

POTENTIALLY HEPTADENTATE SCHIFF'S BASE LIGAND IN THE SYNTHESIS OF HETEROTRINUCLEAR $[\text{Ni}^{\text{II}}\text{La}^{\text{III}}\text{Ni}^{\text{II}}][\text{NO}_3]_3$ COMPLEX

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ABSTRACT

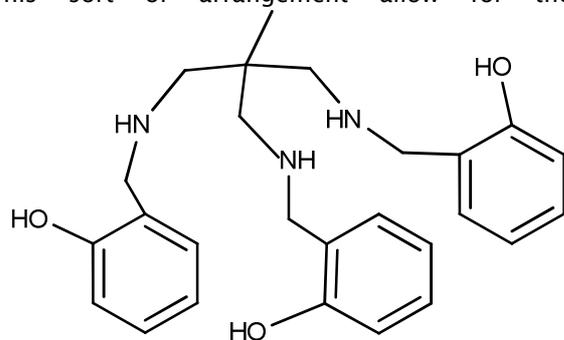
The synthesis and characterisation of a new $[\text{Ni}^{\text{II}}\text{La}^{\text{III}}\text{Ni}^{\text{II}}][\text{NO}_3]_3$ complex has been reported in this paper, the complex was synthesised by refluxing the ligand in the presence of relevant metal salts in the ratio 2:2:1. The technique used in the characterisation shows strong evidence that the compound has formed. The use of infrared spectroscopy was employed to confirm the presence of the imine double bond, which is the primary target of the ligand hydrolysis, while the mass spectra confirm the existence of the molecular compound.

KEYWORDS: Nickel, lanthanum, schiff base, complex, ligand

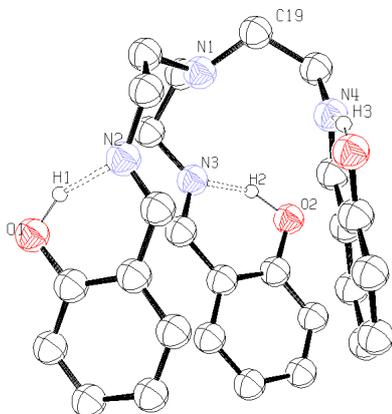
INTRODUCTION

Homotrinnuclear metal complexes of potentially heptadentate schiff base ligands have been reported [Bayly *et al.*, 2003], these metal complexes were mainly for first row transition metal ions [Abdullahi *et al.*, 2009] while the use of hydrogenated amine phenol ligand was employed. The reported homotrinnuclear nickel and zinc complexes were found to be isostructural, with the metal ion M^{2+} (M= Ni or Zn) found sitting in the pocket of the tripodal ligand, the second metal was found to complex at the peripheral of the two monometallic complexes. This sort of arrangement allow for the

measurement of the trimetallic nickel complex, which the μ_{eff} was found to be 6.0 BM. This is an indication that the two nickels adjacent to each other were ferromagnetically coupling, while the two terminal nickels were coupling antiferromagnetically. Similar studies reported [Ohta *et al.*, 2001] a trimetallic motif with the same magnetic coupling orientation, although different ligand system is used, where the tripodal N cap is replaced with carbon while the ethyl backbone was reduced to methyl (figure 1) this reshape of the ligand change it from more flexible to rigid.



a.



b.

Figure 1: a. Chemical drawing showing the picture of potentially hexadentate ligand, b. Crystal structure of potentially heptadentate ligand

Previously, phosphonotrihydrazone (tris [2-(2-hydroxybenzylidene)-1-methylhydrazido] thiophosphorus) ligand was used in the preparation of homotrinnuclear nickel complex [Chandrasekhar *et al.*, 2003], the story is the same as linear trinuclear metal complex is produced with the Ni-Ni-Ni angle measured to be 176.65°. Mixed metal complexes with potentially heptadentate schiff base ligand have been

reported recently [kobayashi *et al.*, 2006]. The two heterotrinnuclear complexes synthesised by kobayashi *et al* are; $[\text{Mn}^{\text{II}}(\text{Ni}^{\text{II}}\text{L}_2)_2] \cdot 2\text{CH}_3\text{OH}$ (figure 2) and $[\text{Fe}^{\text{III}}(\text{Ni}^{\text{II}}\text{L}_2)]\text{NO}_3 \cdot \text{C}_2\text{H}_5\text{OH}$. interestingly, the two complexes have similar structure with the same spin 1-5/2-5, but different magnetic interactions between adjacent metals ions; ferromagnetic ($\text{Ni}^{\text{II}}-\text{Mn}^{\text{II}}$) and antiferromagnetic ($\text{Ni}^{\text{II}}-\text{Fe}^{\text{III}}$).

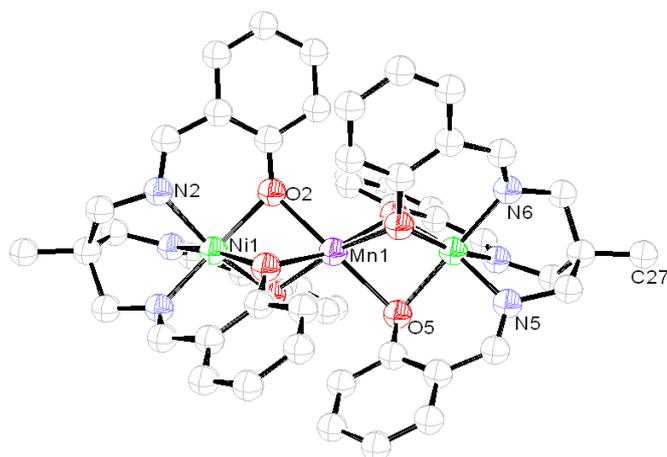


Figure 2: A crystal structure showing the mixed NiMnNi complex using hexadentate ligand (figure 1a)

This work is concerned with the synthesis of heterotrinnuclear metal complex involving nickel ion and lanthanum ion. The expectation is to build a system that carry a diamagnetic ion at the centre and if possible to measure the extent to which the two adjacent Ni^{II} ions couple together.

