Inorganic Chemistry Communications 36 (2013) 212–215

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Quantitative estimation of the antiferromagnetic interaction between Cu(II) and Sm(III) in two dimensional heterometallic coordination polymer with isonicotinic acid as tectons

Sandip Saha [a,*], Debabrata Biswas [a], Partha Pratim Chakrabarty [a], Dieter Schollmeyer [b], Atish Dipankar Jana [c], Hiroshi Sakiyama [d], Masahiro Mikuriya [e]

[a] Department of Chemistry, Acharya Prafulla Chandra College, New Barrackpur, Kolkata 700131, India
[b] Institut fur Organische Chemie, Universit at Mainz, Duesbergweg 10-14, 55099 Mainz, Germany
[c] Department of Physics, Behala College, Parnasree, Kolkata 700 060, India
[d] Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12, Kojirakawa, Yamagata 990-8560, Japan
[e] Department of Chemistry and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansei Gakuin University, Gakuen 2-1, Sanda 669-1337, Japan

ARTICLE INFO

Article history:
Received 17 July 2013
Accepted 29 August 2013
Available online 5 September 2013

Keywords:
Heterometallic
Coordination polymer
Two dimensional
Antiferromagnetic interaction

ABSTRACT

The syntheses, structure and magnetic property of a novel two dimensional 3d–4f coordination polymer $^{2}_{\infty}$[CuSmL$(NO_3)_2$(IN)], 1 (L^{2-} = *N*, *N*′- propylenedi (3-ehoxysalicylideneiminato), the dianion of the Schiff base obtained from the 2:1 condensation of 3-ethoxysalicylaldehyde with 1,3-propanediamine, IN^- = the isonicotinate ion) has been reported. The heterobinuclear units are connected through exo-bidentate ligands IN^-, leading to an extended 2D structure. A fit of the magnetic susceptibility data yields $g_{Cu} = 2.109$, $g_{Sm} = 0.476$, $J_{CuSm} = -0.893$ cm^{-1}, $\theta = -3.37$ K, and TIP = 0.001257 emu K mol^{-1} with a good discrepancy factor of $R_\chi = 4.4 \times 10^{-5}$. This is the first quantitative estimation of the strength of the antiferromagnetic interaction between Cu(II) and Sm(III) ions to the best of our knowledge.

The node-and-spacer approach is a widely used strategy for the construction of a large variety of 3d–4f coordination polymers [1–3]. It relies upon the strong directionality of the coordination bonds established between the metal ions (nodes and connectors) and the exodentate ligands (spacers and linkers) [1–3]. Coordination polymers can be constructed from oligonuclear nodes as well [4–9]. The metal ions interact with the divergent ligand through their easily accessible coordination sites. The presence of two or more metal ions confers a higher geometrical flexibility to the node. Moreover, the metal–metal intra- and inter-node interactions can lead to new redox, electric, or magnetic properties. The exodentate ligands with oxygen donor atoms are supposed to interact preferentially with the oxophilic 4f cations, while the exodentate ligands bearing nitrogen atoms will prefer the Cu(II) ions. Indeed, various network topologies were obtained by employing spacers with only oxygen, only nitrogen, or both oxygen and nitrogen donor atoms [1–9].

A quite interesting tecton in constructing extended structures is the isonicotinate anion, IN^-, an unsymmetrical divergent ligand bearing, at one end, the nitrogen atom and, at the other one, the oxygen atoms from the carboxylato group [7,9–12]. It can coordinate to a metal ion (mainly 3d) through the nitrogen atom and to a metal ion (mainly 4f) with one or two carboxylato oxygen atoms [7,9]. From the magnetic view-point, the understanding of the magnetic properties of complexes that involve 4f ions is still far from being satisfactory. The magnetic properties of the most rare-earth ions are strongly influenced by the orbital component of the magnetic moment. The ligand-field effects and the exchange interactions between the magnetic centers become relevant at the same temperature's range. This makes the analysis of the magnetic behavior of such compounds very difficult [13]. Until now, the generality of Cu–Gd ferromagnetic coupling has been correlated with the large occurrence of approximate pseudo-C_{2v} geometry of these complexes due to the metal ions linked by two phenoxo bridges [14]. The quantitative description of the magnetic properties of Cu(II) and Sm(III)-containing heterometallic complexes is not an easy task because of the ligand-field effect and spin–orbit coupling of the Sm(III) ion [6,15]. A qualitative approach and a semi-quantitative approach have been taken to investigate the magnitude of exchange interaction between Cu(II)–Sm(III) containing 3d–4f coordination polymers [6,15].

