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A new NiCe complex derived from ortho-vanillin: Structural characterization and luminescence properties

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Abstract

In this study, a new heteronuclear NiCe complex $[\text{NiL}_2\text{Ce}(\text{NO}_3)_2(\text{OAc})(\text{H}_2\text{O})(\text{X})] \cdot 1.25\text{H}_2\text{O}$ (where L = ortovanillinato; X: H_2O or CH_3OH) was prepared and characterized by analytical and spectroscopic methods. Molecular structure of the complex was further characterised by single crystal X-ray diffraction study. In the structure of the complex, there are two geometrical isomers with only water as coordinated solvent at the Ni(II) centre, and two others with part water and part methanol at this site. In the structure of the complex, a NiL_2 moiety is bound to the Ce(III) ion *via* two phenolic and two methoxy oxygen atoms of two ligands L. The coordination sphere of the Ce(III) ion is completed by the coordination of oxygen atoms of two bidentate nitrate anions, an acetate which bridges the two metal ions, and a water ligand. Hirshfeld surface analysis was performed to investigate the intermolecular contacts and their percentage contributions within the crystal packing. The complex molecules are linked by hydrogen bond contacts. The complex shows an emission band at 656 nm when excited at 317 nm with large stokes shift. The complex exhibits a reversible redox potential at -0.36 V due to the cerium-based oxidation/reduction process.

Keywords: Ortho-vanillin; NiCe complex; X-ray structure; Emission spectra; Redox potential

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1. Introduction

The lanthanide complexes have wide range of applications in several areas including catalytic, resonance imaging, magnetic and fluorescent materials [1-5]. The magnetic properties of lanthanide complexes have received considerable attention and magnetic behaviours of those complexes can be tuned with ligand modifications [6]. For this purpose, several organic ligands have been used for the synthesis of lanthanide complexes with certain behaviours [7-9]. Due to interesting emission behaviors, trivalent lanthanide complexes have several advantages over organic base fluorescent molecules and nanoparticles. The main advantages of these compounds are well-defined line emission bands, high quantum yields and long lifetimes [10]. The Ln(III) ions show low absorption coefficients from parity forbidden f-f transitions. The emission of Ln(III) ions is usually fulfilled by an indirect sensitization from chromophore ligands (antenna effect) rather than direct excitation of the lanthanide centers [11, 12]. Another indirect sensitization of Ln(III) is to introduce transition metal ions such as Cr(II), Ru(II), Zn(II) and Cd(II) [13-15].

Ortho-vanillin, also known as 3-methoxysalicylaldehyde, has the ability to bind transition metal ions through the phenolic, aldehydic and methoxy oxygen atoms [16-18]. In the transition metal complexes of ortho-vanillin, two ligands are usually coordinated to the metal in a trans arrangement [19]. Due to having relatively hard oxygen donor atoms, ortho-vanillin can also coordinate to the lanthanide ions [20, 21]. A trinuclear Gd(III) complex of ortho-vanillin was synthesized and characterized by X-ray crystallography [22]. Dy(III) complexes of ortho-vanillin were reported to show single-molecule magnet (SMM) behaviour [23]. The heteronuclear 3d-4f complexes show interesting magnetic and emission properties [24, 25]. The salen type multi-dentate ligands derived from ortho-vanillin are often used to prepare such heteronuclear 3d-4f complexes. The transition metal ions in those complexes bind to the N₂O₂ donor sets while the lanthanide ions coordinate to the outer methoxy and phenolic oxygen atoms (O₂O₂) [26].

In our previous work, a Ni(II)-Ce(III) heteronuclear complex derived from salen type ligand was prepared and its luminescence properties were investigated [27]. In this work, a new Ni(II)-Ce(III) heteronuclear complex using ortho-vanillin as ligands was synthesized from one pot reaction. The complex was characterized by the spectroscopic and analytical techniques. Single crystals of the complex were obtained from MeOH-diethylether diffusion and the structure of the new complex was studied by X-ray diffraction study. Finally, absorption and luminescent properties of the complex were investigated in detail.

