Crystal structure and magnetic properties of the layered hybrid organic–inorganic compounds $M_2(\text{OH})_2(\text{C}_{14}\text{H}_8\text{O}_4)$ ($M = \text{Mn}, \text{Fe}$)

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The structure of $M_2(\text{OH})_2(\text{bpdc})$ (bpdc = biphenyl dicarboxylate, $\text{C}_{14}\text{H}_8\text{O}_4$) is distinct from that of the isorecticular compounds $M_2(\text{OH})_2(\text{bdc})$ (bdc = benzene dicarboxylate, $\text{C}_8\text{H}_4\text{O}_4$) ($M = \text{Mn}, \text{Fe}$), in the sense that no disorder of the bpdc molecules from one layer to the other needs to be considered. The global symmetry is lower in the bpdc compounds ($P\bar{1}$) than in the bdc compounds ($C2/m$). Both $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ and $\text{Fe}_2(\text{OH})_2(\text{bpdc})$ order magnetically at 36.8 and 46.5 K, respectively, and can be considered as uncompensated antiferromagnets, whereas $\text{Mn}_2(\text{OH})_2(\text{bdc})$ (Néel temperature $T_N = 38.5$ K) and $\text{Fe}_2(\text{OH})_2(\text{bdc})$ ($T_N = 66$ K) are compensated antiferromagnets.

1. Introduction

Hybrid organic–inorganic compounds of general formula $M_2(\text{OH})_2(L)$, where M stands for a divalent first-row transition metal and L is a dicarboxylate anion ligand of general formula $^-\text{OOC}-\text{C}_6\text{H}_4\text{COO}^-$, were first discovered by Huang *et al.* (2000) for $M = \text{Co}$ and $L = \text{C}_8\text{H}_4\text{O}_2^{2-}$ (benzene-1,4-dicarboxylate, abbreviated to bdc and also called terephthalate). In their study, Huang *et al.* established the crystal structure *ab initio* using X-ray powder diffraction. Subsequently, the study was extended to other 3d transition metal elements, with $M = \text{Cu}$ (Abdelouhab *et al.*, 2005), Mn and Fe (Carton *et al.*, 2007a), and finally Ni (Carton *et al.*, 2007b). The latter nickel-based compound was obtained by dehydration of the $\text{Ni}_3(\text{OH})_2(\text{bdc})_2(\text{H}_2\text{O})$ phase (Mesbah *et al.*, 2014). A zinc-based compound also exists but its crystal chemistry is distinct from the other members of the series (Carton *et al.*, 2009), while the five compounds incorporating magnetic transition metal ions, $M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ and Cu , all adopt a similar crystal structure based on sheets of transition metal hydroxides in octahedral coordination (2D inorganic subnetwork). These sheets are pillared in the third direction by bdc molecules. The bdc molecules are always inclined in the same orientation within a layer, but adopt either the same orientation (ordered structure) or random orientations (disordered structure) from one layer to another. Thus, the slight structural variations between these five compounds mainly concern the order or disorder of bdc molecules (space groups $P\bar{1}$ and $C2/m$, respectively), and to a lesser

degree the coordination polyhedra around the different metals.

The macroscopic magnetic properties of hydroxy-terephthalates of Co^{II} (Huang *et al.*, 2000), Fe^{II} (Mesbah *et al.*, 2010), Ni^{II} (Carton *et al.*, 2007*b*) and Cu^{II} (Abdelouhab *et al.*, 2005) have been extensively investigated. The Co^{II} compound (Huang *et al.*, 2000) presents a complex and original magnetic behavior. An antiferromagnetic long-range order is stabilized at a Néel temperature of $T_{\text{N}} = 48$ K, however, a peak is observed in the imaginary part of the complex magnetic susceptibility χ_{ac} at a slightly lower temperature of 44 K, indicating the appearance of an uncompensated component. The influence of the applied field on the magnetic order was studied by isothermal magnetization measurements, which revealed that three nearly degenerate magnetic states can be stabilized depending on the magnetic field and temperature. At temperatures well below the magnetic ordering, a giant hysteretic effect is observed (the coercive field H_{C} amounts to 5.9 T at 4.2 K). The Cu^{II} compound is ferromagnetic below $T_{\text{C}} = 4.5$ K (Abdelouhab *et al.*, 2005) and the Ni^{II} analogue exhibits a very similar behavior (Carton *et al.*, 2007*b*). Finally, the compounds based on Fe^{II} and Mn^{II} are compensated antiferromagnets with Néel points at 66 K (Mesbah *et al.*, 2010) and 38.5 K (Sibille *et al.*, 2012), respectively. The magnetic structures of the Co^{II} (Feyerherm *et al.*, 2003), Mn^{II} (Sibille *et al.*, 2012) and Fe^{II} (Mesbah *et al.*, 2010) compounds were solved using neutron powder diffraction data. The arrangement of the magnetic moments for these three compounds are identical in terms of couplings but differ in the direction of the magnetic moments, probably due to different single-ion anisotropies.

