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

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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$_3$OH)] 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-

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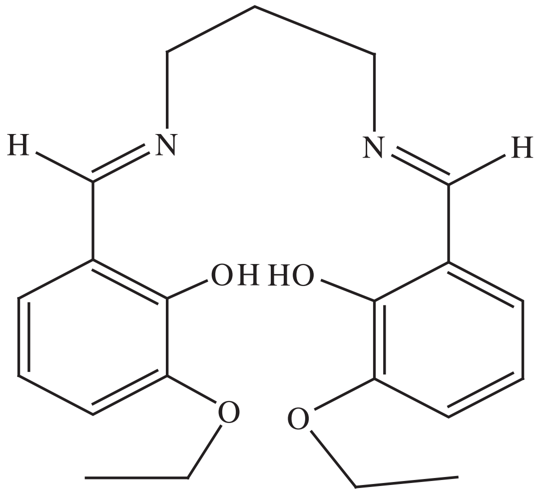

H2L

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 $[\mathrm{Cu(L^{2-})(CH_3OH)}]$ 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 $^{2}_{\infty}[\mathrm{CuSmL(NO_3)_2(IN)}]$, 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 $[\mathrm{CuSm}]_2$ 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)

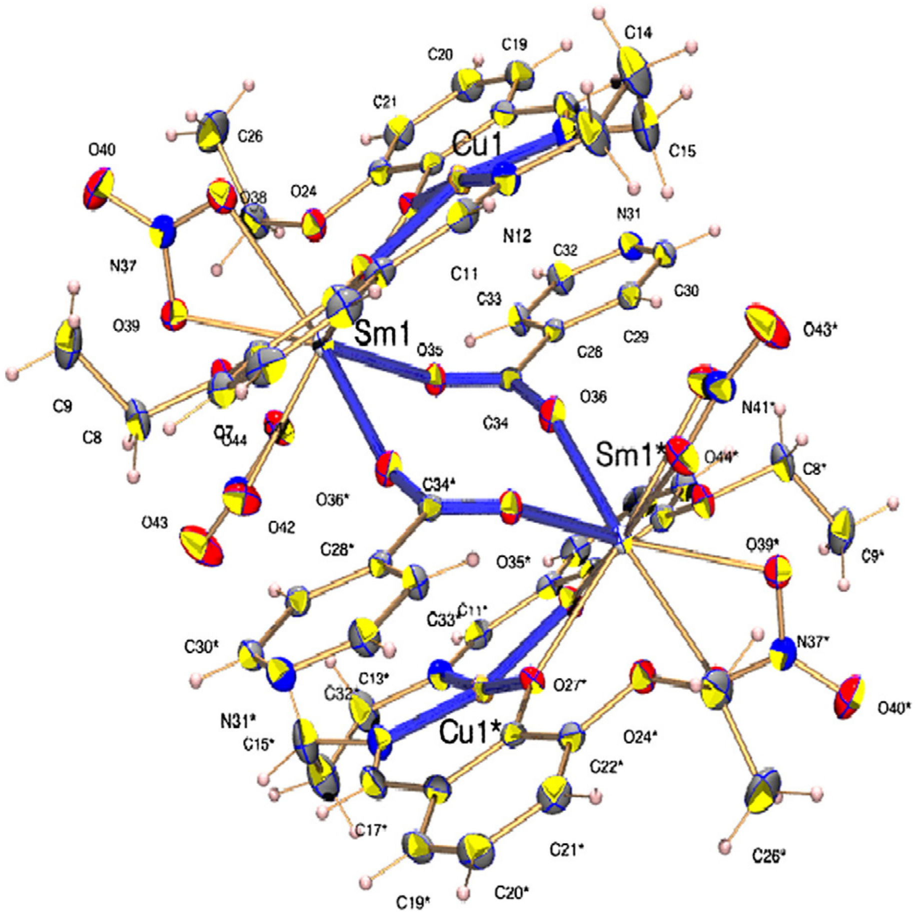

Fig. 1. The ORTEP diagram (30% ellipsoidal probability) of the tetranuclear unit of **1** with atom numbering scheme (* = 1−x,1−y,1−z).

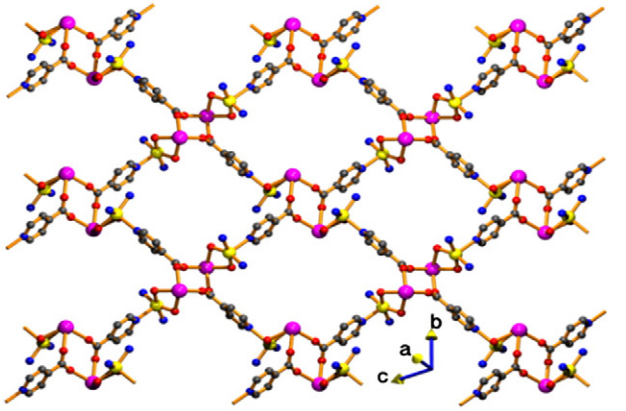

Fig. 2. The two dimensional coordination polymer of **1** by the two way bridging action of the isonicotinate ligand. For the clarity of the picture, besides the isonicotinate ligand only coordinated atoms to the metal centers are shown. Sm is magenta and Cu is yellow.

exhibits a coordination number of 10 (Figure S1), the coordination sphere being formed by oxygen atoms. Four of them arise from the two chelating nitrato ligands, four others from the compartmental ligand (two phenoxo and two ethoxy oxygen atoms), and two oxygen atoms from the bridging carboxylato groups donated by two isonicotinate ligand. The square pyramidal coordination environment of Cu is satisfied by two O atoms and three N atoms. The chelating Schiff base ligand forms the basal plane of the square pyramid of Cu with two O and two N atoms. This axial coordination is by the isonicotinate N atom.

