COVER PAGE**Synthesis, structure and magnetism of two metal(II) compounds
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Synthesis, structure and magnetism of two metal(II) compounds based on two new zwitterionic ligands

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Abstract

Two coordination polymers, $[\text{Co}(\text{L}_1)_{0.5}(\text{N}_3)_2]_n \cdot 3n\text{H}_2\text{O}$ (**1**), $[\text{Cu}_3(\text{OH})_3(\text{L}_2)_3(\text{H}_2\text{O})_{1.5}]_n \cdot n\text{H}_2\text{O}$ (**2**), ($\text{H}_2\text{L}_1 = 1,4\text{-bis(4-carboxylatopyridinium-4-benzoate-1-methylene)benzene}$, $\text{HL}_2 = 4\text{-(4-oxypyridinium-1-yl)benzotetrazolate}$) have been synthesized and studied by means of X-ray crystallography and magnetic analyses. Compound **1** exhibits a 2D braided grid structure, in which 1D $[\text{Co}(\text{N}_3)_2(\text{COO})]_n$ chains are cross-linked by the cationic bis(pyridinium) spacers of the L_1 ligand. Compound **2** is a 1D coordination chain in which the Cu(II) ions are linked by the mixed $(\mu\text{-OH})(\mu\text{-N, N-tetrazolate})$ double bridges. The mixed $(\mu\text{-EO-N}_3)_2(\text{COO})$ triple bridges transmits the ferromagnetic interaction between Co(II) ions, while the antiferromagnetic interaction between Cu(II) ions was induced by the mixed $(\mu\text{-OH})(\mu\text{-N, N-tetrazolate})$ double bridges.

Keywords: tetrazolate, azide, zwitterionic ligands, magnetic properties

1. Introduction

The molecule-based magnetic studies have been of interest in recent years due to their unusual properties and their potential applications [1-4]. The magnetic coupling depends on mainly the nature of the short bridging groups which can connect the paramagnetic centers in close proximity. The azide and carboxylate are the most investigated bridges not only for their efficiency in magnetic coupling (ferromagnetic or antiferromagnetic) but also for their diversity in bridging networks. Therefore, A large number of azide-, carboxylate- or even both co- bridged metal compounds with different dimensionality structures and magnetic behaviors have been reported [5-10]. The most interesting magnetic behavior involving as single-molecule magnets (SMMs), single-chain magnets (SCMs) have been demonstrated. Recently, We have obtained some compounds with azide and carboxylate simultaneously by employing the zwitterionic carboxylates ligands bearing cationic pyridinium and anionic carboxylate groups. These compounds exhibit SCM-type slow relaxation, solvent-modulated SCM behaviors and the coexistence of metamagnetism, antiferromagnetism, and SCM dynamics [11-20]. And the use of zwitterionic ligands, in comparison with the usual anionic carboxylates or hydroxo is an efficient synthetic approach toward 1D coordination motifs with mixed bridges. In order to extend the range of this study, we chose to use the bifunctional zwitterionic ligands bearing both hydroxy and tetrazolate groups, which remain largely unexplored in coordination chemistry. Here, we report on two coordination compounds derived from different paramagnetic centers and two zwitterionic ligands. (Scheme 1), which have not been

explored in coordination chemistry previously. Compound **1**, $[\text{Co}(\text{L}_1)_{0.5}(\text{N}_3)_2]_n \cdot 3n\text{H}_2\text{O}$, exhibits a 2D braided grid coordination network in which the mixed triple bridges result in uniform chains and shows a typical 1D ferromagnetic chain. Compound **2**, $[\text{Cu}_3(\text{OH})_3(\text{L}_2)_3(\text{H}_2\text{O})_{1.5}]_n \cdot n\text{H}_2\text{O}$, exhibits a 1D coordination chain with the mixed double bridges transmitting antiferromagnetic coupling. The L_1 ligand includes dicarboxylates [1,4-bis(4-carboxylatopyridinium-4-benzoate-1-methylene)benzene] which is neutral with self-compensated positive and negative charges, while the L_2 ligand with negative charge includes hydroxy and tetrazolate groups in which the tetrazolate group has been obtained by a in-situ organic reaction: the $[2 + 3]$ cycloaddition of the nitrile with azide.