In the present work, we address the question of the evolution of the magnetic properties as a function of the number of aromatic cycles in $M_2(\text{OH})_2(\text{OOC-C}_{6n}\text{H}_{4n}\text{-COO}^-)$ materials. We study two new compounds where $M = \text{Mn}$ or Fe and $n = 2$ (bpdc = 4,4'-biphenyl dicarboxylate). The crystal structure of materials based on this polyphenyl dicarboxylate is reported for the first time based on synchrotron X-ray powder diffraction (XRPD) data of a $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ sample. For this purpose, efforts were dedicated to improve the crystallinity, which is far less good for these new compounds than in materials based on terephthalate ligands ($n = 1$). Similar studies have already addressed the influence of the interlayer spacing on the magnetic properties of various kinds of organic-inorganic materials composed of magnetic layers and organic spacers of variable lengths. These studies related, for example, to lamellar hydroxide salts (Rabu *et al.*, 1996; Taibi *et al.*, 2002; Park *et al.*, 2005; Si *et al.*, 2012), metallic soaps (Rueff *et al.*, 2002) or metal-organic frameworks (Ban *et al.*, 2014). A number of works have focused on studying the influence of the interlayer spacing especially in model 2D magnets based on Cu^{II} (Laget *et al.*, 1999), while other remarkable investigations have addressed in detail the intercalation of spacers of various lengths in sheets of Co^{II} hydroxide (Laget *et al.*, 1996).

2. Experimental

2.1. Synthesis

4,4'-Biphenyl dicarboxylic acid ($\text{C}_{14}\text{H}_{10}\text{O}_4$, Aldrich, 0.5 mmol = 0.12 g) was dissolved in water (10 ml) through a strong base reaction (NaOH). This starting solution was adjusted to pH 8.0 by adding a solution of NaOH (0.2 M) dropwise. A solution of the desired metal cation ($\text{MnCl}_2 \cdot 0.4\text{H}_2\text{O}$ or $\text{FeCl}_2 \cdot 0.4\text{H}_2\text{O}$, Aldrich, 0.45 mmol = 0.09 g) was then added to the solution containing the organic ligand. The resulting suspension was kept under magnetic stirring and argon flow for a few minutes, while keeping a constant pH of 8.0 by adding drops of a NaOH solution (0.2 M). Powders obtained after hydrothermal treatment (three days, 150°C) were washed with a water-ethanol (1:1) solution and then air-dried. Different problems were encountered during our attempts to synthesize the iron and manganese compounds. $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ could not be obtained repeatedly due to the competition – which is not well understood – with the formation of the hydrated phase $\text{Mn}(\text{H}_2\text{O})_{1.5}(\text{bpdc})$ (Sibille *et al.*, 2018). The isotype with Fe^{II} is simpler to obtain, but in both syntheses the dicarboxylic acid is systematically present in the resulting samples and remains difficult to entirely wash out under pH conditions that do not alter the main product of the synthesis. While the sample of the manganese compound used in this work contained only small amounts of an unidentified impurity (see Section 2.5), a large amount of unreacted 4,4'-biphenyl dicarboxylic acid remained in the sample of the ferrous compound (Fig. S1), which prevented the exploitation of the diffraction data beyond the determination of unit-cell parameters.

