Inorganica Chimica Acta 442 (2016) 64-69

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Coordination of metalloligand [NiL] (H_2L = salen type N_2O_2 Schiff base ligand) to the f-block elements: Structural elucidation and spectrophotometric investigation

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ARTICLE INFO

Article history: Received 25 September 2015 Received in revised form 31 October 2015 Accepted 29 November 2015 Available online 8 December 2015

Keywords: Metalloligand Heterometallic complexes Lanthanide and actinide X-ray crystal structures Spectrophotometric titration

ABSTRACT

To investigate the coordinative interaction of a bidentate metalloligand [NiL] with f-block metal ions, two di-phenoxo bridged Ni-nf (n = 4 and 5) complexes [(NiL)₂Ce(NO₃)₃] (**1**) and [(NiL)UO₂(NO₃)₂] (**2**) have been synthesized and characterized (H₂L = N,N-bis(α -methylsalicylidene)-1,3-propanediamine, a N₂O₂ donor Schiff base ligand). Single crystal structural characterizations revealed that [NiL] formed 2:1 adduct with a lanthanide Ce(NO₃)₃ whereas with the actinyl UO₂(NO₃)₂, 1:1 adduct was obtained. In complex **1** the central Ce(III) ion is connected to two terminal [NiL] metalloligands through $\mu_{1,1}$ -diphenoxido bridges to form a trinuclear coordination cluster with three chelating nitrato coligands (CeO₁₀ tetradecahedron). Whereas in complex **2** one [NiL] is chelated to the U^{VI}O₂²⁺ ion along with two chelating nitrato coligands to form a dinuclear core (UO₈ hexagonal bipyramid). Moreover, to examine the formation of these complexes in solution, we performed UV-Vis spectrophotometric titrations of [NiL] with the respective metal ions which revealed the formation of bimetallic 1:1 and 2:1 complexes for both Ce(III) and UO₂²⁺ ions. However, we got only 1:1 and 2:1 adducts for UO₂²⁺ and Ce³⁺ respectively on crystallization even of varying the stoichiometry of the reactants probably due to the differences in solubility of the adducts formed. © 2015 Elsevier B.V. All rights reserved.

1. Introduction

Apart from their serendipitous assembly, one of the most convenient routes for synthesis of 3d-f complexes is the utilization of compartmentalized ligands those are capable of sorting 3dand f-block metal ions in a planned way *via* different coordination environment [1]. Amongst these compartmentalized ligands, salen type di-Schiff bases or their derivatives are arguably the most investigated ones [1,2]. The success of this strategy relies on the preference of the metal ions toward different coordinating sites. A CSD search shows that the substituted derivatives of salen type ligands (N₂O₄, N₂O₃, N₃O₃, N₃O₆ etc.) are much more useful in this regard compared to their unsubstituted analogs (salen and its homologs: N₂O₂ donor) presumably due to their higher denticity that brings higher selectivity and stability of the complexes [3]. Moreover, for a single compartment, there is a high possibility of transmetallation reaction [4]. It has been observed that neutral [ML] type metalloligands (M = Zn(II), Cu(II) and Ni(II), $H_2L = N_2O_2$ salen type Schiff bases) are capable of behaving as bidentate chelates to produce dinuclear [(ML)M']ⁿ⁺ or trinuclear [(ML)₂M']ⁿ⁺ hetero-metallic complexes if there is no transmetallation [5]. Recently, we reported the formation of complexes of [CuL] with $UO_2(NO_3)_2$ in solid and in solution [6]. However, such investigation combining solid state structure and solution behavior with any [ML] and Ln(III) is scanty. It should be noted that coordination numbers of Ln(III) ions are usually high (8-10) and they allow coordination along all directions. Therefore, they can accommodate easily more than one metalloligands around themselves [7]. On the other hand, in naturally abundant AnO_2^{n+} , coordination of ligand can take place only through equatorial plane and usually dinuclear complex is formed with [ML] type metalloligands [6]. Therefore, a systematic spectroscopic investigation and comparison of host-guest interaction between a metalloligand [ML] and a 4f- or 5f-block metal ion can enlighten the formation of different species in solutions [8]. Such study is of potential importance to understand the solution speciation of these complexes and also to make future synthetic design.

