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Synthesis, crystal structure, photoluminescence and electrochemical properties of a sandwiched Ni₂Ce complex

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Abstract

In this study, a Ni₂Ce complex [(NiL)₂Ce(NO₃)₂](NO₃) was synthesized and characterized by spectroscopic and analytical methods. The structure of the complex was determined by single crystal X-ray diffraction study. In the structure of the complex, a Ce(III) ion is sandwiched between the two NiL units, which are virtually parallel to each other. The Ce(III) center is 12-coordinate, surrounded by 12 oxygen atoms; four are from phenolic groups, four from methoxy groups, and four from two bidentate nitrate ligands. Hirshfeld surface analysis was used to evaluate the inter-molecular interactions within the crystal packing. The complex molecules are linked by H····ONO₂ interactions. The largest contribution is H····O/O····H with 41.6% contribution and followed by H····H contacts with 39.1%. The complex showed an excitation band in the range of 510-580 nm. A band in the range of 520-580 nm observed in the emission spectrum almost completely overlapped. This suggests that the band in the emission spectrum of the complex is not the actual fluorescence emission and is assigned to the Rayleigh scattering band. Electrochemical and thermal behaviours of the complex were also investigated.

Keywords: Heteronuclear complex; Ni₂Ce complex; Molecular structure; Emission; Rayleigh scattering

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1. Introduction

Lanthanide complexes which emit in the near-infrared region have found several applications including fluoroimmuno assays, laser systems, and optical amplification [1]. Due to their interesting spectroscopic and magnetic properties, trivalent lanthanide complexes have received considerable attention [2]. Magnetic and spectroscopic properties of lanthanide complexes can also be tuned by the change of ligand around the metal centres [3]. Therefore, chemists have prepared several Ln(III) complexes with different coordinating ligands [1,4,5]. Recently, the preparation and magnetic properties of 3d-4f heterometallic Schiff base complexes have taken considerable attention, however, there are a few studies on their luminescent properties [6–11]. The reason for this may be because of the fact that some lanthanide ions such as Eu(III) and Tb(III) show strongly emissive and long lived excited states yet do not exhibit intense absorption bands [9]. In the lanthanide(III) complexes, the absorption coefficients of the f-f transitions are usually very low because of parity forbidden f-f transitions. However, this can be overcome by attaching suitable chromophores to the ligands [8,9]. These chromophore groups used as sensitizers can transfer energy to the lanthanide ions causing an efficient emission (the antenna effect). In literature, some 3d-4f heterometallic Schiff base complexes such as CuII-GdIII, NiII-GdIII and ZnII-HoIII have been synthesized and found to exhibit interesting magnetic and luminescent properties [6-9,11–13].

In our previous studies, La(III) and Ce(III) complexes of multidentate Schiff base ligands were prepared and their luminescence properties were investigated [14,15]. As part of our investigations into the structure and applications of 3d–4f heterometallic Schiff base complexes, we report here the synthesis and X-ray crystal structure analysis of a Ni₂Ce complex derived from a Schiff base ligand. Molecular structure of the complex was determined by single crystal X-ray diffraction studies. Luminescence and electrochemical behaviours of the complex were also investigated.

2. Experimental

2.1 General methods

All starting materials and organic solvents were purchased from commercial sources and used as received, unless noted otherwise. IR spectrrum was performed on a Perkin Elmer Paragon 1000 PC. CHN analyses were performed using a CE-440 Elemental analyser. The electronic spectrum in the 200–900 nm range was obtained on a Shimadzu UV-1800 UV-Vis

spectrophotometer. The single-photon fluorescence spectra were collected on a Perkin Elmer LS55 luminescence spectrometer. The thermal analysis of the complex was performed on a Perkin Elmer Pyris Diamond.

The cyclic voltammetry studies at the glassy carbon electrode were carried out using a BAS 100W (Bioanalytical System, USA) electrochemical analyser. A glassy carbon working electrode (BAS; Φ : 3mm diameter), an Ag/AgCl reference electrode (BAS; 3M KCl) and platinum wire counter electrode and a standard one-compartment three electrode cell of 10 mL capacity were used in all experiments. The solution of the complex was prepared in DMF (10^{-4} M) for electrochemical studies.