<Scheme 1>

2. Experimental

2.1 Physical measurements

Elemental analyses were determined on an Elementar Vario ELIII analyzer. The FT-IR spectra were recorded in the range $500\text{--}4000\text{ cm}^{-1}$ using KBr pellets on a Nicolet NEXUS 670 spectrophotometer. Temperature and field dependent magnetic measurements were performed on a Quantum Design MPMSXL5 SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables).

2.2 Materials and synthesis

The reagents and $[\text{HL}_2']\text{Cl}$ (4-(4-oxypyridinium-1-yl)benzonitrile chloride) were obtained from commercial sources and used without further purification. The ligand

([H₂L₁]Cl₂) was prepared according to a procedure for similar compounds [21].

2.2.1 [Co(L₁)_{0.5}(N₃)₂]_n·3nH₂O (1)

A mixture of CoCl₂·6H₂O (0.1 mmol, 0.024 g), [H₂L₁]Cl₂ (0.02 mmol, 0.012 g) and NaN₃ (0.5 mmol, 0.033 g) in water (3 mL) and methanol (2 mL) was stirred for 20 min at room temperature. Slow evaporation of the solution at room temperature yielded yellow crystals of **1** after 5 day. Yield: 51% based on L₁. Anal. Found: C, 43.10; H, 3.87; N, 21.94%. Calcd for C₁₆H₁₇N₇O₅Co: C, 43.06; H, 3.84; N, 21.97%. Main IR (KBr, cm⁻¹): 2089s, 1633m, 1591m, 1561m, 1535m, 1462m, 1384w, 1292m, 1193m, 1161w, 844m, 813m, 765m.

2.2.2 [Cu₃(OH)₃(L₂)₃(H₂O)_{1.5}]_n·nH₂O (2)

A mixture solution of CuCl₂·2H₂O (0.017 g, 0.1 mmol), NaN₃ (0.033 g, 0.5 mmol), and [HL₂']Cl (0.012 g, 0.05 mmol) in water (4 mL) was sealed in a Teflon-lined stainless steel vessel (25 mL), heated at 140 °C for 2 days under autogenous pressure, and then cooled to room temperature. Blue crystals of **2** were obtained in a yield of 45% based on L₂'. Anal. Calcd for C₃₆H₃₂N₁₅O_{8.5}Cu₃: C, 43.18; H, 3.22; N, 20.98. Found: C, 43.14; H, 3.26; N, 20.95. Main IR bands (KBr, cm⁻¹): 3254w, 1639s, 1607 m, 1564m, 1527m, 1446s, 1341 m, 1272 m, 1198 m, 974 m, 843 m, 769w.

2.3 Crystallographic analysis

Diffraction intensity data for **1** and **2** were collected at 293 K and 293 K, respectively, on a Bruker Apex II CCD area detector equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied using the SADABS program [22]. The structures were solved by the direct method and refined

by the full-matrix least-squares method on F^2 , with all non-hydrogen atoms refined with anisotropic thermal parameters [23]. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model, and hydrogen atoms attached to oxygen atoms were located from the difference maps. The disordered coordinated water molecules O5, O9 and O9' sites were refined with occupancies of 0.5. A summary of the crystallographic data, data collection, and refinement parameters are provided in Table 1.

<Table 1>

3 Results and discussion

3.1 IR spectra

The FT-IR spectra of **1** displays the sharp bands at 2089 cm^{-1} , attributable to the $\nu_{\text{as}}(\text{N}_3)$ Vibration. The strong bands at about 1633 and 1462 cm^{-1} can be assigned to the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations, respectively. The FT-IR spectra of **2** displays the strong bands at $1632\text{-}1452\text{ cm}^{-1}$, attributable to the tetrazolate group vibration.

