



## Two 2D grid-based Co(II) amino acid Schiff base complexes with left- and right-handed helical chains: Structures and magnetism



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### ABSTRACT

Two layered Co(II) amino acid Schiff base complexes, [Co(napala)(tbpe)<sub>0.5</sub>]<sub>n</sub> (**1**) and [Co(napgly)(tbpe)<sub>0.5</sub>]<sub>n</sub> (**2**) [H<sub>2</sub>napala = *N*-(2-hydroxy-1-naphthylmethylidene)-D/L-alanine, H<sub>2</sub>napgly = *N*-(2-hydroxy-1-naphthylmethylidene)-glycine and tbpe = *trans*-1,2-bis(4-pyridyl)ethylene], have been synthesized by solvothermal methods and characterized using single-crystal X-ray diffraction. The bridging of Schiff base ligands napala<sup>2-</sup> or napgly<sup>2-</sup> with Co(II) forms one-dimensional (1D) left- and right-handed helical chains which are further pillared by tbpe to build a two-dimensional (2D) grid-based **hcb**-type framework. Moreover, both complexes show high thermal stability and exhibit antiferromagnetic coupling between the Co(II) centers mediated by the *syn-anti*-COO<sup>-</sup> bridges.

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Much of the intense interest in metal amino acid Schiff base complexes stems not only from their fascinating structural features but also from their potential applications in fields as diverse as magnetism, asymmetric catalysis, sensing, nonlinear optics, and biologically active reagents [1–6]. In particular, the majority of amino acid Schiff base ligands applied so far are derived from a condensation reaction of salicylaldehyde derivatives and various amino acids, which contain an imine nitrogen atom, an alkoxide oxygen atom, and carboxylate group(s). It is well documented that the carboxylate group usually shows flexible coordination capability and effectively mediates magnetic exchange between paramagnetic metal centers [7,8]. Therefore, large numbers of 1D helical/zigzag chains [9,10], mono- and polynuclear complexes [11–14] prepared from these tridentate Schiff base ligands have been extensively reported. For example, a novel heptanuclear [Dy(III)<sub>7</sub>] Schiff base cluster was recently reported with single-molecule magnetism behavior and blue-emitting properties [15]. However, the higher dimensional (2D, 3D) coordination polymers in these systems are exceedingly rare [16,17]. Further research is necessary to enrich and develop this field.

In our group we have successfully obtained two 3D and 2D Co(II) Schiff base complexes based on the introduction of rigid N-donor linker 4,4'-bipyridine (bpy) [18]. As our continuous work, we chose longer dipyriddy-based organic tecton *trans*-1,2-bis(4-pyridyl)ethylene (tbpe) as linker to construct high-dimensional coordination polymers. We report in this contribution the syntheses, crystal structures, thermal and magnetic properties of two new Co(II) amino acid Schiff base complexes, [Co(napala)(tbpe)<sub>0.5</sub>]<sub>n</sub> (**1**) and [Co(napgly)(tbpe)<sub>0.5</sub>]<sub>n</sub> (**2**) [H<sub>2</sub>napala = *N*-(2-hydroxy-1-naphthylmethylidene)-D/L-alanine, H<sub>2</sub>napgly = *N*-(2-hydroxy-1-naphthylmethylidene)-glycine]. Both complexes exhibit a 2D grid-based **hcb**-type layer with antiferromagnetically coupled helical chains.

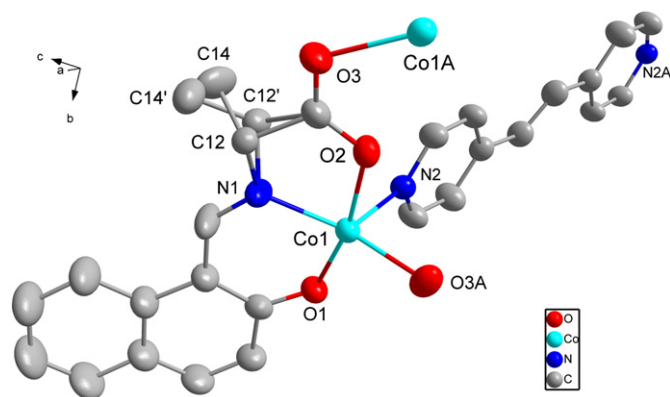
Because the mixing of cobalt salt, Schiff base and/or tbpe in solution usually results in the formation of orange–red precipitates, the solvothermal method, which has been extensively explored as an effective and powerful tool in the construction of high-dimensional coordination polymers, was employed in this work. Dark-red crystalline blocks of complexes **1** and **2** were prepared from the solvothermal reactions of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, corresponding Schiff base ligands and tbpe in a 1:1:0.5 mole ratio [19]. The IR spectra of complexes **1** and **2** (Fig. S1) show strong absorption bands of ν(C=N) stretching vibration at 1610 and 1607 cm<sup>-1</sup>, respectively, suggesting the presence of an imine group. The thermogravimetric analysis (TGA) profiles of the two complexes in Ar flow (Fig. S2) are quite similar, and both exhibit excellent thermal stability. There is no obvious weight loss from RT to 350 °C for **1** and 360 °C for **2** because of the absence of free and coordinating solvent

