



*Dedicated to Professor Cristian Silvestru
on the occasion of his 65th anniversary*

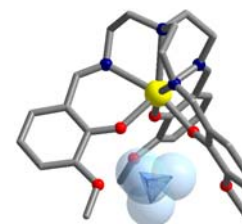
MONONUCLEAR LANTHANIDE(III) COMPLEXES WITH TRIPODAL LIGANDS AS AMMONIUM CATION RECEPTORS

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Synthesis and crystal structures of the mononuclear complexes [Er(valtren)] (1) and [Yb(valtren)] (2), H₃valtren is the Schiff base derived from *o*-vanillin and tris(2-aminoethyl)-amine, are reported herein. The [Er(valtren)] (1) mononuclear complex was used as receptor for ammonium cation and the supramolecular complex [Er(valtren){NH₄}] (PF₆)-3CH₃CN (3) was structurally characterized by X-ray diffraction on single crystal. The ammonium cation is hosted in the external compartment of the tripodal bicompartamental ligand.



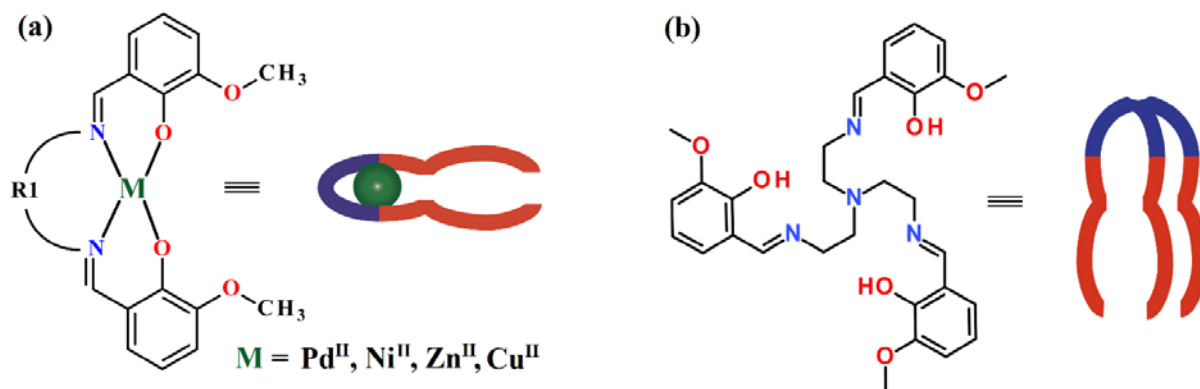
INTRODUCTION

The design and synthesis of molecular receptors able to recognize particular chemical species require topological control of the molecular fragments involved in the non-covalent interactions, which can offer a good electronic and steric complementarity between host and guest. In metallosupramolecular chemistry, the metal ions play a double role: *i*) structural (organising the ligand), and *ii*) functional (carrying magnetic, optical, redox or catalytic properties). Schiff-bases derived from *o*-vanillin and diamines are easily accessible ligands and usually behave as bicompartamental ligands, allowing the synthesis of heterobinuclear 3d-4f complexes¹ or 3d-3d' complexes.² In mononuclear complexes with this type of ligands, the metal ion is hosted into the N₂O₂ compartment (Scheme 1a) and the larger vacant O₂O'₂ compartment can act as a receptor not only toward other metal ions, but also toward hydrogen bond donors (*e.g.* the aqua ligand^{3,4} or ammonium

cation⁵). These planar tectons can be also used in combination with 4-aminopyridine, which acts as coordinating ligand and hydrogen bonds donor, to build various supramolecular architectures: rectangles, zigzag chains or ladders.⁶ The three dimensional version of these bicompartamental ligands can be obtained by reacting *o*-vanillin with tris(2-aminoethyl)-amine (Scheme 1b). Generally, the tripodal ligands were used as receptors for different chemical species: transition metal ions,⁷ lanthanide ions,⁸ anions,⁹ or cations and anions in the same time.¹⁰ In the particular case of the tripodal Schiff base ligand derived from *o*-vanillin and tris(2-aminoethyl)-amine, H₃valtren, the compartments can host one¹¹ or two lanthanide ions.^{8a,b}

In this paper we report on crystal structures of the mononuclear complexes of the anionic valtren³⁻ tripodal ligand with erbium(III) and ytterbium(III) ions, [Er(valtren)] (1) and [Yb(valtren)] (2), and the use of the [Er(valtren)] complex as receptor for the ammonium cation.