3.2 Description of the structures

Compound **1** is a 2D coordination layers based on 1D Co(II) chains with the mixed triple $(\mu\text{-EO-N}_3)_2(\text{COO})$ bridges. The selected bond lengths and angles are summarized in Table 2. The asymmetric unit consists of one Co(II) ion, a half of L_1 ligand, two azide ions and three lattice water molecules. There are two crystallographically independent Co(II) ions, each residing in the $[\text{N}_2\text{O}_4]$ octahedral environment (Fig. 1a). Co1 is completed by four azide ions (N2, N2A, N5, N5A) and

two carboxylate oxygen atoms (O1, O1A). The Co1-N/O distances range from 2.061(7) to 2.133(8) Å. While Co2 residing at an inversion center, is completed by four equatorial azide nitrogen atoms (N2, N2B, N5A, and N5C) and two axial carboxylate oxygen atoms (O2 and O2B). The equatorial Co–N distances (2.063(8) Å and 2.184(8) Å) are slightly longer than the axial Co–O distances (2.022(6) Å). The neighboring Co(II) ions are bridged by two azide ions in the EO mode and one carboxylate groups in the *syn-syn* mode, generating a 1D chain along the *c* direction (Fig. 1b). In the chain, the Co···Co distance separated by the mixed (μ -EO-N₃)₂(COO) triple bridge is 3.124(9) Å, and the Co–N2–Co and Co–N5A–Co bridge angles are 96.2(3)° and 94.7(3)°, respectively. The neighboring chains are cross-linked by the backbones of the L₁ ligands to give a 2D network along the *bc* plane (Fig. 1b). Each L₁ ligand acts as a μ_4 bridge using its two carboxylate groups to ligate four Co(II) ions from two chains. The shortest intralayer Co···Co distance spanned by the L₁ ligands is 22.821(4) Å. Topologically, the carboxylate bridges between the chains as selected atoms and the chains as linear rods, the layer is simplified into a braided grid net for clarity (Fig. 1c). The layers are packed into 3D architectures by weak O–H···O hydrogen bonds which involve carboxylate O atom and all lattice water molecules (Fig. S1): (a) the lattice water molecule (O3) forms three hydrogen bonds with one carboxylate O atom (O1) and two the lattice water molecule (O4, O5) with O3–H3C···O1 = 170°, H3C···O1 = 2.039 Å, and O1···O3 = 2.878 Å; O3–H3C···O1 = 171°, H3D···O4 = 2.201 Å, and O1···O3 = 3.043 Å; O5–H5D···O3 [*x*, -*y*+1, *z*+1/2] = 167°, H5D···O3 = 1.942 Å and O5···O3 = 2.774 Å; (b) the lattice water molecule

(O4) donates its two hydrogen atom to one equivalent lattice water molecules (O4) and the lattice water molecule (O5) from two layers with $O4-H4C\cdots O4[-x+1, y, -z+1/2] = 177^\circ$, $H4C\cdots O4 = 2.169 \text{ \AA}$, and $O4\cdots O4 = 3.017 \text{ \AA}$; $O4-H4D\cdots O5[-x+1/2, y-1/2, -z+1/2] = 177^\circ$, $H4D\cdots O5 = 2.115 \text{ \AA}$ and $O4\cdots O5 = 3.017 \text{ \AA}$. The nearest interlayers $Co\cdots Co$ distances are $12.117(3) \text{ \AA}$.

< Fig. 1.>

<Table 2>

compound **2** is a 1D neutral coordination chains with $(\mu_2\text{-OH})(\mu\text{-tetrazolate})$ double bridges. The selected bond lengths and angles are summarized in Table 3. The asymmetric unit consists of three Cu(II) ions, three L_2 ligands, three $\mu_2\text{-OH}$ groups, one and half coordinated water molecules and one lattice water molecule (Fig. 2a). There are four crystallographically independent Cu(II) ions. Both Cu1 and Cu2 exhibit the distorted square-pyramidal geometry with different degrees of distortion. For Cu1, the basal plane consists of two equivalent $\mu_2\text{-OH}$ group oxygen atoms (O4, O4A) and two equivalent tetrazolate nitrogen atoms (N3, N3A) from two L_2 ligands, and the coordinated water molecule (O5, having an occupancy of 0.5) occupied the axial position. The Cu2 environment is similar with that of Cu1, with two $\mu_2\text{-OH}$ group oxygen atoms (O4, O6) and two tetrazolate nitrogen atoms (N7, N2A) in the basal plane and the coordinated water molecule (O7) at the axial position. The apical Cu-O distance [$2.321(9) \text{ \AA}$ for Cu1, $2.247(5) \text{ \AA}$ for Cu2] is obviously longer than the basal Cu-N/O ones [$1.889(5)\text{-}1.991(6) \text{ \AA}$ for Cu1, $1.880(5)\text{-}1.997(6) \text{ \AA}$ for Cu2]. The distortion parameters τ defined by Addison et. al., [24] are 0.04 and 0.09 for Cu1 and

