Synthesis, Crystal Structure, and Magnetic Properties of a One-Dimensional Polymeric Copper(II) Complex, Containing Unicoordinated Phthalato Bridges

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Introduction

In recent studies[1,2] our attention has been focused on the investigation of the ability of the phthalate dianion (phth) to support long-range ferromagnetic interactions. It was shown that the variations in ω—the angle between the planes of the two carboxylato groups of each phthalato intervening bridge—could play a significant role on the magnetic behavior of the complex. Moreover, it is well-known that, copper(II)−phthalato complexes have been of considerable structural interest.[3,4] To the best of our knowledge, however, it has been found that in almost all cases the phthalate dianion acts as a bridging ligand from both its carboxylate groups. As a consequence, almost all Cu^{II}−phthalato complexes are chain or layer-type polymers in which the phth dianion bridges the Cu ions. There has been only one case[4h] in which phth dianions do not act as bridging ligands, since they are involved in the discrete $[Cu(phthalato)_2(H_2O)_2]^{2-}$ moieties, as well as another one in which they afford discrete dimeric molecules.[5] However, as far as we are aware, the magnetic properties of none of the previous complexes have yet been studied, despite the fact that the transition metal coordination polymers have been the subject of intense research in the last few decades.[6] Moreover, major advances have been made in both their theoretical description and their applications as new materials. Therefore, we thought it was advisable to further explore this very interesting class of compounds. To accomplish this—and contrary to previous experiments which used diethylenetriamine (dien) in the presence of the potential ligand ClO_4^-, yielding a strongly ferromagnetically coupled complex[1]—dien in the presence of a less potential ligand than phth, namely CH_3COO^-, has been used. Again we were pleased to realize that this experimental approach does work. Hence, we report herein on the synthesis, crystal structure, and interpretation of the magnetic behavior of the one-dimensional, polymeric [Cu^{II}(μ-phth)(dien)]$\cdot$0.5CH$_3$OH, (**1**) complex in which each phth dianion bridges the Cu^{II} ions through one of its two carboxylate groups only while its second carboxylate group remains pendant. The key point here is that **1** constitutes the first example of a chain molecule in which neither the benzene ring nor the second carboxylato group of the phth bridging dianion is involved in the intrachain magnetic exchange pathway; the second carboxylato group, however, is involved in the interchain one.

Experimental Section

Preparation of 1. To a bidistilled water solution (6 mL) of Cu(CH$_3$COO)$_2\cdot$H$_2$O (10 mmol) and dien (10 mmol) was added a bidistilled solution (6 mL) of piperidinium phthalate (10 mmol) at room temperature. This resultant clear dark-blue solution, after slow diffusion over methanol in a freezer for 4 days, gave a very small amount of a green powder which was filtered and eliminated. The dark-blue filtrate that remained gave, by slow diffusion over methanol at 7−14 °C within 15 days, a blue crystalline solid (0.64 g, 19% yield) which was collected and dried in air. Anal. Calcd for **1**: C, 43.29; H, 5.52; N, 12.11. Found: C, 43.20; H, 5.55; N, 12.25.

Crystals of **1** suitable for X-ray diffractometry were obtained by slow diffusion over methanol, at 10−16 °C, of a bidistilled water solution (10 mL) of the blue crystalline solid obtained before. The single crystals appeared after 10 days and were analyzed satisfactorily for **1**.

Magnetic and EPR Measurements. Magnetic measurements were carried out on a Quantum Design SQUID susceptometer in the 4.2−300 K temperature range; the magnetic field applied was 6 kG. The susceptibility of the samples was found to be field independent. Mercuric tetrakis(thiocyanato)cobaltate was used as a susceptibility standard. Correction for diamagnetism was estimated by using Pascal's tables. The EPR spectra were recorded at room temperature with a Bruker X-band ER 200D spectrometer equipped with a Hall probe and a Hewlett-Packard frequency meter.