In the present work, we use a metalloligands [NiL] where $H_2L = N,N'$ -bis(α -methylsalicylidene)-1,3-propanediamine to study the complex formation with cerium(III) nitrate and uranyl(VI) nitrate. The formation of the bimetallic dinuclear and trinuclear complexes in solution for both Ce(III) and UO₂²⁺ has been







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characterized by UV–Vis spectrophotometric titration of [NiL] with the respective analyte metal ions. The single crystal X-ray crystallographic analyses of the isolated solid reveal the formation of 2:1 and 1:1 adduct with $Ce^{III}(NO_3)_3$ and $U^{VI}O_2(NO_3)_2$ respectively. It is to be noted that complex **1** is the first trinuclear Ni₂Ln complex derived from salen type N₂O₂ Schiff base ligand. The formation of such trinuclear complex with uranyl is also enlightened from spectrophotometric titration but the crystallographic evidence is unknown till now.

2. Experimental

2.1. Starting materials

2-Hydroxyacetophenone and 1,3-propanediamine were purchased from Spectrochem, India and were of reagent grade. They were used without further purification. Tetrabutyl ammonium perchlorate (TBAP), Ce(NO₃)₃·6H₂O and UO₂(NO₃)₂·6H₂O was purchased from Aldrich.

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care. All uranyl compounds are toxic when ingested, and any contact with the skin should also be avoided because of its mild radioactivity.

2.2. Synthesis of the Schiff base ligand H₂L and ligand complex [NiL]

The Schiff-base ligand (H₂L) and its subsequent Ni-derived "metalloligand" ([NiL]) were synthesized by reported methods [9]. Briefly, 5 mmol of 1,3-propanediamine (0.42 mL) was mixed with 10 mmol of 2-hydroxyacetophenone (1.20 mL) in 20 mL methanol. The resulting solution was refluxed for ca. 2 h, and allowed to cool. The yellow methanolic solution of H₂L was used for complex formation. A methanolic solution (20 mL) of Ni(ClO₄)₂- \cdot 6H₂O (1.825 g, 5 mmol) was added to a methanolic solution of H₂L (5 mmol, 10 mL) and triethyl amine (1.38 mL, 10 mmol) were added to prepare the respective (NiL) crystalline "metalloligand" [NiL].

2.3. Synthesis of complex $[(NiL)_2Ce(NO_3)_3]$ (1)

The "metalloligand" [NiL] (14.7 mg, 0.04 mmol) was dissolved in acetonitrile (10 mL) and to it a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (8.7 mg, 0.02 mmol in 5 mL of acetonitrile) was added, stirred to mix and then allowed to stand overnight at room temperature when reddish X-ray quality single crystals were deposited at the bottom of the vessel.

Yield 0.015 g, 71%, *Anal.* Calc. for $C_{38}H_{40}N_7O_{13}Ni_2Ce$ (1060.27): C, 43.05; H, 3.80; N, 9.25. Found: C, 43.14; H, 3.71; N, 9.18. IR (KBr): $v(C=N) = 1600 \text{ cm}^{-1}$, $v(NO_3^-) = 1477 \text{ cm}^{-1}$ (v_1), 1318 cm⁻¹ (v_2), 1023 cm⁻¹ (v_3).

2.4. Synthesis of complex $[(NiL)UO_2(NO_3)_2]$ (2)

The "metalloligand" [NiL] (14.7 mg, 0.04 mmol) was dissolved in acetonitrile (5 mL) and to it a solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (20.0 mg, 0.04 mmol in 5 mL of acetonitrile) was put in, swirled to mix and then allowed to stand overnight at room temperature when reddish microcrystalline compound deposited at the bottom of the vessel. This compound was collected and redissolved in 5 mL of acetonitrile by warming, and the solution was kept in a long tube for slow evaporation. X-ray quality light orange single crystals of complex **2** appeared after about 15 days.

Yield 0.020 g, 66%, *Anal.* Calc. for C₁₉H₂₀N₄O₁₀NiU (761.11): C, 29.98; H, 2.65; N, 7.36. Found: C, 29.90; H, 2.55; N, 7.27.

IR (KBr): $v(C=N) = 1598 \text{ cm}^{-1}$, $v(U=O) = 927 \text{ cm}^{-1}$, $v(NO_3^-) = 1482 \text{ cm}^{-1}$ (v_1), 1297 cm⁻¹ (v_2), 1029 cm⁻¹ (v_3).