2.2. Synchrotron X-ray powder diffraction

High-resolution X-ray powder diffraction (XRPD) data were collected at ambient temperature with synchrotron radiation on the CRISTAL beamline at SOLEIL (Saint Aubin, France). A monochromatic beam was extracted from the U20 undulator beam using a Si111 double monochromator. Its wavelength ($\lambda = 0.77752$ Å) was refined from a LaB_6 (NIST Standard Reference Material 660a) powder diagram recorded just before the experiment. The high angular resolution is achieved using a two-circle diffractometer (SMP-Lyon) equipped with an analyzer made of 21 perfect Si(111) crystals. The sample enclosed in a capillary ($\Phi = 0.8$ mm) is mounted on a spinner rotating at about 5–10 Hz, in order to improve powder averaging. Diffraction patterns were recorded for 2 h in the angular range $4^\circ < 2\theta < 50^\circ$ with a scan step of 0.002° .

2.3. Indexing

A set of 20 Bragg reflections was selected using the graphical interface of *Materials Studio* (Accelrys, <http://www.accelrys.com/products/mstudio/modeling/crystallization/reflex.html>), then used for indexing via the *X-Cell* software (Neumann, 2003). The triclinic cell $P\bar{1}$ of approximate unit-cell parameters $a \simeq 14.2$ Å, $b \simeq 6.5$ Å, $c \simeq 3.4$ Å, $\alpha \simeq 90^\circ$, $\beta \simeq 97^\circ$

and $\gamma \simeq 92^\circ$ quickly appeared as the most relevant solution. The unit-cell parameters b and c recall the unit cells of the $M_2(\text{OH})_2(\text{bdc})$ compounds (Abdelouhab *et al.*, 2005; Carton *et al.*, 2007a). A Le Bail refinement using 12 parameters (one zero shift, six unit-cell parameters, one isotropic broadening parameter due to particle-size effects and four anisotropic broadening parameters related to micro-strains) leads to satisfactory confidence factors ($R_{\text{wp}} = 0.0135$, $R_p = 0.106$). The LaB₆ standard was used to define the instrumental resolution function. The peak shape profiles were defined by using the Thomson–Cox–Hasting pseudo-Voigt function.

2.4. Structure solution

The starting model was derived from the structure of the $M_2(\text{OH})_2(\text{bdc})$ compounds suggested by the unit-cell parameters. The manganese atoms were positioned at the special positions $1a$ (0,0,0) (site $M1$) and $1g$ ($0, \frac{1}{2}, \frac{1}{2}$) (site $M2$) of space group $P\bar{1}$. The oxygen atom defining the hydroxide group was arbitrarily positioned in analogy with its coordinates in bdc-based materials. Finally, the bpdc molecule was inserted in the structure in the general position (random orientation). The molecule is a rigid body [see Scheme 1, which shows the atomic labels and distances (Å) in the bpdc molecule] and, being centrosymmetric, half of the atoms are sufficient to describe it in the general position of space group $P\bar{1}$.

Scheme 1

2.5. Rietveld refinement

The Rietveld refinement of the structure (Table 1 and Fig. 1) was performed using the *FullProf* software (Rodríguez-Carvajal, 2011). The metal atoms were fixed to their special positions as well as, initially, the oxygen atom defining the hydroxide group. Thus, only the Eulerian angles and the position coordinates of the rigid bpdc block including H atoms are refined in a first step. During this refinement, the bpdc molecule took the position and orientation expected from the structures of the bdc-based materials. In a second step, the refinement is further carried out by releasing the position of the oxygen atom, then four atomic displacement factors (see Table S1), and finally the 12 parameters refined during the Le Bail decomposition.

2.6. Additional characterization

A thermogravimetric analysis of the sample was performed using a TG/ATD 92-16.18 SETARAM instrument between 20°C and 650°C in air, at a heating rate of 1°C min^{−1}. The sample was placed into an alumina container, and data were corrected for the signal of the empty container.

Table 1

Experimental details.

Crystal data	
Chemical formula	$\text{C}_{14}\text{H}_{10}\text{Mn}_2\text{O}_6$
M_r	384.10
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	293
a, b, c (Å)	14.2037 (4), 6.47851 (8), 3.4532 (2)
α, β, γ (°)	90.091 (9), 96.839 (13), 91.7101 (16)
V (Å ³)	315.35 (2)
Z	1
Radiation type	Synchrotron
μ (mm ^{−1})	2.58
Specimen shape, size (mm)	Cylinder, 10 × 0.5
Data collection	
Diffractometer	CRISTAL Beamline, SOLEIL
Specimen mounting	Glass capillary
Data collection mode	Transmission
Scan method	2θ
$2\theta_{\text{min}}, 2\theta_{\text{max}}$ (°) and step values	2.511, 44.003, 0.004
Refinement	
R factors and goodness of fit	$R_p = 0.106$, $R_{\text{wp}} = 0.135$, $R_{\text{exp}} = 0.189$, $R_{\text{Bragg}} = 0.066$, $\chi^2 = 51.1052$
No. of parameters	23
H-atom treatment	H-atom parameters not refined

Computer programs: *FOX* (Favre-Nicolin & Černý, 2002), *FullProf* (Rodríguez-Carvajal, 2011).

