanthanide complexes with the goal of synthesizing volatile compounds for MOCVD (Metal Organic Chemical Vapor Deposition) processes. Mixed lanthanide sandwich complexes containing a cyclooctatetraenyl ligand and a substituted cyclopentadienyl ring, e.g.  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{R})]$  (R = H [2], Me [3], Et [4]), are extremely well suited for these applications. Studies of the compounds  $[(\eta^8\text{-C}_8\text{H}_8)\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)]$  (Ln = Y, Dy, Er) have shown that they can be used as precursors for the production of thin carbon-free lanthanide oxide films by MOCVD methods [5]. In the course of further investigations on this subject we now present the synthesis of (cyclooctatetraenyl)(azacyclopentadienyl)-

lanthanide complexes. The 2,5-di-tert.-butylpyrrolyl was employed as nitrogen heterocycle, because it has already been established as a  $\pi$ -ligand in the lanthanide chemistry [6,7].

(Cyclooctatetraenyl)(pyrrolyl)lanthanide complexes of samarium **1**, thulium **2**, and lutetium **3** were generated by the equimolar reaction of the corresponding (cyclooctatetraenyl)lanthanide chlorides with 2,5-di-tert.-butylpyrrolylsodium in THF at room temperature in reasonable yields. The samarium complex **1**, in contrast to **2** and **3**, contains coordinated THF, which can be removed by drying under high vacuum for several hours.



Ln = Sm **1** x = 1

Ln = Tm **2**, Lu **3**, x = 0

<sup>☆</sup> For part CII see Ref. [1].

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The tert.-butyl groups of the pyrrolyl ring make the complexes **1–3** soluble in aromatic solvents such as toluene or benzene as well as in nonpolar solvents like *n*-hexane. All three compounds decompose rapidly in the presence of air and moisture, but they are stable in an inert atmosphere with decomposition points around 100°C. The C, H, N analyses, <sup>1</sup>H and <sup>13</sup>C NMR of **1** and **3**, and mass spectra of **2** and **3** obtained are in good agreement with the molecular formula. The <sup>1</sup>H and <sup>13</sup>C NMR spectra in benzene-d<sub>6</sub> show the expected number of signals for the π-bound eight and five membered rings. In the <sup>1</sup>H NMR spectrum of the complex **1** the influence of the paramagnetism of the Sm<sup>3+</sup> ion on the protons of the ligands is evident. Thus the signals are broadened and their chemical shifts range from δ 13.02 ppm to 0.19 ppm. Similar values for the protons and the carbon atoms of the C<sub>8</sub>H<sub>8</sub> ring and the coordinated THF have been observed for the compounds [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Sm(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>R)(THF)] (R = H [2], Me [3], Et [4]). The mass spectra, recorded between 80°C and 120°C, show the molecular ion for **2** and **3**, whereas for **1** the fragment with the highest *m/z* value is the molecular ion without THF.