2.5. Physical measurements

Elemental analyses (C, H and N) were carried out using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra (4000–500 cm⁻¹) were recorded by a Perkin-Elmer RXI FT-IR spectrophotometer in KBr pellets. Electronic spectra were collected from spectroscopic grade acetonitrile solution of the complexes (500–200 nm) in a 1 cm optical glass cuvette with a Hitachi U-3501 spectrophotometer. The spectrophotometric titration were performed in presence of a large excess and fixed concentration of a supporting electrolyte TBAP (100 mM) both in analyte and titrant to maintain the ionic strength of the solution. The titrations were performed with 2 mL, 5×10^{-5} M [NiL] solution as analyte with corresponding metal nitrates solution (1 mM) as titrant those were added up to 0.35 mL (metal concentration deviated due to volume correction from 5×10^{-5} M to 4.25×10^{-5} (M).

2.6. Crystallographic data collection and refinement

Suitable single crystals of each of the two complexes were mounted on a Bruker-AXS SMART APEX II diffractometer ready with a graphite monochromator and Mo K α (λ = 0.71073 Å) radiation. The crystals were placed at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. The structures were solved using Patterson method by using the SHELXS 97. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms that were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least squares refinement. Absorption corrections were carried out using the sadabs program [10]. All calculations were carried out using shelxs 97 [11], shelxl 97 [12], platon 99 [13], ortep-32 [14] and WinGX system ver-1.64 [15]. Data collection with selected structure refinement parameters and selected bond parameters for both the complexes are given in Tables 1 and S1, of the supporting information respectively.

3. Results and discussion

3.1. Syntheses and characterizations of the complexes 1 and 2

Recently we successfully synthesized several [(ML)M'X_n] and [(ML)₂M'X_n] type complexes [where, M represent Cu^{II} and Ni^{II} and M' are different s-, p- and d-block elements] [16]. We also reported such complexes where M = Cu^{II} and M' = f-block metal ions derived from the same ligand that forms 2:1 adduct with Tb^{III} and 1:1 adduct with U^{VI}O₂²⁺ [6,7]. In the present endeavor we extend our strategy where M is Ni^{II}. Expectedly, at room temperature (25–30 °C) under specified experimental conditions, we found that [NiL] formed 2:1 adduct with Ce(NO₃)₃ and 1:1 adduct with UO₂(NO₃)₂ (Scheme 1). However it is worth to be mention that even after changing the molar ratio of the reactants i.e., [NiL]:Ce (NO₃)₃ = 1:1 and [NiL]:UO₂(NO₃)₂ = 2:1 only complexes **1** and **2** respectively, were precipitate out from the reaction mixture.

Besides elemental analyses, both the complexes were primarily characterized by IR spectra. The metalloligand [NiL] is neutral and does not possess any counter anion (Fig. S1 of the supporting information), whereas both the complexes contain nitrato

Table	1

Crystal data and structure refinement parameters of complexes 1 and 2.

Compound	1	2
Formula	C38H40N7O13Ni2Ce	C19H20N4O10NiU
Formula weight	1060.27	761.11
Space group	monoclinic	orthorhombic
Crystal system	$P2_1/n$	Pnma
a (Å)	11.181(5)	18.327(6)
b (Å)	20.757(5)	19.940(7)
<i>c</i> (Å)	17.805(5)	6.299(2)
α (°)	90	90
β (°)	103.427(5)	90
γ (°)	90	90
V (Å ³)	4019(2)	2302(1)
Ζ	4	4
D_{calc} (g cm ⁻³)	1.752	2.196
μ (mm ⁻¹)	2.116	7.907
F(000)	2140	1448
R _{int}	0.0585	0.0962
θ range (°)	1.5-25.3	2.0-25.0
Total reflections	28034	14284
Unique reflections	7262	2093
Data with $I > 2\sigma(I)$	5538	1682
R_1^a on $I > 2\sigma(I)$	0.0498	0.0496
$wR_2^{b} (I > 2\sigma(I))$	0.1272	0.1139
Goodness-of-fit $(GOF)^{c}$ on F^{2}	1.049	1.012
<i>T</i> (K)	293	293

^a $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|.$

^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}.$ ^c GOF = $[\Sigma [w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}.$

coligands (Fig. S2 of the supporting information). The presence of the nitrato anion and its bidentate chelation ($\kappa^2 0, 0'$) in each compound are illustrated by its characteristic bands [17]. The broad strong bands of chelated nitrates are assigned at 1477, 1445 cm⁻¹ (B₁), and 1318, 1280 cm⁻¹ (A₁) for **1** as well as 1482, 1444 cm⁻¹ (B₁) and 1384, 1297 cm⁻¹ (A₁) for **2**. The 1350 cm⁻¹ band of the free D_{3h} nitrate ion is absent. A strong and sharp band due to the azomethine [v(C=N)] group of the Schiff base appears at 1600 and 1598 cm⁻¹ for [NiL] for complexes **1** and **2** respectively

which is observed at 1593 cm⁻¹ for free [NiL]. The asymmetric vibration of the O=U=O moiety appears at 927 cm⁻¹ for complex **2** [6].

