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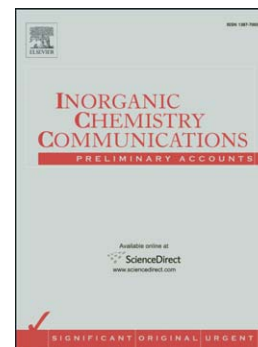
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PII: S1387-7003(15)30169-6
DOI: doi: [10.1016/j.inoche.2015.12.018](https://doi.org/10.1016/j.inoche.2015.12.018)
Reference: INOCHE 6200

To appear in: *Inorganic Chemistry Communications*

Received date: 9 November 2015
Revised date: 17 December 2015
Accepted date: 29 December 2015



Please cite this article as: Ling Li, Ji-Yong Zou, Zhen Gu, Sheng-Yong You, Yan-Hua Chen, Jun Xia, Jian-Zhong Cui, Two cobalt complexes derived from 1*H*-1,2,3-triazole-4,5-dicarboxylic acid: Syntheses, structures and magnetic properties, *Inorganic Chemistry Communications* (2016), doi: [10.1016/j.inoche.2015.12.018](https://doi.org/10.1016/j.inoche.2015.12.018)

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Two cobalt complexes derived from 1*H*-1,2,3-triazole-4,5-dicarboxylic acid: syntheses, structures and magnetic properties

Ling Li,^[a] Ji-Yong Zou,^{*[a]} Zhen Gu,^[a] Sheng-Yong You,^[a] Yan-Hua Chen^[a] Jun Xia^[a] and Jian-Zhong Cui^{*[b]}

[a] Institute of applied chemistry, Jiangxi academy of sciences, Nanchang, 330096, China

[b] Department of Chemistry, Tianjin University, Tianjin, 300072, China.

Abstract

Two cobalt(II) homometallic complexes, $[\text{Co}_2(\text{HTDA})_2(\text{H}_2\text{O})_6 \cdot 2\text{H}_2\text{O}]$ (**1**) and $\{[\text{Co}_3(\text{TDA})_2(\text{H}_2\text{O})_8] \cdot \text{H}_2\text{O}\}_n$ (**2**) ($\text{H}_3\text{TDA} = 1H\text{-}1,2,3\text{-triazole-}4,5\text{-dicarboxylic acid}$) have been synthesized and structurally characterized in detail. Single-crystal X-ray crystallographic study reveals that they crystallize in trigonal space group $R\bar{3}$ and orthorhombic space group $Pna2_1$, respectively. In **1**, two Co^{2+} cations are bonded by two HTDA^{2-} ligands to generate a binuclear Co^{II} unit, which can further be extended to a 3D superamolecular structure via the hydrogen bonds. At variance with **1**, the nearest Co^{2+} cations of **2** are connected via TDA^{3-} ligands to form a 1D coordination polymer and can be further linked to each other to result in a 3D superamolecular framework through the hydrogen bonding interactions as well. The magnetic properties of them were studied in detail.

Keywords: cobalt(II) complexes, H_3TDA ligand, hydrogen bonding interactions, magnetic properties

Crystalline molecular magnetic materials have attracted considerable attention of the academic community in recent years because of their impressive properties and potential applications in high-density data storage devices and nanosized electronics [1]. These materials could be realized by incorporating metal ions or metal clusters and organic ligands into one system via metal-ligand coordinate bonds, resulting in a variety of interesting structures [2]. As a result, much work has been devoted to preparing such multifunctionalized crystalline molecular magnetic materials by employing pure 3*d* or 4*f* or mixed 3*d*-4*f* spin carries to construct

* Corresponding author. E-mail address: zoujiyong@jxas.ac.cn; cuijianzhong@tju.edu.cn.

magnetic moments [3-5]. Among them, the exchange coupled molecular magnetic complexes containing cobalt(II) ions are extraordinary interesting as the systems exhibiting strong orbital contributions to the magnetic moments and thus strong magnetic anisotropy [6]. This orbital magnetism arises from the ground orbital triplet 4T_1 of each cobalt(II) ion in a surrounding cubic crystal. However, it is still a challenge for the interpretation of magnetic data for the coordination complexes with octahedral cobalt(II) centres due to the first order orbital contribution, leading to the difficulties in both syntheses and magneto-structural correlation analyses. And consequently, the precise nature of the magnetic superexchange, the orientation of the local zero-field splitting tensors and how these contribute to the anisotropy of octahedral cobalt(II) centres are undoubtedly critical questions that should be further investigated.

