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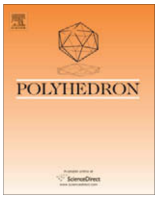

Role of weak interactions in controlling the topology of coordination polymeric chains in $[Pt(CN)_4]^{2-}$ bridged Cu(II) complexes: Syntheses, crystal structure and magnetic studies

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ABSTRACT

Four coordination polymeric complexes, $[\{Cu_2(aepn)_2Pt(CN)_4{\cdot}H_2O\}(H_2O)\{Pt(CN)_4\}]_n$, (**1**), $[\{Cu(dpt)_2Pt(CN)_4\}]_n$ (**2**), $[\{Cu(dien)Pt(CN)_4\}]_n$ (**3**) and $[\{Cu(iprdien)Pt(CN)_4\}]_n$ (**4**) (where aepn = *N*-(2-aminoethyl)-1,3-propanediamine, dpt = 3,3′-imino bispropylamine, dien = diethylenetriamine, iprdien = *N*′-isopropyl-diethylenetriamine), have been synthesized and characterized by X-ray single crystal structure determination and variable temperature magnetic measurements. The formation of the supramolecular assemblies has been rationalized and it has been shown that competition between coordinative forces and hydrogen bonding interactions is crucial in the determination of final solid-state packing. A zig-zag/helical 1D chain (**2** and **3**) appears when the chelating amine at the Cu(II) center is capable of forming the maximum number of hydrogen bonds, on the other hand when one or more of the amine sites are blocked, due to the prevention of the maximization of hydrogen bonding, (4,2) ribbons (**1** and **4**) appear. Variable temperature magnetic measurement shows the presence of weak antiferromagnetic interactions in all the complexes.

1. Introduction

The packing of 1D/2D coordination polymers in the solid-state is generally controlled by weak interactions [1,2] and for 3D coordination polymers these weak forces also can play many important roles [3,4]. Therefore, for the successful design of coordination polymers with specific functional properties, knowledge of the interplay between coordinative forces and weak forces is a prerequisite. It has been shown in many cases that a number of weak forces, by their mutual cooperation, can compete with coordinative forces resulting in a different architecture to the one expected on consideration of the coordinative forces alone [5,6]. For designing coordination polymers of intended dimensionality having a specific property, the proper choice of a suitable metal node and bridging or chelating organic ligands is key. The cyano group, in this respect, has been widely utilized in various fields like luminescence [7,8], catalysis [9,10], molecular sieves [11–14], ion exchange [15], selective binding of guest molecules [16–18] and magnetism [19–24]. Wide varieties of cyanometallate anions have been used for the construction of 1D [25,26], 2D [27–29] and 3D [30–32] coordination polymers or discrete metal clusters [33,34]. Recently, we have reported [35] a number of cyanometallate complexes where $[Ni(CN)_4]^{2-}$ has been utilized to bridge different metal nodes and a new coordination mode of $[Ni(CN)_4]^{2-}$ was observed [36] giving rise to a (4,2) ribbon-like chain (Scheme 1). A literature [37–43] and CSD survey has revealed that these type of cyanometallate bridged 1D coordination polymers usually comes either as a single file zig-zag/helical chain or a (4,2) ribbon-like chain (Scheme 1). Also, coordination polymers of these types of topologies are ideal for testing theoretical models of interacting spin chains in the emerging field of single chain magnets (SCM) [44–46]. Therefore, understanding the reasons that govern the appearance of the above mentioned topologies is important from a crystal engineering point of view. In this paper, we wish to report four new $[Pt(CN)_4]^{2-}$ bridged coordination polymers of Cu(II) and their magnetic properties. A careful analyses of the crystal packing forces reveal that the appearance of a 1D zig-zag/helical or (4,2) ribbon topology is possibly the outcome of subtle competition and cooperation between coordinative and weak forces. We show that among a set of chelating co-ligands that bear lesser hydrogen bonding sites, the coordinative force wins resulting in (4,2) ribbons, but when there are more hydrogen bonding sites, zig-zag or helical chains appear.

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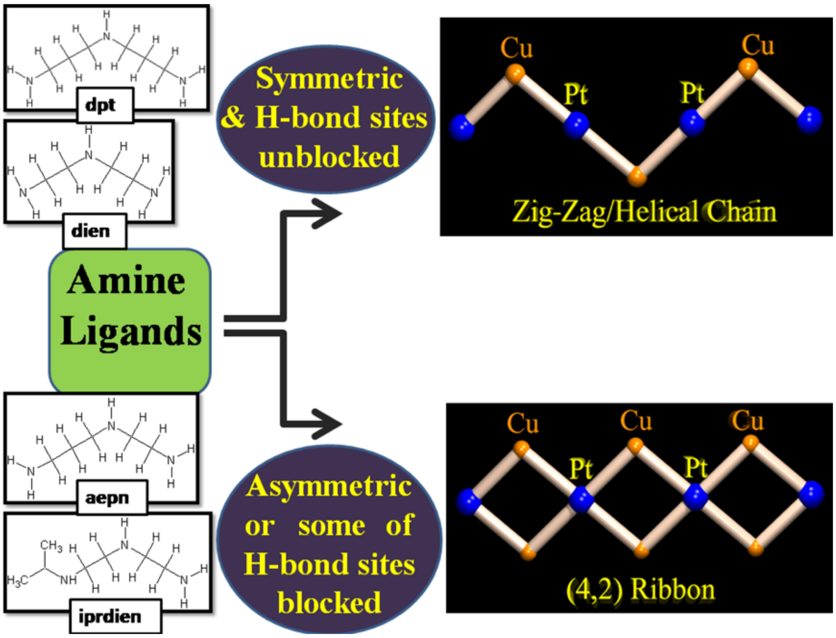

Scheme 1.