2.2 X-ray structures solution and refinement for the complex

Data collection and cell refinement for X-ray crystallography were completed using a Bruker D8 QUEST diffractometer and data reduction was performed using Bruker SAINT. Crystals of the complex exhibited very weak diffraction, satisfactory structure solution was able to be attained. Diffraction data were measured at ambient temperature using Mo- $K\alpha$ radiation with a Bruker ApexII diffractometer [16]. SHELX-2014/6 was used to solve and refine the structures [17,18]. The structure was solved by direct methods and refined on F^2 using all reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters. Details of the crystal data and refinement are given in Table 1.

2.3 Synthesis of $[(NiL)_2Ce(NO_3)_2](NO_3)$

To a stirring solution of 2-hyrdroxy-3-methoxybenzaldehyde (0.152 gr, 1 mmol), $Ni(OAc)_2.4H_2O$ (0.124 gr, 0.5 mmol) and $Ce(NO_3)_3.6H_2O$ (0.217 gr, 0.5 mmol) were added respectively. The resulting clear green reaction solution was refluxed for 2 hours and ethylenediamine (0.06 g, 0.5 mmol) in methanol (5 mL) was added. As soon as ethylenediamine was added, the colour of the reaction solution turned from green to orange-red colour. The reaction solution was further refluxed for 24 h. Upon cooling to the room temperature, the orange precipitate formed was filtered and dried in air. Crystals suitable for X-ray diffraction study were obtained from slow diffusion of diethyl ether into a methanol solution of the complex.

[(NiL)₂Ce(NO₃)₂](NO₃): Colour: Orange-red, Yield: 0.195 g (75%). Elemental analysis data: Anal. (%) Calculated for $C_{36}H_{36}N_7O_{17}Ni_2Ce$ (1096.22 g/mol): C, 39.44; H, 3.31; N, 8.94. Found (%): C, 39.18; H, 3.12; N, 8.65. IR (KBr, v, cm⁻¹): 2946(w), 1619(s), 1561(w),

1456(s), 1294(s), 1284(s), 1232(s), 1172(w), 1081(s), 1036(s), 994(s), 958(s), 862(s), 818(s), 785(s), 735(s), 676(s), 625(w), 603(w), 581(w), 532(w), 491(w).

3. Results and Discussion

The reaction of two equivalents of 2-hyrdroxy-3-methoxybenzaldehyde with one equivalent of $Ni(OAc)_2.4H_2O$ and half equivalent of $Ce(NO_3)_3.6H_2O$ in the presence of one equivalent of ethylenediamine resulted in a Ni₂Ce sandwich complex [(NiL)₂Ce(NO₃)₂](NO₃) (**Fig. 1**). The complex is soluble in most organic solvents such as methanol, ethanol, dimetylformamide and slightly soluble in water.

The FT-IR spectrum of the complex were obtained on KBr disc. In the FT-IR spectrum of free aldeyhde, the characteristic aldehyde group vibration v(C=O) was observed at 1657 cm⁻¹ [**19**] and the aldehyde group vibration v(C=O) was completely absent in the spectrum of the complex [(NiL)₂Ce(NO₃)₂](NO₃), instead a new band due to the imine group v(C=N) appeared which confirms the condensation reaction between the aldehyde and amine groups [**20**]. In the spectrum of the complex, in addition to the v(M-O) band strechings at 581 and 532 cm⁻¹, a band due to v(M-N) stretching was observed 491 cm⁻¹.

