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Research paper

1,4-Cyclohexanedicarboxylato-bridged cobalt coordination polymers: Synthesis, crystal structures and magnetic properties

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ABSTRACT

Three coordination polymers have been synthesized, using self-assembly solution reactions at ambient conditions, combining Co(II) ion with 1,4-ciclohexanedicarboxylic acid, in the presence of 1,10-phenantrolione and two different 2,2′-bipyridines, as co-ligands: $[Co(H_2O)(cdc)(phen)]_n$ (**1**); $\{[Co(H_2O)(cdc)(4dmb)]\cdot 2H_2O\}_n$ (**2**); $\{[Co(H_2O)(cdc)(5dmb)]\cdot 3H_2O\}_n$ (**3**), where cdc = *e,a-cis*-1,4-ciclohexanedicarboxylato, phen = 1,10-phenantroline, 4dmb = 4,4′-dimethyl-2,2′-bipyridine, and 5dmb = 5,5′-dimethyl-2,2′-bipyridine. Crystallographic studies show that these compounds have one-dimensional (1D) structures; Co(II) in **1**–**3** is six-coordinated with a distorted-octahedral coordination sphere. Complexes **2** and **3** exhibit a novel bridging motif of the cdc ligand in its *equatorial, axial cis* configuration. In addition, the solid-state self-assembly of the polymeric structure of **1** gives rise to a 2D supramolecular framework, mainly through hydrogen bonding. In contrast, complex **2** forms an infinite 1D supramolecular array, made of double Co ion rows bridged by hydrogen bonding interactions. Complex **3** generates an intricate 2D supramolecular framework also throughout hydrogen bonding. The thermal stabilities of the three coordination polymers were investigated. Magnetic properties measurements reveal that complexes **1**–**3** exhibit weak antiferromagnetic ordering with $\theta_{(C\text{-}W)} = -9.6$, -5.8 and -7.5 K, and $E_2 = 0.51$, 0.16 and 0.28 cm^{-1}, accordingly to Curie-Weiss model and Rueff phenomenological approach, respectively.

1. Introduction

The design of hybrid metal-organic polymeric and supramolecular architectures, based on crystal engineering, has gained substantial interest in recent years in coordination chemistry, supramolecular chemistry and materials science, since these structures can acquire fascinating arrays and work as functional materials [1]. Crystal engineering refers to the construction of crystal structures from organic and metal-organic compounds using design principles that come from an understanding of the intermolecular interactions in the molecular solids [2]. Several strategies have been developed to synthesize metal mixed ligands coordination polymers of bivalent transition metals containing nitrogen and oxygen donor ligands [3]. Self-assembly of small molecules, compounds or complexes, proved to be a valuable procedure for the synthesis of large structures with a minimum of effort. However, the self-assembly process is sometimes accompanied by an uncertainty halo, due to unpredictable interactions among metal centers and ligands, especially when weak forces (e.g. hydrogen bonding, π-π interactions) and/or solvents, such as water, are involved [4]. Also, supramolecular frameworks based on metal centers and organic ligands have gained interest recently, due to their fascinating structural diversity and their potential applications in catalysis, sensing, porosity and non-linear optics [5]. Among the most used bridging ligands for transition metals are the dicarboxylates [6]. Perhaps the main reason to keep investigating the dicarboxylates as bridging ligands of metal centers, is the, at times, surprising variety of coordination modes that these organic compounds can accomplish, yielding thus interesting extended metal-organic molecular and supramolecular structures possessing divergent dimensionalities and properties [7]. Coordination polymers having cdc as bridging ligand have been prepared, though no so extensive; moreover, most of those compounds have been synthesized using solvothermal or hydrothermal methods [8]. The use of 2,2′-bipyridine as an ancillary ligand had become

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relevant in our previous studies on complexes [9] and coordination polymers [10] of different metals. Therefore, we decided to continue with one of the most studied nitrogen donor ligands [11], but varying its alkyl substituent, in order to verify the influence of the co-ligand on the dimensionalities and crystalline structures of the resulting coordination polymers. So far, few articles have been published on the use of different di-alkyl-2,2′-bipyridines as ancillary ligands, either in transition metal complexes [12] or coordination polymers [13,14].