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Scheme 1

RESULTS AND DISCUSSION

The synthesis of mononuclear complexes of valtren anionic tripodal ligand with various lanthanide(III) ions, $[Ln(\text{valtren})]$, was already reported,¹¹ but the structural information concerning this series of compounds was gathered only by powder X-ray diffraction. Herein we present the structural characterization of $[\text{Er}(\text{valtren})]$ (**1**) and $[\text{Yb}(\text{valtren})]$ (**2**) complexes by X-ray diffraction on single crystal. The two compounds are isostructural and crystallize in the *trigonal P-3* space group. Below we will describe only the structure of compound **1**.

In the $[\text{Er}(\text{valtren})]$ mononuclear complex, the lanthanide ion has a coordination number seven and is located in the inner compartment of the ligand surrounded by the four nitrogen atoms (three imino and one amino) and the three phenoxo oxygen atoms (Figure 1). The external compartment of the ligand delimited by the three phenoxo and three methoxy oxygen atoms is empty. The lanthanide ion and amino nitrogen

atom (N1) lie on a C_3 axis of symmetry. The Ln-N bond lengths in compounds **1** and **2** are: Er1-N1 = 2.874(14), Er1-N2 = 2.447(10) Å, respectively Yb1-N1 = 2.902(8) and Yb1-N2 = 2.432(5) Å. The Ln-O bond lengths are: Er1-O1 = 2.178(7) Å in **1** and Yb1-O1 = 2.166(3) Å in **2**.

The molecule has an overall conical shape. The analysis of the packing diagrams shows that the molecules form piles of cones running along the crystallographic *c* axis. The cones have the same orientation within the pile but alternating in neighbouring piles (Figure 2).

The existence of the empty external compartment containing six oxygen atoms (potentially hydrogen bonds acceptors) prompted us to attempt recognition of a hydrogen bond donor in this cavity of the mononuclear complexes. Because the $[\text{Ln}(\text{valtren})]$ molecules present a C_3 axis of symmetry the ammonium cation is a good candidate to be recognized in the external compartment of the ligand by hydrogen interactions.

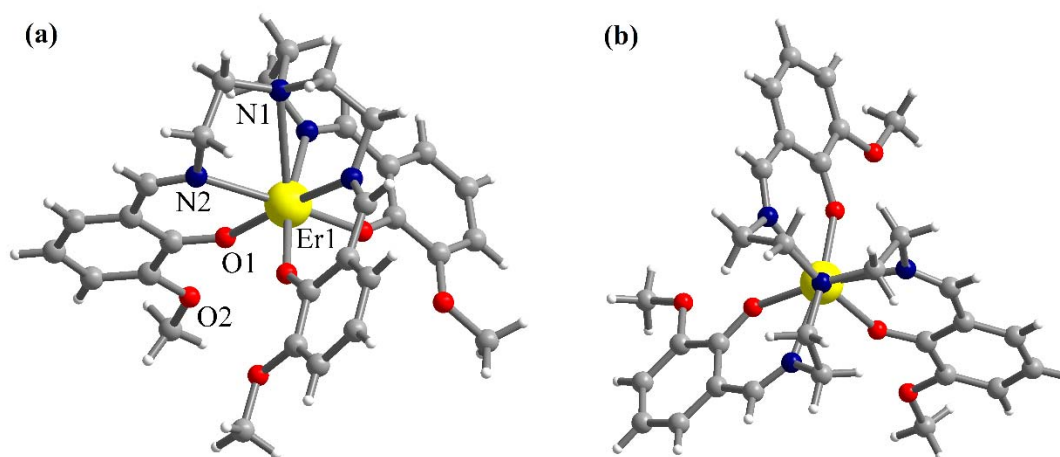


Fig. 1 – (a) Perspective view and (b) top view (along the C_3 axis of the molecule) of the molecular structure of **1** determined by X-ray diffraction on single crystal.