MATERIALS AND METHODS

All the chemicals were used as purchased without further purification. The microanalysis, mass spectra and infrared spectroscopy were run at university of Strathclyde (UK). Briefly, the ligand was prepared by refluxing one mole of triethylamine with three mole of salicylaldehyde in methanol for one hour. The resulting yellow powder was obtained, filtered and air dried.

Complex preparation: 1mole of the ligand (TrenSal = Tris(2-hydroxybenzylaminoethyl)amine) was dissolve in 50ml absolute ethanol, followed by the addition of 1mole equivalent of Nickel acetate. To the mixture was added slowly 0.5mole equivalent $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The resulting cloudy mixture was brought to reflux for 0.5 hours, after which the solution was allowed to cool and the light yellow solid filtered and dried under vacuum. Yield 72%. [Malek *et al.*, 1979]
Infrared spectrum FTIR [$\nu/\text{cm}^{-1}(\text{KBr})$]: 3446 (broad, OH); 1634 (strong, $-\text{C}=\text{N}$); 753 (aromatic); 1301

(C-O); 1470 (NO_3). Mass Spectral analysis (ESI) m/z , 515 (100%, $[(\text{LNi})_2\text{La}]^+$, 1167 (60%, $[(\text{LNi})_2\text{La}]^+$. Elemental analysis, % calculated for $\text{C}_{55}\text{H}_{58}\text{N}_9\text{O}_{10}\text{Ni}_2\text{La}$: C; 52.81, H; 4.43, N; 10.27. % found, C; 52.71, H; 4.14, N; 9.99. λ_{max} (solid reflectance) 594nm

RESULTS AND DISCUSSION

Previously it has been reported that the imine group in the potentially heptacoordinate ligand is prone to hydrolysis as such not many work has been carried out with this ligand but only the flexible hydrogenated [Mustapha *et al.*, 2009] potentially heptadentate ligand. recently there has been a report of tri and tetrametallic complex [Mochizuki *et al.*, 1994] which include d and f metal ions. The report by Mochizuki *et al.*, suggest that such a mixture of d and f metal ions is possible with schiff base ligands. Of recent we reported a $\text{Zn}^{\text{II}}\text{La}^{\text{III}}\text{Zn}^{\text{II}}$ metal complex [Mustapha A., 2009.], the success in the synthesis of the said complex allowed us to concentrate further that in here we reported the analogue of such complex. $\text{Ni}^{\text{II}}\text{La}^{\text{III}}\text{Ni}^{\text{II}}$ reported here is assumed to have same molecular structural arrangement with the homo trimetallic complex [Bayly *et al.*, 2003] above. The infrared spectra proved that the metal complex is symmetrical as there are few absorbance peaks observed in it.

The appearance of a peak at 1634 v/cm^{-1} confirm the presence of -HC=N bond. The mass spectral analysis which was obtained using electrospray ionisation technique confirms the presence of the molecular ion at 1167(60%), with the fragment of such molecule observed to be 515 m/z. The 515 fragment is a mono nuclear LNi^+ , and it's two of this molecule that coordinate to the lanthanum ion to make the trimetallic.

By these analyses carried out we can propose the structure of this complex to be a linear trimetallic molecule, consisting of two nickel centres which are bridged with a lanthanide metal ion. As the tradition of such type complexes coupled with the ionic balance on the ligand, a nitrate counter ion is believed to counter the residual charge on the complex (figure 3).

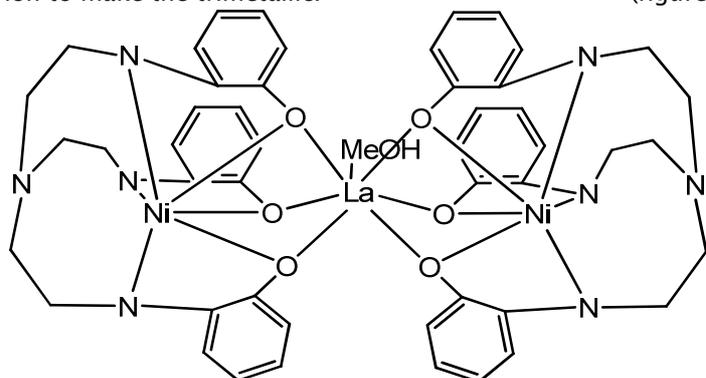


Figure 3: The proposed structure of $[(\text{TtrenSalNi})_2\text{La}]$ complex

The insertion of lanthanum which is a bigger ion into the homotrimetallic d-block metal complexes, indicate that the system can be viewed as a puzzle, where the mixed trimetallic complex can be formed, which can contain either d or f block metal. This will in turn help in designing metal complexes of single molecule magnet (SMM).

CONCLUSION

The synthesis of trimetallic NiLaNi complex with potentially heptadentate schiffbase is reported for the first time. The analysis of such complex using infra red, mass spectrometry and elemental analysis confirm the synthesis. The likes of these compounds are very significant, as they are very useful as single molecular magnet molecules. Therefore we will focus our attention in producing these complexes especially with metals that has high number of unpaired electrons.

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