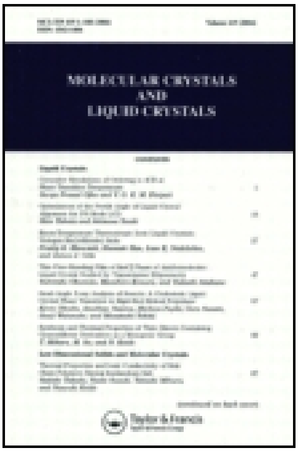

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A Novel Class of Layered Molecular Antiferromagnets

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A Novel Class of Layered Molecular Antiferromagnets

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The synthesis, structure and magnetic properties of a novel series of layered compound containing interlayer dicarboxylate anions, where the interlayer separation has been tuned from 9.9 to 13.8 Å, are reported. They display collinear antiferromagnetism (AF) just below the Néel temperature and in small applied fields canted AF below a second transition. At higher fields metamagnetic behavior is observed which exhibits no hysteresis in the collinear state and wide hysteresis, attaining 5.2 Tesla at 2K, below the canting temperature. The phase diagram is also presented.

Keywords: carboxylate, clay, cobalt, high coercive field, metamagnet, layer.

INTRODUCTION

The prospect of creating novel magnetic materials from purely organic, metal-organic hybrid and coordination polymers have aroused the interest of synthetic and physical chemists and theoretical and experimental physicist alike [1]. This was fuelled by several key findings, such as long range magnetic ordering in a purely organic compound [2], Curie temperature getting higher than room temperature [3], coercive field exceeding five Tesla [4] and the observation of quantum effects in single molecule magnets [5]. There is

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therefore a strong drive to better existing limits and several approaches are emerging. Molecule based magnetic materials exhibit the whole range of magnetic properties known for metallic and conducting solids [6]. In addition, several properties are unique to molecule-based compounds and especially those having structural and magnetic anisotropy. Two examples are the one-dimensional compounds such as $Fe(cp^*)_2X$ or Mn(TPP)X, where X is a coordinating cyano-ligand (TCNQ, TCNE, etc) [7] and the two-dimensional metal-hydroxide compounds [4]. Both display antiferromagnetism for moment carriers at fairly large distances and wide hysteresis loops with large coercive fields. Furthermore, for the latter set a canted AF state is established at a temperature lower than the Néel temperature that is not quite what is normally described in most textbooks on magnetism [6].

Here, we describe the syntheses, structural characterization and a study of the magnetic properties of a novel family of layered cobalt hydroxide interleaved with aromatic dicarboxylate anions.

EXPERIMENTAL

All reagents, $Co(H_2O)_6(NO_3)_2$, NaOH, terephthalic acid ($C_8H_6O_4$), carboxy cinnamic acid ($C_{10}H_8O_4$), 1,9'-naphthalene dicarboxylic acid ($C_{12}H_8O_4$) and 4,4'-biphenyl dicarboxylic acid ($C_{14}H_8O_4$) were obtained from Fluka or Aldrich and used as received. The acid (1mmol) is suspended in 100ml water and slowly neutralized with NaOH (2mmol). To the clear solution $Co(H_2O)_6(NO_3)_2$ (1mmol) was added to give a purple precipitate. A further 2mmol of NaOH was added to give a blue to green solid. $Co_2(OH)_2$(dicarboxylate) was obtained by heating the latter at 80°C until it is transformed to a pale pink solid or placed in a hydrothermal bomb at 120°C overnight. The compounds were authenticated by chemical and thermogravimetric analyses.

The physical techniques and sampling methods have been previously described [4, 8].

RESULTS AND DISCUSSION

The reaction of cobalt nitrate with a base in the presence of an anion (X^-) or di-anion (XX^{2-}) results a range of colored compounds from pink to purple to green and blue; amongst them are the layered compounds of general formula: $Co_5(OH)_8(X)_2{\cdot}xH_2O$ or $Co_5(OH)_8(XX){\cdot}xH_2O$ which are green or blue [4, 9] and $Co_2(OH)_2(XX)$ which are pale pink [4]. Several anions containing different coordination groups have been employed for the former series and for the latter only dicarboxylate anions have been found to stabilize such composition and structure.

