Crystal structure and magnetic behavior of Cu_3(O_2C_16H_23)_6·1.2 C_6H_12. An unexpected structure and an example of spin frustration


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This paper is published in homage to our late friend Olivier Kahn, who led the way in molecular magnetochemistry.

Abstract – A copper(II) carboxylate has been obtained from the reaction of basic copper carbonate, CuCO_3·Cu(OH)_2, with 2,4,6-triisopropylbenzoic acid. It contains a trinuclear Cu_3^{2+} core with three-fold symmetry, with each pair of copper atoms bridged by two carboxylate ligands. The Cu···Cu separations are 3.131(3) Å, precluding any direct bonding. Magnetic susceptibility data from 1.8 to 380 K at 1 000 G indicate a doublet ground state, (g ≈ 2.1) between 10–50 K (µ_eff = 1.80 µ_B). Above 50 K, the magnetic moment increases to 2.69 µ_B at 380 K, as expected for an equilateral triangular system of Cu^{II} with antiferromagnetic interactions between spin carriers. © 2001 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

copper / carboxylate / crystal structure / trinuclear complex / magnetic properties

1. Introduction

The chemistry of copper(II) complexes with various carboxylates has been very broadly researched with numerous studies on magnetic properties of the tetracarboxylate bridged compounds having two axial ligands L, Cu_2(O_2CR)_4L_2 (figure 1a) [1–10]. These studies have focused on the factors influenc-
ing the magnitude of the intramolecular magnetic exchange interaction that occurs between the two CuII ions in this type of compound. Several crystal structures have been reported for Cu$_2$(O$_2$CR)$_4$ without any exogenous ligands, but these were found to have a well-known chain structure built on the long Cu–O axial contacts in the solid state (figure 1b) [11–18]. For these non-adduct copper(II) carboxylates, relatively few studies have been reported on the magneto-structural correlations [6, 17, 18].

Coordination flexibility of copper atoms, combined with the electronic and steric diversity of R groups in carboxylate anions O$_2$CR$^-$, still leads to novel and interesting results in such an ‘old-fashioned’ chemistry as copper carboxylates. For example, we recently prepared a remarkable copper(II) trifluoroacetate, Cu$_2$(O$_2$CCF$_3$)$_4$, which was shown to have a unique chain motif in the crystaline form, different from that in any other carboxylate. This structure is with- out any exogenous ligands, but these were found to have a well-known chain structure built on the long Cu–O axial contacts in the solid state (figure 1b) [11–18]. For these non-adduct copper(II) carboxylates, relatively few studies have been reported on the magneto-structural correlations [6, 17, 18].

Coordination flexibility of copper atoms, combined with the electronic and steric diversity of R groups in carboxylate anions O$_2$CR$^-$, still leads to novel and interesting results in such an ‘old-fashioned’ chemistry as copper carboxylates. For example, we recently prepared a remarkable copper(II) trifluoroacetate, Cu$_2$(O$_2$CCF$_3$)$_4$, which was shown to have a unique chain motif in the crystaline form, different from that in any other carboxylate (figure 1b) [19]. It is therefore important to mention that prior to this work only one CuII carboxylate compound has been isolated in the solid state containing discrete hexanuclear molecules in which phenoxyacetate groups form both syn–syn and syn–anti bridges [20]. In the latter the Cu atoms together formed a compressed trigonal anti-prism with six long edges (Cu–Cu 5.65 Å) bordering the equilateral triangular faces and six shorter edges (Cu–Cu 3.53 Å).

As a part of our studies on the interaction of the 2,4,6-triisopropylbenzoate (TiPB) ligand with the first row transition metals [21], and with our interest in the coordination chemistry of copper in general, we extended our research to the CuII–TiPB system. The TiPB ligand was already shown to be sufficiently bulky to prevent self-association in the CrIII case, resulting in a discrete dinuclear compound Cr$_2$(TiPB)$_4$ with a supershort Cr–Cr bond [21]. Therefore, we believed that TiPB would be a good candidate to attempt the isolation of the first discrete CuII carboxylate, Cu$_2$(O$_2$CR)$_4$, that has no axial ligation, either by exogenous ligands or by self-association.

