

Synthesis of the first mono(cyclopentadienyl)lanthanide Schiff base complex bearing C_2 -symmetric tetradentate ligand: crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]_2(\mu\text{-THF})(\text{THF})$

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Abstract

Reaction of YbCl_3 with 3 equimolar CpNa (Cp = cyclopentadienide) in THF, followed by treatment with *trans*-(±)-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine led to the isolation of first mono(cyclopentadienyl) lanthanide Schiff base complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]_2(\mu\text{-THF})(\text{THF})$ (**1**). The molecular structure of **1** shows that it is a dimer in which the two $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]$ units connecting via a bridging THF oxygen and two bridging oxygen atoms from Schiff base ligands. © 1998 Elsevier Science S.A.

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1. Introduction

The chiral lanthanide complexes have been paid more attention recently in both synthesis and application [1–5]. However, the Schiff base complexes of lanthanides synthesizing in nonaqueous are rare [6]. Nitrogen atoms of Schiff base and other N–O chelating ligands can bond to the rare earth centers via their lone-electron pairs [6–8], hence we are interested in studying the properties of this kind of complexes and have isolated the first bis(cyclopentadienyl)-lanthanide Schiff base complex with a chiral bidentate Schiff base as ligand [9]. Furthermore, mono(cyclopentadienyl) rare earth chalcogenides prepared from the exchanging reaction

between Cp_3Ln and alcohols or phenols are also very rare and no X-ray crystal structure are available for complexes by this method [10,11]. In this communication, we describe the synthesis and molecular structure of the title complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]_2(\mu\text{-THF})(\text{THF})$, the first example of mono(cyclopentadienyl)lanthanide Schiff base complex bearing C_2 -symmetric ligand obtained from the exchanging reaction between Cp_3Ln and corresponding Schiff base.

2. Experimental

YbCl_3 and three equimolar of CpNa in THF at room temperature, followed by sequent treatment with either one equimolar or 0.5 equimolar quantity of *trans*-(±)-*N,N'*-bis(salicylidene)-1,2-cyclohexanediamine give to the formation of the title complex in 51% yield. Complex **1** has been characterized by elemental analysis,

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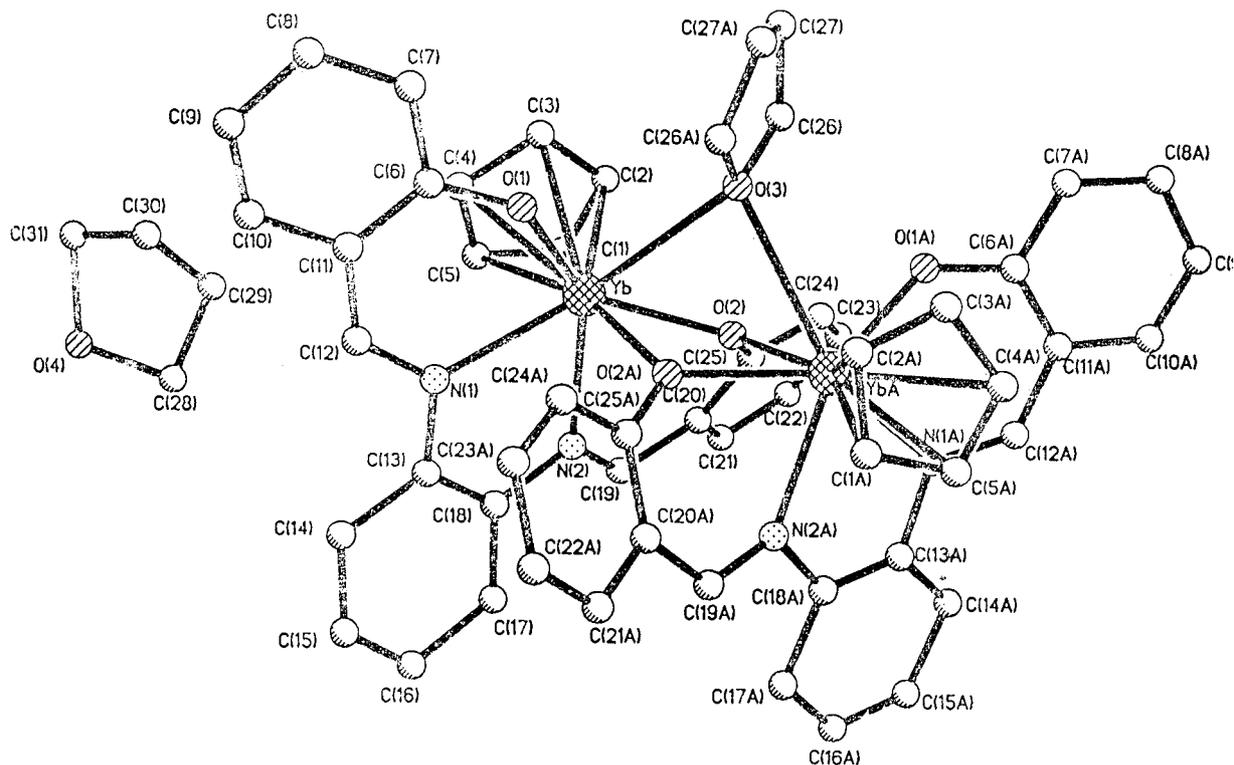