X-ray Crystallography. Table 1 lists the crystallographic data. A blue prismatic crystal of **1** with approximate dimensions 0.08 × 0.12 × 0.50 mm was mounted in air. Diffraction measurements were made on a Crystal Logic dual goniometer diffractometer using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range $11 < 2\theta < 23°$, and they appear in Table 1. Intensity data were recorded using a $\theta-2\theta$ scan to $2\theta(\max) = 50°$ with scan speed 1.0 deg/min and scan range (2θ deg) 2.3 plus $\alpha_1\alpha_2$ separation. Three standard reflections monitored every 97 reflections showed less than 3% variation and no decay. Lorentz and polarization corrections were applied using Crystal Logic software. Symmetry equivalent data were averaged with $R = 0.0209$ to give 2653 independent reflections from a total 2726 collected. The structure was solved by direct methods using SHELXS-86[7] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93[8] using

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Table 1. Crystal and Refinement Data for **1**

empirical formula	$C_{12.5}H_{19}CuN_3O_{4.5}$
fw	346.85
temp (°C)	25
cryst syst	monoclinic
space group	*I*2/*a*
a (Å)	24.602(5)
b (Å)	7.849(2)
c (Å)	15.711(3)
β (deg)	97.970(5)
V (Å^3)	3004.7(11)
Z	8
ρ_{calcd} (g cm^{-3})	1.533
ρ_{obsd} (g cm^{-3})	1.510
λ(Mo Kα) (Å)	0.710 73
μ(Mo Kα) (cm^{-1})	0.148
w [a]	$a = 0.0637$, $b = 20.6390$
R indices [2199 refs, $I > 2\sigma(I)$][b]	$R1 = 0.0534$, $wR2 = 0.1446$

[a] $w = [\sigma^2(F_o)^2 + (aP)^2 + bP]^{-1}$ and $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. [b] *R*1 based on *F*; w*R*2 based on F^2

Table 2. Selected Bond Lengths (Å) and Angles (deg) of **1**

Cu···Cu[a]	4.122(1)	Cu···Cu[b]	7.636
Cu−N(1)	2.009(4)	C(1)−C(2)	1.532(7)
Cu−N(2)	1.997(4)	N(1)−C(1)	1.472(7)
Cu−N(3)	2.012(5)	O(1)−C(5)	1.235(6)
Cu−O(1)	2.332(4)	O(3)−C(12)	1.223(6)
Cu−O(2)	1.975(3)	O(4)−C(12)	1.254(7)
Cu−Cu−Cu	144.4(1)[c]	N(2)−Cu−O(1)	93.4(2)
N(1)−Cu−O(2)	98.8(2)	N(1)−Cu−O(1)	88.2(2)
N(2)−Cu−O(2)	166.7(2)	N(3)−Cu−O(2)	92.3(2)
N(2)−Cu−N(1)	85.2(2)	Cu−O(1)−C(5)	172.2(4)
N(3)−Cu−O(1)	86.0(2)	Cu−O(2)−C(5)[#1,d]	109.2(3)
N(3)−Cu−N(2)	84.9(2)	O(3)−C(12)−O(4)	124.5(5)
N(1)−Cu−N(3)	168.2(2)	O(1)−C(5)−O(2)[#2]	124.4(4)
O(2)−Cu−O(1)	99.37(2)	C(7)-C(6)−C(11)	119.3(5)

[a] Closest intrachain. [b] Closest interchain. [c] The "Cu-angle" along a zigzag chain. [d] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, $y + {}^1/_2$, $-z + {}^3/_2$; #2, $-x + 1$, $y - {}^1/_2$, $-z + {}^3/_2$.

2652 reflections and refining 267 parameters. All hydrogen atoms were located by difference maps and their positions refined isotropically; H atoms for the solvent molecule were not included in the refinement. All non-hydrogen atoms were refined anisotropically. Final values for *R*, R_w, and GOF for all data are 0.0649, 0.1574, and 1.107, respectively. The maximum and minimum residual peaks in the final difference map were 0.906 and −0.957 e/Å^3, respectively. The largest shift/esd in the final cycle was 0.009.