Suitable single crystals of **1** were obtained by cooling a saturated *n*-hexane solution. The X-ray crystal structure analysis [8] revealed two symmetrically independent molecules per asymmetric unit. The solid-state structure of **1** is shown in Fig. 1. It confirms the sandwich arrangement. The Sm<sup>3+</sup> ion has a pseudo-trigonal planar coordination sphere consisting of one η<sup>8</sup>-bound cyclooctatetraene unit, one η<sup>8</sup>-bound nitrogen heterocycle, and one coordinated THF ligand. The (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub>-Sm-(pyr<sup>\*</sup>)<sub>c</sub>, (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub>-Sm-O(THF), and (pyr<sup>\*</sup>)<sub>c</sub>-Sm-O(THF) angles sum to 359.9(1) Å (molecule 1) and 360.0(1) Å (molecule 2), indicating perfect planarity of the lanthanide cation, the oxygen atom, and the ring centers. The formal coordination number at the lanthanide ion is nine. The C<sub>8</sub>H<sub>8</sub> system is approximately planar with a maximal deviation from the ring plane of 0.051(8) Å (molecule 1) and 0.052(9) Å (molecule 2), whereas the heterocycle is planar within the standard deviation. The average Sm-C(η<sup>8</sup>) distances (2.646(7) Å for molecule 1, 2.638(7) Å for molecule 2) and Sm-O(THF) bond lengths (2.507(4) Å for molecule 1, 2.524(4) Å for molecule 2) are in good agreement with the corresponding bond distances in [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Sm(η<sup>5</sup>-2,4-C<sub>7</sub>H<sub>11</sub>)(THF)] (2,4-C<sub>7</sub>H<sub>11</sub> = 2,4-dimethylpentadienyl) (d(Sm-C(η<sup>8</sup>)) = 2.66 Å, d(Sm-O(THF)) = 2.50(1) Å) [12] and [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Sm(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)(THF)<sub>2</sub>] (d(Sm-C(η<sup>8</sup>)) = 2.68(4) Å, d(Sm-O(THF)) = 2.60(5) and 2.652(5) Å) [13], taking the different coordination numbers into consideration. The distance between the Sm<sup>3+</sup> ion and the center of the pyrrolyl in **1** is 2.462(3) Å (molecule 1) and 2.460(3) Å (molecule 2) and the ring slippage has a value of 0.158 Å (molecule 1) and 0.168 Å (molecule 2).

## 2. Experimental section

All experiments were carried out under nitrogen using standard Schlenk and vacuum techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. The starting materials [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Ln(μ-Cl)(THF)]<sub>2</sub> [14,15] and Na[pyr<sup>\*</sup>] were synthesized using literature procedures [7,16].

### 2.1. Synthesis of [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Sm(η<sup>5</sup>-pyr<sup>\*</sup>)(THF)] (**1**)

0.60 g (0.83 mmol) [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Sm(μ-Cl)(THF)]<sub>2</sub> was suspended in 50 ml THF, and 0.33 g (1.66 mmol)