A Fourier transform infra-red (FTIR) spectrum was recorded for $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ using a Bruker 80v spectrometer in the spectral region 500–4000 cm^{−1}. The specimen was prepared as a disk of dried KBr (100 mg) mixed with a small amount of the sample (3 mg). A dried KBr disk was used as baseline correction.

Figure 1

Observed (red), Rietveld calculated (black), and difference line of the synchrotron XRPD patterns ($\lambda = 0.77752$ Å) for $\text{Mn}_2(\text{OH})_2(\text{C}_{14}\text{H}_8\text{O}_4)$, $R_{\text{Bragg}} = 0.066$. The green vertical bars indicate the Bragg positions. Excluded regions correspond to contributions from an unidentified minor impurity.

2.7. Macroscopic magnetic measurements

DC and AC magnetic susceptibility measurements were carried out between 2 K and 300 K using a 'physical property measurement system' (PPMS) from Quantum Design. The DC curves were recorded under an applied magnetic field of 0.1 T upon cooling in order to detect the transition temperatures and to extract the molar Curie constant (C_M), the paramagnetic Curie–Weiss temperature (θ_{CW}) and the effective moment (μ_{eff}) from the paramagnetic state. The thermal dependence of the χ_{AC} was recorded without bias DC field, from 300 K to 2 K, using an alternative magnetic field $\mu_0 H_{AC} = 0.5$ mT, and a frequency of 1000 Hz. Isothermal magnetization curves were recorded at low temperatures in applied magnetic fields up to 9 T.

3. Results and discussion

3.1. Thermal properties

Fig. 2 shows the experimental weight loss as a function of temperature for $Mn_2(OH)_2(bpdC)$. The one-step weight loss is similar to that observed in $Mn_2(OH)_2(bdc)$ (see Fig. S2). The measurement demonstrates that the material remains stable

Figure 2
Thermogravimetric analysis of $Mn_2(OH)_2(bpdC)$ recorded upon heating in air.

Figure 3
FTIR spectra of $Mn_2(OH)_2(bpdC)$ recorded in transmission. Red dots correspond to bands assigned to the breathing vibration of the aromatic rings.

up to about 280°C, the temperature at which the material starts to decompose in air. The product of this decomposition is Mn_2O_3 manganese oxide, which was identified by XRPD. The theoretical weight loss for the reaction $Mn_2(OH)_2(C_{14}H_8O_4) \rightarrow Mn_2O_3$ is 58.9%, in reasonable agreement with the experimental weight loss of 54.5% given the contamination of the sample by a few mass % of bpdC acid.

3.2. FT-IR spectroscopy

The FT-IR spectrum of the sample (Fig. 3) has the following characteristic bands: (i) a sharp and intense band at 3616 cm^{-1} attributed to the stretching of O–H bonds (*i.e.* hydroxide group), (ii) a weak band around 3060 cm^{-1} attributed to stretching vibrations of C–H groups on phenyl rings, (iii) a band at 1543 cm^{-1} assigned to the antisymmetric stretching mode of the carboxylate function $\nu_{as}(COO^-)$ and the corresponding symmetrical stretching band $\nu_s(COO^-)$ at 1373 cm^{-1} . The small frequency difference between the stretching modes $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ ($\Delta\nu_{as-s} = 171\text{ cm}^{-1}$) is characteristic of bridging carboxylates, in agreement with the crystal structure.

Figure 4
Structure of $Mn_2(OH)_2(bpdC)$, projection along **b** (left) and **c** (right). H atoms are omitted for clarity.

Figure 5
Inorganic sub-network of $Mn_2(OH)_2(bpdC)$, projection along **a**.

Table 2

Mn–O distances (Å) in $\text{Mn}_2(\text{OH})_2(\text{bpdc})$.

Significant differences appear in the standard uncertainties on these distances, depending on the nature of the oxygen atom, because oxygen atoms belonging to carboxylate groups are treated as part of a rigid body.

