

Structure and Magnetic Properties of a New Cobalt(II) Thiophenedicarboxylate Coordination Polymer Showing Unprecedented Coordination

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A new carboxylato-bridged Co^{II} network of formula {Co((κ^1 - κ^1)-(κ^1 - μ_2)- μ_4 -TDC)(μ_2 -H₂O)_{0.5}(H₂O)}_n (H₂TDC = 2,5-thiophenedicarboxylic acid) has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and IR and UV–visible spectroscopies. The title compound is made of chains of Co^{II} dimers interconnected by TDC²⁻ ligands, showing an unprecedented asymmetric tetradentate coordination mode of the carboxylate functions. Magnetic measurements show weak ferromagnetic interactions between the Co ions within the dimers.

Syntheses, structures, and properties of coordination polymers still arouse considerable research interests because of their potential applications in materials science.¹ Carboxylic acids have been successfully used as building blocks for the design of various coordination polymers, in areas such as gas storage and separation, catalysis, sensors, and magnetism.^{2–4}

Following our research on the grafting of thiophenedicarboxylates into layered magnetic transition-metal hydroxides⁵

and in order to overcome the difficulty encountered for the anionic exchange of 2,5-thiophenedicarboxylic acid (H₂TDC) into cobalt hydroxide layers, we have extended our approach to the direct synthesis of extended polymeric magnetic networks incorporating the TDC²⁻ ligand. The magnetic properties of such extended networks have been very scarcely studied. To the best of our knowledge, only one recent paper reports the magnetic properties of two Co- and Fe-based compounds built from the combination of TDC²⁻ with 4,4'-bipyridine.⁶

It has been shown that H₂TDC shows various binding modes such as monodentate, bridging bidentate, or bridging tridentate, which makes it a useful building block in the elaboration of coordination polymers.^{7–9}

Several one-, two-, or three-dimensional Mn^{II}, Co^{II}, Cu^{II}, and Zn^{II} compounds have been obtained by mixing H₂TDC and N ligands.^{6,10} 1-D polymeric chains have been obtained with this ligand and triorganotin.¹¹ Finally, 2-D and 3-D metal organic frameworks (MOFs) have been reported with Tb^{III}² or Cu^{II}.³ In these MOFs, the TDC²⁻ ligand exhibits a symmetric tetradentate (κ^1 - κ^1)-(κ^1 - κ^1)- μ_4 coordination mode.

We report here the synthesis, crystal structure, and magnetic properties of a new Co^{II}(TDC) compound, where TDC²⁻ exhibits the unprecedented asymmetric tetradentate (κ^1 - κ^1)-(κ^1 - μ_2)- μ_4 coordination mode.

The title compound {Co(TDC)(H₂O)_{1.5}}_n (**1**) was synthesized as dark-pink crystals by a hydrothermal method from

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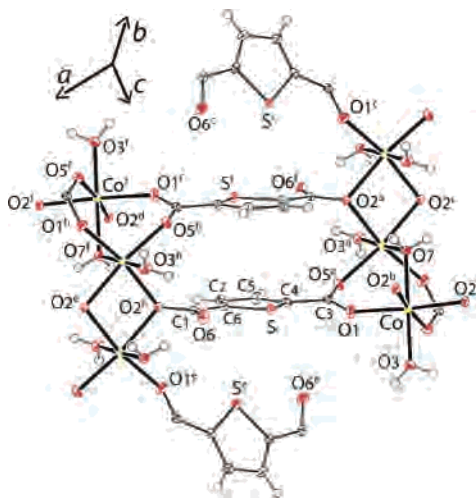


Figure 1. ORTEP view of compound **1**. The ellipsoids enclose 50% of the electronic density. The water molecules are labeled O3 and O7. Symmetry operators for equivalent positions are as follows: $a = 1 - x, y, 3/2 - z$; $b = 1 - x, 2 - y, 1 - z$; $c = x, 2 - y, 1/2 + z$; $d = 1/2 + x, -1/2 + y, 1 + z$; $e = 3/2 - x, -1/2 + y, 3/2 - z$; $f = 3/2 - x, 3/2 - y, 2 - z$; $h = 1/2 + x, 3/2 - y, 1/2 + z$.