Significantly, one of the essential prerequisites in the construction of crystalline molecular magnetic materials is the magnetic exchange pathways, which are confirmed to be a required factor of the influence on the magnetic coupling effect. An appropriate magnetic exchange media should be arranged in a special topological motif via the spin carries and more readily to communicate magnetic information. 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H_3TDA) has been proved to be a promising magnetic exchange media to communicate magnetic information and has been extensively studied as an effective magnetic exchange pathways, but it still deserved to be further investigated [3b,3c,7]. In this contribution, two cobalt(II) homometallic complexes, $[Co_2(HTDA)_2(H_2O)_6 \cdot 2H_2O]$ (**1**) and $\{[Co_3(TDA)_2(H_2O)_8] \cdot H_2O\}_n$ (**2**) have been obtained and structurally characterized by infrared spectra, thermogravimetric analysis, elemental analysis, powder X-ray diffraction and single-crystal X-ray diffraction. The magnetic properties were studied in detail to determine the following magnetic parameters: $g = 2.47$, $D = 36.85 \text{ cm}^{-1}$, $zJ = -0.61 \text{ cm}^{-1}$, and $R = 0.9979$ for **1**; $A + B = 9.79 \text{ cm}^3 \text{ K mol}^{-1}$, $E_1 = -31.27 \text{ K}$, $E_2 = -1.55 \text{ K}$ and $R = 0.9998$ for **2**, respectively, suggesting dominant antiferromagnetic interaction between Co^{2+} ions.

Reaction of $CoCl_2 \cdot 6H_2O$ and H_3TDA in the presence of 1*H*-1,2,4-triazole (HTZ) in the mixture of water and C_2H_5OH at room temperature, gives the crystals of **1** in *ca.* 58% yield, where HTZ was absence in the final product and H_3TDA was partially deprotonated, forming $HTDA^{2-}$ ligand (scheme 1a). This structure was isomorphous with the known structure $[Co_2(HTDA)_2(H_2O)_6 \cdot 5H_2O]$ [8], which crystallizes in trigonal space group $R\bar{3}$ and consists of two Co(II) ions, two $HTDA^{2-}$ ligands, six coordinated water molecules and five free water molecules, generating a binuclear Co^{II} unit (Fig 1a). Co1 adopts a slightly distorted octahedral $\{CoO_4N_2\}$ coordination geometry with one oxygen atom(O1A), two nitrogen atoms(N1A and N2) from two $HTDA^{2-}$ ligands and three oxygen atoms (O5, O6 and O7) from three water molecules. The binuclear Co^{II} units can be linked each other to a 3D superamolecular structure

via the hydrogen bonds, which further consolidate the structure of **1** (Fig 1b). The differences between them are the number of free water molecules. Therefore, the detailed structure of **1** is accordingly ignored here.

(Insert scheme 1)

(Insert Fig. 1)