2. Results and discussion

2.1. Synthesis and structure

The standard literature procedure has been used to prepare the title copper(II) carboxylate, Cu(TiPB)$_2$ (1) [1, 22]. The reflux reaction of the heterogeneous mixture containing the parent 2,4,6-triisopropylbenzoic acid (HTiPB) and insoluble basic copper carbonate, CuCO$_3$Cu(OH)$_2$, in ethanol slowly afforded a blue-green solution. Several blue crystals of the composition Cu$_2$(TiPB)$_4$(C$_2$H$_6$OH)$_2$ (2) [23] have been isolated directly from the reaction mixture upon cooling to room temperature. Evaporation of all the solvent after removal of the unreacted copper carbonate from the blue solution resulted in a green residue. The green solid was dissolved in cyclohexane and the solution was placed in the refrigerator for a week, affording green crystals of 1. After dissolving crystals of 1 in ethanol, followed by keeping the ethanol solution in the freezer for a few days, characteristic blue crystals of 2 reappeared. Both the distinctive color change and the results of elemental analyses were indicative of the reversible transformations from the bis-adduct (2) to the unligated copper complex (1) and back. The compound Cu$_2$(TiPB)$_4$(C$_2$H$_6$CO$_2$) (3) has also been made. The identities of the compounds 1, 2, and 3 were also confirmed by the crystal structure determinations [23, 24].

The crystal structure of 1 consists of the discrete molecules Cu$_4$(O$_2$C$_{16}$H$_{23}$)$_6$ having a triangular arrangement of the CuII atoms with a 3-fold axis passing through the center of the equilateral triangle (figure 2). Two disordered cyclohexane molecules with partial occupancies were located in the asymmetric unit giving a total of 1.2 molecules of solvent per Cu$_3$ moiety. Each pair of copper atoms in the Cu$_3$ unit is bridged by two TiPB carboxylate ligands in the syn–syn mode. This structure is without any precedent in the chemistry of copper carboxylates, although close analogues are found in palladium systems, Pd$_4$(O$_2$CR)$_6$ [25].
The copper(II) centers in 1 are in a square planar environment of four oxygen atoms with the two equatorial Cu–O distances being slightly different, 1.891(3) and 1.948(3) Å. The O(1)–Cu–O(1) and O(2)–Cu–O(2) angles are 159.8(2)° and 175.0(2)°, respectively, while O(1)–Cu–O(2) angles are averaged to 90.4(1)°. The Cu–Cu distances, 3.131(3) Å, are longer than what might be expected for Cu–Cu bonds. Similarly, in all Pd₃(O₂CR)₆ molecules, the Pd–Pd distances range from 3.10 to 3.25 Å, greatly exceeding the usual length for Pd–Pd bonds, and thus underscoring the absence of bonded interactions [25].

2.2. Magnetic behavior

Magnetic susceptibility measurements were performed on a polycrystalline sample of 1 at 1 000 G. As the plot in figure 3 indicates, $\mu_{\text{eff}}$ is constant between 10 and 50 K at 1.80 $\mu_B$. These data are consistent with the presence of a doublet ground state with a $g$ value near 2.1. At lower temperatures (below 10 K), the small decrease of the effective moment is probably due to some very small antiferromagnetic interaction ($|\theta| < 0.1$ K) between the Cu(II) trimers ($S = 1/2$). Field dependence of the magnetization at 1.8 K can be fitted to the Brillouin function for an $S = 1/2$ magnetic spin which allows us to better determine the $g$ value as 2.071(5). Above 50 K, the magnetic moment gradually increases without saturation from 1.80 $\mu_B$ to 2.69 $\mu_B$ at 380 K. This temperature dependence is expected for an equilateral triangular system of Cu(II) with antiferromagnetic interactions between spin carriers [26–30]. Since the crystal structure revealed that the Cu triangle is rigorously equilateral with a 3-fold axis, the magnetic exchange parameters are equal (figure 4). The appropriate spin Hamiltonian is given in equation (1), with an isotropic exchange interaction $J$

$$H = -2J(S_1S_2 + S_2S_3 + S_3S_1)$$

This interaction splits the three degenerate energy levels into a quartet state with a total spin $S_T = 3/2$ (where $S_T = 1/2$ and two degenerate doublet states with $S_T = 1/2$ (figure 4). This situation is a classic example of spin frustration for $S = 1/2$ spin carriers arranged in an equilateral triangle. The susceptibility as a function of temperature derived from this Hamiltonian can be expressed as equation (2)

