Journal of Solid State Chemistry 181 (2008) 3229–3235

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Ab-initio crystal structure of hydroxy adipate of nickel and hydroxy subarate of nickel and cobalt from synchrotron powder diffraction and magnetic properties

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ARTICLE INFO

Article history:
Received 22 February 2008
Received in revised form
27 June 2008
Accepted 29 June 2008
Available online 23 August 2008

Keywords:
Hybrid compound
Crystal structure
Rietveld analysis
Magnetic properties

ABSTRACT

Organic–inorganic hybrid compounds $Ni(II)_5(OH)_6(C_6H_8O_4)_2$ **(1)**, $Ni(II)_5(OH)_6(C_8H_{12}O_4)_2$ **(2)** and $Co(II)_5(OH)_6(C_8H_{12}O_4)_2$ **(3)** have a similar layered structure as determined *ab initio* from synchrotron powder diffraction analysis. The metal sites are octahedrally coordinated by O atoms. The slabs are built from edge-sharing octahedra in such a way that channels with an average size of 4 Å are formed. Bis-bidentate and bridging dicarboxylate anions lead to a 3D framework. The compounds **(1)** and **(2)** order antiferromagnetically below $T_N = 26.5$ and 19.3 K, respectively, while **(3)** is ferrimagnetic with $T_C = 16.2$ K. Crystal data for compounds are as follows: **(1)** $a = 11.6504(1)$ Å, $b = 6.8021(3)$ Å, $c = 6.3603(1)$ Å, $\alpha = 73.52(1)^\circ$, $\beta = 99.69(1)^\circ$, $\gamma = 96.16(1)^\circ$, $R_B = 0.070$, 668 reflections; **(2)** $a = 13.9325(1)$ Å, $b = 6.7893(1)$ Å, $c = 6.3534(4)$ Å, $\alpha = 73.63(1)^\circ$, $\beta = 95.14(1)^\circ$, $\gamma = 91.80(1)^\circ$, $R_B = 0.052$, 804 reflections; **(3)** $a = 13.9806(1)$ Å, $b = 6.9588(1)$ Å, $c = 6.3967(1)$ Å, $\alpha = 73.05(1)^\circ$, $\beta = 94.51(1)^\circ$, $\gamma = 92.19(1)^\circ$, $R_B = 0.048$, 410 reflections. The space group is $P-1$ for the three compounds.

1. Introduction

Over the past two decades, hybrid metal-organic materials have been intensively investigated, with a particular interest for the magnetic, optical and electrical properties associated with the various crystallographic structures. A recent review article surveys the progress that has been made on this subject [1]. As these metal-organic compounds often consist of more or less open or porous networks, these materials also find application as catalysts or for gas adsorption applications [2–5]. Among these compounds, those based on carboxylates are of particular interest. Review papers have been published that discuss the structural properties and strategies of chemical synthesis [6], magnetic properties, etc. [7]. Another one, focused especially on cobalt and nickel carboxylates [8], is also available.

In this paper, we investigated hybrid compounds based on dicarboxylate linkers for several reasons. These compounds can be synthesized easily under mild conditions of temperature and pressure and are thermally stable up to 400 °C. The dicarboxylates tend to form highly crystalline products. This facilitates the determination of their crystallographic structures more accurately than in the corresponding monocarboxylates. Moreover, due to the covalent bonds between the organic and mineral network, it is possible to imagine coupling between the properties of the two sub-networks. For example, it was shown that in Ni(II)-layered organic–inorganic compounds, the magnetic properties of the layers of nickel hydroxide influence the optical properties of the grafted luminescent molecules [9].

These compounds are synthesized in basic media to support the presence of hydroxides. *M* is a divalent transition metal element from the first series of the Periodic Table. The crystal structures of many such compounds have been accurately determined. In most cases the metal is located exclusively in an octahedral site, coordinated by O [10–26]. The oxygen atoms usually come from the hydroxide and/or carboxylate groups, but in some cases they come from the water molecules. The octahedra are connected via edge- or corner-sharing, which often leads to the formation of 1D chains [10–15] or 2D planes [16–25]. In the latter case, the planes can leave holes leading to porous materials [20,25]. Less frequently, the connection of the octahedra may lead to 3D networks [26].