While hydrothermal reaction of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and H_3TDA in the presence of benzotriazole (HBTZ) in water at 150°C , gives the crystals of **2** in *ca.* 35% yield, where HBTZ was absence in the final product as well but H_3TDA was completely deprotonated, forming TDA^{3-} ligand (scheme 1b). Single-crystal X-ray diffraction analysis reveals that **2** crystallizes in orthorhombic space group $Pna2_1$. Each unit cell contains crystallographically independent three Co(II) ions, two TDA^{3-} ligands, eight coordinated water molecules and one free water molecule (Fig. 2a). Co1 adopts a slightly distorted octahedral $\{\text{CoO}_4\text{N}_2\}$ coordination geometry with one oxygen atom (O5), two nitrogen atoms (N2 and N4) from two TDA^{3-} ligands and three oxygen atoms (O12, O13 and O14) from three water molecules. Similar to Co1, Co2 is hexa-coordinated by one oxygen atom (O4), two nitrogen atoms (N3 and N5) from two TDA^{3-} ligands and three oxygen atoms (O9, O10 and O11) from three water molecules as well, forming a slightly distorted octahedral $\{\text{CoN}_2\text{O}_4\}$ coordination geometry. Different from the coordination environments of Co1 and Co2, Co3 is coordinated by two oxygen atoms (O1A and O8), two nitrogen atoms (N1A and N6) from two TDA^{3-} ligands and two oxygen atoms (O15 and O16) from two water molecules forming an octahedral $\{\text{CoO}_4\text{N}_2\}$ coordination geometry. The bond lengths of Co-N are in the range of 2.081(9)-2.154(9) Å and those of Co-O are in the range of 2.050(7)-2.195(7) Å, respectively. Obviously, the bond lengths of Co-N and Co-O fall in the normal values of the previously reported Co-based complexes [6,9]. There are two different types of TDA^{3-} ligands: one chelates two Co^{II} ions (Co1 and Co2) through the carboxylate oxygen atom (O4) and the triazole nitrogen atoms (N2 and N3), one crystallographically equivalent Co3A ion through the same carboxylate oxygen atom O1 and triazole nitrogen atom N1 neighboring to N2 atom. Interestingly, the other one chelates three Co^{II} ions (Co1, Co2 and Co3) through the carboxylate oxygen atoms (O5 and O8) and the triazole nitrogen atoms (N4, N5 and N6). In this case, three Co^{II} ions are simultaneously coordinated by two TDA^{3-} ligands to form a trinuclear Co^{II} unit, further bridging each other to form a 1D coordination polymer (Fig 2b). The 1D coordination polymer can be further packed together via hydrogen bonds to result in a 3D superamolecular framework (Fig. 2c), consolidating the structure of **2**. Significantly, such low-nuclearity complexes of **1** and **2** assembled with H_3TDA ligand and Co(II) ions are still rare and only a hexanuclear complex $[\text{Co}_6(\text{TDA})_4(\text{H}_2\text{O})_{14} \cdot 5\text{H}_2\text{O}]$ [7b] could be found in recent literature. In most case, H_3TDA is a promising candidate to generate 3D coordination polymers due to its intrinsic nature of the coordination modes [3b,3c,7a].

To confirm its crystalline phase purity, the XRPD experiments of **1** and **2** have been carried out at room temperature. The diffraction peaks of bulk sample are consistent with the simulated pattern in terms of the single crystal data, indicating the presence of mainly one crystalline phase in the corresponding sample of **1** and **2**, respectively (Figs. S1 and S2). The TGA have been also performed under an N₂ atmosphere (Figs. S3 and S4). The TGA curve of **1** shows a weight loss of 6.81% before 100 °C, corresponding to the removal of two uncoordinated water molecules (calcd. 6.29 %). After the loss of all free water molecules, 19.47 % weight loss was observed before 200 °C, suggesting the removal of six coordinated water molecules (calcd. 18.88 %). With the temperature increasing, **1** began to decompose. Whereas the TGA curve of **2** shows a weight loss of 2.43% before 120 °C, corresponding to the removal of one uncoordinated water molecule (calcd. 2.78 %). After the loss of all free water molecules, 21.85 % weight loss was observed before 330 °C, indicating the removal of six coordinated water molecules (calcd. 22.25 %). After the loss of all water molecules, no weight loss is observed, indicating the decomposition of **2**. The IR spectrum (Figs. S5 and S6) band at 3403 cm⁻¹ for **1** and 3431 cm⁻¹ for **2** is assigned to the OH stretching vibration, respectively. The characteristic band at 1713 cm⁻¹ for **1** and 1615 cm⁻¹ for **2** can be attributed to the $\nu_{\text{C=O}}$ stretching vibration of the carboxyl group and the band at 1380 cm⁻¹ for **1** and 1389 cm⁻¹ for **2** is assigned to $\nu_{\text{C-O}}$. Band at 1154 cm⁻¹ for **1** and 1129 cm⁻¹ for **2** belongs to the triazolate ring.