$$\chi = \frac{Ng^2}{4k_BT} \left( 1 + \frac{g\mu_B T}{k_B T} \right)$$

Figure 3. Temperature dependence of the effective magnetic moment at 1 000 G. The solid line is the best fit obtained with equation (2) with $J = -108$ K and $g = 2.07$. Figure 4. Scheme of the spin topology in 1 and its energy diagram in the case of an antiferromagnetic interaction (where $J$ is the magnetic exchange).
An excellent fitting of the experimental data was obtained with the parameters $J = -108$ K and $g = 2.07$ (figure 3). The $J$ value is lower than the ones observed in copper carboxylate dimers in which Cu(II) centers are bridged by four ligands [31]: $J = -240$ K for [Cu(OAc)$_2$H$_2$O]$_2$ [32], $J = -258$ K for 2, and $J = -276$ K for 3 [33]. The fact that in the new Cu(II) trimer each spin carrier is linked to the others by only two carboxylate groups could play a role in lowering the $J$ value. However, it must be pointed out that, since spin-spin coupling is effected by the details of orbital overlaps, the geometric constraints of the trimer will also influence the magnitude of superexchange through the bridges. The system we have studied is an excellent example of spin frustration [34].

3. Experimental

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Starting materials, 2,4,6-trisopropylbenzoic acid and CuCO$_3$·Cu(OH)$_2$, were commercial samples. All solvents were dried before use. Elemental analyses were performed by Canadian Microanalytical Services, Ltd. The IR spectrum was collected on a Perkin-Elmer 16PC FT-IR spectrophotometer using a KBr pellet.

3.1. Synthesis of Cu$_3$(TiPB)$_6$ (1)

In a typical reaction, 50 mL of ethanol was added to a mixture of 0.884 g (4 mmol) CuCO$_3$·Cu(OH)$_2$ and 0.993 g (4 mmol) 2,4,6-trisopropylbenzoic acid. The suspension was refluxed for 3 to 10 days; the yield of the heterogeneous reaction is a function of reflux time. After refluxing, the suspension was cooled and filtered over Celite to afford a blue-green solution. The solvent was removed in vacuo, and the remaining solid was heated to 100 °C to sublime remaining HTiBP. The heat also removes axially ligated ethanol, as evidenced by the change in color of the solid from blue-green to dark green. The solid was then dissolved in 10 mL cyclohexane, in color of the solid from blue-green to dark green.

3.2. Crystallographic studies

The X-ray study of Cu$_3$(O$_2$C$_{16}$H$_{33}$)$_6$·1.2 C$_6$H$_{12}$ (1·1.2 C$_6$H$_{12}$) was carried out on a Nonius FAST diffractometer with an area detector using Mo Kα radiation at 213(2) K. Fifty reflections were used in cell indexing and 250 reflections in cell refinement (15° < 2θ < 42°) [24]. A total of 2 436 independent reflections in the range 4.5° < 2θ < 45° were collected, 2 075 with $I \geq 2 \sigma (I)$. Data were corrected for Lorentz and polarization effects by the MADNES program [35, 36]. Reflections profiles were fitted and values of $F^2$ and $\sigma (F^2)$ for each reflection were obtained by the program PROCOR [37, 38]. Systematic absences in the data uniquely determined the space group for 1·1.2 C$_6$H$_{12}$ to be trigonal $P3_3_1c$ (No. 163).

The coordinates of copper atoms were found in direct-method $E$ maps using the structure solution program SHELXTL [39]. The positions of the remaining atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-93 program [40]. The isopropyl groups of the ligand were found to be disordered over two different rotational orientations. The hydrogen atoms were included in the structure factor calculations at idealized positions. Two molecules of disordered cyclohexane with partial occupancies have been located in the structure. Anisotropic displacement parameters were assigned to all non-hydrogen atoms, except the disordered carbon atoms. All calculations were performed on a DEC Alpha running VMS. Final refinement of 178 parameters and 11 restraints resulted in $R_I = 0.086 \, 0$ and $wR_2 = 0.218 \, 9$ for all data, and $R_I = 0.075 \, 4$ and $wR_2 = 0.204 \, 8$ for data with $I \geq 2 \sigma (I)$.

3.3. Magnetic measurements

Magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University). Data were collected from 1.8 to 380 K at 1 000 G on finely divided polycrystalline samples (23.77 mg for 1). The data were corrected for the sample holder and for the experimental diamagnetic contribution (~4·0·10$^{-4}$ emu CGS·K·mol$^{-1}$). This value is in good agreement with the value of ~7·4·10$^{-4}$ emu CGS·K·mol$^{-1}$ calculated from Pascal constants [41], taking into account that a trimer of Cu(II) should exhibit a TIP contribution of 2·10$^{-4}$ emu CGS·K·mol$^{-1}$ [26].
Supplementary material

Crystallographic data, atomic coordinates, displacement parameters and a full list of bond lengths and angles for 1 1.2 C6H12 have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK as deposition number CCDC 153277, and can be obtained by contacting the CCDC.

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References