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Four 3,5-diamino-1,2,4-triazole-based cobalt(II/III) complexes incorporating with 5-substituted isophthalate coligands: Synthesis, structure and magnetism

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ABSTRACT

Four 3,5-diamino-1,2,4-triazole (Hdatrz)-based cobalt(II/III) coordination polymers, {[Co$_2$(Hdatrz)(NH$_2$-ip)$_2$]·0.5H$_2$O}$_n$ (**1**), [Co(CH$_3$OH)(Hdatrz)(CH$_3$-ip)]$_n$ (**2**), {[Co$_2$(datrz)$_2$(CH$_3$-ip)]·2.5H$_2$O}$_n$ (**3**) and {[Co(datrz)(NO$_2$-ip)]·H$_2$O}$_n$ (**4**) (NH$_2$-ip^{2-} = 5-aminoisophthalate, CH$_3$-ip^{2-} = 5-methylisophthalate and NO$_2$-ip^{2-} = 5-nitroisophthalate), were hydro-/solvothermally synthesized by changing the substituents attached on the isophthalate coligand, which were structurally and magnetically characterized. Complex **1** is a corrugated layer with dimeric {Co$_2$(μ-N1,N2-Hdatrz)}$^{4+}$ subunits extended by three-connected NH$_2$-ip^{2-} connectors. Constructed from the same mixed ligands, both **2** and **3** exhibit robust three-dimensional (3D) frameworks consisting of helical {Co(μ-N1,N4-Hdatrz)}$^{2+}$ chain and corner-sharing triangular {Co$_2$(μ_3-N1,N2,N4-datrz)$_2$}$^{2+}$ layer, respectively. By contrast, two bis-monodentate NO$_2$-ip^{2-} and two μ-N1,N4-datrz$^-$ anions connect tetrahedral Co(III) sites into a (4, 4) grid-like layer of **4**. Thus, the substituent of the isophthalate coligand is observed to virtually influence the overall structures of the resulting complexes by changing the binding modes of the coligand and coordination polyhedra. Additionally, complex **1** exhibits a metamagnetic transition from antiferromagnetic ordering to weak ferromagnetic state. Instead, typically antiferromagnetic interactions are respectively mediated by the cyclic triazolate ligand along the helical chain of **2** and in the distorted triangular layer of **3**.

1. Introduction

Structural design and functional modification of paramagnetic coordination polymers (CPs) have always received enormous interest in crystal engineering, magnetic materials science and theoretical understandings on the magnetostructural relationships [1–2]. Among diverse paramagnetic transition metal ions with different numbers of unpaired d electron, cobalt ion has becoming one of good candidates as a spin carrier resulting from its strong single-ion anisotropy and unquenched spin–orbit coupling [3,4]. Up to date, lots of interesting Co^{II}-containing CPs, such as isolated helical/bent chains, coplanar/wave-like layers and extended microporous/pillared-layer frameworks, have been consequently obtained by varying the organic magnetic mediators, which have exhibited intriguingly long-range magnetic ordering and/or single-chain magnetic behaviors [5–9]. On the other hand, hetero-bridge-involved magnetic systems constructed from heterocyclic triazolate and bent carboxylate mediators have recently drawn great attention due to their collaborative effect on structural and magnetic adjustments of the resulting CPs [10–12]. Crystallographically, both the cyclic triazolate and the deprotonated carboxylate group can adopt various binding modes to aggregate discrete spin carriers into dense subunits with variable core numbers and core topologies, accompanying the transfer of the typically anti- and/or ferromagnetic interactions with variable coupling constants. Especially, the type of superexchange interaction for bidentate bridging carboxylate is found to be conformation-dependent. Moreover, the rigid phenyl-based polycarboxylates can behave as polytopic connectors to essentially extend the versatile subunits into intriguing polymeric frameworks, in which the intralayer/interchain distance separated by the phenyl moiety is suitable to induce interesting metamagnetic