3.2. Description of the structures

The molecular structure of complexes **1** and **2** along with partial atomic numbering scheme is shown in Figs. 1 and 2 respectively where the detailed crystallographic and structural parameters are given in Tables 1 and S1 of the supporting information.

Complex **1** is comprised of a trinuclear Ni¹¹₂Ce¹¹¹ coordination cluster having formula $[(NiL)_2Ce(NO_3)_3]$. In the complex the central metal ion is Ce(III) which is coordinated by two terminal metalloligands. This complex crystallizes in the monoclinic crystal system with $P2_1/n$ space group where the overall molecule is asymmetric. Two neutral metalloligands are chelated in a transoid orientation to the central Ce. Three chelating nitrato ($\kappa^2 0, 0'$) coligands complete the deca-coordination of Ce^{III}. Thus the vertexes of the coordination polyhedron of the Ce^{III} ion is constructed by ten oxygen atoms with average Ce–O bond distances of 2.58(2) Å. The four of the ten oxygen atoms namely O(1), O(2) and O(3), O(4) that belong to the two metalloligands are at distances of 2.411(5)-2.667(4) Å and the remaining six oxygen atoms O(5), O(7); O(8), O(10); O(11), O(13) are from three nitrato coligands are at distances of 2.555(5)-2.648 (5) Å. The coordination polyhedron of the Ce^{III} atom can be preeminently described as a distorted tetradecahedron geometry [18]. Six oxygen atoms, i.e., O(1), O(2), O(3), O(4), O(8) and O(10), form nearly an equatorial plane, whereas O(5), O(7), and O(11), O(13) set of atoms are at the opposite sides of this plane in such a manner that the O(5)-Ce(1)-O(7) and O(11)-Ce(1)-O(13) planes are nearly orthogonal to the equatorial plane [81.5(1)° and 77.5(1)° respectively] as well as to each other $[78.6(2)^{\circ}]$. The root mean squared (r. m. s.) deviation of the six equatorially coordinated O-atoms from the mean plane passing through them is 0.445(13) Å with the metal atom 0.027(1) Å for Ce(1) from this plane toward axially coordinated nitrate coligand (N(7)).



Scheme 1. Syntheses of the metalloligand and complexes 1 and 2.



Fig. 1. The ORTEP diagram of complex **1** with partial atomic numbering scheme. Ellipsoids are drawn at 30% probability; color Scheme Ce violate, Ni green, O red, N blue, C brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. The ORTEP diagram of complex **2** with partial atomic numbering scheme. Ellipsoids are drawn at 30% probability; color Scheme U yellow others unchanged. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In case of **2** a [NiL] metalloligand is coordinated to a UO_2^{2+} to form a dinuclear compound of formula [(NiL)UO₂(NO₃)₂] which crystallizes in the orthorhombic crystal system with Pnma space group [6]. A mirror plane of symmetry (symmetry code: a = x, 1/2 - y, z) passes through the Ni(1) and $[UO_2]^{2+}$ of the molecule (Fig. S3 of the supporting information). The metalloligand is chelated in a bidentate fashion through $\mu_{1,1}$ -bridging phenoxido O atoms to the uranium atom U(1) which has a pair of *trans*-coordinated oxido atoms. Two chelating nitrato ($\kappa^2 0,0'$) coligands complete the octa-coordination of the actinide ion. Thus, the vertexes of the coordination polyhedron of the U(VI) ion in complex 2 are constructed by eight oxygen atoms with average U-O bond distances of 2.29(2) Å. The four of the eight oxygen atoms namely O (1), O(1a) and O(5), O(6) belonging to the [NiL] metalloligand and trans-uranyl oxido atoms are at distances of 2.390(5) Å and 1.753(8), 1.734(8) Å respectively. The remaining oxygen atoms O(2), O(3) and their symmetry related ones are from chelating nitrato coligands at distances of 2.527(6) and 2.513(6) Å respectively.