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.48 g, 2 mmol), H_2TDC (0.34 g, 2 mmol), and NaOH in water ($2 \text{ mol} \cdot \text{L}^{-1}$, 20 mL) in a sealed bomb (125 mL) at 180°C over 22 h. **1** crystallizes in the monoclinic space group $C2/c$.¹² Its structure consists of 1-D chains of octahedral Co^{II} dimers, organized in layers parallel to the (b,c) planes and connected to one another via the TDC^{2-} units along the a axis (Figure 1 and the Supporting Information).

All of the Co^{II} ions are crystallographically equivalent and lie in a slightly distorted octahedral environment consistent with the UV–visible spectrum (Figure S5 in the Supporting Information). The axial positions are occupied by two water molecules, whereas the equatorial positions are occupied by four O atoms from four different TDC^{2-} groups. Two Co^{II} ions are bridged by two $(\kappa^1-\mu_2)$ -carboxylate groups, forming the repeating dinuclear unit. These diamond-core dimers are then connected along the c axis by two $(\kappa^1-\kappa^1)$ -carboxylate functions and one bridging water molecule. The distances between the metal centers within the chain are 3.212 and 3.583 Å in and between the dimers, respectively. Finally, one interchain and two intrachain hydrogen-bonding interactions are found respectively between an O atom of the bidentate carboxylate and a terminal water molecule of another chain ($\text{O5} \cdots \text{O3} = 2.747 \text{ \AA}$) and between the H atoms of the two water molecules and the noncoordinated O atom of the monodentate carboxylate group ($\text{O6} \cdots \text{O7} = 2.642 \text{ \AA}$ and $\text{O6} \cdots \text{O3} = 2.813 \text{ \AA}$) (Figure S1 in the Supporting Information). Accordingly, the C1–O6 bond length is not as short as expected for a terminal C–O (C1–O6 = 1.247 Å).

Each chain of dimers is connected to four other chains in the a direction by TDC^{2-} ligands. Each TDC^{2-} ligand thus

(12) Crystal data for **1**: $\text{C}_6\text{H}_5\text{SCoO}_5.5$, $M_w = 256.10 \text{ g} \cdot \text{mol}^{-1}$, monoclinic, space group $C2/c$, $a = 19.828(5) \text{ \AA}$, $b = 7.513(5) \text{ \AA}$, $c = 10.730(5) \text{ \AA}$, $\beta = 103.440(5)^\circ$, $V = 1554.65(13) \text{ \AA}^3$, $Z = 4$, $d_c = 2.188 \text{ g} \cdot \text{cm}^{-3}$, $T = 173(2) \text{ K}$, 7242 reflections, 135 parameters refined, $R1 = 0.0313$, $wR2 = 0.0649$.

Table 1. Coordination Modes of the Carboxylate Functions of TDC^{2-}

Monodentate ^{7,8}	Bidentate ^{7,10}
 $\kappa^1\text{-TDC}^{2-}$	 $(\kappa^1)-(\kappa^1)-\mu_2\text{TDC}^{2-}$
Tridentate ^{6,8}	Tetradentate ^{2,3,10}
 $(\kappa^1)-(\kappa^1-\kappa^1)-\mu_3\text{TDC}^{2-}$	 $(\kappa^1-\kappa^1)-(\kappa^1-\kappa^1)-\mu_4\text{TDC}^{2-}$
 $(\kappa^2)-(\kappa^1-\kappa^1)-\mu_3\text{TDC}^{2-}$	 $(\kappa^1-\kappa^1)-(\kappa^1-\mu_2)-\mu_4\text{TDC}^{2-}$ (this work)