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transition [13,14]. More interestingly, the chemical modifications for the triazolate ligands can change their crystallographically symmetry and influence their binding behaviors towards the spin carriers, which can potentially lead to the asymmetric superexchange pathways for interesting canted antiferromagnetism. Apparently, the mixed carboxylate–triazolate mediators can play important and complicated roles for the resulting structures and magnetic properties of the resulting samples. To continuing the magnetostructural investigations of the triazolate–carboxylate-Co(II) ion-involved systems [15,16], self-assembly reactions of 3,5-diamino-1,2,4-triazole (Hdatrz) and inorganic Co^{II} sources were performed in the presence of different 5-substituted isophthalic acids (R-H_2ip) (R = –NH_2, –CH_3 and –NO_2). The particular purpose of the present contribution is to investigate the steric and/or electronic effect of the substituent appended around the isophthalate on the structure and magnetic properties. Herein, we report the syntheses, crystal structures and magnetic properties of the resulting four CPs.

2. Experimental

2.1. Materials and Instruments

All initial chemicals were commercially purchased (Hdatrz was from Acros and other analytical-grade reagents were from Tianjin Chemical Reagent Factory) and used as received without further purification. Elemental analyses for C, H and N were carried out with a CE-440 (Leeman-Labs) analyzer. Fourier transform (FT) IR spectra (KBr pellets) were taken on an Avatar-370 (Nicolet) spectrometer in the range 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) experiments were performed on a Shimadzu simultaneous DTG-60A compositional analysis instrument from room temperature to 800 °C under N_2 atmosphere at a heating rate of 5 °C/min. Powder X-ray diffraction (PXRD) patterns were obtained from a Rigaku D/max-2500 diffractometer at 60 kV and 300 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 2 deg/min and a step size of 0.02° in 2θ. The simulated PXRD patterns were calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4 program provided by the Cambridge Crystallographic Data Center. Magnetic susceptibilities were acquired on a Quantum Design (SQUID) magnetometer MPMS-XL-7 with crystalline samples, in which the phase purity of the samples were determined by PXRD experiments. The data were corrected for TIP and the diamagnetic corrections were calculated using Pascal's constants. The diamagnetism from the sample container were also corrected.

2.2. Preparation of {[Co_2(Hdatrz)(NH_2-ip)$_2$]·0.5H_2O}$_n$ (**1**)

A mixture containing $Co(NO_3)_2·6H_2O$ (58.2 mg, 0.2 mmol), Hdatrz (19.8 mg, 0.2 mmol) and NH_2-H_2ip (36.2 mg, 0.2 mmol) was dissolved in mixed H_2O–CH_3OH (v:v = 1:1, 10.0 mL) solution, and the initial pH value of the reactant mixture was adjusted to 6 by triethylamine. The resulting mixture was then transferred into a Teflon-lined stainless steel vessel (23.0 mL) and heated at 165 °C for 96 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 2.9 °C h^{-1}, red block-shaped crystals suitable for X-ray analysis were obtained directly, washed with water and dried in air (Yield: 50%, based on NH_2-H_2ip). *Anal.* Calc. for $C_{36}H_{32}Co_4N_{14}O_{17}$: C, 37.01; H, 2.76; N, 16.78. Found: C, 37.04; H, 2.65; N, 16.72%. IR (KBr pellet, cm^{-1}): 3409 (br), 3319 (w), 3167 (w), 1625 (s), 1588 (s), 1559 (s), 1481 (s), 1449 (s), 1386 (s), 1322 (w), 1011 (m), 985 (m), 952 (w), 797 (w), 778 (w), 724 (w), 666 (w).