2. Experimental

2.1 General methods

Ortho-vanillin, Ni(OAc)₂·4H₂O and Ce(NO₃)₃·6H₂O and solvents were purchased from commercial sources and used without further purification. The FT-IR spectrum was taken on a Perkin Elmer Paragon 1000 PC. CE-440 Elemental analyser was used for the elemental analysis of carbon, hydrogen and nitrogen. The absorption spectra were studied on a Shimadzu UV-1800 UV-Vis. spectrophotometer. The fluorescence spectra were collected on a Perkin Elmer LS55 luminescence spectrometer. The thermal analysis was carried out on a Perkin Elmer Pyris Diamond. The cyclic voltamograms at the glassy carbon electrode were obtained using a BAS 100W (Bioanalytical System, USA) electrochemical analyser.

2.2 X-ray structures solution and refinement for the complex

Data collection and cell refinement were performed using a Bruker D8 QUEST or Apex II diffractometer and data reduction was performed using Bruker SAINT [28]. Diffraction data were measured at 150(2) K using Mo-*K*α radiation. SHELX-2014/6 was used to solve and refine the structures [29-31]. The structure of the complex was solved by charge flipping method and refined on F^2 using all reflections [29-31]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters. H atoms bonded to oxygen atoms were located from difference maps and their positional and temperature factors were constrained. Further details of the crystal data and refinement are given in Table 1. The H atoms on the minor occupancy coordinated water sites could not be reliably located, so were not refined.

For the complex, there are four unique complex molecules and five water molecules of crystallisation in the asymmetric unit. Two of the metal complexes have the formula: [CeNi(C₈H₇O₃)(NO₃)₂(O₂CCH₃)(OH₂)₂] with a fully occupied water ligand coordinated to the Ni ion; the other two have the formulae: [CeNi(C₈H₇O₃)(NO₃)₂(O₂CCH₃)(OH₂)_x(CH₄O)_y] where x = 1.47(2) and y = 0.53(2) for one, and x = 1.26(2) and y = 0.74(2) for the other where the water coordinated to Ce is fully occupied, but that on Ni(II) is either water or methanol.

2.3 Synthesis of $[NiCe(L)_2(NO_3)_2(OAc)(H_2O)(X)] \cdot 1.25H_2O$

Ortho-vanillin (0.304 g, 2.00 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (0.248 g, 1 mmol) was dissolved in methanol (20 mL) and refluxed for 2 h. To the refluxing solution, $Ce(NO_3)_3 \cdot 6H_2O$ (0.43 g, 1 mmol) was added in MeOH (20 mL) followed by addition of NaOH (0.08 g, 2 mmol). The clear green solution was refluxed for 24 h and cooled to room temperature. The solvent was removed on a rotary evaporator. The green colored product was washed with diethylether (10 mL) and dried in air. X-ray quality crystals were grown by MeOH- diethyl ether diffusion.

$[NiCe(L)_2(NO_3)_2(OAc)(H_2O)(X)] \cdot 1.25H_2O$ (X: H_2O or MeOH): Colour: Green powder, yield: 0.301 g (84%). Elemental analyses for $C_{18}H_{21}N_2O_{16}NiCe \cdot 3H_2O \cdot CH_3OH$ (MW: 806.26 g/mol): Calcd.: C, 28.30; H, 3.88; N, 3.47. Found: C, 28.12; H, 3.27; N, 3.12%. IR (KBr, cm^{-1}): 3405, 2945, 1620, 1572, 1492, 1351, 1245, 1182, 1087, 1032, 984, 960 cm^{-1} .

