

Crystal structure, magnetic properties and spectroscopic characterization of a rare *syn–anti* acetato-bridged zig-zag chain copper(II) complex

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Abstract

The reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with dpa (in which dpa = *N,N*-bis(pyridin-2-ylmethyl)amine) in the presence of CH_3COOH results in the formation of a linear chain copper(II) complex, $\{[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 0.5\text{THF}\}_n$ (**1**), containing *syn–anti* acetato bridges. The copper(II) atoms display a slightly distorted square-pyramidal geometry with a N_3O_2 chromophore group and with Cu–O distances of 1.950(2), 2.388(3) Å and Cu–N distances which vary from 1.984(3) to 1.998(3) Å. The intra chain Cu···Cu separation is 4.039 Å. The EPR spectra of solid **1** shows at RT an unresolved $S = 1/2$ signal with g_{\perp} of 2.06 and g_{\parallel} of 2.24; the frozen solution EPR has values of g_{\perp} of 2.04, g_{\parallel} of 2.26 and A_{\parallel} of 17.9 mT, typical for a $\text{CuN}_3\text{O}(\text{O})$ chromophore. The magnetic susceptibility measurements (5–300 K) agree with a very weak ferromagnetic chain interaction between the Cu centres with a J value of 0.21 cm^{-1} .

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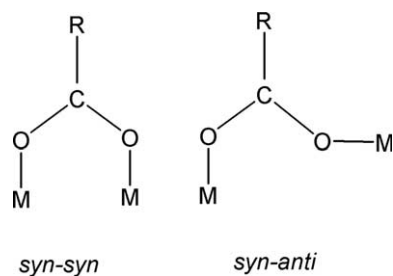
Keywords: Copper; Acetato bridge; Polynuclear

1. Introduction

During the past decades, metal–carboxylate chemistry has received a great deal of attention in several different fields ranging from metallobiochemistry to catalysis and materials chemistry. The main interest in this chemistry arises from: (i) the versatility of the coordination modes of the simple carboxylate anions which leads to fascinating molecular architectures; (ii) the key role of the carboxylate as ligand in biological systems involving mono- or polynuclear active sites; and (iii) the property of carboxylate bridge to exhibit an exchange path mediating the interaction among spins that are localized on

paramagnetic centres. Carboxylate ligands exhibit several coordination modes to the metal centre leading to a variety of polynuclear complexes ranging from discrete entities to multi-dimensional systems. One-dimensional copper(II) compounds containing carboxylate bridges are especially important in the area of molecule based-magnets [1,2] and high-temperature oxide-superconductors [3]. With the tridentate ligand used in this study, *N,N*-bis(pyridin-2-ylmethyl)amine (abbreviated as dpa), only a few Cu(II) X-ray structures are reported with dpa as the only coordinating ligand [4–8]. With acetate as a bridging ligand, several interesting structures with special magnetic properties have been reported for a number of dinuclear Cu(II) compounds [9–13]. The acetate ligand can adopt two different bridging conformations, the *syn–syn* mode and the *syn–anti* mode (see

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Scheme 1.

Scheme 1). Specially, the *syn-anti* mode confirmation is very rare and only a limited number of X-ray structures have been reported with this *syn-anti* acetate bridging mode [9,10,12,14–20].

However, to the best of our knowledge, so far only one polymeric Cu(II) structure with an N-containing ligand has been published with acetate as the bridging molecule in a $[-\mu\text{-OAc-Cu}-\mu\text{-OAc-Cu}]_n$ fashion [9].

In this study, we report the synthesis, spectroscopic characterization and magnetic properties of $\{[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 0.5\text{THF}\}_n$, a new polymeric copper(II) compound with an infinite zig-zag chain structure, having the acetate ligand in a *syn-anti* bridging mode.

2. Experimental

2.1. General remarks and physical measurements

All starting reagents and solvents were purchased from commercial sources and were used as received. C, H, N analyses were performed on a Perkin–Elmer 2400 Series II analyzer. Infrared spectra ($4000\text{--}300\text{ cm}^{-1}$) were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. Ligand field spectra were obtained on a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. Magnetic susceptibility measurements ($5\text{--}300\text{ K}$) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.2. Synthesis of the compound

To an acetonitrile solution (10 ml) containing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.37 g, 1 mmol) and dpa (0.2 g, 1 mmol) was added slowly an acetonitrile (5 ml) solution containing CH_3COOH (0.02 g, 0.33 mmol) and Et_3N (0.03 g, 0.33 mmol). The reaction mixture was stirred for

10 min and was then filtered to remove the impurities. The resulted blue filtrate was diluted with 10 ml of THF and it was allowed to stand at room temperature. After 2 days dark blue crystals were obtained. Yield: 0.31 g (ca. 66%). *Anal.* Calc. for $\text{C}_{16}\text{H}_{19}\text{ClCuN}_3\text{O}_{6.5}$: C, 42.1; H, 4.2; N, 9.2. Found: C, 42.7; H, 4.5; N, 8.9%. UV–Vis ($\lambda_{\text{max}}/\text{nm}$): 632, 380, 314, 279.

The positive ion mass spectrum of a fresh solution of the compound in acetonitrile exhibits a prominent signal at $m/z = 320$ (relative intensity $I = 100\%$ in the range $m/z = 100\text{--}500$). This signal matches very well with the calculated isotopic distribution for $[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})]^+$.

2.3. X-ray crystallography and data collection

Intensity data for a single crystal were collected using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) on a Nonius KappaCCD diffractometer. The structure was solved by automated Patterson methods using DIRDIF-99 [21] and was refined on F^2 by least-squares procedures using SHELXL-97 [22]. A SADABS multiscan correction [23] was applied. The hydrogen atoms of the methyl group were refined as rigid rotors to match maximum electron density in a difference Fourier map. All other hydrogens were placed at calculated positions and were refined riding on the parent atoms. The THF molecule is disordered around a centre of symmetry. A suitable disorder model could be defined in which the THF molecule partly occupies one of the two possible positions and orientations, each having a site occupation factor of 0.5. Geometric calculations and molecular graphics were performed with the PLATON package [24]. Crystallographic data are listed in Table 1.

Table 1
Crystallographic data for the $\{[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 0.5\text{THF}\}_n$

Chemical formula	$\text{C}_{16}\text{H}_{19}\text{ClCuN}_3\text{O}_{6.5}$
Molecular weight	456.34
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
a (\AA)	10.6956(6)
b (\AA)	7.7949(3)
c (\AA)	23.3892(13)
β ($^\circ$)	99.064(5)
V (\AA^3)	1925.63(17)
Z	4
D_{calc} (Mg m^{-3})	1.574
μ (Mo $\text{K}\alpha$) (mm^{-1})	1.314
Crystal size (mm)	$0.26 \times 0.20 \times 0.07$
T (K)	208
Data collected	39520
Unique data	4417
R_{int}	0.045
$R(F)$ [$I > 2\sigma(I)$]	0.0570
R_w (F^2)	0.1475
S	1.06
$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ (e \AA^{-3})	–0.65 and 1.33

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