

A two-dimensional magnetic architecture with bridging polynitrile and 2,2'-bipyrimidine ligands

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Abstract. A new polymeric, two-dimensional compound $[\text{Co}_2(\text{bpym})(\text{dcne})_4(\text{H}_2\text{O})_2]$ (**1**) ($\text{dcne} = [(\text{CN})_2\text{CC}(\text{O})\text{OEt}]^- = 2,2\text{-dicyano-1-ethoxyethenolate anion}$ and $\text{bpym} = 2,2'\text{-bipyrimidine}$) has been synthesized and characterized by X-ray crystallography. The structure is monoclinic space group $P2_1/a$ and consists of two-dimensional networks of octahedrally coordinated Co(II) ions, bridged by bis-bidentate 2,2'-bipyrimidine and $\mu_2\text{-dcne}$ anions. Magnetic measurements revealed a broad maximum in the χ_m vs T plot at 20 K which is characteristic of antiferromagnetic exchange between the high spin cobalt(II) centres.

Key words. Cobalt complexes, magnetic measurements, 2,2'-bipyrimidine.

1. INTRODUCTION

By taking into account the crucial role of the bridging ligands in determining the magnetic properties of polynuclear or polymeric derivatives, we have combined two types of bridging ligands with transition metal ions to generate new molecular architectures associated with new properties. In this context, focusing on polynitrile ligands [1-5], we recently described two compounds, $[\text{Fe}_2(\text{dca})_4(\text{bpym})]\cdot\text{H}_2\text{O}$ and $[\text{Fe}_2(\text{dca})_4(\text{bpym})(\text{H}_2\text{O})_2]$ ($\text{bpym} = 2,2'\text{-bipyrimidine}$ and $\text{dca}^- = \text{dicyanamide anion}$) in which the Fe(II) ions are bridged by bis-bidentate bpym and dicyanamide ligands [4]. We now report the synthesis, structural characterization and magnetic properties of the new polymeric compound $[\text{Co}_2(\text{bpym})(\text{dcne})_4(\text{H}_2\text{O})_2]$ (**1**) with the dcne^- anion ($[(\text{CN})_2\text{CC}(\text{O})\text{OEt}]^- = 2,2\text{-dicyano-1-ethoxyethenolate anion}$).

2. RESULTS AND DISCUSSION

The reagents bpym (0.126 mmol) and K(dcne) (0.504 mmol) were successively added with continuous stirring to a hot aqueous solution of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.252 mmol). The resulting solution was slowly evaporated to yield orange crystals of **1**, which were removed by filtration.

2.1 Structure

In this structure [6], each metal ion is in a highly distorted octahedral CoN_5O environment occupied by two *cis*-bridging dcne^- ligands, one bis-chelating bpym, and two unidentate ligands (one terminal dcne and one water molecule) in a *cis*-arrangement (Figure 1). The selected bond lengths listed in the legend of figure 1 reveal the distorted octahedral environment of the metal ion. As observed in several bpym coordination compounds [4, 7], a significant distortion also arises from the small bite angle of the bpym ligand ($76.46(7)^\circ$). The extended structure is best described as dcne -bridged, zigzag-chains, running along the [100] direction, which are connected to each other, in the [010] direction, by the bis-chelating bpym ligand (Figure 1). The shortest Co...Co separation through the bpym bridges (5.785 Å) is close to the values reported for other cobalt(II)-bpym derivatives [7]. The metal-metal

separation through the dcne⁻ bridge (8.088 Å) is longer than the analogous distance observed in the 1-D compound [Co(dcne)₂(H₂O)₂] (7.4270 Å) [5].

2.2 Magnetic Properties

The magnetic properties of compound 1 are displayed in figure 1 as the thermal dependences of the χ_m and $\chi_m T$ product, where χ_m is the magnetic susceptibility per mol of two metal ions. The room temperature value of 5.38 emu.K.mol⁻¹ is in the range expected for two octahedral high spin Co(II) ions. When the temperature is lowered, a decrease in the $\chi_m T$ product is observed. This feature is attributed to the anisotropy of the Co^{II} ions. Below 150 K there is a change in slope, and the $\chi_m T$ product decreases more rapidly until it reaches values close to zero at very low temperatures. This indicates the presence of nearest neighbor antiferromagnetic interactions. This conclusion is corroborated by the presence of a maximum in the χ_m vs. T plot around 20 K. A simple model to fit these data is not available due to the high anisotropy of the Co^{II} ions, and therefore no quantitative data can be extracted at this point.

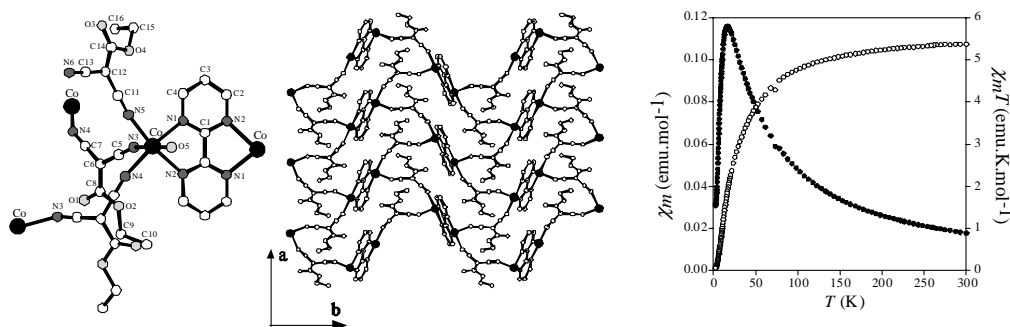


Figure 1. Asymmetric unit, two-dimensional structure (the two terminal ligands are omitted for clarity) and thermal variations of χ_m (●) and $\chi_m T$ (○) for 1. Selected bond lengths (Å) and bond angles (°): Co-N1 2.154(2); Co-N2 2.187(2); Co-N3 2.109(2); Co-N4 2.120(2); Co-N5 2.063(2); Co-O5 2.053(2); N1-Co-N2 76.46(7); N1-Co-N4 169.96(8); N1-Co-N5 94.12(8); N2-Co-N4 94.08(8); N2-Co-N5 170.27(8); N2-Co-O5 86.20(7).

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