

# Triple-decker naphthalene complex of thulium(III); synthesis and molecular structure of $[\{\text{Tm}(\text{dme})\}_2(\eta^2\text{-C}_{10}\text{H}_8)_2(\mu^2\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)]$

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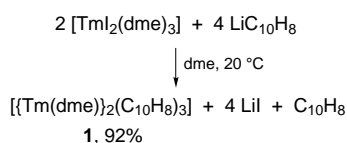
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The reaction of thulium(II) iodide with 2 equiv. of lithium naphthalenide in dme (dme = 1,2-dimethoxyethane) yields a binuclear thulium(III) complex with one bridging and two terminal dianions of naphthalene  $[\{\text{Tm}(\text{dme})\}_2(\eta^2\text{-C}_{10}\text{H}_8)_2(\eta^2\text{-}\eta^4\text{:}\eta^4\text{-C}_{10}\text{H}_8)]$  **1**.

Recently, the first molecular complex of divalent thulium,  $[\text{TmI}_2(\text{dme})_3]$ <sup>1</sup> was synthesized and characterized crystallographically. To develop the chemistry of divalent thulium further we studied its reaction with lithium naphthalenide. Previously, it had been shown that exchange reactions of the lanthanoid dihalides,  $[\text{LnI}_2(\text{thf})_2]$  (Ln = Sm, Eu, Yb), and cyclopentadienyl lanthanoid dihalides,  $[\text{Ln}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]$  (Ln = Y, Gd, Er, Tm, Lu), with alkali-metal naphthalenides in thf or dme resulted in the formation of naphthalene lanthanoid complexes of the type  $[\text{Ln}(\text{C}_{10}\text{H}_8)(\text{thf})_2]$ <sup>2</sup> or  $[\text{Ln}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_{10}\text{H}_8)(\text{dme})]$ .<sup>3,4</sup> While the latter complexes were fully characterized by structural and spectroscopic analyses, no structural information on the cyclopentadienyl-free complexes was obtained owing to difficulties in the preparation of crystalline samples suitable for X-ray analysis. In the case of lanthanoid triiodides, including  $[\text{TmI}_3(\text{dme})_3]$ , reactions with  $\text{LiC}_{10}\text{H}_8$  in various molar ratios gave no products that could be identified. The only exception was the structurally characterized complex of lanthanum  $[\{\text{LaI}_2(\text{thf})_3\}_2(\text{C}_{10}\text{H}_8)]$  isolated from the reaction of equimolar amounts of  $[\text{LaI}_3(\text{thf})_3]$ , naphthalene and Li in dme.<sup>5</sup>

Here we report that the treatment of a  $[\text{TmI}_2(\text{dme})_3]$  solution in dme with  $\text{LiC}_{10}\text{H}_8$  in a 1 : 2 molar ratio leads to the formation of the binuclear naphthalene complex **1** in good yield (Scheme 1).



Scheme 1

The black crystals of **1** are sparingly soluble in dme and thf and insoluble in hydrocarbon solvents. They decompose slowly in solution at room temperature. In the solid state decomposition is observed above *ca.* 100 °C. The complex gave satisfactory elemental analysis for thulium (calc. 37.43; found 36.71%). Total elemental analysis could not be performed because of an extreme sensitivity of the complex to moisture and air. Careful oxidation of **1** in air leads to the formation of naphthalene in about 90% yield, in good agreement with the composition of the complex. The magnetic moment of **1** (6.59  $\mu_{\text{B}}$ /Tm, 293 K) is somewhat lower than the value typical for thulium(III) derivatives (7.1–7.5  $\mu_{\text{B}}$ ).<sup>6</sup> That might be explained by the existence of an intramolecular antiferromagnetic Tm–Tm interaction. The observed magnetic moment is significantly different from the  $\mu_{\text{eff}}$  of  $[\text{TmI}_2(\text{dme})_3]$  (4.5  $\mu_{\text{B}}$ )<sup>1</sup> confirming the oxidation of

thulium during the course of the reaction. One can suggest that the reaction proceeds *via* the formation of  $[\text{Tm}^{2+}(\text{C}_{10}\text{H}_8)^{2-}]$  a transient intermediate, which then reacts with free naphthalene, contained in the solution of  $\text{LiC}_{10}\text{H}_8$ , to give **1**. However, it should be noted, that in spite of the high reduction potential of  $\text{Tm}^{\text{II}}$  (*ca.* –2.3 V),<sup>7</sup>  $[\text{TmI}_2(\text{dme})_3]$  does not react with free naphthalene.

The IR spectrum<sup>†</sup> of **1** contains the absorption bands of the bridging (1500, 1400  $\text{cm}^{-1}$ ) and terminal naphthalene dianions (1250  $\text{cm}^{-1}$ ) which were observed previously in the complexes  $[\{\text{LaI}_2(\text{thf})_3\}_2(\mu\text{-C}_{10}\text{H}_8)]$ <sup>5</sup> and  $[\text{Lu}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_{10}\text{H}_8)(\text{dme})]$ .<sup>3</sup> An X-ray crystal structure analysis confirms this assignment.