The UO₈ coordination polyhedron can be described by distorted hexagonal bipyramid. Six oxygen atoms, i.e., O(1), O(2), O(3) and their symmetry related ones form an equatorial plane. The axial positions are occupied by the oxygen atoms of uranyl ion with short U–O distances which are typical of the double uranyl bond, commonly found for hexavalent uranium [6,19]. The *trans* OUO angle which is $178.7(4)^{\circ}$ show slight deviation from linearity (180°). The r. m. s. deviation of the six equatorially coordinated O-atoms from the mean plane passing through them is 0.014 (16) Å with a deviation of 0.105(1) Å for U(1) from this plane toward axially coordinated O(6) atom.

The nickel atoms in both the complexes show a square-planar geometry being coordinated by two $\mu_{1,1}$ -phenoxido oxygen atoms and the two imine nitrogen atoms of the tetradentate Schiff base ligand with the Ni-N and Ni-O bond distances ranges between 1.866(6)–1.913(6) Å and 1.837(5)–1.868(4) Å. respectively. The r. m. s. deviations of the four coordinating atoms of each of the Schiff bases around Ni(1) and Ni(2) for 1 from the mean plane passing through them are 0.0065(11) Å and 0.089(14) Å whereas the same is 0.000(13) Å for 2. The metal centers deviate by 0.022(1) Å and 0.024(1) Å for 1 and 0.025(1) Å for 2 from the respective plane. This square-planar geometry for each Ni center is also verified by the so-called τ_4 index that measures the distortion between a perfect tetrahedron ($\tau_4 = 1$) and a perfect square planar geometry ($\tau_4 = 0$) with the formula: $\tau_4 = [360 - (a + b)]/141^\circ$, where "*a*" and "*b*" (in degrees) are the two largest angles around the central metal in the complex [20]. The τ_4 values for Ni(1) and Ni(2) in complex **1** 0.091 and 0.121 respectively and that for Ni(1) in case of 2 is 0.108, confirming a slightly distorted square planar geometry for these metal centers. The structure of $\mathbf{1}$ shows that weak C-H···O and C–H \cdots π interactions form a three dimensional supramolecular packing. A brief description of these interactions has been included in the Supporting information. The same for 2 is similar to one of our previously reported compounds hence is not described here again [6].

Both complexes **1** and **2** contain a heteronuclear 3d-nf(n = 4 or5) core formed by the coordination of the two phenoxido oxygen atoms of the "metalloligand". [NiL] to the f-block metal ions. Therefore, in both structures the metalloligand behaves as chelating bidentate ligand to f-block metal ions. It is worth to note that there are numerous crystallographic evidences of polynuclear 3d-4f (3d = Zn to V and 4f = different lanthanides) and 3d-5f complexes (3d = Zn, Cu, Ni, Co etc. and 5f = Th, U) derived from N_2O_4 type Schiff base ligands [21,4a,22]. On the other hand, crystal structures of only very few heterometallic 3d-4f (3d = Zn, Cu and Ni; 4f = different lanthanides) and 3d-5f complexes (3d = Cu and Ni and $5f = UO_2^{2+}$ with salen type ligands (N₂O₂ donor) are known [23,6,24]. Moreover, among these complexes, Cu(II) is much more frequently used than the other 3d-metal ions [7,23b,25]. With Ni (II), one structure of dinuclear Ni–UO₂ complex [24] and five structures of dinuclear Ni-Ln(III) complexes [Ln = Pr, Gd and Lu] were found with N₂O₂ donor ligands [23a,26]. In all five Ni-Ln(III) complexes the acetylacetonate type anionic coligands encapsulate the Ln ion in such a way that trinuclear Ni₂Ln structure cannot be formed. However, in the present case, nitrate coligand with smaller biting angle opens up the possibility for the Ln (here Ce) to accommodate two [NiL] metalloligands in the coordination sphere. It is also observed that in all the reported complexes of f-block metal ions, the geometry of [NiL] metalloligands ($H_2L = N_2O_2$ ligand) is square planar.