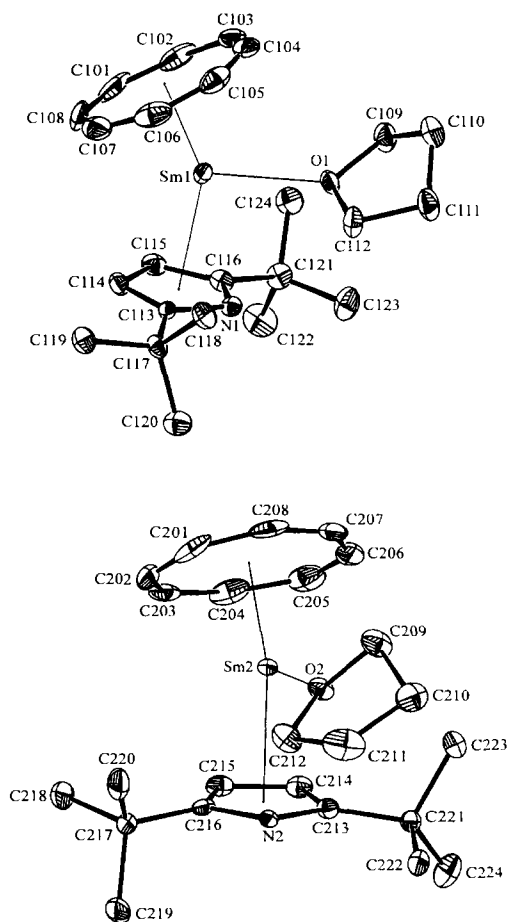


Fig. 1. ORTEP [11] diagram of **1** with the probability ellipsoids drawn at the 30% level. Selected distances [Å] and angles [°]: Sm1-(C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 1 1.913(3), Sm1-C101 2.624(7), Sm1-C102 2.613(7), Sm1-C103 2.663(6), Sm1-C104 2.697(6), Sm1-C105 2.656(6), Sm1-C106 2.631(7), Sm1-C107 2.632(7), Sm1-C108 2.655(7), Sm1-(pyr<sup>\*</sup>)<sub>c</sub> 1 2.462(3), Sm1-C113 2.726(6), Sm1-C114 2.798(6), Sm1-C115 2.772(6), Sm1-C116 2.699(6), Sm1-N1 2.653(4), Sm1-O1 2.507(4), Sm2-(C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 2 1.913(3), Sm2-C201 2.654(7), Sm2-C202 2.626(7), Sm2-C203 2.635(6), Sm2-C204 2.647(7), Sm2-C205 2.605(7), Sm2-C206 2.611(7), Sm2-C207 2.653(7), Sm2-C208 2.675(7), Sm2-(pyr<sup>\*</sup>)<sub>c</sub> 2 2.460(3), Sm2-C213 2.708(6), Sm2-C214 2.789(6), Sm2-C215 2.793(6), Sm2-C216 2.704(6), Sm2-N2 2.647(4), Sm2-O2 2.524(4); (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 1-Sm1-(pyr<sup>\*</sup>)<sub>c</sub> 1 144.48(11), (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 1-Sm1-O1 114.78(13), (pyr<sup>\*</sup>)<sub>c</sub> 1-Sm1-O1 100.65(12), (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 2-Sm2-(pyr<sup>\*</sup>)<sub>c</sub> 2 143.78(11), (C<sub>8</sub>H<sub>8</sub>)<sub>c</sub> 2-Sm2-O2 116.47(14), (pyr<sup>\*</sup>)<sub>c</sub> 2-Sm2-O2 99.71(12).

Na[pyr<sup>\*</sup>] was added at room temperature. The mixture was stirred for a further 12 h. The solvent was removed under vacuum and the residue extracted with 60 ml *n*-hexane. The clear solution was concentrated to 20 ml and on cooling to –28°C provided the product in a crystalline form. Yield 0.51 g (61%) purple crystals. M.p. 97°C (dec.). Anal. Found: C, 56.73, H, 6.92, N 3.11. C<sub>24</sub>H<sub>36</sub>NOSm Calc.: C, 57.09, H, 7.19, N 2.77. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 200 MHz): δ: 13.02 (br s, 2H, pyr<sup>\*</sup> –CH), 10.45 (br s, 8H, C<sub>8</sub>H<sub>8</sub>), 5.40 (m, 4H, THF), 1.99 (m, 4H, THF), 0.19 (br s, 18H, <sup>t</sup>Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>, 50.32 MHz): δ: 143.26 (C<sup>t</sup>Bu), 109.59 (pyr<sup>\*</sup>–CH), 82.92 (C<sub>8</sub>H<sub>8</sub>), 74.77 (THF), 35.46 (CMe<sub>3</sub>), 28.99 (Me), 26.19 (THF). MS (70 eV, 120°C, <sup>152</sup>Sm): m/z (%) = 434 (5) [M–THF]<sup>+</sup>, 330 (16) [Sm(pyr<sup>\*</sup>)]<sup>+</sup>, 256 (1) [Sm(C<sub>8</sub>H<sub>8</sub>)]<sup>+</sup>, 164 (100) [C<sub>11</sub>H<sub>18</sub>N]<sup>+</sup>, and additional fragments.

### 2.2. Synthesis of [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Tm(η<sup>5</sup>-pyr<sup>\*</sup>)] (2)

Following the procedure described for **1**. 0.54 g (0.71 mmol) [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Tm(μ-Cl)(THF)]<sub>2</sub> was treated with 0.28 g (1.39 mmol) Na[pyr<sup>\*</sup>]. Yield 0.33 g (53%) orange crystals. M.p. 125°C (dec.). Anal. Found: C, 52.99, H, 6.11, N 3.45. C<sub>20</sub>H<sub>28</sub>NTm Calc.: C, 53.22, H, 6.25, N 3.10. MS (70 eV, 80°C): m/z (%) = 451 (26) [M]<sup>+</sup>, 347 (3) [Tm(pyr<sup>\*</sup>)]<sup>+</sup>, 273 (11) [Tm(C<sub>8</sub>H<sub>8</sub>)]<sup>+</sup>, 164 (100) [C<sub>11</sub>H<sub>18</sub>N]<sup>+</sup>, and additional fragments.