Results and Discussion

Selected bond lengths and angles are listed in Table 2. In **1**, the Cu(dien) moieties are bridged sequentially by phthalato dianions, coordinated in an anisobidentate fashion through the O(1) and O(2) atoms of one of their carboxylato groups; the second carboxylato group of each phthalato bridge remains pendant. Thus, infinite chains along the *b* axis are formed (Figure 1). Neighboring chains are interconnected by a dense network of hydrogen bonds linking mainly, the pendant carboxylato oxygens of each phth bridge with the amine groups of a dien molecule of a neighboring chain. The copper environment is 4+1 distorted square pyramidal. The equatorial plane includes the O(2) carboxylato atom and the three N(1), N(2), and N(3) atoms of one dien molecule; the carboxylato O(1) of another phthalato bridge occupies the apical position. (Cu−N = 1.997(4)−2.009(4) Å, $Cu-O_{short}$ = 1.975(3) Å, and $Cu-O_{long}$ = 2.332(4) Å; still all angles of the square pyramid range from 84.9 to 99.4°). In each infinite chain along *b*, the equatorial planes of neighboring square pyramidal environments, being the magnetic orbitals of the complex (vide infra), have a dihedral angle of 41.7° while alternate planes are parallel to each other. The Cu−Cu−Cu angle between three successive Cu ions along each chain is 144.4(1)°, hence each Cu chain should be better described as a zigzag. The intrachain Cu−Cu separation is 4.122(1) Å, the closest interchain being 7.636 Å.

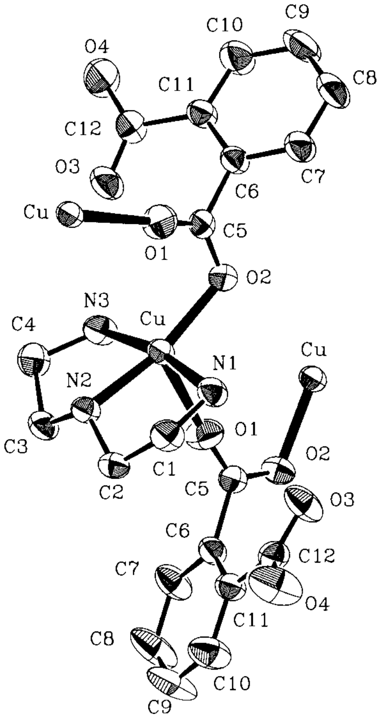


Figure 1. One-dimensional structure of **1** showing 50% thermal ellipsoids.

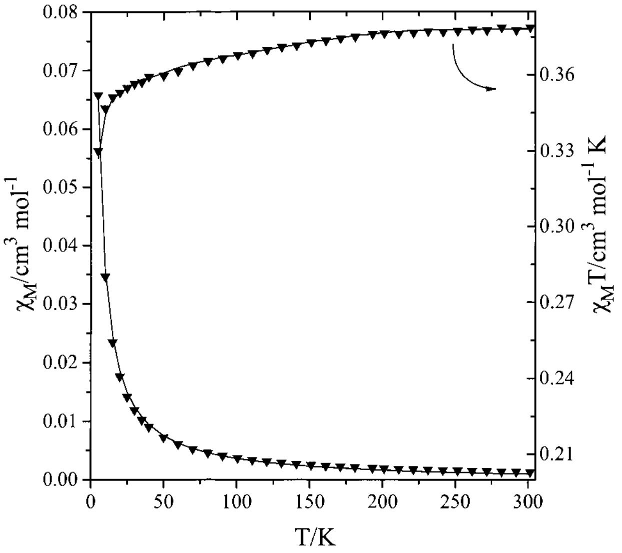


Figure 2. Experimental (▲) and calculated (—) χ_M and $\chi_M T$ versus *T* curves for **1**.

Variable-temperature (5.1−301 K) magnetic susceptibility data were collected for solid sample of **1**. Its $\chi_M T$ versus *T* plot, χ_M being the corrected molar magnetic susceptibility per copper(II) and T the temperature, is shown in Figure 2. At 301 K, $\chi_M T$ is equal to 0.379 cm^3 K mol^{-1}, as expected for a noncoupled Cu(II) ion. Upon cooling from room temperature, $\chi_M T$ decreases slightly and reaches a value of 0.353 cm^3 K mol^{-1} at ca. 20 K, where upon it decreases again down to a value of 0.330 cm^3 K mol^{-1}, at 5.1 K. Deviations from Curie behavior, not inconsistent with weak intramolecular antiferromagnetic (AF) interactions, are observed for the high temperature range;

still a very weak interchain antiferromagnetic interaction superimposes itself on the intrachain antiferromagnetic coupling below 20 K.