Cu2, respectively, suggesting the square pyramidal geometries. In addition, the basal atoms around Cu1 and Cu2 show good coplanar, with their deviations from the mean square plane being smaller than 0.0053(3) Å and 0.0066(3) Å, respectively and the metal ions (Cu1, Cu2) are out of the mean basal plane by 0.1109(5) and 0.2149(6) Å, respectively. Both Cu3 and Cu4 exhibit the similar distorted square geometry with different weak coordination. Cu3 are coordinated by two oxygen atoms (O6 and O8) from μ_2 -OH group and two nitrogen atoms (N8 and N13A) from tetrazole group. Cu4 are also coordinated by two oxygen atoms (O8 and O8B) from μ_2 -OH group and two nitrogen atoms (N12 and N12A) from tetrazole group. The four atoms around Cu3 and Cu4 show good coplanar, with their deviations from the mean square plane being smaller than 0.0066(4) Å for Cu3 and 0.0065(3) Å for Cu4 and the Cu3 is out of the mean basal plane by 0.0975(6) Å, while the Cu4 and four square atoms show very good coplanar. It is noted that both Cu3 and Cu4 are weakly coordinated respectively by O9' and O9, O9B (O9' and O9, both having an occupancy of 0.5) from the water molecules, with a long Cu-O distance of 2.476(4) Å for Cu3 and 2.691(7) Å for Cu4. If those weak coordinations are included, the geometry around Cu3 may be described as a square-pyramidal with the distortion parameters $\tau = 0.17$, while the Cu4 is a axially elongated octahedral geometry. Adjacent Cu(II) ions are doubly linked by one μ_2 -OH and one μ -N,N-tetrazolate bridges to generate an infinite 1D chain along the *b* direction in which the Cu(II) ions alternate in the -Cu1-Cu2-Cu3-Cu4-Cu3-Cu4-Cu1- sequence. The double bridges between Cu(II) ions are somewhat different in terms of their structural parameters: the Cu1...Cu2 distance is 3.066(1) Å, with Cu-O-Cu =

121.4(3)°, the Cu2···Cu3 distance is 3.342(1) Å, with Cu-O-Cu = 126.9(3)° and the Cu3···Cu4 distance is 3.206(1) Å, with Cu-O-Cu = 116.3(3)°. Each L₂ ligand uses only two tetrazole nitrogen atoms to bridge two metal ions, with the μ₂-OH oxygen atom (O1, O2, O3) left uncoordinated. The uncoordinated μ₂-OH oxygen atom forms four hydrogen bonds with three coordinated water molecules (O5, O7, O9) from another chains. The relevant hydrogen-bonding parameters are listed in Table S1. Through these hydrogen bonds, the coordination chains are organized into a 2D hydrogen bonded layers along the *ac* plane (Fig. 2c).

< Fig. 2 >

<Table 3>

3.3 Magnetic properties

The magnetic susceptibility (χ) of compound **1** was measured under 1000 Oe in the range of 2-300 K (Fig. 3). The χT value per Co(II) ion at the room temperature is about 2.89 emu K mol⁻¹, much higher than the high-spin Co(II) ion for an S=3/2 ion (1.875 emu K mol⁻¹), but in the usual range for octahedral Co(II) with an unquenched orbital momentum. As the temperature is lowered, the χT value first increases slowly, and then drops slightly to a round minimum, and then increases rapidly to a maximum at 3.0 K, while the χ value increases monotonously. The data above 140 K follow the Curie-Weiss law with $C = 2.69$ emu K mol⁻¹ and $\theta = 23.4$ K. The above behaviors indicate the presence of intrachain ferromagnetic interactions, which is in coincidence with previous compounds with the mixed (EO-N₃)₂(COO) triple bridges between Co(II) ions [14, 16, 25, 26]. The abrupt decrease of χT may be due to the saturation

effect and/or the interchain antiferromagnetic interactions.