Fig. 1. The X-ray crystal structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]_2(\mu\text{-THF})(\text{THF})$ (**1**), showing the atom numbering scheme and the hydrogen atoms are omitted for clarity. Selected bond lengths: Yb–C(1) 2.72(3) Å, Yb–C(2) 2.69(3) Å, Yb–C(3) 2.67(3) Å, Yb–C(4) 2.69(3) Å, Yb–C(5) 2.72(3) Å, Yb–O(1) 2.15(2) Å, Yb–O(2) 2.252(14) Å, Yb–O(2a) 2.312(14) Å, Yb–O(3) 2.83(2) Å, Yb–N(1) 2.43(2) Å and Yb–N(2) 2.43(2) Å.

infrared spectroscopy.² Complex **1** is slightly soluble in THF, insoluble in nonpolar solvents such as toluene, benzene and hexane, etc. Yellow single crystals of **1** suitable for X-ray crystallography were grown in THF.

The infrared spectrum shows a strong band at 1618 cm^{-1} (C=N), as expected slightly lower than that of the free ligand (1621 cm^{-1} for C=N in ligand).

3. Results and discussion

The crystal structure of **1** is shown in Fig. 1, together with selected bond distances.² Complex **1** is a dimer composed of two $[(\eta^5\text{-C}_5\text{H}_5)\text{Yb}(\mu\text{-OC}_{20}\text{H}_{20}\text{N}_2\text{O})]$ units and two THF molecules (one bridging located on the crystallographic 2-fold axis, the other free), and the shadow of **1** looks like a butterfly. If the THF molecule on general position is not considered, the main body of the molecular structure of the title complex possesses the C_2 -symmetry. The 9-coordinated ytterbium are each bonded to two nitrogen atoms and two oxygen atoms of Schiff base ligands, one Cp ring and two bridging oxygen atoms (one from bridging THF molecule, the other from Schiff base ligand of another ytterbium center) to form a distorted pentagonal bipyramidal geometry, with two N and two O atoms of Schiff base ligand and one O atom from bridging THF molecule occupying the pentagonal plane while the centroid of Cp ring and the bridging Schiff base oxygen atom in apical sites. The Yb–C distances range from 2.67(3) to 2.72(3) Å and average 2.70(3) Å, which is longer than

² Selected data for complex **1**. Anal.: $\text{C}_{58}\text{H}_{66}\text{N}_4\text{O}_6\text{Yb}_2$ requires Yb: 27.44%. Found: Yb, 27.21%. IR (KBr pellets): $\nu_{(\text{C}=\text{N})} = 1618 \text{ cm}^{-1}$. M.p. 226°C (dec.). Single-crystal X-ray studies of **1**: Crystal data for $\text{C}_{58}\text{H}_{66}\text{N}_4\text{O}_6\text{Yb}_2$, $M_r = 1261.23$, monoclinic, $a = 17.780(4)$ Å, $b = 12.234(2)$ Å, $c = 26.420(5)$ Å, $\beta = 96.75(3)^\circ$, $V = 5707(2)$ Å³ (by least-squares analysis of 30 strong reflections), space group C_2/c (No. 15), $Z = 4$, $D_c = 1.468 \text{ g cm}^{-3}$, $F(000) = 2520$, $\mu = 3.307 \text{ mm}^{-1}$, $T = 293(2)$ K, crystal size $0.40 \times 0.20 \times 0.20 \text{ mm}^3$. Data were collected on a Siemens P4 four-circle diffractometer using graphite mono-chromated ($\lambda_{\text{Mo K}\alpha} = 0.71073$ Å) radiation in $\omega - 2\theta$ scan mode, 5099 reflections were collected, index ranges $-1 \leq h \leq 19$; $-1 \leq k \leq 13$; $-29 \leq l \leq 28$, producing 3977 unique data ($R_{\text{int}} = 0.0456$ after absorption correction). The corrections were made for Lorentz-polarization effects and for empirically absorption. The structure were solved by heavy atom methods (SHELXTL-90) and then subjected to full-matrix least-squares refinement based on F^2 (SHELXTL-93). Final wR_2 and R_1 values are 0.1202 and 0.1303 for all data and 348 parameters (ρ_{max} , ρ_{min} : 0.889 and $-1.412 \text{ e \AA}^{-3}$). Corresponding wR_2 and R_1 for 3977 independent data with $I > 2\sigma(I)$ are 0.0576 and 0.1083, respectively. Full tables of bond lengths and angles, anisotropic displacement parameters of nonhydrogen atoms, hydrogen atom parameters, and tables of structure factors (on both hard copy and diskette) have been sent to the Editors for deposition.

the corresponding Yb–C (2.60(2) Å) in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb}(\text{OC}_{10}\text{H}_7)(\text{THF})$ [12]. The bond length of Yb–O(3) (2.83(2) Å) is also significantly longer than that in $(\eta^5\text{-C}_5\text{H}_5)_2\text{Yb}(\text{OC}_{10}\text{H}_7)(\text{THF})$. Moreover, the distance of Yb–O(3) is longer than those of Yb–O (bridging oxygen atoms, 2.252(14) Å for Yb–O(2) and 2.312(14) Å for Yb–O(2a)).

4. Conclusion

The formation of the title complex indicates that $\text{CpLn}(\text{OR})_2(\text{THF})_n$ -type complexes can be obtained from the reaction of Cp_3Ln with functional alcohols or phenols.

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