Static (dc) magnetic susceptibilities of **1** and **2** have been measured in an applied magnetic field of 1 kOe in the temperature range of 300-2 K. As shown in Fig. 3, the observed $\chi_{\text{M}}T$ values at room temperature are 5.78 cm³ K mol⁻¹ for **1** and 9.16 cm³ K mol⁻¹ for **2**. The corresponding expected theoretical $\chi_{\text{M}}T$ values are 3.76 cm³ K mol⁻¹ for **1** and 5.65 cm³ K mol⁻¹ for **2**, calculated from the isolated Co(II) ions ($S = 3/2$, $g = 2$). The observed $\chi_{\text{M}}T$ values at room temperature are much higher than the corresponding calculated $\chi_{\text{M}}T$ values for the free high-spin Co(II) ions in an octahedral coordination environment, which can be attributed to the contribution of the spin-orbit coupling [10]. With decreasing the temperature, $\chi_{\text{M}}T$ values decrease gradually, reaching a minimum of 1.30 cm³ K mol⁻¹ for **1** and 1.66 cm³ K mol⁻¹ for **2** at 2 K. The decrease of $\chi_{\text{M}}T$ values could be attributed to antiferromagnetic interactions and/or zero-field splitting (ZFS) effects [11]. The fitting by Curie-Weiss law with the data above 50 K for **1** and 10 K for **2**, gives $C = 5.88$ cm³ K mol⁻¹, $\theta = -8.59$ K for **1** and $C = 10.03$ cm³ K mol⁻¹, $\theta = -28.72$ K for **2**. The large and negative Weiss constant suggests dominant antiferromagnetic interactions as well as the spin-orbit coupling. Measurements of the field (H) dependence of the magnetizations (M) for **1** and **2** at 2 K have been also performed, exhibiting a rapid increase with the increasing fields and a lack of saturation. The magnetizations at 2 K increase up to 4.74 N β for **1** and

3.18 N β for **2**, respectively, far from the expected saturation, further implying the presence of the antiferromagnetic interactions between Co²⁺ ions for **1** and **2**.

(Insert Fig. 3)

According to the crystal structure of **1**, it is difficult to model the magnetic behavior by deducing an exact expression including J parameters even if the orbital contributions of Co(II) ions are ignored. The data can be fitted by an expression for $S = 3/2$ system with dominant zero-field splitting effects [12], rather than an equation for Co(II) with ground state of ⁴T_{1g}.

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{kT} \frac{1+9e^{-2x}}{4(1+e^{-2x})} \quad (1)$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{kT} \frac{4+\frac{3}{x}(1-e^{-2x})}{4(1+e^{-2x})} \quad (2)$$

$$\chi' = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} \quad (3)$$

$$\chi = \frac{\chi'}{1 - \left(\frac{2zJ}{Ng^2\beta^2}\right)\chi'} \quad (4)$$

Where g is the Lande g value, x is $D/(kT)$, D is the magnitude of the ZFS, z is the number of neighbors and J is the magnitude of the intermolecular interactions. The best agreements between model and experiment by fitting $\chi_M T$ above 2 K for **1** using a least-squares analysis lead to the following parameters: $g = 2.47$, $D = 36.85 \text{ cm}^{-1}$, $zJ = -0.61 \text{ cm}^{-1}$ and $R = 0.9979$ ($R = 1 - \sum\{(\chi_M T_{\text{calc}} - \chi_M T_{\text{obs}})/\sum(\chi_M T_{\text{obs}})\}^2$) for **1**. The obtained values of **1** are in good agreement with the previously reported $S = 3/2$ system with dominant zero-field splitting effects [7d,13]. The magnetic data and fitting parameters suggested antiferromagnetic interactions between the adjacent Co²⁺ ions for **1**.