Octahedral Co (II) at low temperature is often handled as an Ising-like ion based on the Hamiltonian $\mathbf{H} = -J_{\text{eff}}\sum \mathbf{S}_i\mathbf{S}_{i+1}$, with effective $S_{\text{eff}} = 1/2$ spin [27, 28]. Thus, the fit of the low-temperature χ data between 8 and 35 K to the Ising chain model was attempted using the following expressions

$$\chi = (\chi_{//} + 2\chi_{\perp})/3 \quad (1)$$

$$\text{with } \chi_{//} = (N\beta^2 g_{//}^2 / 4kT) \exp(J_{\text{eff}}/2kT) \quad (2)$$

$$\chi_{\perp} = (N\beta^2 g_{\perp}^2 / 2J_{\text{eff}}) [\tanh(J_{\text{eff}}/4kT) + (J_{\text{eff}}/4kT) \text{sech}^2(J_{\text{eff}}/4kT)] \quad (3)$$

The data in low temperature regions are well simulated by the expressions with $J = 8.1 \text{ cm}^{-1}$, $g_{//} = 10.6$ for **1** with $g_{\perp} \approx 0$. The J value is similar to that reported for some previous Co(II) compounds with similar two EO azides and one carboxylate bridges [14, 16, 26, 27]. A collection of the structural and magnetic data for the previous Co(II) compounds with similar bridges have been given elsewhere [14]. All of the Co(II) compounds with similar bridges exhibit ferromagnetic interactions with the J values lying in range of 8-14 cm^{-1} . The ferromagnetic interactions decreases as the Co-N distance decreases. Compound **1** exhibits ferromagnetic interactions and follows the general trend.

< Fig. 3 >

The field-dependent isothermal magnetization data measured at 0-50 kOe at 2 K are shown in Fig. 4. As the field is lifted, the magnetization increases slowly and reaches 2.2 $N\beta$ at 50 kOe, which is in the usual range of 2-3 $N\beta$ for Co(II) [29, 30]. The experimental values are higher than the predicted values by the Brillouin function for

two isolated Co(II) ions with $S_{\text{eff}} = 1/2$, clearly confirming the presence of ferromagnetic interactions. No evident hysteresis was observed by cycling the field between -50 and 50 kOe at 2 K and no imaginary signals was also observed under $H_{\text{dc}} = 0$ kOe at different frequencies (Fig. S2 of the ESI†).

< Fig. 4 >

The magnetic susceptibilities of compound **2** was measured in the range 2-300 K under 1 kOe. The χT value per formula at 300 K is about 0.99 emu K mol⁻¹, lower than the spin-only value (1.125 emu K mol⁻¹ with $S = 1/2$) expected for three uncoupled Cu(II) ions. Upon cooling to 2 K, the χT value decreases continuously, while the χ value increases smoothly. The data above 160 K follow the Curie-Weiss law with $C = 1.87$ emu K mol⁻¹ and $\theta = -301.3$ K. The above features indicates overall antiferromagnetic interactions between Cu (II) ions.

According to the structural analysis, the magnetic behaviors could be nearly analyzed by a 1D magnetic system based on the spin Hamiltonian $H = \mathbf{H} = J\sum \mathbf{S}_i \mathbf{S}_{i+1}$ [31]. The magnetic behaviours of **2** can be described by the Bonner-Fisher (eqn 4-6) [32] model.

$$x_{\text{chain}} = \frac{Ng^2\beta^2}{kT} \left(\frac{A}{B} \right) \dots\dots\dots (4)$$

$$A = 0.25 + 0.74975x + 0.075235x^2$$

$$B = 1 + 0.9931x + 0.172135x^2 + 0.757825x^3$$

$$x = x_{\text{chain}} / [1 - (zj'x_{\text{chain}}) / Ng^2\beta^2] \dots\dots\dots (5)$$

$$x' = x(1 - \rho) + \frac{Ng^2\beta^2\rho}{2kT} + TIP \dots\dots\dots (6)$$

where $x = |J| / 2kT$, the zj' parameter in the molecular-field approximation is the