The UV-Vis absorption spectrum of the complex was investigated in the 250-800 nm range in DMF (10⁻⁵ M). In the UV-vis spectrum of the complex, there is only one absorption band in the range of 330-460 nm which was assigned to the π - π * transition. In the spectrum of the complex no M \rightarrow L, L \rightarrow M or d-d transitions were observed at the concentration studied. The single-photon fluorescence spectra of the complex were collected on a Perkin Elmer LS55 luminescence spectrometer in DMF solution (10⁻⁵ M). The emission and excitation spectra of the complex are shown in **Fig. 2**. The complex showed an excitation band in the range of 510-580 nm ($\lambda_{max} = 543$ nm). In the emission spectrum of the complex showed a band in the range of 520-580 nm which almost completely overlapped with the excitation spectrum is not the actual fluorescence emission and this was assigned to the Rayleigh scattering band.

Cyclic voltammetry studies of the complex was performed in DMF solution (10^{-4} M) using 0.1 M NBu₄BF₄ as supporting electrolyte [**21**]. The obtained electrochemical data are summarized in **Table 2**. The electrochemical curves of the complex are shown in **Fig 3**. The complex shows two anodic peak potential at about -0.36 and 0.53 V at all scan rates. The oxidation process may be referred to Ce(III) \rightarrow Ce(IV) + e⁻ [**5**, **22**] and the oxidation process is not reversible. In the reverse scan, the complex in DMF solution exhibited two cathodic peak potentials in the -0.54 – (+ 0.46) V range. While the anodic potential values almost remain invariable upon the increase in the scan rate, the cathodic peak potentials shifted to the more negative regions.

Thermal behaviour of the synthesized complex was studied under nitrogen atmosphere in the temperature range of 20–1000 °C with a heating rate of 10 °C/min. The thermal curves for the complex are shown in **Fig. 4**. The thermal decomposition of complex $[(NiL)_2Ce(NO_3)_2](NO_3)$ showed a mass loss between 50-150 °C with about 2% of the total mass. This mass loss may be due to the moisture in the sample. The molecular skeleton of the complex is thermally stable up to 260 °C and thermal decomposition of the complex $[(NiL)_2Ce(NO_3)_2](NO_3)$ occurred in three steps. In the first step, a sharp mass loss was observed between 260 and 375 °C with approximately 26% of the total mass. This mass loss was accompanied by an exothermic at about 290 °C. The mass loss in the first step can be attributed to the removal of the coordinated and non-coordinated nitrate anions. In the second decomposition step, almost 22% of the total mass was lost between 375 and 740 °C. The rest of the organic moiety of the compound decomposed up to higher temperatures (1050 °C) leaving metal oxides as final residue. At 1050 °C, the 45% of the total mass remained and this mass corresponds to the metal oxide (NiO + Ce₂O₆).

3.1 Molecular structure of the complex [(NiL)₂Ce(NO₃)₂](NO₃)

Single crystals of the complex suitable for X-ray diffraction study were grown from slow diffusion of diethyl ether into a DMF solution of the complex over two weeks. The structure of the complex was solved in orthorhombic unit cell and C222₁ space group. X-ray structure of the complex is depicted in **Fig. 5**. The structure of the complex contains a trinuclear Ni₂Ce coordination cluster with the formula of $[(NiL)_2Ce(NO_3)_2](NO_3)$. In the complex, two Ni(II) ions are coordinated to the inner N₂O₂ cores of the two Schiff-base ligands with square planar geometries. The Ce(III) ion is sandwiched between the two NiL units, which are virtually parallel to each other. The molecule sits on two fold rotation axis

passing through the Ce(III) atom. The asymmetric unit, thus, contains half of the structure. The Ce(III) center is 12-coordinate, surrounded by 12 oxygen atoms; four are from phenolic groups, four from methoxy groups, four from two bidentate nitrate ligands. There is also a third NO₃ anion present in the crystal lattice but is not within bonding distance with any of the metal ions. The bond lengths and angles are given in the supplementary file. The Ce-O distances are in the range of 2.539(13)-2.96(2) Å and Ce-O_{phenol} distances are shorter than Ce-O_{methoxy} distances. The azomethine bond distances are within the range of C=N bond distances.