Atom	Atom	Distance	Atom	Atom	Distance
Mn1	OH ⁱ or OH ⁱⁱ	2.09 (3)	Mn2	M_{26} or M_{26}^{iv}	2.1586 (2)
	M_{25}^{i} or M_{25}^{ii}	2.1336 (1)		OH or OH ^{iv}	2.260 (9)
	OH or OH ⁱⁱⁱ	2.23 (3)		M_{26}^{i} or M_{26}^{v}	2.2860 (3)

Symmetry codes: (i) $x, y, z - 1$; (ii) $-x, -y, -z + 1$; (iii) $-x, -y, -z$; (iv) $-x, -y + 1, -z + 1$; (v) $-x, -y + 1, -z + 2$; (vi) $-x - 1, -y + 1, -z + 2$.

3.3. Structural description

The hybrid compound $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ has a structure very similar to $\text{Mn}_2(\text{OH})_2(\text{bdc})$. These two compounds are isorecticular in the sense they have the same structural topology, while the Fe and Mn based compounds are isotype when associated with the same molecule (bdc or bpdc). The space group $P\bar{1}$ of $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ indicates the absence of disorder of the orientation of bpdc molecules, as in the case of copper hydroxy-terephthalate (Abdelouhab *et al.*, 2005). Fig. 4 presents two general views of the structure.

A view from the top of the 2D inorganic subnetwork is depicted in Fig. 5. The Mn–O distances are given in Table 2. The comparison with the values of terephthalate-based materials can be made using Table S2.

3.4. Magnetic properties

Macroscopic magnetic measurements were performed on $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ as well as on the $\text{Fe}_2(\text{OH})_2(\text{bpdc})$ isotype. Fig. 6 shows the DC magnetic susceptibility curves recorded between 300 K and 2 K with a static field of 0.1 T. These curves show a small increase in susceptibility as temperature decreases and then a much higher increase at low temperature with inflection points at 36.8 K (manganese compound) and 46.5 K (iron compound). Below these transition temperatures, the magnetic susceptibility tends to saturates, before another increase of weaker amplitude is observed, which might indicate either the onset of a second transition or parasitic paramagnetism. The signal recorded around 250 K for

Figure 6

Magnetic susceptibility curves as a function of temperature $\chi_{\text{DC}}(T)$ of $\text{M}_2(\text{OH})_2(\text{bpdc})$ compounds with $M = \text{Mn}^{\text{II}}$ and Fe^{II} .

Table 3

Geometrical parameters (Å, °) of the magnetic exchange pathway in $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ and $\text{Mn}_2(\text{OH})_2(\text{bdc})$ for comparison.

Atom	Atom	Atom	bpdc	bdc
Mn1	Mn1 ⁱ		3.453 (1)	3.398
Mn2	Mn2		3.453 (1)	
Mn1	Mn2 ⁱ		3.673 (1)	3.677
Mn1	Mn2			
Mn2	O _{COO}	Mn2 ^{vi}	101.92 (1)	98.2
Mn1	OH	Mn1 ^{vi}	105.9 (11)	102.7
Mn2	OH	Mn1	109.4 (8)	115.3
Mn1 ^{vi}	OH	Mn2	115.1 (8)	

Symmetry codes: (i) $x, y, z - 1$; (vi) $-x - 1, -y + 1, -z + 2$.

$\text{Fe}_2(\text{OH})_2(\text{bpdc})$ is attributed to the presence of magnetic impurities (small amounts of iron oxides).

The temperature dependence of the reciprocal susceptibility of $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ is shown in Fig. 7. The adjustment of this curve between 80 and 300 K to the Curie–Weiss law gives a Curie constant of $4.44 \text{ cm}^3 \text{ K mol} (\text{Mn}^{\text{II}})^{-1}$

Figure 7

Inverse magnetic susceptibility curve as a function of temperature $\chi_{\text{DC}}^{-1}(T)$ of $\text{Mn}_2(\text{OH})_2(\text{bpdc})$.

Figure 8

$\chi_{\text{AC}}(T)$ curves for $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ (left) and $\text{Fe}_2(\text{OH})_2(\text{bpdc})$ (right).

Figure 9
Isothermal magnetization cycles for $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ (left) and $\text{Fe}_2(\text{OH})_2(\text{bpdc})$ (right).