2. Experimental

2.1. Materials

High purity (98%) *N*-(2-aminoethyl)-1,3-propanediamine (aepn), diethylenetriamine (dien), 3,3′-imino bispropylamine (dpt), N′-isopropyldiethylenetriamine (iprdien) and potassium tetracyanoplatinate(II) were purchased from the Aldrich Chemical Co. Inc. and were used as received. All others chemicals were of AR grade.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet 520 FTIR spectrometer. The magnetic measurements were carried out on polycrystalline samples using a Quantum Design MPMS SQUID magnetometer working in the temperature region 300–2 K. Diamagnetic corrections were estimated from Pascal's table [47].

2.3. Synthesis

2.3.1. $[\{Cu_2(aepn)_2Pt(CN)_4 2H_2O\}\cdot 2(H_2O)\cdot\{Pt(CN)_4\}]_n$ (**1**)

N-(2-aminoethyl)-1,3-propanediamine (aepn) (2 mmol, 0.234 g) was added dropwise to an aqueous solution (10 cm^3) of $Cu(ClO_4)_2{\cdot}6H_2O$ (2 mmol, 0.741 g) with constant stirring for a few minutes. To the resulting deep blue solution, an aqueous solution (10 cm^3) of $K_2[Pt(CN)_4]{\cdot}2H_2O$ (2 mmol, 0.754 g) was added slowly and the reaction mixture was stirred for 1 h and then filtered and the filtrate was kept in a $CaCl_2$ desiccator. Shiny deep blue single crystals suitable for X-ray analysis were obtained after a few days. Yield 65%. *Anal.* Calc. for $C_{18}H_{38}Cu_2N_{14}O_4Pt_2$ (**1**): C, 20.95; H, 3.71; N, 19.00. Found: C, 20.75; H, 3.64; N, 19.16%. IR spectra (KBr disk; cm^{-1}) 3300–3500 [ν(O–H)]; 3200–3400 [ν(N–H)]; 2141 [ν(C–N)].

2.3.2. $[\{Cu(dpt)Pt(CN)_4\}]_n$ (**2**)

Complex **2** was synthesized by the same procedure adopted for **1** using 3,3′-imino bispropylamine (dpt), (2 mmol, 0.262 g) instead of aepn. Yield 70%. *Anal.* Calc. for $C_{10}H_{17}CuN_7Pt$ (**2**): C, 24.29; H, 3.44; N, 19.84. Found: C, 24.25; H, 3.41; N, 19.82%. IR (KBr disk; cm^{-1}) 3200–3400 [ν(N–H)]; 2138 [ν(C–N)].

2.3.3. $[\{Cu(dien)Pt(CN)_4\}]_n$ (**3**)

Complex **3** was synthesized by the same procedure adopted for **1** using diethylenetriamine (dien) (2 mmol, 0.206 g) instead of aepn. Yield 70%. *Anal.* Calc. for $C_8H_{13}CuN_7Pt$ (**3**): C, 20.61; H, 2.79; N, 21.04. Found: C, 20.59; H, 2.76; N, 21.01%. IR (KBr disk; cm^{-1}) 3200–3400 [ν(N–H)]; 2155 [ν(C–N)].

2.3.4. $[\{Cu_2(iprdien)_2Pt(CN)_4\}\cdot 2(ClO_4)\cdot 2(H_2O)]_n$ (**4**)

Complex **4** was synthesized by the same procedure adopted for **1** using N′-isopropyldiethylenetriamine (iprdien) (2 mmol, 0.284 g) instead of aepn. Yield 70%. *Anal.* Calc. for $C_{18}H_{32}Cu_2N_{10}PtCl_2O_8$ (**4**) C, 23.65; H, 3.82; N, 15.14. Found: C, 23.75; H, 3.52; N, 15.39%. IR (KBr disk; cm^{-1}) 3200–3400 [ν(N–H)]; 2190, 2181, 2140 [ν(C–N)].

2.4. Crystallographic data collection and refinement

Diffraction data collection of all four complexes was carried out on a Bruker SMART diffractometer, equipped with a graphite monochromator and Mo Kα radiation ($\lambda = 0.71073$ Å). The data integration and reduction were processed with SAINT [48] software. An empirical absorption correction was applied to the collected reflections with SADABS [49] using XPREP [50]. The structures were solved by the Patterson method. Metal atoms in all four complexes were located from the *E*-maps. Other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The water hydrogen atoms in **1** were located from the difference Fourier map and refined isotropically but the positions of the hydrogen atoms attached to the carbon atoms were calculated geometrically with a fixed thermal parameter 1.2 times that of their parent atoms. Water hydrogen atoms in **4** could not be located from the difference Fourier map. Crystallographic data and experimental details for the structural analyses are listed in Table 1. Large residual electron densities in **1** and **3** are within 1 Å of the heavy metals (Pt) and are due to a series truncation error having no chemical significance. All calcula-