In this article, we describe the synthesis, crystalline molecular and supramolecular structures, thermal analyses and magnetic properties of three coordination polymers of three coordination polymers of formulae $[Co(H_2O)(cdc)(phen)]_n$ (**1**), $\{[Co(H_2O)(cdc)(4dmb)]\cdot 2H_2O\}_n$ (**2**) and $\{[Co(H_2O)(cdc)(5dmb)]\cdot 3H_2O\}_n$ (**3**) (cdc = *e,a-cis*-1,4-ciclohexanedicarboxylato, phen = 1,10-phenantroline, 4dmb = 4,4′-dimethyl-2,2′-bipyridine, and 5dmb = 5,5′-dimethyl-2,2′-bipyridine).

2. Experimental section

2.1. General considerations

All chemicals were of analytical grade, purchased commercially (Aldrich) and used without further purification. All syntheses were carried out under aerobic and ambient conditions. Elemental analyses for C, H, N were obtained by standard methods using a Vario Micro-Cube analyzer. IR spectra of the complexes were determined in a FT-IR Shimadzu spectrophotometer, IR Prestige-21, from 4000 to 500 cm^{-1}. Thermogravimetric analyses were performed in a SDT Q600 TA Instruments analyzer, under N_2 atmosphere, at a heating rate of 10 °C min^{-1}, from 20 to 700 °C. Magnetic characteristics of the complexes were determined with a MPMS Quantum Design magnetometer, with measurements performed at zero field cooling (ZFC) and field cooling (FC) from 2 to 300 K and decreasing. The applied magnetic field was 1000 Oe, and diamagnetic corrections were estimated using Pascal's constants as -250×10^{-6} cm^3mol^{-1}.

2.2. Preparation of $[Co(H_2O)(cdc)(phen)]_n$ (*1*)

Initially, sodium 1,4-cyclohexanedicarboxylate was prepared by adding an aqueous solution of NaOH (5 mL; 0.16 M) to a methanol solution (5 mL) of 1,4-cyclohexanedicarboxylic acid (0.0688 g; 0.4 mmol). A solution of 1,10-phenantroline (0.0744 g; 0.4 mmol) in methanol (5 mL) was added to the solution of sodium 1,4-cyclohexanedicarboxylate while stirring. Then, a de-ionized water solution (10 mL) of $Co(NO_3)_2\cdot 6H_2O$ (0.1164 g; 0.4 mmol) was added. A red-brown translucent solution was obtained. After five days, purple-brown crystals were achieved; these were filtered out and washed with de-ionized water. Yield: 49% based on metal precursor. Elemental analysis (%), $C_{20}H_{20}N_2O_5Co$, cal.: C, 56.21; H, 4.71; N, 6.55; found: C, 56.25; H, 4.64; N, 6.50. IR cm^{-1} (ATR): 3228 (m, br), 2924 (m), 1554 (s), 1516 (m), 1427 (m), 1404 (m), 1203 (s), 1146 (s), 964 (s), 910 (s), 841 (m, sh), 725 (m, sh), 671 (m, sh).

2.3. Preparation of $\{[Co(H_2O)(cdc)(4dmb)]\cdot 2H_2O\}_n$ (*2*)

Comparable conditions as in the synthesis of **1** were used, except that a solution of 4,4-dimetil-2,2′-bipyridine (0.0720 g; 0.4 mmol) in methanol (10 mL) was added to the solution of sodium 1,4-cyclohexanedicarboxylate while stirring. Yield: 43% based on metal precursor. Elemental analysis (%), $C_{20}H_{28}N_2O_7Co$, cal.: C, 51.39; H, 6.03; N, 5.99; found: C, 51.06; H, 6.02; N, 6.03. IR cm^{-1} (ATR): 3259 (m, br), 2943 (w), 1616 (m, sh), 1538 (s), 1512 (m), 1457 (m, sh), 1409 (s), 1014 (w, sh), 914 (m), 829 (m, sh), 767 (m, sh).