3. Results and Discussion

In current study work, a new heterodinuclear NiCe complex was synthesised and characterized. The reaction of two equivalents of 2-hydroxy-3-methoxybenzaldehyde (HL) with one equivalent of $Ni(OAc)_2 \cdot 4H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ in the presence of two equivalents of NaOH gave a NiCe heteronuclear complex (**Fig. 1**). The green colored complex is soluble in methanol, ethanol, dimethylformamide and slightly soluble in water and not soluble in diethyl ether. The FT-IR spectra of the complex was obtained to determine the characteristic stretching bands. The FT-IR spectrum of the complex shows a broad band at around 3400 cm^{-1} due to $\nu(O-H)$ stretches of water or methanol molecules in the structure of the complex. In the FT-IR spectrum of the free HL ligand (ortho-vanillin), the carbonyl group stretching $\nu(C=O)$ was seen at 1657 cm^{-1} [32] and upon coordination to the Ni(II) center, this stretch shifted to 1623 cm^{-1} , confirming the coordination of the aldehyde oxygen atom to the metal centre. In the spectrum of the complex, the bands observed at 592 and 569 cm^{-1} were assigned to $\nu(M-O)$ stretches.

The thermal stability of the new hetero-dinuclear NiCe complex was studied under N_2 atmosphere in the temperature range of 20–1000 °C with a heating rate of 10 °C/min (see supplementary data). Thermal degradation of the complex under nitrogen atmosphere occurs in several steps. Thermal decomposition of the complex starts at about 50 °C. In the range of 50-200 °C, approximately 10% of the total mass was lost. This mass loss can be attributed to

gradual loss of solvate water from the structure of the complex. The loss of solvate water by thermal decomposition is followed by two endothermic peaks at about 75 and 175 °C. The molecular backbone of the complex started to decompose at about 200 °C and decomposes in five consecutive steps. In the first two decomposition steps (200-305 °C and 305-410 °C), almost 45% of the total mass was lost and this loss was attributed to the removal of the coordinated external ligands (CH₃OH, H₂O, AcO⁻ and NO₃⁻). The first two decomposition steps at 200-305 °C and 305-410 °C were followed by two exothermic peaks at 280 and 390 °C, respectively. In the other decomposition steps, the rest of the organic moieties of the complex were lost gradually up to higher temperatures leaving metal oxides as the final residue. At 1000 °C, almost 35% of the total mass remained and this corresponds to the metal oxides (NiO + CeO₂).

3.1 Molecular structure of [(NiL₂)Ce(NO₃)₂(OAc)(H₂O)(X)]·5H₂O

The crystals of the complex have *triclinic* symmetry and the structure was solved in space group $P\bar{1}$. The asymmetric unit comprises four independent metal complexes plus five water molecules of crystallisation. There are two geometrical isomers with only water as coordinated solvent at the Ni(II) centre, and two others with part water and part methanol at this site. The asymmetric unit of the complex is shown in [Fig. 2](#). In each independent complex molecule (prefixed with A-D in [Fig. 2](#)), the Ni(II) ion is six-coordinate binding to the two aldehyde and two phenolate oxygen atoms of two L ligands, one water or methanol oxygen and one acetate oxygen atom. The acetate ion and phenolate oxygen atoms bridge the Ni(II) and Ce(III) atoms. The Ce(III) ion in each complex molecule is ten-coordinate binding to the two phenolate, two methoxy, four oxygens of two nitrate ions, an acetate oxygen and a water oxygen atom.

Hirshfeld surface of the complex was generated to investigate the inter-molecular interactions in the structure [[32](#), [33](#)]. The finger print plots and percentage contribution of different intermolecular contacts are given in [Figs. 3&4](#). Each molecule from the asymmetric unit stacks linearly along the *a* axis. The molecules are held together *via* a complex network of hydrogen bonds between neighbouring molecules and bridging interactions involving the waters of crystallisation ([Fig. 5](#)). The H····O/O····H hydrogen bond contacts play an important role in crystal packing with 42.8% contribution. These contacts are shown as red spots in the *d_n* surface. The fingerprint plot of the complex shows two spikes for H····O/O····H contacts. The H····H and C····H contacts also stabilise the structure of the

complex with 36.1% and 12.5% contributions, respectively. In the structure, phenyl rings show stacking interactions and C···C stacking contacts make 4.7% contribution to the overall stability of the complex.