This work attempts to contribute toward the development of new compounds in the *M*(II)-OH/dicarboxylates system. The main goal was to establish relations between the crystal structure and magnetic properties in the entitled compounds. The magnetism of the metal hydroxycarboxylates is relatively well understood [7,27] for compounds where the metal hydroxide layers form a brucite-like structure. In metal-hydroxy-dicarboxylates where the mineral

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0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.06.059

sub-unit differs and does not adopt a brucite-like arrangement, the magnetic behaviors are less well understood. For example, one can find ferrimagnetic compounds with ‘chains’ [10,11,13] or ‘planes’ [20,24,25,28], ferromagnetic compounds with ‘planes’ [19], antiferromagnetic compounds with ‘chains’ [14,15] or canted antiferromagnetics with ‘planes’ [16]. Conversely, the aforementioned compound with the 3D mineral network [26] remains paramagnetic at low temperature. In this work, three new compounds were synthesized by the hydrothermal route: Ni(II)5(OH)6(C6H8O4)2, Ni(II)5(OH)6(C8H12O4)2 and Co(II)5 (OH)6(C8H12O4)2. Their crystal structures were determined from synchrotron X-ray powder diffraction (XRPD) measurements and their magnetic, optical and thermal properties are characterized.

2. Experimental

2.1. Synthesis, thermal and chemical analyses

The nickel hydroxy adipate $Ni(II)_5(OH)_6(C_6H_8O_4)_2$ **(1)** was synthesized by the hydrothermal route from a mixture (2:3) of $Ni(NO_3)_2 \cdot 2H_2O$ (Aldrich, 98%) and adipic acid $C_6H_8O_4H_2$ (Aldrich, 98%) in aqueous solution, typically $Ni(NO_3)_2 \cdot 2H_2O$ (1.50 g, 6.8 mmol), $C_6H_8O_4H_2$ (1.50 g, 10.3 mmol,). The pH of the solution was increased up to 8 by the addition of NaOH (0.1 M). About 20 ml of the starting mixture was homogenized and transferred into a 25 ml teflon-walled acid digestion bomb, and then heated under autogenous pressure for 72 h at 150 °C. The reaction product was collected by filtration, washed twice with a mixture of distilled water and anhydrous ethanol (1/1) and then dried at room temperature. The same procedure was applied for $Ni(II)_5(OH)_6(C_8H_{12}O_4)_2$ **(2)** with subaric acid $C_8H_{12}O_4H_2$ (Aldrich, 98%) (1.79 g, 10.3 mmol), $Ni(NO_3)_2 \cdot 2H_2O$ (1.50 g, 6.8 mmol) and for $Co(II)_5(OH)_6(C_8H_{12}O_4)_2$ **(3)** with subaric acid $C_8H_{12}O_4H_2$ (1.79 g, 10.3 mmol), $Co(NO_3)_2 \cdot 2H_2O$ (Aldrich, 98%) (1.50 g, 6.85 mmol).

Thermogravimetric (TG) measurements were performed with a ‘TG/ATD 92–16.18’ SETARAM instrument between 20 and 600 °C in air and using a heating rate of 1°/min. The thermal curves for **(1)**, **(2)** and **(3)** are reported in Fig. 1. For each compound the weight loss occurs in a single stage, at 320 °C for **(1)**, and at 300 °C for **(2)** and **(3)**. It is ascribed to the transformation from **(1)** or **(2)** to NiO (as determined by X-ray diffraction, PDF: 44–1159) (43.5% obs; 45.5% calc **(1)**, 48.5% obs; 47.5% calc **(2)**) and from **(3)** to CoO (PDF: 75–0533) (45.3% obs; 45.3% calc **(3)**).

Chemical analysis: **(3)** C (obs: 26.20%; calc 25.92%), Co (obs: 36.02%; calc 30.24%); H (obs: 4.08%; calc 4.05%).

2.2. IR and UV spectroscopy

The IR spectrum was recorded with a ‘Spectrum one FT-IR’ spectrometer (Perking Elmer Instrument) in the ATR mode using the ‘Universal Sampling Accessory’.