2.4. Preparation of $\{[Co(H_2O)(cdc)(5dmb)]\cdot 3H_2O\}_n$ (*3*)

Similar conditions as in the synthesis of **1** were used, except that a solution of 5,5′-dimethyl-2,2′-bpyridina (0.0720 g; 0.4 mmol) in methanol (10 mL) was added to the solution of sodium 1,4-cyclohexanedicarboxylate. Yield: 64% based on metal precursor. Elemental analysis (%), $C_{20}H_{30}N_2O_8Co$, cal.: C, 49.49; H, 6.23, N, 5.77; found: C, 50.02; H, 6.05; N, 5.58. IR cm^{-1} (ATR): 3420 (w, br), 2940 (w, sh), 1527 (s), 1470 (m, sh), 1427 (m, sh), 1404 (s, sh), 1349 (m, sh), 1254 (m, sh), 1144 (w, sh), 1044 (m, sh), 902 (w, sh), 841 (m, sh), 757 (m, sh), 687 (m, sh), 587 (m, sh).

3. X-ray crystallography

Crystallographic data for **1**–**3** were collected on a Bruker APEX II CCD Diffractometer, for **1** and **2** at 100 K and for **3** at 296 K, using Mo-Kα radiation (k = 0.71,073 Å) from an Incoatec IμS source and Helios optic monochromator [15]. Suitable crystals were coated with hydrocarbon oil (Parabar), picked up with a nylon loop, and mounted in the cold nitrogen stream of the diffractometer. The structures were solved using intrinsic phasing (SHELXT) [16] and refined by full-matrix least-squares on F^2 [16] using the shelXle GUI [17]. The hydrogen atoms of the C—H bonds were placed in idealized positions whereas the hydrogen atoms from water molecules were localized from the difference electron density map, and their position was refined with U_{iso} tied to the parent atom with distance restraints. In compound **2**, the hydrogens from water molecules that are not coordinated to cobalt present positional disorder in two positions, the occupation was set at 50% and their position were localized from the difference electron density map and refined using DFIX instruction. The hydrogens for methyl group (C11) present positional disorder in two positions that was solved using AFIX 123 constraint to fix the positions of hydrogens and the occupancy was fixed in 50%. The crystallographic data and refinement details for the polymers are summarized in Table S1. Selected bond lengths, angles and hydrogen bonding interactions for **1**–**3** are listed in Tables S2, S3 and S4, respectively.

4. Results and discussion

4.1. Synthesis and IR spectra

Using a very simple methodology of self-assembling solution reactions, equivalent amounts of 1,4-cyclohexanedicarboxylic acid, $Co(NO_3)_2$, and 1,10-phenantroline, 4,4′-dimethyl-2,2′-bipyridine and 5,5′-dimethyl-2,2′-bipyridine, respectively, were mixed in water-methanol solutions under ambient conditions. Slow evaporation of solvents yielded reddish-brown crystals of complexes **1**–**3**. These crystals are insoluble in common solvents.The IR spectra of the complexes show the typical bands (*vide supra*) expected for carboxylate ligands coordinated to Co(II) [18,19], along to the bands corresponding to the auxiliary ligands (Figs. S1–S3). Since the cdc bridging ligand has the same coordination modes in polymers **1**–**3**, relatively few variances can be observed in the IR spectra of these complexes. These IR spectra show two sets of asymmetric stretches for the carboxylate moiety at 1554 and 1516 cm^{-1}, 1538 and 1512 cm^{-1}, 1527 and 1470 cm^{-1}, with the corresponding symmetric stretches at 1404 and 1427 cm^{-1}, 1409 and 1457, 1404 and 1427 for **1**–**3**, respectively. The differences between asymmetric and symmetric stretch for the carboxylate ion ($\Delta\nu_{COO}^{-}$, cm^{-1}) are 150 and 89, 129 and 55, and 123 and 43, for **1**–**3**, respectively. These sets of bands can be assigned, correspondingly, to the bidentate chelate and monodentate coordination modes of the cdc ligand found in these complexes [20].