($8.88 \text{ cm}^3 \text{ K mol}^{-1}$), in good agreement with the expected value for a free ion $S = 5/2$ ($4.38 \text{ cm}^3 \text{ K mol}^{-1}$). The large and negative value of the Weiss temperature [$\theta_p = -205$ (1) K] indicates the dominant antiferromagnetic character of the exchange interactions of the inorganic subnetwork. AC magnetic susceptibility data for both compounds are illustrated in Fig. 8. In both cases a peak is observed at the magnetic transition in the in-phase component of the magnetization, accompanied by a signal in the out-of-phase part. In the case of $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ the peak is at 36.1 K in χ_{AC}' and 34.8 K in χ_{AC}'' . For the iron compound the signal in χ_{AC} at the transition is comparatively less sharp, and centered around 38.5 K in χ_{AC}' and 33.4 K in χ_{AC}'' . The presence of signals in the imaginary part of the alternative susceptibility indicates the existence of a ferromagnetic component, which was not observed in $\text{Mn}_2(\text{OH})_2(\text{bdc})$ and might be related to the lower symmetry of the present structure. In the case of the iron compound, the peak in χ_{AC}' occurs at a significantly lower temperature than that in χ_{AC}'' , which recalls the behavior of $\text{Co}_2(\text{OH})_2(\text{bdc})$ (Huang *et al.*, 2000).

The measurement of the isothermal magnetization in the ordered regime (Fig. 9), reveals the opening of hysteretic cycles. The saturation is not reached in an applied magnetic field of 9 T applied field and the remanent magnetization, of the order of $0.05 \mu_B \text{ mol}^{-1}$, remains small even at the lowest temperatures. This value excludes a ferromagnetic ordering but rather indicates the stabilization of an uncompensated antiferromagnet, in agreement with the AC and DC susceptibility data.

3.5. Comparison with bdc-based compounds

The Fe^{II} and Mn^{II} bdc-based compounds exhibit a compensated antiferromagnetic behavior with Néel points at $T_N = 66 \text{ K}$ (Mesbah *et al.*, 2010) and 38.5 K (Sibille *et al.*, 2012), respectively. On the basis of the results obtained here, a detailed comparison of the structural variations existing between $\text{Mn}_2(\text{OH})_2(\text{bdc})$ and $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ is made in Table 3, where the local exchange pathway parameters are reported. The values of the reported distances and angles only differ by $0.05 \text{ \AA}$ and 5° , respectively, which appears rather small to explain a significant change of magnetic interactions

between the bdc- and bpdc-based compounds. Thus we suggest that the lower symmetry of the bpdc-based materials plays a role in the stabilization of a ferromagnetic component.

Finally, results have already been published for the compound $\text{Co}_2(\text{OH})_2(\text{bpdc})$ (Kurmoo & Kumagai, 2002). In this study an X-ray diffraction pattern is presented and the authors consider, based on the results of the thermogravimetric analysis, that the structure of the compound is similar to that of the hydroxy-terephthalate, which is verified more precisely here for the manganese analog. The results presented by Kurmoo & Kumagai (2002) also show that the macroscopic magnetic behavior of $\text{Co}_2(\text{OH})_2(\text{bpdc})$ is similar to that of $\text{Co}_2(\text{OH})_2(\text{bdc})$.

4. Conclusion

Efforts devoted to improve the crystallinity and the purity of $\text{M}_2(\text{OH})_2(\text{bpdc})$ compounds, which are significantly more challenging to prepare than their bdc analogs, have led to assess the isotype crystal structure by refining that of $\text{Mn}_2(\text{OH})_2(\text{bpdc})$. The structure is distinct from that of $\text{Mn}_2(\text{OH})_2(\text{bdc})$ in the sense that no disorder of the molecules from one layer to another needs to be considered. However, the global symmetry is lower in the bpdc ($P\bar{1}$) than in the bdc compound ($C2/m$). Both $\text{Mn}_2(\text{OH})_2(\text{bpdc})$ and $\text{Fe}_2(\text{OH})_2(\text{bpdc})$ order magnetically and are best described, according to macroscopic data, as uncompensated antiferromagnets. These results add to the knowledge on this interesting family of layered hybrid compounds and also inspire further works to fully understand the original magnetic properties of these materials and the role played by the disorder of the molecules from one layer to the other.

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