X-ray Powder Diffraction and Crystal Structure

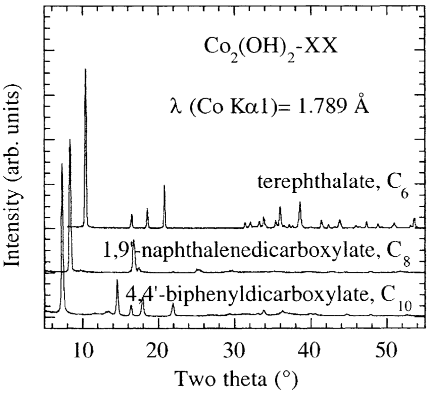

FIGURE 1 Powder X-ray diffraction pattern of $Co_2(OH)_2$(dicarboxylate)· (Co-Kα1, λ = 1.789Å).

The XRD patterns for the $Co_2(OH)_2$(dicarboxylate) compounds are shown in Fig. 1. The patterns are dominated by a progression of the *00ℓ* Bragg reflections corresponding to the basal spacing characteristic of layered structures. The close similarity in the strong reflections, the EXAFS and the color of the compounds suggest that they are isostructural. The basal spacing (*d_{001}*) increases systematically with the length of the anion (Fig. 2). A fit of the distance versus the number of carbon atoms in the bridge to $d_0+R_{av}\cos\theta$ (d_0 = inorganic layer thickness, R_{av} = average C-C distance and fixed to 1.02Å and θ is the tilt angle of the anion) gives d_0 of 4.08Å and θ of 17°. Both in good agreement with 4.2Å for the sum of two slightly tilted Co-O bonds in *trans*-position and 17.12° obtained from the observed structure (*vide supra*).

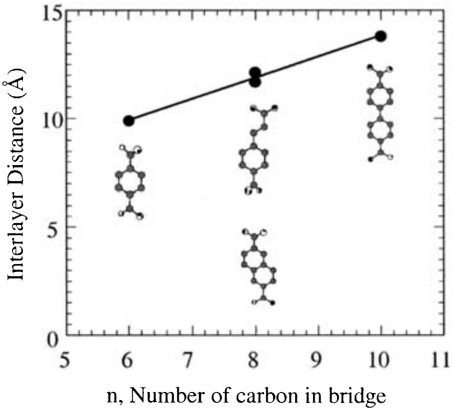

FIGURE 2 The dependence of d_{001} as a function of the number of carbon atoms (n) in the dicarboxylate bridge.

The highly crystalline terephthalate salt gave a better diffraction pattern, especially at higher angles, than the other salts. This allowed its unit cell parameters to be determined using TREOR and refined using the LeBail pattern matching. The structure was solved by Rietvelt refinement of the experimental powder diffraction using GSAS. The carbon atoms of the terephthalate were located by difference Fourier maps.

The crystals of the terephthalate salt belong to the monoclinic system, space group *C2/m*, a=19.9520(15), b=3.2862(3), c=6.2952(4) Å, β=95.84(1)°, V=410.6(1) $Å^3$. The structure (figure 3) is formed of two types of edge sharing CoO_6 chains running parallel that are connected to each other by the μ^3-OH to form layers. The coordination about the cobalt in the two chains is different. The cobalt atom in one chain is coordinated in the equatorial positions by four oxygen atoms from carboxylate groups and two OH groups in the *trans*-position. In the other chain it is four OH in equatorial positions and two O from the carboxylate groups. Every octahedron displays six different Co-O bond distances. The chains are tilted with respect to one another and each carboxylate group forms three bonds to the cobalt atoms to complete its coordination sphere. The terephthalate bridges the layers to form the three dimensional structure.