The Sm–Sm distance in a tetranuclear unit is 5.588 Å. Sm1–O35 and Sm1–O36 distances are 2.3859(19) Å and 2.342(2) Å, respectively. Other relevant bond distances and angles are given in Table S1 and Table S2. The coordination layers which are the (−101) planes successively stack (Figure S2).

The magnetic data of **1** was recorded from 4.5 to 300 K under 0.1 T field. The $\chi_M T$ value for **1** decreases slowly from 0.868 emu K mol^{-1} at 300 K to 0.427 emu K mol^{-1} at 20 K and then more rapidly to 0.197 emu K mol^{-1} at 4.5 K. A fit of the data (Fig. 3) was calculated using the following equation:

$$\chi = \frac{N\beta^2}{k(T-\theta)} \frac{10\,g_2{}^2 + 28\,g_2{}^2 \exp\left[\frac{2\,J_{\mathrm{CuSm}}}{kT}\right]}{5 + 7\exp\left[\frac{2\,J_{\mathrm{CuSm}}}{kT}\right]} + \mathrm{TIP},$$

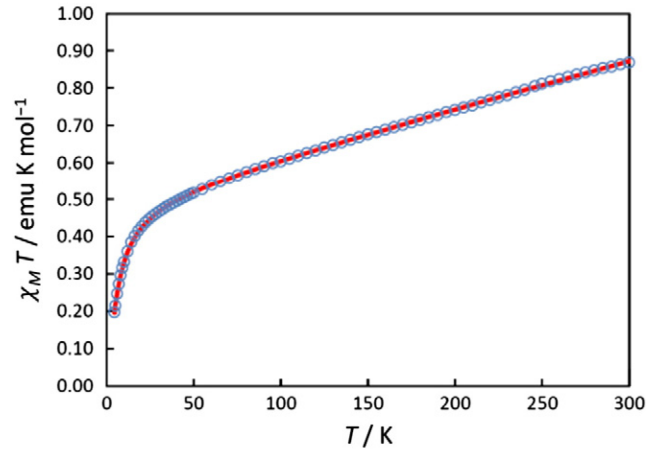

Fig. 3. Temperature dependence of the $\chi_M T$ versus T for **1** plot is shown with data represented by open circles and the solid-line fit obtained using the parameters described in the text.

where $g_2 = -\frac{1}{6}g_{\mathrm{Cu}} + \frac{7}{6}g_{\mathrm{Sm}}$ and $g_3 = \frac{1}{6}g_{\mathrm{Cu}} + \frac{5}{6}g_{\mathrm{Sm}}$. The ^{6}H state of Sm(III) splits into six states – $^6H_{5/2}$, $^6H_{7/2}$, $^6H_{9/2}$, $^6H_{11/2}$, $^6H_{13/2}$, and $^6H_{15/2}$from the lower energy – due to the spin–orbit coupling, and the second lowest $^6H_{7/2}$ state is ~700 cm^{-1} (7λ/2) higher than the lowest $^6H_{5/2}$ state [20]. Therefore, the interaction was considered between Cu(II) ion ($S_{\mathrm{Cu}} = 1/2$) and the lowest $^6H_{5/2}$ state of Sm(III) ion ($J = 5/2$), and the effect of the second lowest $^6H_{7/2}$ state was included in TIP as shown in the following equations:

$$\mathrm{TIP} = \mathrm{TIP}_{\mathrm{Cu}} + \mathrm{TIP}_{\mathrm{Sm}}$$

$$\mathrm{TIP}_{\mathrm{Sm}} = \frac{2\,N\beta^2\left(g_J - 1\right)\left(g_J - 2\right)}{3\,\lambda}.$$

The best-fitting parameters are $g_{\mathrm{Cu}} = 2.109$, $g_{\mathrm{Sm}} = 0.476$, $J_{\mathrm{CuSm}} = -0.893$ cm^{-1}, $\theta = -3.37$ K, and TIP $= 0.001257$ emu K mol^{-1} with a good discrepancy factor of $R_\chi = 4.4\times 10^{-5}$. If $\mathrm{TIP}_{\mathrm{Cu}}$ is assumed to be 0.000060 emu K mol^{-1}, $\mathrm{TIP}_{\mathrm{Sm}}$ will be 0.001197 emu K mol^{-1}and λ will be calculated as 207.6 cm^{-1}, which is normal for Sm(III) complex [20]. The g_{Sm} value of 0.476 is noteworthy; it corresponds to $(5\,g_J)/3 = 10/21$ (~0.476) in the cubic ligand field [21] where the g_J value for Sm(III) ion is 2/7 (~0.286). It is generally difficult to determine J_{CuSm} and θ correctly when both are in the same sign; however, the discrepancy factor became a minimum with the best-fitting parameters.