3.3. Spectrophotometric investigations

The crystallographic data suggest that [NiL] form 2:1 adduct with $Ce(NO_3)_3$ and 1:1 adduct with $UO_2(NO_3)_2$ as expected. However, [ML]s are known to form both 2:1 and 1:1 adduct with

lanthanides but only 1:1 adduct with actinyls in the solid state [6,7c]. To have an idea, at least qualitatively about the stoichiometry of these adducts formed in the solution, we undertake spectrophotometric titration. The study of the equilibria in acetonitrile solution between the [NiL] and the respective metal ions, we monitor the spectral changes in the UV–Vis region by adding increasing amounts of metal nitrates [27]. Such spectral changes are attributed to cation-metalloligand binding. The associated interactions are usually ascribed to (i) an electrostatic part due to ion–dipole interaction, (ii) a polarization part arising from ion-induced dipole interaction, and/or (iii) a charge-transfer part. In the metal ion-Lewis base association, the electrostatic part prevails and the metal-to-ligand charge-transfer band of the free metalloligand is expected to illustrate a hypsochromic shift on complexation with the added metal ion [28].

The free metalloligand [NiL] in acetonitrile (5×10^{-5} M) shows intense bands at 399 and 344 nm which are assigned to metal-to-ligand charge-transfer transitions (Fig. 3). Upon gradual addition of metal nitrate solutions (1 mM) to a solution of the metalloligand (2 mL, 5×10^{-5} M), these bands show concomitant lowering of absorption intensity. Notably, for both cases, a new absorption band centered at 325 and 306 nm, for Ce(NO₃)₃ and UO₂(NO₃)₂ respectively, appears with increasing intensity, which is attributed



Fig. 3. Spectrophotometric titration of fixed concentration of 5×10^{-5} M of [NiL] by 1×10^{-3} M solution of Ce(NO₃)₃ (upper panel) and UO₂(NO₃)₂ (lower panel).

to the formation of ground-state complexes. The intensity of these bands becomes highest when the amounts of the respective metal nitrates are half of that of [NiL] suggesting the formation of 2:1 adducts. On further addition of the metal nitrates, the intensity this band starts to decrease and another band centered at 367 and 352 nm, for Ce(NO₃)₃ and UO₂(NO₃)₂ respectively, appears. The intensity of this band increases with addition of corresponding metal nitrates indicating the formation of 1:1 adduct. Appearances of well anchored isobestic points centered at $\lambda = 345$ nm for Ce (NO₃)₃ and $\lambda = 335$ nm for UO₂(NO₃)₂ are consistent with the existence of an equilibrium between free metalloligand [NiL] and the 1:1 and 2:1 complexes in solutions.

The spectrophotometric data qualitatively suggest the formation of 1:1 and 2:1 adduct in solution for both Ce³⁺ and UO₂²⁺ ions as observed earlier with s- or d-block metal ions [29]. However, during crystallization we got only 1:1 and 2:1 adducts for uranyl and Ce³⁺ respectively even of changing the stoichiometry of the reactants possibly because of the differences in solubility of the adducts formed.

4. Conclusion

Two heterobimetallic nickel(II)-cerium(III) and nickel(II)-uranium(VI) complexes have been synthesized by reacting a Ni(II)metalloligand derived from a N₂O₂-donor salen-type Schiff base, with Ce(NO₃)₃·6H₂O and UO₂(NO₃)₂·6H₂O. Single crystal X-ray crystallographic data show that in case of Ce^{III}, a trinuclear coordination cluster is formed whereas a dinuclear complex is obtained by using $U^{VI}O_2^{2+}$. Thus, the present study shows that the strategy of using a Ni-based N₂O₂ metalloligand can be used in an easy and effective manner in isolating heterometallic 3d-nf systems (n = 4 and 5). However, the spectrophotometric study in solution suggests the formation of 1:1 and 2:1 adducts for both Ce³⁺ and UO_2^{2+} ions with the appearances of well-anchored isobestic points. Combining these results, one can envisage that although various species exist in solution, only one of them may be isolated exclusively in the solid state, possibly depending upon the solubility of the species. This study will encourage the comparisons and differences of host-guest interactions between bidentate ligands/ metalloligands with lanthanide and actinyl ions in the solution and in solid state.

Acknowledgements

A.G. thank the Department of Science and Technology (DST), New Delhi, India, for financial support (SR/S1/IC/0034/2012) as well as for the DST-FIST funded single crystal X-ray diffractometer facility at the department of chemistry, University of Calcutta. S. Ghosh is thankful to the University Grants Commission (UGC), New Delhi, for the Senior Research Fellowship.

Appendix. A. Supplementary material

CCDC 1427294 and 1427295 contains the supplementary crystallographic data for the complexes **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2015.11.029.

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