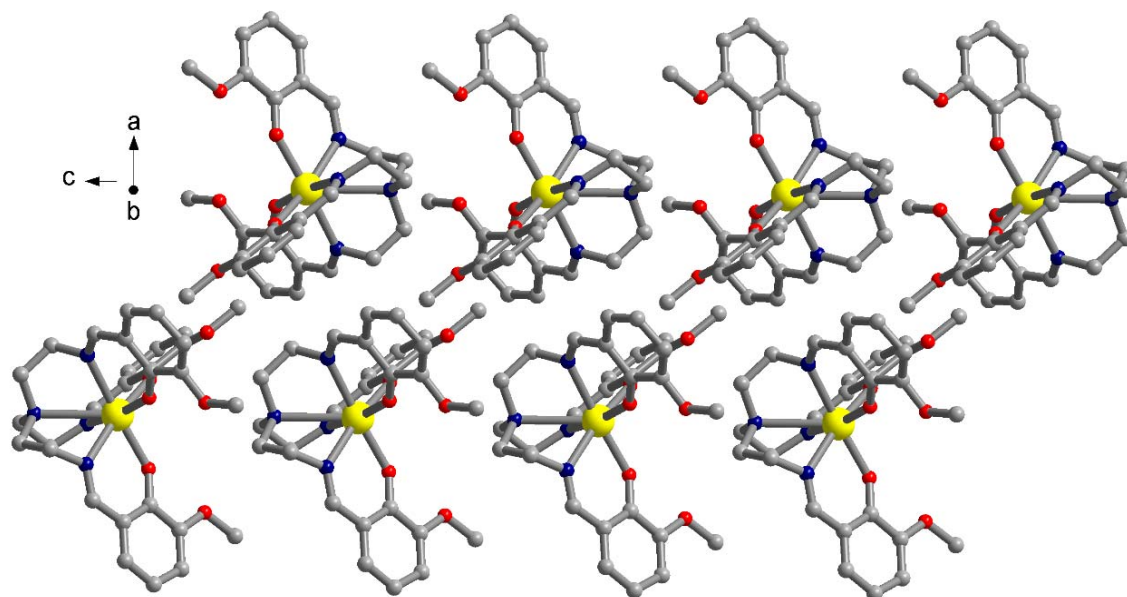


Fig. 2 – Packing diagram in crystal **1** showing two neighbouring columns of [Er(valtren)] molecules running along the crystallographic *c* axis.

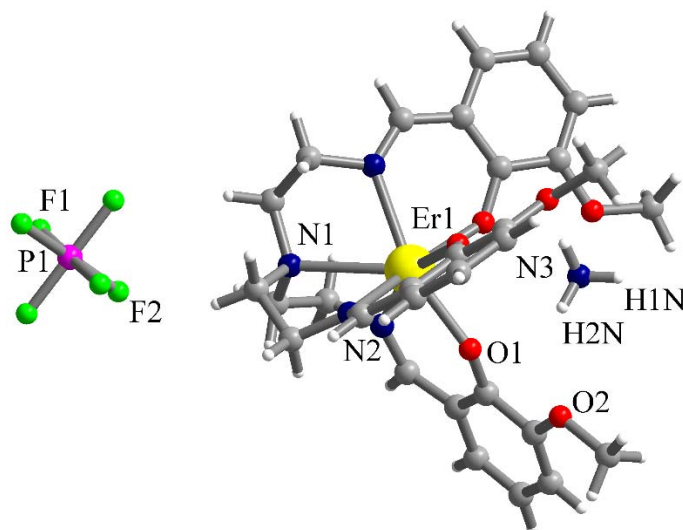


Fig. 3 – Perspective view of the supramolecular complex [Er(valtren){NH₄]}(PF₆) in crystal **3** (the acetonitrile solvent molecules were omitted for clarity).