Hirshfeld surface analysis was used to evaluate the inter-molecular interactions within the crystal packing [23, 24]. The Hirshfeld surface for $[(NiL)_2Ce(NO_3)_2](NO_3)$ was obtained to determine the interaction sites and contribution of different intermolecular contacts within the crystal structure. The fingerprint plot of the complex shows two spikes indexed as (1) and (2) corresponding to H····O/O····H and H·····H contacts, respectively (**Fig. 6a**). The complex molecules are linked by H····ONO₂ interactions and these contacts are observed in the d_n surface as intense red spots. Relative contribution of the different intermolecular contacts to the Hirshfeld surface of the molecule is shown in **Fig. 6b**. The largest contribution is H····O/O····H with 41.6% contribution and followed by H····H contacts with 39.1%. There is also π - π (phenyl-pheyl) stacking interactions are seen in the shape index.

4. Conclusions

In this work, an heteronuclear Ni₂Ce complex was synthesized and characterized by spectroscopic and analytical methods. The structures of the complex was evaluated by single crystal X-ray diffraction study. The structure of the complex contains a trinuclear Ni₂Ce coordination cluster with the formula of $[(NiL)_2Ce(NO_3)_2](NO_3)$. The Ce(III) ion is sandwiched between the two NiL units, which are virtually parallel to each other. The complex showed an excitation band in the range of 510-580 nm ($\lambda_{max} = 543$ nm) which almost completely overlapped with the band (520-580 nm range) in the emission spectrum. This band was then assigned to the Rayleigh scattering band. Finally, the electrochemical behaviour of the complex was also investigated in DMF solution.

Supplementary Information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC number for the complex is 1559335. Copies of this information can be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 335033; email deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Table 2 Electrochemical data of the complex.)



Fig. 1 Schiff base ligand and Ni₂Ce complex.



Fig. 2 UV-vis (a) and excitation-emission spectra (b) of the complex (10^{-5} M) .







Fig. 4 Thermal curves for the complex.



Fig. 5 Molecular structure of [(NiL)₂Ce(NO₃)₂](NO₃), hydrogen atoms are not shown for clarity.



Fig. 6 a) Finger print plot b) Contribution of different intermolecular contacts c) Shape index, (white circle shows π - π interaction site) d) π - π interaction within the structure.

Identification code		$[(NiL)_2Ce(NO_3)_2](NO_3)$
Empirical formula		C ₃₆ H ₃₆ N ₇ O ₁₇ CeNi ₂
Formula weight	ţ	1096.26
Crystal size (m	m ³)	0.13 x 0.09 x 0.08
Crystal color		Orange
Crystal system		Orthorhombic
Space group		C2221
Unit cell	a (Å)	9.132(5)
	b (Å)	21.223(12)
	c (Å)	20.763(12)
	α (°)	90
	β (°)	90
	γ (°)	90
Volume (Å ³)		4024(4)
Z		4
Abs. coeff. (mn	n ⁻¹)	2.124
Refl. collected		26421
Ind. Refl. [R _{int}]		4001 [0.1781]
Final R indices	[I>2sigma(I)]	0.0921, 0.2358
R indices (all da CCDC	ata)	0.1493, 0.2758 1559335

 Table 1 X-ray data for the complex.

....493, 155933.

Scan rate(mV/s)	$E_{pa}(\mathbf{V})$	$E_{pc}(\mathbf{V})$	<u>Epa/Epc</u>	$E_{1/2}(\mathbf{V})$	$\Delta E_{\rm p}({\rm V})$
100	-0.57, 0.51	0.46, -0.54	1.05	0.56	-0.03
250	-0.58, 0.52	0.41, -0.60	0.96	0.59	0.02
500	-0.59, 0.53	0.39, -0.65	0.90	-	0.06
750	-0.60, 0.54	0.35, -0.68	0.88	-	0.08
1000	-0.61, 0.55	0.31, -0.70	0.87	-	0.09

 Table 2 Electrochemical data of the complex.

Highlights

- ➤ A Ni₂Ce complex was synthesized and characterized.
- > The structure of the complex was determined by X-ray diffraction study.
- > Inter-molecular interactions were determined by Hirshfeld surface analysis.
- > Electrochemical and thermal behaviour of the complex were investigated.

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