exhibits two different modes of coordination of its carboxylate units. One carboxylate function is monodentate and coordinated to two Co ions ($\kappa^1-\mu_2$) in one chain; the other carboxylate function is in bridging bidentate mode ($\kappa^1-\kappa^1$). This tetradentate asymmetric coordination mode is observed for the first time in complexes with the TDC^{2-} ligand (Table 1). Based on the Cambridge Crystallographic Database, this asymmetric coordination mode of carboxylate functions is rare. To our knowledge, two examples of cobalt and zinc benzenetetracarboxylate show the two coordination modes ($\kappa^1-\kappa^1$) and ($\kappa^1-\mu_2$),¹³ but no dicarboxylate ligand having this ($\kappa^1-\kappa^1$)-($\kappa^1-\mu_2$)- μ_4 coordination has ever been described.

Compound **1** was also investigated by Fourier transform IR spectroscopy (Figure S4 and Table S2 in the Supporting Information).¹⁴ A broad feature is observed in the 3300–3500 cm^{-1} region and is attributed to the antisymmetric and symmetric stretching modes of the coordinated water molecules, whereas the band at 1630 cm^{-1} is attributed to their bending mode. The asymmetric stretching band of the carboxylate function, $\nu_{\text{as}}(\text{COO})$, is almost not modified in **1** compared to $\text{Na}_2(\text{TDC})$ (1565 and 1560 cm^{-1} , respectively), whereas the symmetric stretching band is clearly split in two in **1** [1390 and 1345 cm^{-1} in **1** and 1385 cm^{-1} in $\text{Na}_2(\text{TDC})$]. These two $\Delta\nu$ values [$\Delta\nu = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$] can be attributed respectively to the bridging bidentate coordination mode ($\kappa^1-\kappa^1$) ($\Delta\nu = 175 \text{ cm}^{-1}$) and to the bridging monodentate coordination mode ($\kappa^1-\mu_2$) ($\Delta\nu = 220 \text{ cm}^{-1}$) of the carboxylate functions of TDC^{2-} .¹⁵ The other bands observed between 1460 and 1540 cm^{-1} are attributed to in-plane ring vibrations.¹⁶

Thermogravimetric analysis (TGA) for **1** reveals four successive weight losses in the temperature range 30–900 $^\circ\text{C}$ (Figure 2). The first one, between 160 and 300 $^\circ\text{C}$, is

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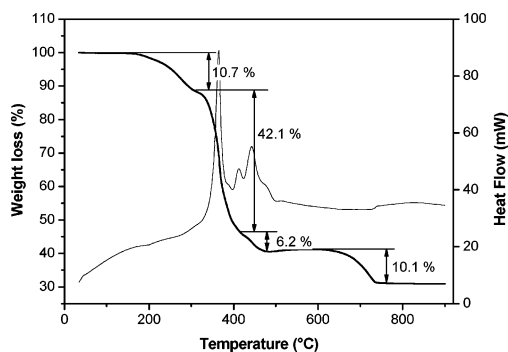


Figure 2. TGA and thermal differential analysis curves for **1**.

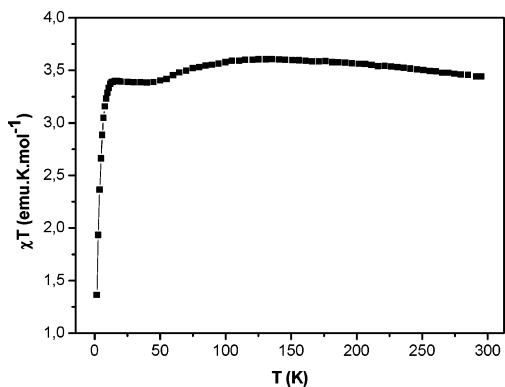


Figure 3. χT vs T curve for **1** recorded under a 0.05 T applied field.