According to the contribution of the spin-orbit coupling to the magnetic data as well as the crystal structure of **2**, the observed $\chi_M T$ data for **2** can be fitted by the following expression [14]:

$$\chi T = A \exp(E_1/T) + B \exp(E_2/T) \quad (5)$$

Where $A + B$ equals the curies constant, E_1 is the spin-orbit coupling constant and E_2 is the activation energy of the antiferromagnetic interactions. The best agreements between model and experiment by fitting $\chi_M T$ over the whole temperature for **2** using a least-squares analysis lead to the following parameters: $A + B = 9.79 \text{ cm}^3 \text{ K mol}^{-1}$, $E_1 =$

-31.27 K, $E_2 = -1.55$ K and $R = 0.9998$ ($R = 1 - \sum \{(\chi_M T_{\text{calc}} - \chi_M T_{\text{obs}}) / \sum (\chi_M T_{\text{obs}})\}^2$) for **2**. The negative value of E_2 further indicates that dominant antiferromagnetic interactions between Co(II) ions in **2**.

In summary, the structures and magnetic properties of two cobalt(II) homometallic complexes based on 1*H*-1,2,3-triazole-4,5-dicarboxylic acid have been reported. Complex **1** is a binuclear Co^{II} complex whereas **2** is a 1D coordination polymer, which can be extended to be a 3D superamolecular structure via the hydrogen bonds. The magnetic studies indicates the presence of dominant antiferromagnetic interactions between Co(II) ions in **1** and **2**. This work illustrates a rational way by employing azolate-dicarboxylic acid bridging ligand to explore homometallic complexes and provides a promising field to construct crystalline molecular magnetic materials. Further synthetic studies on the azolate-carboxylic acid chemistry to construct crystalline molecular magnetic materials are in progress in our lab.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (No. 21561014, 21562023 and 21271137) and Postgraduate Foundation (2014-YYB-21 and 2014-YYB-22) of Jiangxi Academy of Sciences are greatly acknowledged.

Appendix A. Supplementary data

CCDC 930109 for **1** and CCDC 1430720 for **2** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data are available in the online version, at doi: xx.xxxx/j.inoche, 2015.xxx.xx.

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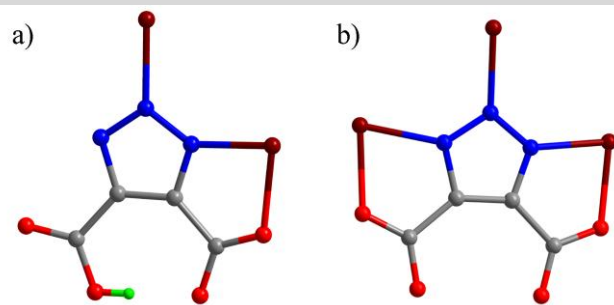
Figure Captions:

Scheme 1. Coordination modes of H₃TDA in **1** and **2**.

Fig. 1. (a) The coordination environments of Co(II) ions in **1** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) -x, -y+1, -z]; (b) The 3D superamolecular structure via the hydrogen bonds of **1**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

Fig. 2. (a) The coordination environments of Co(II) ions in **2** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) -x+3/2, y-1/2, z+1/2]; (b) The 1D coordination polymer of **2**; (c) The 3D superamolecular structure via the hydrogen bonds of **2**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

Fig 3. (a) Temperature dependence of $\chi_M T$ and χ_M of **1**; (b) Field dependence of magnetizations for **1** at 2 K; (c) Temperature dependence of $\chi_M T$ and χ_M of **2**; (d) Field dependence of magnetizations for **2** at 2 K. The red solid line represents the best theoretical fittings.



Scheme 1 Coordination modes of H₃TDA in **1** and **2**.