In this communication we report on the synthesis [16], crystal structure and first time quantitatively estimated antiferromagnetic interaction between Cu(II) and Sm(III) ions of a novel 2-D coordination polymer $^{2}_{\infty}$[CuSmL$(NO_3)_2$(IN)], **1** which has been obtained by reacting the green colored copper complex [Cu(L^{2-})(CH_3OH)] with Samarium nitrate and Sodium isonicotinate [L^{2-} = *N*, *N*′- propylenedi(3-ehoxysalicylideneiminato), the dianion of the Schiff base obtained from the 2:1 condensation of 3-ethoxysalicylaldehyde with 1,3-

* Corresponding author. Tel.: +91 33 25373297.
E-mail address: sandipsaha2000@yahoo.com (S. Saha).

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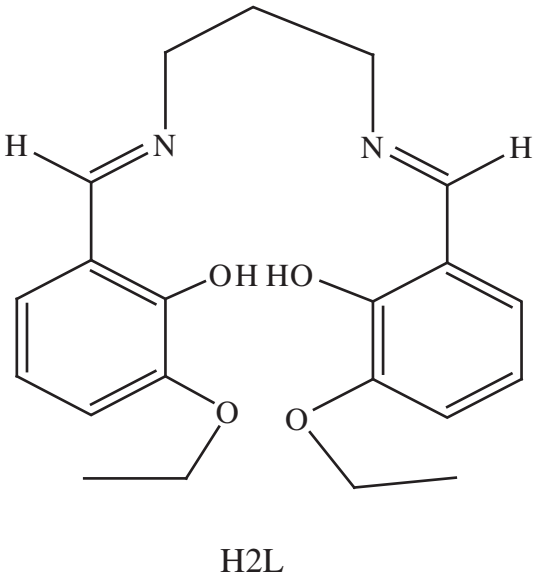
http://dx.doi.org/10.1016/j.inoche.2013.08.032



Scheme 1. Schematic presentation of the Schiff base used in the synthesis.

propanediamine] (Scheme 1). Any group have not reported on the variable temperature magnetic study of these particular types of two dimensional 3d–4f coordination polymers containing IN^- to the best of our knowledge.

The heterobinuclear 2-D complex belonging to the hexadentate Schiff base containing 3d–4f family has some common features [17,18]: the copper(II) ion is hosted within the inner compartment (the N_2O_2 site) of the organic ligand, leading to the $[Cu(L^{2-})(CH_3OH)]$ moiety, which is then coordinated through the empty outer O_4 cavity to the Sm(III) ion (two oxygen atoms arise from the phenoxo groups, the two others from the ethoxy ones). The nitrato ions act as bidentate ligands toward the Sm(III) ion. When one nitrato ligand is replaced with one isonicotinato group, the desired 2-D compound results. The same strategies were employed in earlier two cases to obtain these types of complexes [7,9]. By slow evaporation of the resulting mixture, the green crystals of the compound with the formula $^2{}_\infty[CuSmL(NO_3)_2(IN)]$, were obtained. The crystals were suitable for X-ray diffraction analysis [19]. The infrared spectrum of **1** shows the characteristic bands of both nitrato (1384 cm^{-1}) and carboxylato groups ($\nu_{as} = 1470\ cm^{-1}$ and $\nu_s = 1308\ cm^{-1}$), indicating the substitution of one nitrato ion by isonicotinato anion.

