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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 $[NiL_2Ce(NO_3)_2(OAc)(H_2O)(X)]\cdot 1.25H_2O$ (where L = orthovanillinato; X: H_2O or CH_3OH) was prepared and characterised by analytical and spectroscopic methods. The molecular structure of the complex was further characterised by a single crystal X-ray diffraction study. In the structure of the complex there are four molecules in the asymmetric unit, with two having 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 inter-molecular 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.

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1. Introduction

Lanthanide complexes have a wide range of applications in several areas including catalysis, resonance imaging, magnetic and fluorescent materials [1–5]. The magnetic properties of lanthanide complexes have received considerable attention and the magnetic behaviour can be tuned with ligand modifications [6]. For this purpose, several organic ligands have been used for the synthesis of lanthanide complexes with particular characteristics [7–9]. Due to their interesting emission behaviour, trivalent lanthanide complexes have several advantages over organic-based florescent 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 (antena 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 relativity hard oxygen donor atoms, ortho-vanillin can also coordinate to lanthanide ions [20,21]. A trinuclear Gd(III) complex of ortho-vanillin was synthesised and characterised 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 N_2O_2 donor sets while the lanthanide ions coordinate to the outer methoxy and phenolic oxygen atoms (O_2O_2) [26].

In our previous work, a Ni(II)eCe(III) heteronuclear complex derived from a salen type ligand was prepared and its luminescence properties were investigated [27]. In this work, a new Ni(II)eCe(III) heteronuclear complex using ortho-vanillin as ligands was synthesised via a one-pot reaction. The complex was characterised by

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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. Finally, absorption and luminescent properties of the complex was investigated in detail.

2. Experimental

2.1. General methods

Ortho-vanillin, $Ni(OAc)_2{\cdot}4H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, and solvents were purchased from commercial sources and used without further purification. The FT-IR spectrum was recorded on a Perkin Elmer Paragon 1000 PC. A 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 were obtained using a BAS 100 W (Bioanalytical System, USA) electrochemical analyser using a glassy carbon electrode.

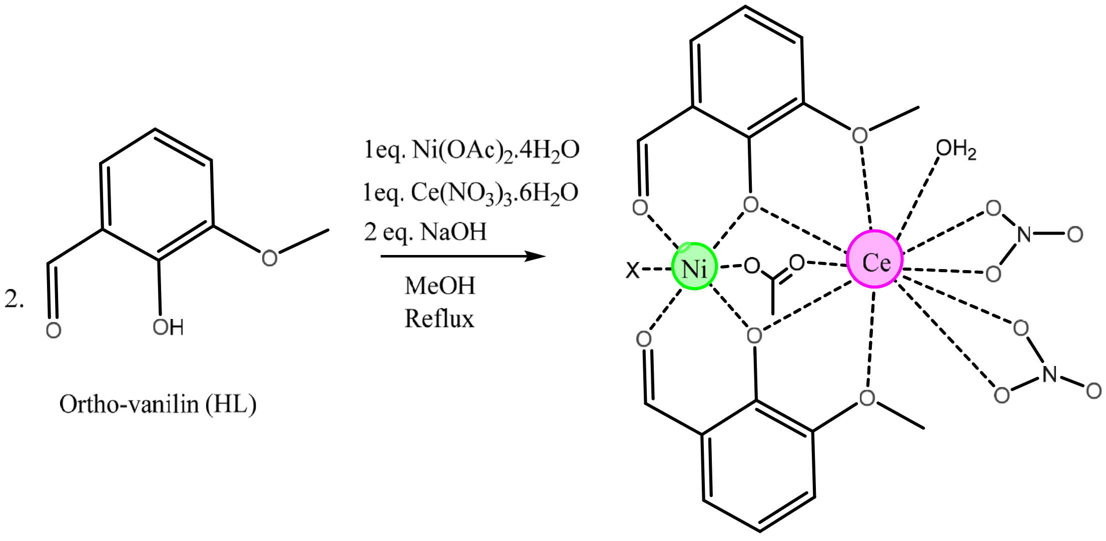
Table 1
X-ray data for the complex.

Empirical formula	$C_{73.32}H_{96.63}Ce_4N_8Ni_4O_{69}$
Formula weight	2989.31
Crystal size (mm^3)	0.20 × 0.08 × 0.04
Crystal colour	Green
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell *a* (Å)	9.2061(9)
b (Å)	22.683(2)
c (Å)	26.087(3)
α (°)	80.3211(13)
β (°)	85.7890(13)
γ (°)	86.6485(14)
Volume (Å3)	5349.6(9)
Z	2
Abs. coeff. $\mu(mm^{-1})$	2.47
Refl. collected	59816
Ind. Refl. [R_{int}]	21898 [0.071]
$R[F^2 > 2\sigma(F^2)]$	0.0545
$wR(F^2)$	0.1316
GOOF, *S*	1.015
Largest diff peak/hole (e Å^{-3})	1.95/−1.11
CCDC	1842328

2.2. X-ray structures solution and refinement for the complex

Data collection and cell refinement were performed using a Bruker Apex II CCD diffractometer and data reduction was performed using Bruker SAINT [28]. Diffraction data were measured at 150(2) K using Mo-$K\alpha$ radiation. SHELXT and SHELXL-2018/3 were used to solve and refine the structure respectively [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. The H atoms on the minor occupancy coordinated water sites could not be reliably located, so were not refined. Where H atoms on water molecules of crystallisation could not be reliably included in the model due to likely H atom disorder, they were omitted. Further details of the crystal data and refinement are given in Table 1 and in the paragraph below.

There are four unique complex molecules and five water molecules of crystallisation in the asymmetric unit. Two of the metal complexes have the formula: $[CeNi(C_8H_7O_3)(NO_3)_2(O_2CCH_3)(OH_2)_2]$ with a fully occupied water ligand coordinated to the Ni(II) ion; the other two have the formulae: $[CeNi(C_8H_7O_3)(NO_3)_2(O_2CCH_3)(OH_2)_x(CH_4O)_y]$ where $x = 1.45(2)$ and $y = 0.55(2)$ for one, and $x = 1.23(2)$ and $y = 0.77(2)$ for the other, where the water coordinated to Ce is fully occupied, but that on Ni(II) is either water or methanol.



X: H_2O or CH_3OH

Fig. 1. The synthesis of the heteronuclear NiCe complex.

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