In an attempt to probe deeper into the magnetic exchange interactions, the magnetic behavior of **1** is closely combined with its molecular and crystal structure. As was shown in the previous section, **1** has a rather long Cu−O(1) separation (2.332(3) Å); hence, the unpaired electron around each Cu^{II} magnetic center is described by an x^2-y^2 type magnetic orbital pointing from the metal toward its four nearest-neighbor N(1), N(2), N(3), and O(2) atoms. Consequently, the spin density on atom O(1) should be very low and/or zero. In **1** the closest Cu−Cu separation within the chain is 4.122(1) Å, while that between the chains is 7.636 Å. The high temperature range observed AF is, therefore, due to intrachain interaction. Since the crystal structure indicates an one-dimensional zigzag structure, the magnetic data from room temperature down to 4.2 K were least-squares fitted with an 1-D magnetic model—a linear antiferromagnetic chain with $S = {}^1/_2$[9]—with a mean field correction[10] to account for the interchain interactions. A very good fit ($R = 0.78 \times 10^{-5}$) was derived with $J = -0.49$ cm^{-1}, $zJ' = -0.38$ cm^{-1}, and $N\alpha = -0.42 \times 10^{-3}$ cm^3 mol^{-1}. [All symbols have their usual meaning except during the fitting procedure the g value was kept constant and equal to the experimental g_{av} value ($g = 2.08$) of the axial EPR spectrum of **1**].

Finally, it is also clear from the structure that only one exchange pathway for intrachain interaction is possible: that through the one carboxylato group of each phth bridging two successive Cu^{II} ions along the chain. However, the ability of the carboxylato group to propagate the exchange interaction between two Cu^{II} ions has been well demonstrated.[11,12] In particular, a syn-syn configuration leads[11] to high J/k value, and a syn-anti one to a very low value.[12] This latter is the case with **1**, in which the contributions of the 2p orbitals of the O(1) and O(2), belonging to the magnetic orbitals centered on the two successive Cu^{II} ions, are unfavorably oriented to give a strong overlap (see in Chart 1). This, along with the very low spin density on O(1), could account well for the very weak intramolecular AF in **1**. Moreover, the hydrogen bonds could propagate[13] the very weak interchain interaction calculated. In particular, these bonds link the O(3) and O(4) atoms of the second—pendant—carboxylato group of each phth bridge with the N atoms of the neighboring dien molecules, belonging to the magnetic orbitals of the neighboring and/or same chains (see in Chart 2). Consequently, of the two carboxylato groups of each phth bridge, one is involved in the intrachain and the second in the interchain magnetic exchange pathway.

Chart 1. The Syn−Anti Configuration of the Bridging Carboxylato Group of Each phth Bridge in 1

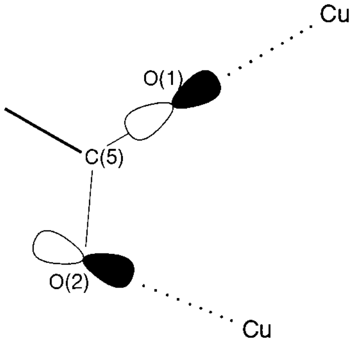
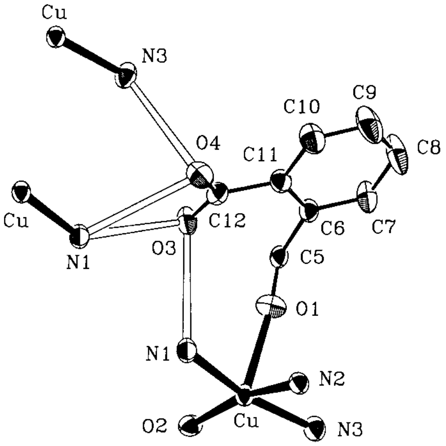


Chart 2. Some of the Inter- and Intrachain Hydrogen Bonds (open lines) in **1**; Most Atoms Have Also Been Omitted for Clarity



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Supporting Information Available: One X-ray crystallographic file, in CIF format, is available on the Internet only. A table listing experimental and theoretical magnetic susceptibility data is also available (1 page). Ordering and access information is given on any current masthead page.

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