The crystal structure of **1** is in line with our expectations. Indeed, a two dimensional coordination polymer is generated out of the binuclear [CuSm] units due to the use of isonicotinate ligand. Isonicotante gereatestetranuclear $[CuSm]_2$ units (Fig. 1) by the syn–syn bridging mode of the carboxylato group connecting two Sm(III) ions from the adjacent dinuclear [CuSm] units. Sm(III) occupies the center of inversion and is doubly bridged by two isonicotinate ligands. Each isonicotinate also binds to the Cu center of another symmetry related dinuclear [Cu–Sm] unit. This binding to Cu is in axial direction of the square pyramidal coordination environment of Cu. This two way bridging action of isonicotinate gives rise to a two dimensional coordination polymer (Fig. 2). The coordination layer is the (−101) plane. Each Sm(III)

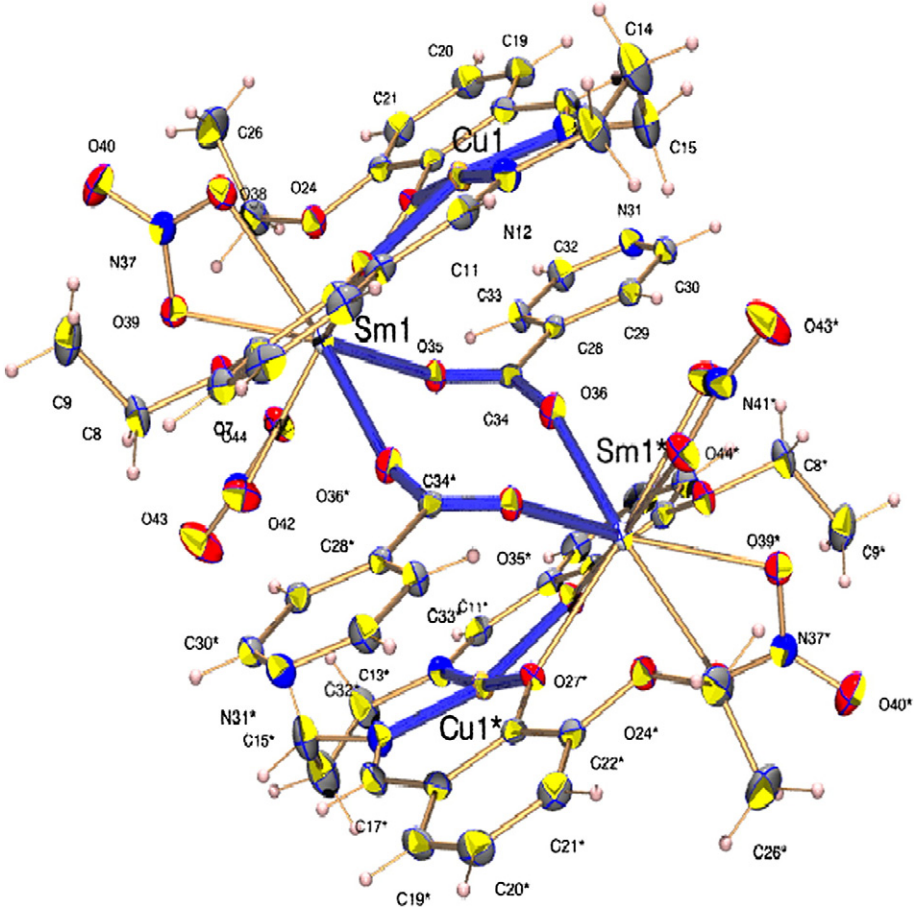


Fig. 1. The ORTEP diagram (30% ellipsoidal probability) of the tetranuclear unit of **1** with atom numbering scheme (* = 1−x,1−y,1−z).