Consequently, the slow decrease in $\chi_M T$ from 300 K to 20 K is due to the $\mathrm{TIP}_{\mathrm{Sm}}$ caused by the excited $^6H_{7/2}$ state, and the rapid drop below 20 K is due to the intramolecular antiferromagnetic interaction between Cu(II) and Sm(III) ions and the intermolecular antiferromagnetic interactions including Sm(III) · · · Sm(III) interaction. Similar behavior was reported earlier [15], however, the antiferromagnetic interaction was not estimated at that time. The interdimer interaction was considered using theta. So, the interaction through the bis-isonicotinato bridge is included in theta. Actually, the observed interdimer antiferromagnetic interaction (minus theta) is larger than usual, so the interaction through the bis-isonicotinato bridge is also expected as antiferromagnetic. In our analysis, exchange interaction (J_{CuSm}) can be estimated between Cu(II) and Sm(III) ions, using an equation for 1/2–5/2 system. Any other groups have not used this approach before for magnetic data fitting of these types of systems. Therefore, it also precludes its comparison with those of the other known Cu(II)–Sm(III) systems [6,15].

In conclusion, we have synthesized a novel two dimensional 3d–4f coordination polymer. With the choice of Cu as one of the metals it generally gives rise to square planar Cu coordination environment with hexadentate Schiff bases and suitable choice for the second metal can give rise to various functional materials especially magnetic one. In the present study with an intention of designing higher dimensional magnetic systems we deliberately used Sm as the second metal and isonicotinate ligand (IN$^-$) as the co-ligand which is suitable for bridging metal nodes. Additionally, it can also be concluded that further extension of the approach used for magnetic data fitting will afford to estimate the magnetic interaction in various heterometallic coordination polymers.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.08.032.

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[16] The Schiff base ligand H2L was synthesized by refluxing1,3-propane diamine (0.074 ml, 1.0 mmol) with 3-ethoxy salicylaldehyde (0.332 g, 2.0 mmol) in methanol (10 mL) for two hrs. The ligand was not isolated; instead the resulting yellow methanolic solutions were subsequently used for complex formation. A clear solution of Cu(CH3COOH)2. H2O (0.199 g, 1.0 mmol) in methanol (10 mL) was added to a 10 mL methanolic solution of the L, and the mixed solution was stirred for 0.5 h. The green colored complex [Cu(L2−)(CH3OH)] was isolated and this complex was further used for the complex preparations L2− = N, N′-propylenedi(3-ehoxysalicylideneiminato, the dianion of the Schiff base).Complex [Cu(L^{2-})(CH_3OH)]: Yield 65%. Anal.: Cacld.for $C_{22}H_{28}CuN_2O_5$: C: 56.95; H: 6.04; N: 6.04%. found: C: 56.00; H: 6.55; N: 6.40%. IR (KBr pellets, cm^{-1}): $\nu(CH_3OH)$ 3400, $\nu(C = N)$ 1631.Prepared Cu-complex (0.1124 g, 0.25 mmol) was dissolved in to 10 ml methanol and mixed with 10 ml methanolic solution of Samarium nitrate (0.113 g, 0.25 mmol) with constant stirring for 2 hrs. Then 10 ml water solution of sodium isonicotinate (0.037 g, 0.25 mmol) was added in the previous mixture. The mixed solution was stirred for another 1 hr, and the green color solution was isolated. On slow evaporation of the resulting green colored solution the green block shaped single crystals of the complex **1** was separated out in a few days. The crystals were filtered and washed with methanol and dried in air.Complex **1**: Yield 70%. Anal.: Cacld. for (complex 1)$C_{27}H_{28}CuN_5SmO_{12}$: C: 39.11; H: 3.37; N: 8.44%. found: C: 39.12; H: 3.39; N: 8.41%.IR (KBr pellets, cm^{-1}): $\nu(C = N)$ 1628, $\nu(NO_3)$ 1384, $\nu_{as}(COO^-)$ 1470, $\nu_s(COO^-)$ 1308.

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[19] Crystal Data for **1**: F W, 828.43; monoclinic, Space group $P2_1/n$; Unit cell dimensions a = 12.0007(5) Å, b = 15.5179(5) Å, c = 16.1233(6) Å, β = 100.2352(12); cell volume, 2954.79 $Å^3$; Z = 4; D_c = 1.862 g/cm^3; μ = 2.761 mm^{-1}; T = 293 K, Reflections collected: 7021; Independent reflections: 5946; Final R indices: R = 0.0237, wR2 = 0.0641. The crystallographic data for 1 was collected on a STOE IPDS 2 T device with a STOE detector equipped with graphite monochromated MoK_α radiation (λ = 0.71073 Å). CCDC-937393 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge for the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif. CIF file for 1. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for these structures have also been deposited with the Cambridge Crystallographic Data Centre. They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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