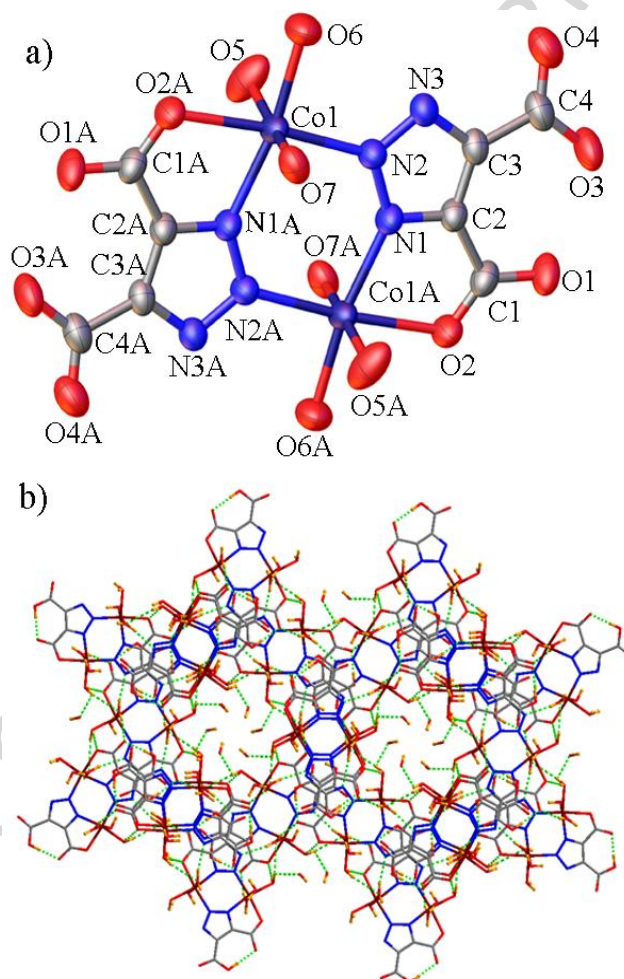


Fig. 1. (a) The coordination environments of Co(II) ions in **1** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) $-x, -y+1, -z$]; (b) The 3D superamolecular structure via the hydrogen bonds of **1**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

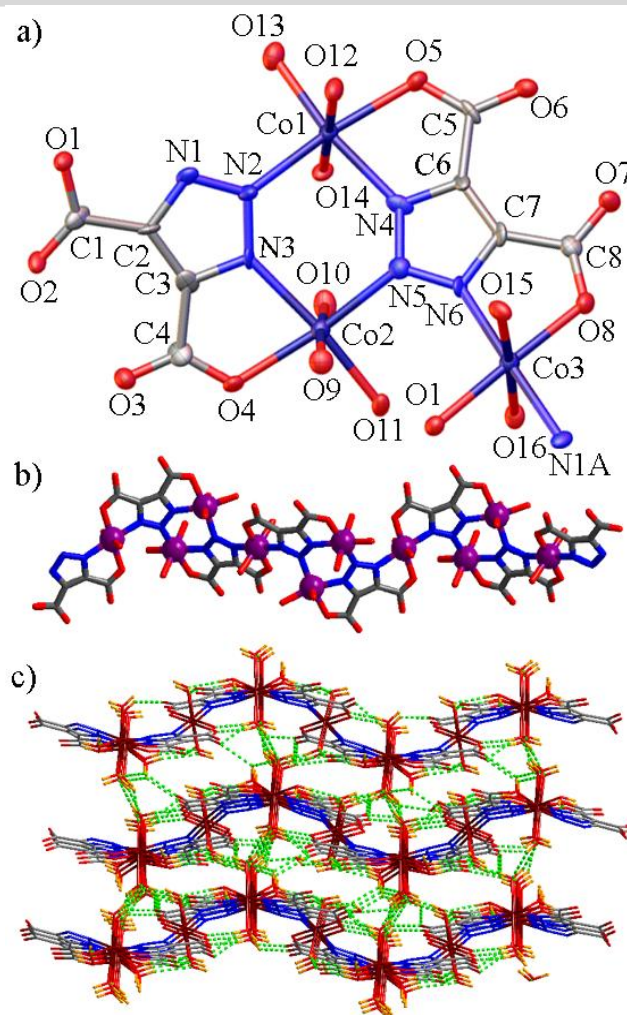


Fig. 2. (a) The coordination environments of Co(II) ions in **2** (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms and uncoordinated water molecules were omitted for clarity. [Symmetry code: (A) $-x+3/2, y-1/2, z+1/2$]; (b) The 1D coordination polymer of **2**; (c) The 3D superamolecular structure via the hydrogen bonds of **2**. purple: Co; red: O; blue: N; black: C, yellow: H. The green dashed lines stand for the hydrogen bonds.