By stirring equimolar amounts of **1** and NH₄PF₆ in acetonitrile, the turbid mixture turns to a clear solution after 20-30 minutes. The slow evaporation at room temperature of the clear solution affords the yellow crystals of the supramolecular complex [Er(valtren){NH₄]}(PF₆)·3CH₃CN (**3**) after one week.

The structural investigation by X-ray diffraction on single crystal confirms that the [Er(valtren)] moiety still possesses the *C*₃ symmetry and the ammonium cation is located in the external compartment of the ligand (Figure 3). The Er(III) ion is also heptacoordinated by four nitrogen atoms (three imino and one amino) and three phenoxo oxygen atoms. The bond lengths for the

coordination environment are Er1-N1 = 2.701(9), Er1-N2 = 2.458(5) and Er1-O1 = 2.193(4) Å. The P1, N1, Er1, N3 and H1N atoms lie on the same *C*₃ axis of symmetry.

The distances for the hydrogen interactions are: (N3)H2N···O1 = 2.48 Å and (N3)H2N···O2 = 2.43 Å, while the corresponding angles are: N3-H2N···O1 = 119.2° and N3-H2N···O2 = 139.8°.

In crystal **3**, the conical complexes are organized in base to base pairs formed by two cones with opposite orientation. Between the bases of the cones are located the crystallization acetonitrile molecules and on the top of the cones are placed the PF₆⁻ anions (Figure 4).

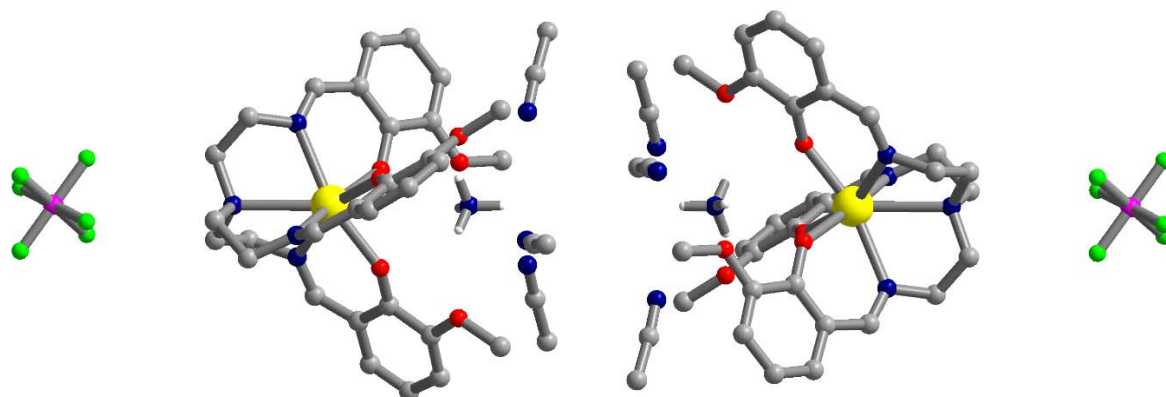


Fig. 4 – Packing diagram in crystal **3** showing a pair of supramolecular complexes.

EXPERIMENTAL

Materials and methods

Synthesis of the complexes

All the chemicals used as well as all the solvents were purchased from commercial sources. All manipulations were performed under aerobic conditions.

The mononuclear complexes [Er(valtren)] (**1**) and [Yb(valtren)] (**2**) were obtained using the same synthetic procedure: 0.3 mmol of *o*-vanillin were added to 100 mL solution containing 0.1 mmol of tris(2-aminoethyl)-amine in a mixture of CH₃OH and CHCl₃ (1:1). Subsequently, 0.1 mmol of Er(NO₃)₃·5H₂O, respectively Yb(NO₃)₃·5H₂O, and 0.5 mmol of triethylamine were added to the reaction mixtures and stirred for one hour. By slow evaporation of the solutions the yellow needle like crystals of **1** and **2** were obtained. The crystals were collected by filtration and washed with diethyl ether.