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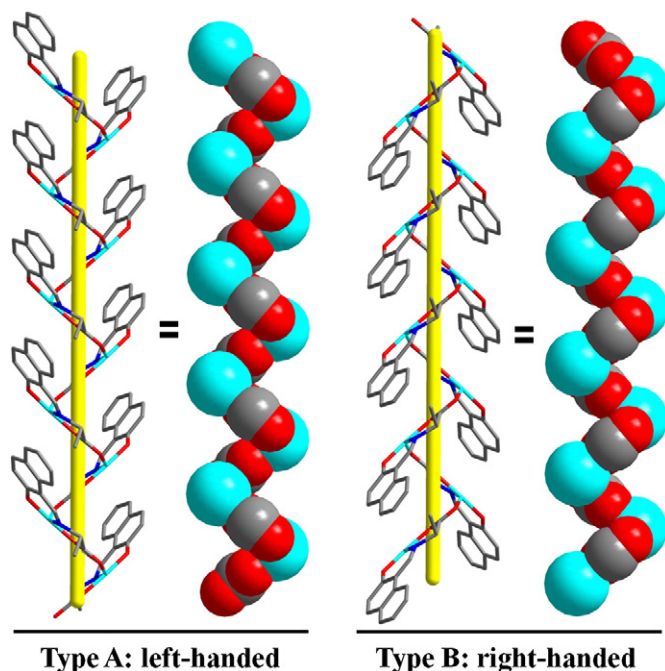
molecules in the crystal structures. The measured PXRD patterns match well with the simulated patterns derived from single-crystal analysis (Fig. S3), indicating the structural consistency and crystalline phase purity of the bulk products for the two compounds.

Single-crystal X-ray diffraction study [20] reveals that both complexes crystallize in the centrosymmetric monoclinic crystal system with space group of  $P2_1/c$  and exhibit a similar 2D grid-based network. Herein, only **1** will be discussed in detail as example. The coordination environments of **2** are also shown in Fig. S4. As depicted in Fig. 1, the asymmetric unit of complex **1** consists of one crystallographically independent Co(II) ion, one napala<sup>2-</sup> anion and half of a bridging tbpe co-ligand. The Co(II) center with distorted [CoN<sub>2</sub>O<sub>3</sub>] square-pyramidal coordination geometry ( $\tau = 0.354$ ) [21] is five-coordinated by one imine nitrogen (N1), three oxygen atoms (O1, O2 and O3A) of hydroxyl and carboxylic part of two tridentate napala<sup>2-</sup> ligands, and also one tbpe nitrogen atom (N2). The equatorial plane is defined by N1, O1, O2 and O3A, and the axial site is occupied by N2 with a Co–N2 distance of 2.089 Å. The average Co–O bond length is 2.045 Å and the Co–N<sub>imine</sub> bond distance is 2.008 Å (Table S1), which are with the range reported for other Co(II) complexes [18,22–24]. Each deprotonated tridentate napala<sup>2-</sup> ligand chelates to Co1 atom, forming two almost coplanar five- and six-membered rings with a dihedral angle of 6.98°, and connects the adjacent metal ion in a *syn-anti*  $\mu_2$ : $\kappa^2$ O:O' carboxylate bridging mode. Based on this connection mode, the neighboring Co(II) ions are bridged by the deprotonated carboxylate groups of the napala<sup>2-</sup> Schiff bases to generate the left- and right-handed [Co( $\mu_2$ -napala)]<sub>n</sub> helical chains [25], running along a crystallographic 2<sub>1</sub> screw axis with a pitch of 6.701 Å in the *b* direction (Fig. 2). Notably, the helical chain configuration in **1** is quite different from the earlier reported fan-shaped Co<sub>4</sub>( $\mu_2$ -napala)<sub>4</sub> molecular square assembled by the same napala<sup>2-</sup> Schiff bases and cobalt ions [18].