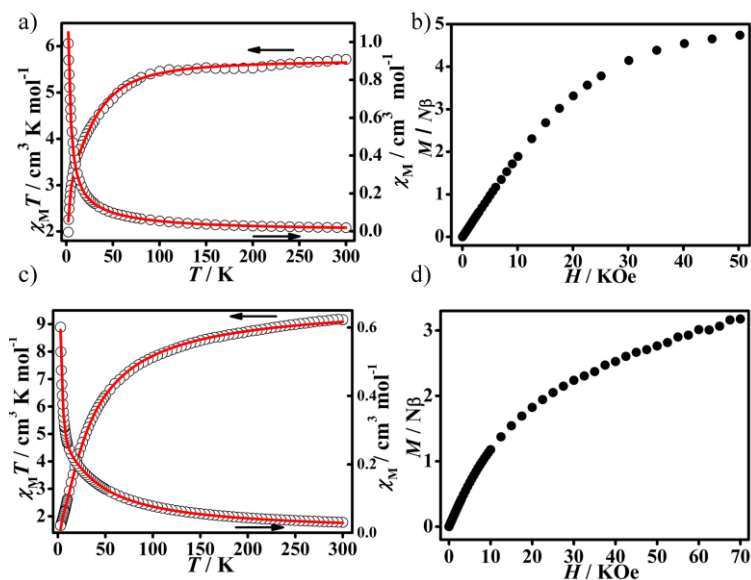
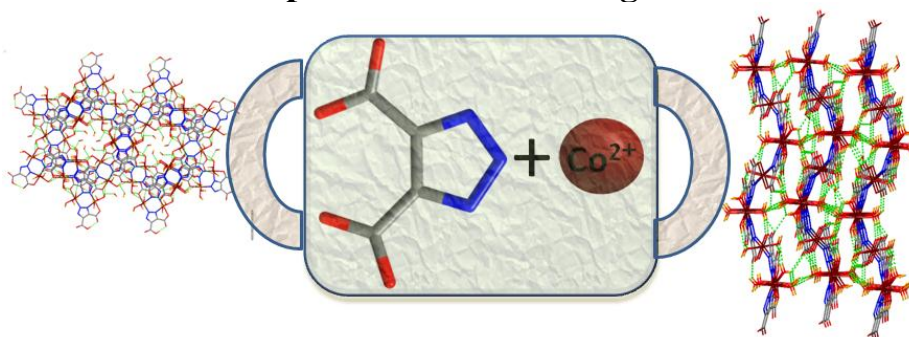


Fig 3. (a) Temperature dependence of $\chi_M T$ and χ_M of **1**; (b) Field dependence of magnetizations for **1** at 2 K; (c) Temperature dependence of $\chi_M T$ and χ_M of **2**; (d) Field dependence of magnetizations for **2** at 2 K. The red solid line represents the best theoretical fittings.

Graphical Abstract Pictogram



Graphical Abstract Synopsis

Two cobalt(II) homometallic complexes derived from 1*H*-1,2,3-triazole-4,5-dicarboxylic acid were synthesized and fully characterized. The magnetic properties were studied in detail to determine the following magnetic parameters: $g = 2.47$, $D = 36.85 \text{ cm}^{-1}$, $zJ = -0.61 \text{ cm}^{-1}$, and $R = 0.9979$ for **1**; $A + B = 9.79 \text{ cm}^3 \text{ K mol}^{-1}$, $E_1 = -31.27 \text{ K}$, $E_2 = -1.55 \text{ K}$ and $R = 0.9998$ for **2**, respectively, suggesting dominant antiferromagnetic interaction between Co^{2+} ions.

Research Highlights

- Two cobalt(II) complexes derived from azolate-carboxylic acid were synthesized and characterized.
- Dominant antiferromagnetic interactions between Co^{2+} ions in them were found.

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