UV–visible spectra were performed for compounds **(1)**, **(2)** and **(3)** with a CARY 4000 spectrometer operating in the 175–900 nm range.

2.3. Magnetic measurements

DC and AC magnetic susceptibility measurements were carried out with a PPMS Quantum Design [29], between 5 and 300 K for **(1)**, **(2)** and **(3)**. The χ_{DC} curves were recorded under a field of 10 kOe to determine the molar Curie constant (C_M), the paramagnetic Curie temperature (θp) and the effective moment (μ_{eff}). The χ_{AC} dependences with temperature were collected using a frequency of 100 Hz and alternative magnetic field $H_{AC} = 5$ Oe. No correction for diamagnetism was applied.

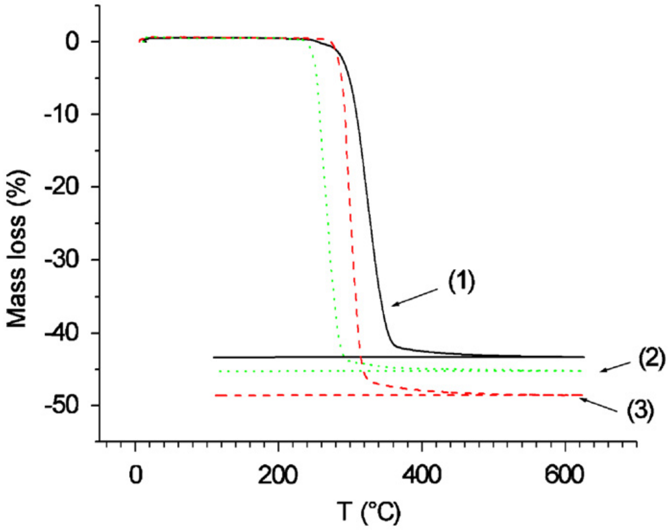

Fig. 1. TGA curve of **(1)**, **(2)** and **(3)**.

2.4. XRPD and ab-initio structure determination

XRPD data were collected at 100 K using synchrotron radiation (ESRF, ID 31, the transmission Debye Scherrer geometry). The diffractometer was equipped with a primary Si(111) double-crystal monochromator and nine sensitive linear position detectors with crystal analyzers [30]. The sample of a fine powder form was introduced in a Lindeman tube ($\Phi = 0.8$ mm). Data were recorded using a wave length of 0.85124 Å, in the 2θ range 4–60° with an interval of 0.003° and a total counting time of 2 h. Crystal data and structure refinement parameters are reported in Table 1.

2.4.1. Indexing

Standard peak search methods with Reflex program from Material Studio (MS) system software (Accelrys) [31] were used to locate the diffraction maxima; indexing was performed with the Xcell [32] program. For the three compounds, the solutions were found in the triclinic system aP. The lattice parameters, presented in Table 1, were refined by the Rietveld method.

2.4.2. Resolution

The three structures were solved in the space group $P-1$ applying optimization methods (parallel tempering) in the direct space, using the FOX program [33]. On the basis of thermal and chemical analyzes and expected density as well as UV–visible results (see hereafter), the asymmetric unit was filled for each model with three independent $M(II)O_6$ octahedra and one linear dicarboxylate molecule $C_6H_8O_4$ for **(1)**; $C_8H_{12}O_4$ for **(2)** and **(3)**—introduced as rigid bodies in the starting models without their H atoms. The optimization led to initial models in agreement with the chemical formulae $Ni(II)_5(OH)_6(C_6H_8O_4)_2$ for **(1)**, $Ni(II)_5(OH)_6(C_8H_{12}O_4)_2$ for **(2)** and $Co(II)_5(OH)_6(C_8H_{12}O_4)_2$ for **(3)**. All three structures contain three metallic sites ($M1$, $M2$ and $M3$) and seven O sites (4 O_{carb} and 3 O_{OH}); **(1)** contains six, whereas **(2)** and **(3)** contain eight C-sites, respectively. The $M1$ site is located in the inversion center.

Structural models were refined by the Rietveld method using the FULLPROF program [34]. A total of 46 and 52 intensity-dependent parameters for **(1)** and **(2)**, **(3)**, respectively, including