



Research paper

Synthesis, structure and magnetic properties of three $\text{Cu}_2\text{Ln}^{\text{III}}$ complexes (Ln = Pr, Nd and Sm) with an unsymmetrical Schiff base ligand

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ABSTRACT

Three heterometallic trinuclear complexes of general formula, $[(\text{CH}_3\text{CN})\text{CuL}]_2(\mu\text{-NO}_3)_2\text{Ln}(\text{NO}_3)$ [Ln = Pr (1), Nd (2) and Sm (3)] have been synthesized by reacting a neutral metalloligand [CuL], derived from a N_2O_2 donor unsymmetrically di-condensed di-Schiff base, H_2L (where $\text{H}_2\text{L} = N\text{-}\alpha\text{-methylsalicylidene-}N'\text{-salicylidene-1,3-propanediamine}$) with the respective lanthanide nitrates in 2:1 ratios. X-ray single-crystal structure reveals that these isomorphous complexes (1–3) possess C_2 -symmetric trinuclear units where two terminal metalloligands are coordinated to the central Ln(III) ion in *transoid* manner. In all three complexes, distorted tetradecahedron coordination geometry is formed around the Ln(III) ion by four μ_2 -phenoxido oxygen atoms from two (CuL) units and three chelating nitrate coligands. The two terminal Cu(II) ions possess distorted octahedral geometry. The dc magnetic susceptibilities and field dependent magnetization measurements of all three complexes reveal the occurrence of antiferromagnetic interactions between Cu(II) and Ln(III) ions.

1. Introduction

N,O-donor multi-dentate ligands have played a crucial role in developing the synthesis of heterometallic complexes in the last few decades [1]. One of the strategies for such synthesis relies on the use of ligands containing more than one pocket (compartments) with dissimilar donor atoms where sequestration of different metal ions takes place depending on their hardness and sizes [2]. Another very simple strategy is to use the neutral complexes of single-compartmental salen type N_2O_2 donor tetradentate di-Schiff base ligands [salen = *N,N'*-ethylenebis(salicylideneimine)] as ‘metalloligand’ [3]. The coordinating ability of the phenoxido oxygen atoms to another metal ion is exploited in this strategy to synthesise heterometallic complexes of various nuclearity and shapes [4]. Among the divalent first transition elements, Cu(II) forms the most stable complexes with these Schiff bases and hence, these chelates have been used quite frequently as metalloligands as most of the other metal ions cannot replace Cu(II) from the ligand compartment [3e-f,4c-d]. The Schiff base ligands are usually symmetric dicondensation products of the di-amine and salicylaldehyde derivatives in which N,O-donor arms are chemically equivalent (Scheme 1). Recently, we have shown that when the diamine is asymmetrically dicondensed, the two N,O-donor arms of the resulting di-Schiff base differ from each other resulting in intriguing structural modification compared to their symmetrical analogues

specially in $[(\text{CuL})_2\text{Ln}]$ complexes [5]. Literature shows that quite a few $[(\text{CuL})_2\text{Ln}]$ complexes are reported and in most of them Ln is heavier ($4f^n$, $n \geq 7$) presumably due to their interesting magnetic properties [6]. However, no such structurally characterized complex of lighter lanthanides ($4f^n$, $n < 7$) other than Ce(III) is reported till date [6a]. The structures of these reported Ce(III) complexes are often found to differ from those of heavier lanthanides due to larger size of Ce(III) [7].

Another interesting difference between the heavier and lighter lanthanides has been found in the magnetic exchange coupling interactions with neighbouring paramagnetic 3d-metal ions [8]. Albeit the coupling is dependent on the nature of bridges and the 3d metal ions, it is predicted that, in general, the coupling should be antiferromagnetic for $n < 7$ and ferromagnetic for $n \geq 7$ [9]. Quite a few studies have been reported verifying this proposition with $[(\text{CuL})_2\text{Ln}]$ complexes where Ln = heavier lanthanides [5,6b,10] but for the lighter lanthanides such structurally and magnetically characterized complexes are limited only to Ce(III) [7,11].

Herein, we report the synthesis of three new trinuclear complexes, $[(\text{CH}_3\text{CN})\text{CuL}]_2(\mu\text{-NO}_3)_2\text{Ln}(\text{NO}_3)$ where Ln(III) = Pr(III), Nd(III) and Sm(III) for complexes 1, 2 and 3 respectively, using Cu(II) metalloligand (CuL) ($\text{H}_2\text{L} = N\text{-}\alpha\text{-methylsalicylidene-}N'\text{-salicylidene-1,3-propanediamine}$). Structures of all three complexes have been determined by single crystal X-ray diffraction. The temperature dependent magnetic measurements of all three complexes have been studied.

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