

# Interactions of trivalent lanthanide cations with tetradentate Schiff bases: New lanthanide(III) complexes from (1*S*,2*S*,*N*<sup>1</sup>*E*,*N*<sup>2</sup>*E*)–*N,N'*-bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine

Mantha Tsiouri <sup>a</sup>, Nick Hadjiliadis <sup>a,\*</sup>, Taner Arslan <sup>b</sup>, Benson M. Kariuki <sup>c</sup>,  
John C. Plakatouras <sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, University of Ioannina, 451 10 Ioannina, Greece

<sup>b</sup> Osmangazi University, Science and Arts Faculty, Chemistry Department, 26480 Eskisehir, Turkey

<sup>c</sup> School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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## Abstract

The novel lanthanide(III) complexes [Ln(NO<sub>3</sub>)<sub>3</sub>(MeOH)L] (Ln = La **1**, Pr **2**), and [Ln(NO<sub>3</sub>)<sub>3</sub>L]·MeOH (Ln = Sm **3**, Gd **4**) where L = *N,N'*-bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine, have been obtained by direct reaction of the Schiff base ligand and the corresponding hydrated lanthanide(III) nitrates in methanol. All complexes were characterized spectroscopically and thermogravimetrically. Complexes **2** and **3** were also characterized with crystallographic studies. In the molecular structure of **2**, Pr(III) is surrounded by all four nitrogen atoms of the Schiff base and seven oxygen atoms belonging to three bidentate chelating nitrate ligands and a coordinated methanol molecule, while in **3**, Sm(III) is surrounded by all four nitrogen atoms of the Schiff base and six oxygen atoms belonging to three bidentate chelating nitrate ligands.

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Schiff base metal complexes have a key role in the development of coordination chemistry, resulting in an enormous number of publications, ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of metal complexes [1].

The lanthanide cations can promote Schiff base condensation and can give access to complexes of otherwise inaccessible ligands. This fact, in combination with the applications of lanthanide macrocyclic complexes emerging from biology and medicine have boosted research on these areas [2]. A large number of articles have been published on lanthanide complexes with the hexadentate Schiff base derived by the

condensation of 2,6-diacetylpyridine and ethylenediamine [3–14]. These complexes are stable enough under physiological conditions. However, only recently, research work dealing with the various aspects involving different physicochemical properties and complexation behaviour of tetradentate Schiff bases has appeared in the literature, primarily focusing in the separation of actinides from lanthanides in nuclear reprocessing [15] and catalytic properties [16].

Previously, we have reported the synthesis and the structural and spectroscopic characterization of lanthanide complexes with *N,N'*-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine [17] and *N,N'*-bis(pyridin-2-ylmethylene)benzene-1,2-diamine [18].

It was found that the ethylenediamine ‘hinge’ of the di-Schiff base ligand eliminates the possibility of coplanar coordination of the four nitrogen donors [17] while when we changed the ethylenediamine moiety with 1,2-

\* Corresponding authors. Tel.: +30 651 98417/98420; fax: +30 651 44831.

E-mail addresses: [nhadjis@cc.uoi.gr](mailto:nhadjis@cc.uoi.gr) (N. Hadjiliadis), [iplakatu@cc.uoi.gr](mailto:iplakatu@cc.uoi.gr) (J.C. Plakatouras).

phenylenediamine to force planar coordination of the tetradentate di-Schiff base, we ended up with the lanthanide cations outside of the four nitrogens plane [18].

Herein, we report the synthesis [19] and characterization [20] of lanthanide(III) complexes with the Schiff base *N,N'*-bis(pyridin-2-ylmethylene)cyclohexane-1,2-diamine. Though interactions of lanthanide cations with that Schiff base have been studied in some extent in acetonitrile [16] the system provides new interesting results that justify our choice.

Complexes **1–4** were prepared by direct reaction of the hydrated lanthanide nitrate salts and the Schiff base ligand in methanol in 1:1 metal to ligand molar ratio. Attempts to prepare the 1:2 complexes using larger excess of the ligand and different solvents lead to impure products with unidentified formulae.

The crystal structure of complex **2** (Fig. 1a) consists of dimeric hydrogen bonded  $[\text{Pr}(\text{NO}_3)_3(\text{MeOH})\text{L}]_2$  units held together with stacking interactions between the pyridine rings. The  $\text{Pr}^{\text{III}}$  atom is surrounded by seven oxygen atoms belonging to three bidentate chelating nitrate ligands and a coordinated methanol and four (two imino and two pyridine) nitrogen atoms belonging to the Schiff base ligand.

The Pr–O bond distances span the range 2.562–2.763 Å and they are in good agreement with previously reported values [5,6,15–18], taking into account the lanthanide contraction. Though neutral, the methanol moiety appears to be coordinated to  $\text{Pr}^{\text{III}}$  stronger than the nitrates (mean  $\text{Pr–O}_{\text{nitrate}} = 2.642$ ,  $\text{Pr–O}_{\text{methanol}} = 2.562$  Å). It is responsible for the formation of the hydrogen bonded dimer (Fig. 1b). It interacts with a nitrate ligand coordinated to an adjacent praseodymium atom. There are no important differences in the coordination characteristics of the nitrate ligands. They can be considered symmetrically chelated and the Pr atom is coplanar to all of them, since all the  $\text{Pr–O}_{\text{coordinated}}\text{–N–O}_{\text{free}}$  are larger than  $170^\circ$ . The mean Pr–N distance is 2.680 Å, and is in agreement with our previous data [17,18]. The 4N group of atoms deviates from the planarity as a result of the *trans* geometry of the cyclohexane moiety and the Pr atom is positioned 1.01 Å outside of the best fitted plane. The coordination geometry about praseodymium is too distorted to allow us assignment to a regular polyhedron.