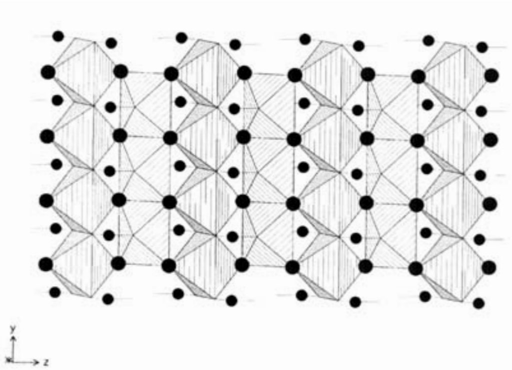

FIGURE 3 View of the structure of a layer of $Co_2(OH)_2$(terephthalate) showing the hydroxide and connecting carboxylate bridges.

X-ray Absorption Spectroscopy

The cobalt K-edge XAS spectra of $Co_2(OH)_2$(dicarboxylate) compounds and of the reference Co^{II} compound, $Co_2(OH)_3(NO_3)$, have been recorded at 80 K at the ESRF synchrotron facility (Figure 4). The pre-edge feature, originating from the 3d ← 1s transition, is observed at 7705 eV and the K-edge at 7719 eV for all the compounds confirming the presence of only Co^{2+}. The weak intensity of the pre-edge feature is consistent with octahedral geometry [10].

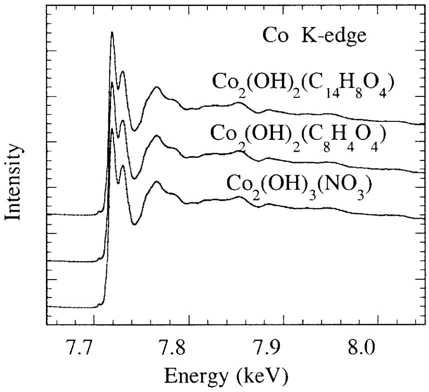

FIGURE 4 Co-K-edge XAS of $Co_2(OH)_2$(dicarboxylate) and $Co_2(OH)_3NO_3$.

Infrared Spectra

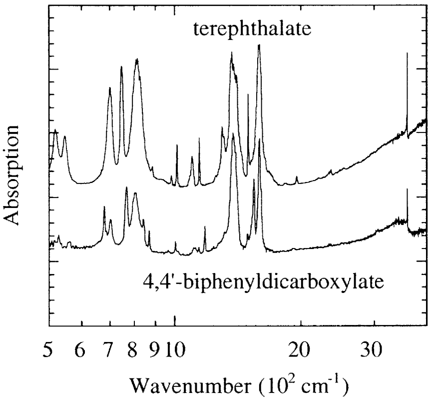

FIGURE 5 IR Absorption spectra of $Co_2(OH)_2$(dicarboxylate).

The infrared spectra (Figure 5) were used to identify the presence of the anions and its mode of coordination to the cobalt layers. The sharp OH band at 3600cm^{-1} suggests only hydroxide is present in these compounds [11]. The energies of the asymmetric and symmetric stretching vibrations (1590 and 1380cm^{-1}, respectively) and the bending mode at 810cm^{-1} of the carboxylate groups are neither consistent with a monodentate nor bidentate coordination to one metal. In our case the carboxylate coordination is asymmetric with an oxygen atom binds to one cobalt atom on one chain and the other to two cobalt atoms on an adjacent chain.

Magnetic Properties

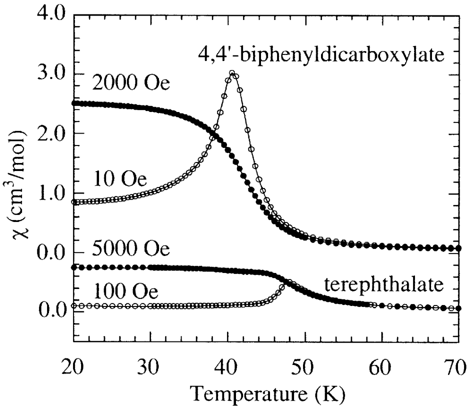

FIGURE 6 Temperature and field dependence of the magnetic susceptibility of $Co_2(OH)_2$(dicarboxylate).