interactions interchain. The best fit of the data yields $J = 196.34 \text{ cm}^{-1}$ (the J value is negative meaning, because eqn 4-6 are the positive equation), $g = 2.01$, and $\rho = 0.009$. The J value shows the strong antiferromagnetic coupling through the mixed (tetrazolate)(OH) double bridges. According to spin polarization mechanism, the tetrazole N-N two-atoms bridge induces antiferromagnetic coupling between Cu(II) ions. In some Cu(II) systems, it is experimentally verified that the μ_2 -OH bridges induces antiferromagnetic coupling for Cu-O-Cu angles $>97.5^\circ$ [33] and the magnitude increases as the Cu-O-Cu angle increases. All Cu-O-Cu angles in **2** lie in the range of $116.3\text{--}126.9^\circ$. Hence, **2** exhibits a stronger antiferromagnetic interaction, which is due to the increase of net orbital overlap as the number of relevant magnetic orbitals increases, that is to say, the orbital complementarity between the μ_2 -OH and tetrazolate bridges. This consideration is supported in the systems with μ -OH or μ -H₂O and carboxylate mixed bridges [34, 35].

< Fig. 5 >

4. conclusions

we have synthesized and characterized two new Co(II) / Cu(II) complexes built from different zwitterionic ligands. Compound **1** contains the uniform chain with $(\mu\text{-EO-N}_3)_2(\mu\text{-COO})$ triple bridges, which induces ferromagnetic interactions between Co(II) ions. A rare Cu(II) chain with $(\mu_2\text{-OH})(\mu\text{-tetrazolate})$ double bridges mediates the strong antiferromagnetic coupling. This work demonstrated that the nature of the zwitterionic ligand plays a very important in generating the chain with the mixed

bridges. The zwitterionic ligands bearing different functional groups may lead to diverse magnetic systems with novel mixed bridges.

5. Supplementary material

CCDC-1458062 (**1**) and 1458063 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/ data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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Captions of Scheme and Figures

Scheme 1. (top) Chemical structure of **1**, (bottom) Synthesis of **2** using in-situ organic reactions.

Fig. 1. (a) Local coordination environments of the Co center and the ligands in **1**. Symmetry codes: A $-x+1, y, -z+1/2$; B $-x+1, -y+1, -z+1$; C $x, -y+1, z+1/2$; D $-x+1, -y, -z+2$. (b) A layer with mixed $(\mu\text{-EO-N}_3)_2(\mu\text{-COO})$ bridges. (c) Schematic illustrations showing the interchain connection topologies: the green rods stand for the mixed-bridged chains, the blue and red lines for simplified linkers.

Fig. 2. (a) Local coordination environments of the Cu center and the ligands in **2**. Symmetry codes: A $-x+1, y, -z+1/2$; B $-x+1/2, -y+1/2, -z+1$. (b) A chain with mixed $(\mu\text{-EO-N}_3)_2(\mu\text{-COO})$ bridges. (c) 2D network formed by interchain hydrogen bonds.

Fig. 3. Temperature dependence of χT for **1**. Inset: the black line represents the best fit of χ -T plot to the Ising model.

Fig. 4. Isothermal magnetization of **1** at 2 K. The solid line represents the Brillouin calculation for noninteracting $S = 2 \times S_{\text{eff}}$ state with $g=2.0$.

Fig. 5. Temperature dependence of χ and χT for **2**. The solid lines represent the fitted curves.

Fig. S1. The 3D packing of the layers in **1**.

Fig. S2. $\chi'(T)$ and $\chi''(T)$ plots for **1** at frequencies of 1, 11, 111, 333, and 997 Hz with $H_{\text{dc}} = 0$ and $H_{\text{ac}} = 3.0$ Oe.

Fig. S3. Hysteresis measurement of **1** at 2 K.

Two coordination polymer containing Co(II) / Cu(II) chains with different mixed bridges was derived from two new zwitterionic ligands; The $(\mu\text{-EO-N}_3)_2(\text{COO})$ triple bridges transmit ferromagnetic interactions in **1**, while the double $(\mu\text{-OH})(\mu\text{-N,N-tetrazolate})$ antiferromagnetic interactions in **2**.

Table 1 Crystal data and structure refinement for compounds **1** and **2**.