related to the dissociation of coordinated water molecules (obsd 10.7%; calcd 10.6%). The second one, from 300 to 410 °C, corresponds to the exothermic dissociation and combustion of the C_6H_2S moiety (obsd 42.1%; calcd 41.5%). The exothermic peaks just above 470 °C are due to the oxidation of Co^{II} to Co^{III} with the loss of one O atom (obsd 6.2%; calcd 6.2%). The product obtained between 470 and 600 °C is amorphous; it is necessary to increase the temperature to 710 °C to lose $5/3$ O atoms (obsd 10.1%; calcd 10.4%) and to form the cobalt oxide Co_3O_4 (the nature of which has been checked by powder X-ray diffraction). The final fractional weight of the Co_3O_4 residue is in agreement with the expected Co content in **1** (obsd 22.7%; calcd 23.0%).

The temperature dependence of the magnetic susceptibility of **1** in the 295–1.8 K range is shown in Figure 3. Between 295 and 150 K, the χT product follows the Curie–Weiss law with a Curie constant of $3.53 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ in agreement with high-spin Co^{II} ions in octahedral geometry¹⁷ and a positive Weiss temperature ($\theta = 2.63 \text{ K}$) indicating ferromagnetic interactions.

Accordingly, the slight increase of the χT product from room temperature ($3.44 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) to 135 K ($3.61 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) suggests the presence of weak ferromagnetic interactions between the Co ions within the dimeric subunits.¹⁸ The subsequent decrease to 45 K and the almost

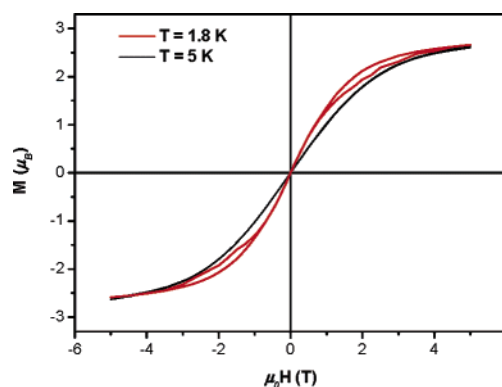


Figure 4. Magnetization cycle for **1** at 5 K (black) and 1.8 K (red).

constant value of χT down to 16 K ($3.40 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$) may indeed be rationalized in considering the spin–orbit coupling of the Co^{II} ions, which stabilizes a pseudo-spin value $S = 1/2$ for each Co^{II} ion at low temperature. The associated g value of 5.2 determined from the magnetization at high field ($2.6 \mu_B$; Figure 4) is within the expected range.¹⁷ The ferromagnetic coupling within the dimeric subunits leads to consideration of magnetic entities with a pseudo-spin value $S = 1$ and $g = 5.2$ resulting in $\chi T = 3.38 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ that matches the experimental value of $\chi T = 3.40 \text{ emu}\cdot\text{K}\cdot\text{mol}^{-1}$ at the plateau. Finally, the decrease of χT below 16 K may be attributed to antiferromagnetic coupling between the dimers within the chain and/or between the chains.

The magnetization vs field at a sweeping rate of $1 \text{ mT}\cdot\text{s}^{-1}$ at 5 K does not show any hysteresis, whereas at 1.8 K, a small opening is observed between 0.8 and 4.3 T (Figure 4). Such a feature has already been observed for polynuclear paramagnetic compounds and attributed to a phonon bottleneck phenomenon.¹⁹

We have described here the hydrothermal synthesis and structure of a new Co^{II} coordination polymer in which the TDC^{2-} ligand exhibits an unprecedented asymmetric tetradentate coordination mode $(\kappa^1-\kappa^1)-(\kappa^1-\mu_2)-\mu_4$. The overall magnetic behavior of this compound is antiferromagnetic, but a weak ferromagnetic coupling is observed between two Co^{II} linked by two μ_2-O of two TDC^{2-} ligands. The coordination properties of TDC^{2-} with other transition-metal ions in the same reaction conditions are under investigation in our laboratory.

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Supporting Information Available: Detailed experimental procedures, crystal data, and IR and UV–visible data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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