Costes and co-workers have prepared several NiLn (Ln: Gd, Ce, Tb and Y) complexes derived from ortho-vanillin [34-36]. The treatment of complex $[\text{Ni}(\text{o-van})_2(\text{H}_2\text{O})_2]$ with $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ gave heteronuclear NiLn complexes (where o-van is ortho-vanillin). The structures of the reported complexes were found to be solvent (used in the reaction) dependent [36]. In the Ni(II) complex of ortho-vanillin, two ligands are arranged in *trans* positions. Introduction of a Ln(III) ion leads the rearrangement of the ligands in a *cis* position to provide a binding site for a Ln(III) ion [34-36]. The reaction of $[\text{Ni}(\text{o-van})_2(\text{H}_2\text{O})_2]$ with $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ gave heterodinuclear NiCe complex with the formula of $[\text{Ni}(\text{o-van})_2(\text{H}_2\text{O})_2\text{Ce}(\text{NO}_3)_3]$ [36]. In the structure of the reported complex, each Ni(II) is six-coordinated binding to the phenolate and aldehyde oxygen atoms of two ortho-vanillin ligands and two water molecules at the axial positions. The Ce(III) ions are ten-coordinate which binds to the bridging phenolate, methoxy oxygen atoms of the o-vanillin ligands and three chelating nitrate anions [36]. In the structure of the complex in this work, the acetate anion occupied one of the axial position which bridges Ni(II) and Ce(III) ions. The other axial position of Ni(II) ion is occupied by either H_2O or CH_3OH .

3.2 UV-Vis. and photoluminescence spectra of the complex

The UV-Vis. absorption spectrum of the complex was studied in the 250-800 nm range in DMF (10^{-5} M). In the spectrum of the complex (Fig. 6), there is a broad absorption band at 335-435 nm range. The absorption band can be assigned to the π - π^* electronic transitions due to the π -electrons in the phenyl ring. The emission and excitation spectra of complex are shown in Fig. 6. Upon excitation at 317 nm, complex exhibits only one emission band at 656 nm (λ_{max}) with high emission intensity with stokes shift of 339 nm. This emission band was assigned to the π - π^* transition. The large stokes shift may due to the M→L and L→M charge transitions.

3.3 Electrochemical studies

Cyclic voltammograms (CV) of the complex was studied in DMF (10^{-4} M) using 0.1 M NBu_4BF_4 as supporting electrolyte. The CV curves and electrochemical data are given in Fig 7 & Table 2. The complex shows one anodic peak potential at about -0.36 V at all scan rates. At 250 scan rate (mV/s), the anodic peak potential is reversible and the metal based oxidation

process is as follow: $\text{Ce(III)} \rightarrow \text{Ce(IV)} + e^-$ [37, 38]. The complex exhibited two cathodic peak potentials in the -0.50 - $(+ 0.80)$ V range. The cathodic peak potential observed in the $+0.67$ - $(+0.80)$ V range is due to irreversible reduction of metal ions. While the anodic peak potentials (E_{pa}) almost remain constant with the increase of the scan rate, the cathodic peak potentials (E_{pc}) shifted to more negative values.

4. Conclusions

A new hetero dinuclear NiCe complex derived from ortho-vanillin ligand was synthesized and characterized by spectroscopic and analytical methods. Molecular structure of the complex was determined by single crystal X-ray diffraction studies. In the structure of the complex, two ortho-vanillinato ligands coordinate to a Ni(II) and a Ce(III) through oxygen atoms. The molecules in the structure are linked by hydrogen bond contacts ($\text{OH} \cdots \text{O}$). The photoluminescence and electrochemical behaviors of the complex were studied in DMF solution. The complex gives an emission band at 656 nm (λ_{exc} : 317 nm) with large stokes shift. Thermal stability of the complex was studied under nitrogen atmosphere.

Supplementary Information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC number for the complex is 1842328. 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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