As shown in Fig. 3a, these two types of helical chains are further linked alternately by pillar-like N-donor tbpe molecules to build a 2D corrugated sheet in the *ac* plane. The nearest Co(II)···Co(II) distances across the *syn-anti*-COO<sup>-</sup> and the  $\mu_2$ -tbpe bridges are 4.964 Å and 13.523 Å, respectively. These values are comparable to those previously reported in the Co(II) complexes linked by two mixed heterobridges (*syn-anti*-COO<sup>-</sup> and  $\mu_2$ -tbpe) [26–29]. Topological analyses of 2D layer using TOPOS software [30] suggest the formation of a noninterpenetrated three-connected **hcb** net [31] with the Co(II) center and the participating ligands (napala<sup>2-</sup> and tbpe) representing the 3-c node and the linkers, respectively (Fig. 3b). The adjacent neutral layers of **1** are joined together to form a 3D supramolecular network through



**Fig. 1.** Coordination environments of Co(II) ions in **1** with the ellipsoids drawn at the 50% probability level. All the hydrogen atoms are omitted for clarity. (symmetry codes: A,  $-x + 3/2, y - 1/2, -z + 1/2$ ; B,  $-x + 2, -y, -z$ ; C,  $-x + 3/2, y + 1/2, -z + 1/2$ ).



**Fig. 2.** Two types of 2<sub>1</sub> helical chains constructed by  $\mu_2$ -napala<sup>2-</sup> Schiff base ligands and Co(II) ions, left-handed helix (A) and right-handed helix (B).

C–H··· $\pi$  stacking interactions [32,33] between the naphthyl rings (Fig. S5).

The variable-temperature magnetic susceptibilities of **1** and **2** were determined in the 2 K to 300 K temperature range under 1 kOe. The temperature-dependence of  $\chi_M T$  and  $1/\chi_M$  plots is displayed in Fig. 4. The  $\chi_M T$  values (2.67 cm<sup>3</sup> K mol<sup>-1</sup> for **1** and 3.05 cm<sup>3</sup> K mol<sup>-1</sup> for **2**) at room temperature are slightly larger than that (1.87 cm<sup>3</sup>·K·mol<sup>-1</sup>) expected for one uncoupled high-spin  $S = 3/2$  Co(II) cations. These findings are expected for an orbital contribution. For **1**, Upon lowering the temperature,  $\chi_M T$  first decreases gradually to a minimum of 0.83 cm<sup>3</sup>·K·mol<sup>-1</sup> at 4.5 K, and then increases reaching a peak value of 0.95 cm<sup>3</sup>·K·mol<sup>-1</sup> at 2.5 K. After further cooling,  $\chi_M T$  value drops sharply. Best-fitting the susceptibility data at 16–300 K with the Curie–Weiss law yields  $C = 2.83$  cm<sup>3</sup> K mol<sup>-1</sup> and  $\theta = -18.65$  K. The initial decrease of  $\chi_M T$  and the negative  $\theta$  value signify the presence of possible antiferromagnetic exchange interactions between the spin carriers. Spin–orbit coupling and zero-field splitting may also contribute to this decay [34–36]. Thus, the slight increase of  $\chi_M T$  below 4.5 K may indicate the occurrence of weak ferromagnetism in this system. For **2**, the plot  $1/\chi_M$  vs  $T$  above 16 K follows the Curie–Weiss law with  $C = 3.22$  cm<sup>3</sup> K mol<sup>-1</sup> and  $\theta = -21.46$  K. Upon cooling,  $\chi_M T$  continuously decreases to reach a minimum of 0.63 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. This behavior may indicate antiferromagnetic coupling between the neighboring Co(II) centers at high temperature.

From the crystal structure as described above, the individual 1D helical chain in the 2D layers of the present complexes should be essentially responsible for the interesting magnetic exchange couplings because the long Co(II)···Co(II) separation across the  $\mu_2$ -tbpe linker excludes an efficient magnetic couplings. Therefore, the magnetic data of **1** and **2** above 16 K can be fitted by Fisher's 1D Heisenberg chain model [37–39] ( $S = 3/2, \hat{H} = -2J\hat{S}_a\hat{S}_b$ ) expressed by the following analytical equation:

$$\chi_M = \frac{Ng^2\beta^2S(S+1)}{3kT} \times \frac{1+u}{1-u}$$

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