Selected IR data for **1** and **2** (KBr pellet, cm⁻¹): **1** - 3050w, 2926w, 1626vs, 1597m, 1547w, 1470s, 1446s, 1407m, 1333s, 1241s, 1219s, 1166w, 1083w, 1064w, 1034w, 967w, 859w, 741m, 629w, 536w; **2** - 3413w, 3052w, 2928w, 2856w, 1626vs, 1597w, 1548w, 1471s, 1448s, 1407m, 1334s, 1241s,

1221s, 1166w, 1083w, 1063w, 1034w, 968w, 918w, 861w, 745m, 627w, 536w.

The supramolecular complex [Er(valtren){NH₄}(PF₆)·3CH₃CN (**3**) was obtained as yellow crystals by slow evaporation at room temperature of the solution containing 0.05 mmol of [Er(valtren)] and 0.05 mmol of NH₄PF₆ in 75 mL of acetonitrile. Selected IR data for **3** (KBr pellet, cm⁻¹): 3647w, 3333w, 3191w, 2904w, 2843w, 1621vs, 1551m, 1469s, 1452s, 1408m, 1317m, 1239m, 1218s, 1170w, 1107w, 1081m, 1034m, 967m, 916w, 843vs, 739s, 626w, 558m.

X-Ray crystallography

X-ray diffraction measurements were performed on a STOE IPDS II diffractometer, operating with Mo-Kα (λ = 0.71073 Å) X-ray tube with graphite monochromator. The structures were solved by direct methods (using SHELXS-2013 or SHELXS-2014 crystallographic software) and refined by full-matrix least squares techniques based on *F*². The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using SHELXL-2018 or SHELXL-2014 crystallographic software package. A summary of the crystallographic data and the structure refinement for the three compounds are given in Table 1. CCDC reference numbers: 2000488-2000490.

Table 1

Crystallographic data, details of data collection and structure refinement parameters for compounds **1-3**

Compound	1	2	3
Chemical formula	C ₃₀ H ₃₃ N ₄ O ₆ Er	C ₃₀ H ₃₃ N ₄ O ₆ Yb	C ₃₆ H ₄₆ ErF ₆ N ₈ O ₆ P
<i>M</i> (g mol ⁻¹)	712.86	718.64	999.04
Temperature, (K)	293(2)	293(2)	173(2)
Wavelength, (Å)	0.71073	0.71073	0.71073
Crystal system	Trigonal	Trigonal	Trigonal
Space group	<i>P</i> -3	<i>P</i> -3	<i>R</i> -3
<i>a</i> (Å)	14.0384(14)	13.9972(8)	13.0523(18)
<i>b</i> (Å)	14.0384(14)	13.9972(8)	13.0523(18)
<i>c</i> (Å)	8.2966(8)	8.3337(4)	43.514(9)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
<i>V</i> (Å ³)	1416.0(3)	1414.00(18)	6420(2)
<i>Z</i>	2	2	6
<i>D</i> _c (g cm ⁻³)	1.672	1.688	1.550
μ (mm ⁻¹)	3.014	3.358	2.076
<i>F</i> (000)	714	718	3018
Goodness-of-fit on <i>F</i> ²	1.068	1.091	1.039

Table 1 (continued)

Final RI , wR_2 [$I > 2\sigma(I)$]	0.0720, 0.1449	0.0402, 0.0823	0.0546, 0.1189
RI , wR_2 (all data)	0.1153, 0.1712	0.0609, 0.0906	0.0773, 0.1306
Largest diff. peak and hole ($e\text{\AA}^{-3}$)	3.526, -1.094	0.966, -0.547	2.072, -1.454

Physical measurements. The IR spectra (KBr pellets) were collected on a Bruker Tensor 37 spectrophotometer in the 4000 - 400 cm^{-1} range.

CONCLUSIONS

In this article, we describe the crystal structures of the mononuclear complexes [Er(valtren)] and [Yb(valtren)] containing the bicompartamental tripodal Schiff base ligand derived from *o*-vanillin and tris(2-aminoethyl)-amine. The [Er(valtren)] complex proved to be a good receptor for the ammonium cation, which is encapsulated in the external compartment of the ligand by hydrogen interactions.

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