

A one-dimensional copper (II) coordination polymer $[\text{Cu}_3(\text{ampym})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]_n$ (ampym = 2-aminopyrimidine) containing both end-on and end-to-end azido bridges

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Abstract

A new polynuclear copper (II) complex, derived from the azido-bridging ligand and 2-aminopyrimidine, has been synthesized and its 3-D structure has been determined by X-ray diffraction methods at two different temperatures. The compound crystallizes in the triclinic system $P\bar{1}$ space group, with the central copper atom lying on an inversion centre. The crystal structure is built up by trinuclear units (each of them contains two double end-on azido bridges) linked through two azide ions in an end-to-end (EE) fashion, to yield the polymer chain $[\text{Cu}_3(\text{ampym})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]_n$. Magnetic susceptibility measurement shows a ferromagnetic interaction above 30 K, whereas a weak anti-ferromagnetic interaction prevails in the range of 30–2 K.

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1. Introduction

Investigation into the structural and magnetic properties of the polynuclear transition metal complexes [1] has been a fascinating subject in the field of coordination chemistry, materials chemistry and condensed matter physics [2]. The use of a variety of different bridging ligands has afforded an interesting array of molecular systems with new architecture. Among them, the azido ion is known to be a versatile ligand for generating such bridged systems [3,4], and particularly, it is a most effi-

cient ligand as regards the super exchange pathways between paramagnetic centres. The amount of work concerning magneto-structural studies of azido bridged compounds with first-row transition metal ions is really impressive [5]. The main reasons for the success of the azido ligand stem from: (1) the remarkable ability to transmit large ferromagnetic or anti-ferromagnetic interactions when adopting the end-on (EO mode) or end-to-end (EE mode) bridging modes; (2) its great coordinative versatility (it can behave like a terminal monodentate or a bridging di-, tri- and tetradentate ligand) which leads to a great variety of structural types, with the possibility of giving three dimensional compounds [6]. In addition, the azide group has been used

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to study the interaction between small molecules and the metal centre of metalloenzymes [7]. It is now well established that the nature of the magnetic interaction in azido-bridged complexes depends on the mode of coordination between the metal ions and the bridging azido group [6]. In symmetric dibridged end-on azido dimers, the interaction is known to be ferromagnetic [8], while with one (or more) symmetric end-to-end azido bridges the interaction is strongly antiferromagnetic [9]. Complexes with asymmetric end-to-end azido bridges are usually weakly antiferromagnetic, whereas complexes with asymmetric end-on azido bridges are rare and show a weak to moderately strong ferromagnetic interaction.

Structural and magnetic studies of metal complexes with 2-aminopyrimidine (abbreviated as ampym) are of considerable interest due to the coordination diversity exhibited by the ligand, allowing also bridging between metal ions [10]. Metal compounds with ampym have been widely investigated [11,12]. In the case of copper (II) complexes, the structures appear to depend on the nature of the used anion and on the synthetic method. For example, with halides, mononuclear and polymeric compounds have been obtained in which ampym acts as monodentate or didentate ligand [12]. With other anions like sulfate [13], triflate [45], nitrate [46] and dicyanamide [47], mononuclear or polynuclear Cu(II) compounds have been obtained with ampym acting as a monodentate ligand, while reaction of ampym with copper (II) tetrafluoroborate results in the formation of a very complicated trinuclear-based polymeric complex [48].

Since coordination compounds with either azido bridges or ampym ligand have shown very interesting structural and magnetic properties, most remarkably the combination of ampym and azide has not yet been studied. In fact, one would expect copper (II) complexes containing both ampym and azido ligands to result in some special properties, as both ligands can mediate magnetism. In this paper, we present the synthesis, structural characterization and magnetic study of the polymeric complex $[\text{Cu}_3(\text{ampym})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]_n$. The magnetism of this compound can be nicely explained by its lattice structure.

2. Experimental

2.1. General remarks

All reagents and solvents were purchased from commercial sources and used as received. C, H, N analyses were carried out on a Perkin–Elmer 2400 series II analyzer. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 spectrophotometer equipped with a Golden Gate Diamond ATR device, using the diffuse

reflectance technique. X-Band EPR spectra were recorded at room temperature and at 77 K on a Jeol RE2X electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. The UV–Vis spectrum of the compound was recorded in the 250–800 nm range on a Cary 50 Varian UV–Vis–NIR spectrometer. The ligand-field spectrum of the solid compound was recorded in the range of 200–2000 nm on a Perkin–Elmer Lambda 900 UV–Vis–NIR spectrometer in the diffuse reflectance mode with MgO as a reference. Electrospray ionization mass spectrum (ESI-MS, positive ion) in a methanol solution was recorded on a Thermo Finnigan AQA apparatus.

2.2. Synthesis of $[\text{Cu}_3(\text{ampym})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]_n$

Warning! The reported azido complex is potentially explosive. Even though no explosions occurred in our hands, only small amounts of material should be prepared, and it should be handled with care.

Copper (II) nitrate trihydrate (4.0 mmol, 0.38 g) and 2-aminopyrimidine (1.5 mmol, 0.36 g) were dissolved and mixed in 40 cm³ of acetone. An aqueous solution of NaN₃ (2.5 mmol, 0.16 g) was slowly added to this mixture under stirring. DMF (15 mL) was subsequently added to dissolve the precipitate and the final clear solution was allowed to evaporate slowly in the air. Crystals suitable for X-ray were obtained after 1 week. Yield 56%. *Anal.* Calc. for C₁₄H₂₄Cu₃N₂₆O₂: C, 21.6; H, 3.1; N, 46.7; Cu, 24.5. Found: C, 21.5; H, 2.8; N, 46.3; Cu, 24.7%. IR (cm⁻¹): 3319.9 (m), 3138.1 (m), 2070.0 (s), 2037.2 (s), 1643.8 (s), 1567.5 (s), 1501.7 (m), 1367.6 (s), 1285.3 (s), 1098.6 (m), 790.1 (s), 667.8 (s), 590.9 (m), 483.7 (s), 366.2 (m).

2.3. Crystallographic data collection and refinement

The molecular structure of $[\text{Cu}_3(\text{ampym})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]_n$ was determined by single-crystal X-ray diffraction methods at 298 and 173 K. Crystallographic and experimental details for the structure are summarized in Table 1.

For the room temperature structure, intensity data and cell parameters were recorded at room temperature (25 °C) on a Bruker AXS Smart 1000 single-crystal diffractometer (Mo K α radiation) equipped with a CCD area detector. The data reduction was performed using the SAINT and SADABS programs [18]. The structure was solved by Direct Methods using the SIR97 program [51] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program [52]. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were found in the difference Fourier map with the exception of the six methyl-hydrogens of the coordi-

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