The temperature dependence of the susceptibility of two representative compounds is shown in figure 6 for two applied fields. In low field, all the compounds behaves in a similar manner; their moment decreases to a minimum at ~120 K as the temperature is lowered from room temperature, followed by a continuous rise to a maximum at ~50 K. This behavior is typical of frustrated spin systems for homo-metallic compounds. The data in the range 150-300 K fit the Curie-Weiss law with C = 4.7(2) cm^3K/mol and Θ varies between -20 and -80 K. The Curie constants are consistent to that expected for the sum of two octahedral Co^{II} ions. The negative Weiss temperatures suggest dominant short-range antiferromagnetic exchange. Below 50K two transitions are evidenced in the small field (1 Oe) dc and ac magnetization; first a long range AF ordering (T_N) and a few degrees lower ($T_{canting}$) spontaneous magnetization due to a slight canting of the moments. The latter is accompanied by the observation of a bifurcation point in the zero-field cool and field cool measurement and a very weak and sharp out-of-phase component in the zero-field ac-susceptibility (not shown). At a field higher than the threshold field the magnetization saturates as for metamagnets [12].

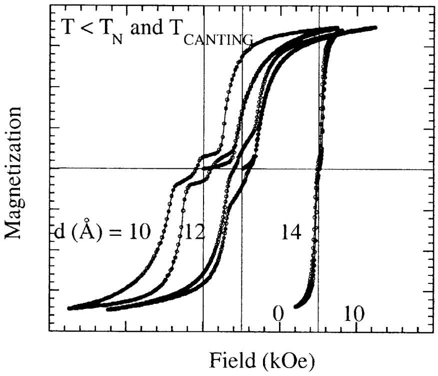

FIGURE 7 Isothermal magnetization of $Co_2(OH)_2(XX)$, XX= terephthalate (left), 1,9'-naphthalenedicarboxylate (middle) and 4,4'-biphenyldicarboxylate, just below the canting temperature.

Above T_N the isothermal magnetization of all the compounds display linear dependence until close to T_N where a Brillouin type of behavior is observed. Between T_N and $T_{canting}$ a characteristic reversible metamagnetic behavior is observed with a critical field increasing sharply as the temperature is lowered. Below $T_{canting}$, hysteresis sets in and its width widens as the temperature is lowered (Figure 7); two different loops are observed one around zero field and the other around the critical field. The unusual features characterizing this class of antiferromagnets are (a) the hysteresis, (b) the double hysteresis loops, (c) the width of the hysteresis loop that reaches ±5.2 Tesla at 2K [4] and (d) the separation of the two phase transitions contrary to what is expected for a Dzyaloshinskii and Moriya (DM) mechanism [13]. The magnetization increases linearly up to 25 Tesla suggesting slow reversal due to strong AF coupling and strong magnetocrystalline anisotropy. The critical field depends on the interlayer spacing; it decreases as the layers are separated, confirming that exchange through bonds is more likely to be the mechanism of long range magnetic ordering rather than exchange through space (dipolar).

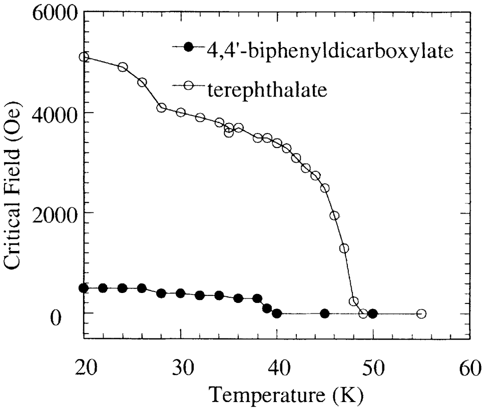

FIGURE 8 Temperature – field phase diagram for the $Co_2(OH)_2$(dicarboxylate) compounds.

CONCLUSION

This novel class of layered cobalt-hydroxide antiferromagnets presents unique and characteristic magnetic properties, *viz*: two successive magnetic transitions, metamagnetism with hysteresis and coercivity. Neutron diffraction and magnetic resonance studies are required to understand the different magnetic states and to determine the mechanism of long range magnetic orderings.

Acknowledgments

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