The crystal structure of complex **3** (Fig. 2) consists of  $[\text{Sm}(\text{NO}_3)_3\text{L}]$  units held together with stacking interactions between the pyridine rings and MeOH molecules. The  $\text{Sm}^{\text{III}}$  atom is surrounded by six oxygen atoms belonging to three bidentate chelating nitrate ligands and four (two imino and two pyridine) nitrogen atoms belonging to the Schiff base ligand. The mean Sm–O bond distance is 2.518 Å while the mean Sm–N bond distance is 2.570 Å. Both values are shorter than the corresponding for **2**, reflecting the lanthanidic contraction, since the charge density in Sm is bigger than Pr. As a consequence Sm atom is closer to the best plane through the four nitrogen donors (0.48 Å). Considering nitrate ligands as a point, the geometry about the Sm atom can be better described as pentagonal bipyramidal with the equatorial plane occupied by the four nitrogen atoms of

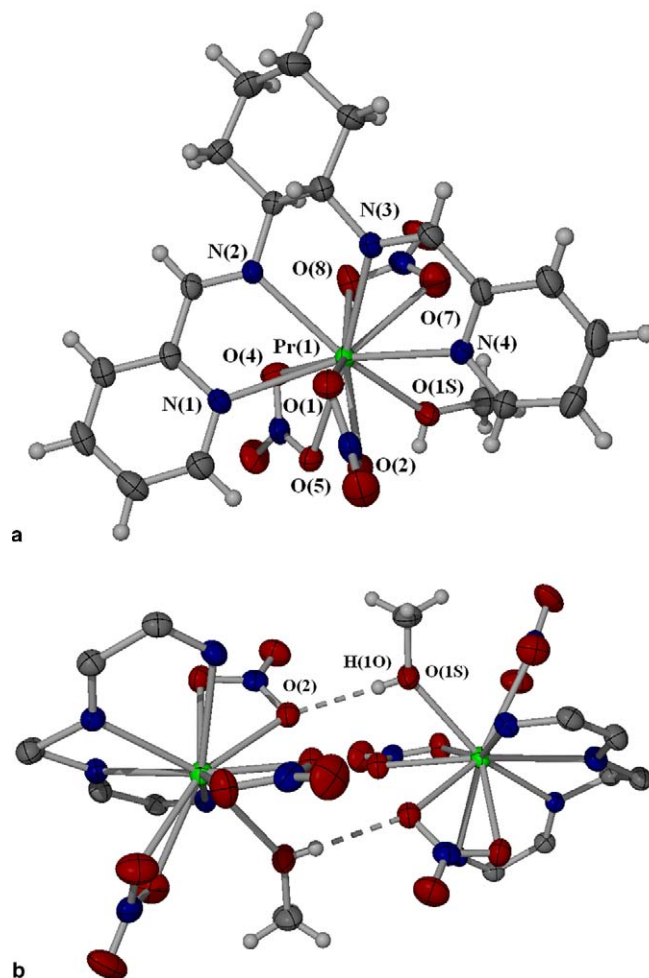


Fig. 1. (a) A presentation of complex **2** with 40% probability ellipsoids. Labels for non-coordinating atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Pr(1)–O(1S) 2.561(4), Pr(1)–O(2) 2.576(3), Pr(1)–O(4) 2.606(4), Pr(1)–N(2) 2.606(3), Pr(1)–O(8) 2.619(4), Pr(1)–O(5) 2.640(3), Pr(1)–O(1) 2.640(4), Pr(1)–N(3) 2.675(4), Pr(1)–N(4) 2.679(4), Pr(1)–O(7) 2.756(4), Pr(1)–N(1) 2.759(4), O(1S)–Pr(1)–O(2) 78.67(12), O(1S)–Pr(1)–O(4) 84.91(13), O(1S)–Pr(1)–N(2) 154.09(12), O(1S)–Pr(1)–N(3) 122.97(12), N(2)–Pr(1)–N(3) 60.69(11), O(1S)–Pr(1)–N(4) 72.55(12), N(2)–Pr(1)–N(4) 121.61(11), N(3)–Pr(1)–N(4) 61.91(11), O(1S)–Pr(1)–O(7) 66.35(13), O(1S)–Pr(1)–N(1) 127.59(12), O(2)–Pr(1)–N(1) 73.46(11), N(2)–Pr(1)–N(1) 61.15(11), N(3)–Pr(1)–N(1) 108.71(12), N(4)–Pr(1)–N(1) 133.06(12). (b) The hydrogen bonded dimer in **2**. The structural characteristics of the H-bonds are: O(1S)–H(10) 0.72(4), H(10)  $\cdots$  O(2) 2.31(5), O(1S)  $\cdots$  O(2) 2.955(6) Å, O(1S)–H(10)  $\cdots$  O(2) 150(5) $^\circ$ . Symmetry operation to generate equivalent atoms:  $1 - x, -y, -z$ .

the di-Schiff base and one nitrate ligand, while the apical positions by the other two nitrate ligands.

Comparison of the infrared spectra of the prepared complexes can lead us rather safely to the conclusion that the four complexes are isostructural or at least that both the nitrate and the Schiff base ligands are coordinated in the same manner. Assignment of the nitrate bands has been made as reported previously [25].

The room temperature effective magnetic moments of complexes **2**, **3** and **4** show little deviation from the Van Vleck theoretical values.

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