Compound	1	2
Formula	C ₁₆ H ₁₇ CoN ₇ O ₅	C ₃₆ H ₃₂ Cu ₃ N ₁₅ O _{8.5}
<i>Mr</i>	446.30	1001.39
Crystal system	Monoclinic	Monoclinic
Temperature/K	293(2)	298(2)
space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> /Å	15.5000(15)	22.900(2)
<i>b</i> /Å	24.557(2)	13.2900(11)
<i>c</i> /Å	11.4779(9)	26.240(2)
<i>α</i> /°	90	90
<i>β</i> /°	118.473(2)	102.602(2)
<i>γ</i> /°	90	90
<i>V</i> /Å ³	3840.4(6)	7793.6(12)
<i>Z</i>	8	8
<i>D_c</i> /g cm ⁻³	1.544	1.707
<i>μ</i> /mm ⁻¹	0.938	1.698
Reflns collected	7375	19775
Unique reflns	3385	6876
<i>R</i> _{int}	0.1868	0.1433
GOF on <i>F</i> ²	1.080	1.023
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)]	0.1172	0.0624
<i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.1995	0.1190

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Co1-N5	2.061(7)	Co2-O2	2.022(6)
Co1-O1	2.122(6)	Co2-N2	2.063(8)
Co1-N2	2.133(8)	Co2-N5A	2.184(8)
N5A- Co1-N5	173.8(5)	O2- Co2-O2A	180.00(19)
N5- Co1-O1	98.7(3)	O2- Co2-N2A	93.3(3)
N5- Co1-O1A	85.9(3)	N2- Co2-N2B	180.000(1)
O1A- Co1-O1	86.4(4)	O2- Co2-N2	86.7(3)
N5A- Co1-N2	83.5(3)	O2- Co2-N5A	86.0(3)
N5- Co1-N2	92.2(3)	O2- Co2-N5C	94.0(3)
O1A- Co1-N2	176.6(3)	N2- Co2-N5A	82.2(3)
O1- Co1-N2	91.2(3)	N2- Co2-N5C	97.8(3)
N2- Co1-N2A	91.4(5)	N5A- Co2-N5C	180.000(1)
Symmetry codes: A -x+1,y,-z+1/2; B -x+1,-y+1,-z+1; C x,-y+1,z+1/2			

Table 3 Selected bond lengths (Å) and angles (°) for compound **2**

Cu1-O4	1.889(5)	Cu2-O7	2.247(5)
Cu1-N3	1.991(6)	Cu3-O6	1.855(5)
Cu1-O5	2.321(9)	Cu3-O8	1.882(4)
Cu2-O6	1.880(5)	Cu3-N13B	1.985(6)
Cu2-O4	1.903(4)	Cu3-N8	1.992(6)
Cu2-N2A	1.989(6)	Cu4-O8	1.893(4)
Cu2-N7	1.997(6)	Cu4-N12	1.969(6)
O4- Cu1-O4A	172.2(3)	O6- Cu2-O7	95.5(2)
O4- Cu1-N3	93.1(2)	O4- Cu2-O7	100.20(19)
O4A- Cu1-N3	86.6(2)	N2A- Cu2-O7	99.0(2)
N3- Cu1-N3A	174.6(4)	N7- Cu2-O7	90.8(2)
O4- Cu1-O5A	85.6(4)	O6- Cu3-O8	178.2(2)
O4- Cu1-O5	102.1(4)	O6- Cu3-N13B	91.4(3)
N3- Cu1-O5A	95.7(8)	O8- Cu3-N13B	87.0(2)
N3- Cu1-O5	89.6(8)	O6- Cu3-N8	86.3(3)
O5- Cu1-O5A	17.3(6)	O8- Cu3-N8	95.4(2)
O6- Cu2-O4	164.3(3)	N13B- Cu3-N8	167.9(3)
O6- Cu2-N2B	91.7(2)	O8- Cu4-O8B	180.000(1)
O4- Cu2-N2A	85.9(2)	O8- Cu4-N12	92.6(2)
O6- Cu2-N7	85.4(2)	O8B- Cu4-N12	87.4(2)
O4- Cu2-N7	94.4(2)	O8- Cu4-N12	92.6(2)
N2A- Cu2-N7	170.0(3)	N12- Cu4-N12B	180.00(18)
Symmetry codes: A -x+1, y, -z+1/2; B -x+1/2, -y+1/2, -z+1.			

Figure(s)

Figure(s)

Figure(s)**(a)** **(b)** **(c)**

Figure(s)

Figure(s)

Figure(s)