2.3. Preparation of [Co(CH_3OH)(Hdatrz)(CH_3-ip)]$_n$ (**2**)

A mixture of Hdatrz (19.8 mg, 0.2 mmol), CH_3-H_2ip (36.0 mg, 0.2 mmol) and $Co(OAc)_2·4H_2O$ (24.9 mg, 0.1 mmol) was dissolved in mixed H_2O–CH_3OH (v:v = 1:1, 10.0 mL) solution, and the initial pH value of the reactant mixture was adjusted to *ca.* 6 by slow addition of triethylamine with constant stirring. The resulting mixture was then transferred into a Teflon-lined stainless steel vessel (23.0 mL) and heated at 160 °C for 96 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 1.4 °C h^{-1}, red block-shaped crystals suitable for X-ray analysis were obtained directly, washed with water and dried in air (Yield: 50%, based on Co^{II} salt). *Anal.* Calc. for $C_{12}H_{15}CoN_5O_5$: C, 39.14; H, 4.11; N, 19.02. Found: C, 39.14; H, 4.12; N, 19.05%. IR (KBr pellet, cm^{-1}): 3445 (s), 3333 (w), 3070 (w), 1670 (s), 1633 (s), 1546 (s), 1439 (s), 1370 (s), 1246 (w), 1083 (m), 1032 (m), 817 (w), 783 (m), 751 (w), 723 (m).

2.4. Preparation of {[Co_2(datrz)$_2$(CH_3-ip)]·2.5H_2O}$_n$ (**3**)

A mixture of Hdatrz (19.8 mg, 0.2 mmol), CH_3-H_2ip (18.0 mg, 0.1 mmol) and $Co(NO_3)_2·6H_2O$ (23.2 mg, 0.08 mmol) was dissolved in mixed H_2O–C_2H_5OH (v:v = 3:7, 10.0 mL) solution, and the initial pH of the reactant mixture was adjusted to *ca.* 7 by slow addition of triethylamine with constant stirring. The resulting mixture was then transferred into a Teflon-lined stainless steel vessel (23.0 mL) and heated at 150 °C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 5.2 °C h^{-1}, blue block-shaped crystals suitable for X-ray analysis were obtained directly, washed with water and dried in air (Yield: 40%, based on Co^{II} salt). *Anal.* Calc. for $C_{13}H_{19}Co_2N_{10}O_{6.5}$: C, 29.06; H, 3.56; N, 26.07. Found: C, 29.04; H, 3.53; N, 26.10%. IR (KBr pellet, cm^{-1}): 3446 (br), 3349 (w), 3244 (w), 1622 (s), 1582 (s), 1517 (s), 1380 (s), 1144 (w), 1107 (w), 1044 (w), 803 (w), 776 (m), 735 (m).

2.5. Preparation of {[Co(datrz)(NO_2-ip)]·H_2O}$_n$ (**4**)

A mixture of Hdatrz (9.9 mg, 0.1 mmol), NO_2-H_2ip (21.1 mg, 0.1 mmol) and $Co(NO_3)_2·6H_2O$ (14.5 mg, 0.05 mmol) was dissolved in doubly distilled water (15.0 mL), and the initial pH of the reactant mixture was adjusted to *ca.* 6 by slow addition of triethylamine with constant stirring. The resulting mixture was then transferred into a Teflon-lined stainless steel vessel (23.0 mL) and heated at 140 °C for 72 h under autogenous pressure. After the mixture was cooled to room temperature at a rate of 3.2 °C h^{-1}, pink block-shaped crystals suitable for X-ray analysis were obtained directly, washed with water and dried in air (Yield: 50%, based on Co^{II} salt). *Anal.* Calc. for $C_{20}H_{18}Co_2N_{12}O_{14}$: C, 31.27; H, 2.36; N, 21.88. Found: C, 31.25; H, 2.37; N, 21.86%. IR (KBr pellet, cm^{-1}): 3422 (br), 3336 (w), 3270 (w), 3083 (w), 1620 (s), 1571 (s), 1533 (s), 1366 (s), 1348 (s), 1200 (w), 1102 (w), 1068 (w), 822 (w), 785 (w), 753 (w), 735 (m), 718 (s), 669 (w), 563 (w), 525 (w), 477 (w), 433 (w).

2.6. X-ray data collection and structure determinations

Diffraction intensities for **1**–**4** were collected on a computer-controlled Bruker APEX–II QUAZAR diffractometer equipped with a graphite-monochromated Mo Kα radiation with a radiation wavelength of 0.71073 Å by using the φ–ω scan technique at 173 (for **1** and **2**), 296 (for **3**), and 150 K (for **4**), respectively. There was no evidence of crystal decay during data collection. Semiempirical multi-scan absorption corrections were applied by SADABS [17], and the program SAINT was used for integration of the diffraction profiles [18]. The structures were solved by direct