Crystals formed directly in the reaction procedure were suitable for X-ray diffraction.‡ An ORTEP representation of the molecular structure of **1** is shown in Fig. 1. The molecule rests on the inversion centre located in between C(11) and C(11'), so only half of the molecule is unique. Both of the naphthalene rings of the bridging ligand are bent along the axis defined by the 1,4 naphthalene positions. The dihedral angle between the planes represented by C(12)C(13)C(14)C(15) and C(11)C(11')C(15)C(12) is 19.28°, this value is somewhat higher than in the lanthanum(III) complex  $[\{\text{LaI}_2(\text{thf})_3\}_2(\mu\text{-C}_{10}\text{H}_8)]$  containing a bridging naphthalene dianion (15.2°).<sup>5</sup> The terminal naphthalene ligands display a different geometry: the naphthalene ring C(2)–C(4) remains flat, while the other ring is bent. The dihedral angle between the planes C(5)C(6)C(9)C(10) and C(6)C(7)C(8)C(9) (26.22°) is smaller than in complex  $[\text{Lu}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_{10}\text{H}_8)(\text{dme})]$  (30°).<sup>3</sup> The thulium–bridging naphthalene bonding mode is the same as that observed in the lanthanum complex mentioned above. Four Tm–C distances lie in a narrow range (2.59–2.62 Å) and are 0.2 Å shorter than in the lanthanum complex. This is in agreement with the difference in ionic radii between Tm and La.<sup>8</sup> The bonding mode of Tm with the terminal naphthalene ligand is quite different. The Tm–C(6) and Tm–C(9) distances are much

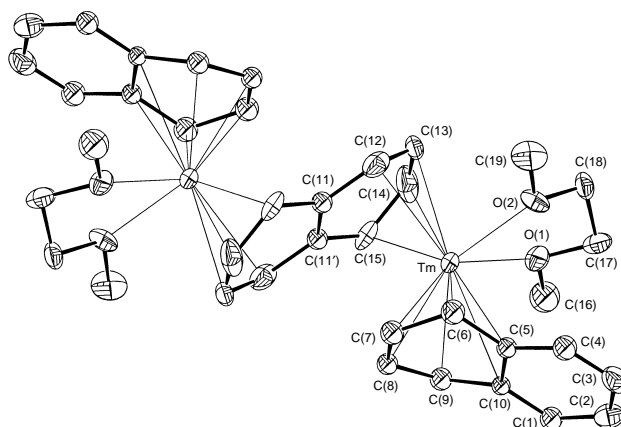


Fig. 1 ORTEP representation of the molecular structure of **1**

shorter than Tm–C(7) and Tm–C(8) (2.41, 2.43, 2.54, 2.54 Å, respectively). The overall geometry of this fragment is almost identical to that observed in the complex [Lu( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(C<sub>10</sub>H<sub>8</sub>)(dme)]. The Tm–C(terminal C<sub>10</sub>H<sub>8</sub>) bond lengths are also close to Lu–C distances (2.406, 2.397, 2.579, 2.562 Å) owing to the nearly identical ionic radii of Tm and Lu (CN = 8: 0.994 and 0.977 Å, respectively).<sup>8</sup> Redistribution of C–C bond lengths in the naphthalene ligands and their non-planar shape reflect a dianionic nature of the ligands: the distances C(13)–C(14) and C(7)–C(8) become shorter (1.35, 1.31 Å) while all other C–C bonds are elongated compared to free naphthalene.<sup>9</sup> The naphthalene ring which is not coordinated to the Tm atom retains its aromaticity with similar C–C distances. Thus, the negative charge in the bridging naphthalene ligand is delocalized between all carbon atoms, but in the terminal naphthalene it is concentrated mainly on the C(6) and C(9) positions.

Previously we had shown that naphthalene complexes of the lanthanoids are very reactive towards organic and organometallic substances.<sup>2,10,11</sup> To illustrate the reactivity of **1** we carried out its reaction with cyclopentadiene. As might be anticipated the reaction proceeded smoothly at room temp. to give [Tm( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>] in good yield. We hope to use **1** for the synthesis of previously inaccessible complexes of thulium.

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#### Footnotes and References

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† Spectroscopic data: IR(Nujol): 1330 1270s, 1250, 1200, 1185, 1160, 1130, 1100, 1060s, 1035, 1020s, 980, 870s, 790, 750, 730, 700s, 490, 450 cm<sup>-1</sup>.

‡ Crystal data for **1**: C<sub>38</sub>H<sub>44</sub>O<sub>4</sub>Tm<sub>2</sub>, *M* = 902.59, *T* = 173(2) K, monoclinic, space group *P*2<sub>1</sub>/*n*; *a* = 7.722(2), *b* = 15.687(5), *c* = 13.605(04) Å,  $\beta$  = 100.16(2)°, *U* = 1622.2(8) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.848 g cm<sup>-3</sup>,  $\mu$  = 5.473 mm<sup>-1</sup>, *F*(000) = 884, crystal size 0.09 × 0.09 × 0.03 mm. A total of 1932 unique reflections with  $\theta$  = 2–20.9°, were collected. Reflections with *I* > 2 $\sigma$ (*I*) 1706, *R* [for *I* > 2 $\sigma$ (*I*)] = 0.0452. An Enraf-Nonius CAD4 diffractometer with monochromated Mo-K $\alpha$  radiation was used ( $\lambda$  = 0.710 69 Å). Data were corrected for Lorenz, polarization and absorption effects. CCDC 182/559. Details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-406861.

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