### 2.3. Synthesis of [(η<sup>8</sup>-C<sub>8</sub>H<sub>8</sub>)Lu(η<sup>5</sup>-pyr<sup>\*</sup>)] (3)

Following the procedure described for **1**. 0.93 g (1.20 mmol) [(η<sup>5</sup>-C<sub>8</sub>H<sub>8</sub>)Lu(μ-Cl)(THF)]<sub>2</sub> was treated with 0.48 g (2.38 mmol) Na[pyr<sup>\*</sup>]. Yield 0.47 g (43%) colorless crystals. M.p. 128°C (dec.). Anal. Found: C, 52.20, H, 5.99, N 3.20. C<sub>20</sub>H<sub>28</sub>LuN Calc.: C, 52.52, H, 6.17, N 3.06. <sup>1</sup>H NMR (benzene-d<sub>6</sub>, 200 MHz): δ: 6.30 (s, 8H, C<sub>8</sub>H<sub>8</sub>), 5.53 (s, 2H, pyr<sup>\*</sup>–CH), 1.16 (s, 18H, <sup>t</sup>Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (benzene-d<sub>6</sub>, 50.32 MHz): δ: 154.70 (C<sup>t</sup>Bu), 104.64 (pyr<sup>\*</sup>–CH), 92.47 (C<sub>8</sub>H<sub>8</sub>), 33.26 (CMe<sub>3</sub>), 30.95 (Me). MS (70 eV, 110°C, <sup>175</sup>Lu): m/z (%) = 457 (21) [M]<sup>+</sup>, 353 (2) [Lu(pyr<sup>\*</sup>)]<sup>+</sup>, 279 (12) [Lu(C<sub>8</sub>H<sub>8</sub>)]<sup>+</sup>, 164 (100) [C<sub>11</sub>H<sub>15</sub>N]<sup>+</sup>, and additional fragments.

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- [8] Crystal data for **1**: C<sub>24</sub>H<sub>36</sub>NOSm; *M*<sub>r</sub> = 504.92; crystal size 0.21 × 0.27 × 0.24 mm<sup>3</sup>; unit cell dimensions: *a* = 11.131(2) Å, *b* = 20.023(3) Å, *c* = 20.118(5) Å, β = 91.16(2)°; cell volume 4482.8(14) Å<sup>3</sup>; crystal system monoclinic; space group P2<sub>1</sub>/c (no. 14) with *Z* = 4; ρ<sub>calcd</sub> = 1.496 g cm<sup>-3</sup>; absorption coefficient: 2.632 mm<sup>-1</sup>; *F*(000): 2056; diffractometer: Enraf-Nonius CAD-4, Mo K<sub>α</sub> radiation = 0.71069 Å, graphite monochromator; temperature: 163(2) K; reflections collected: 7531, independent reflections: 6980 [*R*(int) = 0.0286]; corrections: Lorentz, polarisation and absorption effects; solution: Patterson (SHELXS-86 [9]), difference Fourier methods (SHELXL-93 [10]); refinement: full-matrix least-squares on *F*<sup>2</sup>: all non-hydrogen atoms anisotropic, hydrogen atoms calculated in idealized positions (d(C–H) = 0.96 Å, *U*<sub>iso</sub> = 0.08 Å<sup>2</sup>); goodness-of-fit on *F*<sup>2</sup>: 0.795, 6966 observed reflections for 499 refined parameters; *R*1 = 0.0309, *wR*2 = 0.0874 (*I* > 2σ(*I*)) with a residual electron density of max. 0.948 e Å<sup>-3</sup>, min. –0.817 e Å<sup>-3</sup>. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-404220.
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