Z. Kristallogr. Suppl. **26** (2007) 581-586

Structures of transition metal hydroxy-terephthalates

A. Carton[1], A. Mesbah[1], M. François[1*], P. Rabu[2]

[1]Laboratoire de Chimie du Solide Minéral, Université H. Poincaré, Nancy I, France
[2]Institut de Physique et Chimie des Matériaux de Strasbourg, France
[*]michel.francois@lcsm.uhp-nancy.fr

Keywords: Hybrid compounds, synchrotron powder diffraction, hydroxycarboxylates, Ab-initio structure determination

Abstract. The structures of hydroxyterephthalates of transition metal M (M = Mn, Fe, Ni and Zn) have been determined from synchrotron powder diffraction data. Mn and Fe based compounds are isotype with $Co_2(OH)_2tp$ (tp = $C_8H_4O_4$). Divalent metallic cations in the hydroxide layers are in octahedral O-coordination. The structures of Zn and Ni based compounds present new structures which were determined by ab initio methods. $Zn_2(OH)_2tp$ structure differs mainly from the formers by the pentahedral O-coordination of Zn^{2+} cations. Nickel based compound crystallises with the formula unit $[Ni_3(OH)_2(tp)_2(H_2O)_4].2H_2O$. The structure is build up from 1D chain of nickel octahedra. The repeating unit of the chain consist of two edges sharing octahedra linked to a third octahedra vertex. In all these structures, tp anions are bridging and bidentate conferring a 3D and 2D character to Mn, Fe, Zn and Ni based compounds respectively.

Introduction

The transition metals hydroxycarboxylates are hybrid materials of particular interest for the studies of magnetism in low dimensional systems. Indeed, these structures are usually formed from inorganic metal hydroxide 2D layers spaced by organic species. Magnetism-structure relationship have been extensively studied [1-5]. Moreover and more generally, the main potentiality of these hybrids would be to create multifunctional materials. For example, the mineral component could bring magnetic properties in case of unsaturated 3d level of divalent metal while complex organic chromophoric molecules could bring optical properties as it was made in MPS3 lamellar compound [6]. Unfortunately, the number of accurate crystallographic structures for this specific materials are not so numerous, probably because single crystals are difficult to obtain, thus limiting the fundamental knowledge of the relationship structure-properties. Nevertheless structures of model compounds using 1,4-benzene-dicarboxylate, so called terephthalate or $C_8H_4O_4^{2-}$, as the organic species have been already established: $Co_2(OH)_2tp$ [7], $Cu_2(OH)_2tp$ [8]. Our goal was to complete the first transition metal hydroxy-terephthalate series. In this paper, we report the unknown structures of the Mn, Fe, Ni and Zn based compounds, established from synchrotron powder diffraction data.

Experimental

X Ray analysis, indexing and resolution

The powders were synthetised by hydrothermal method. Details can be found in [8,9]. The X ray powder diffraction data were recorded thanks to synchrotron radiation. The table 1 list the experimental details for the four analysed compounds named MOHtp (M = Mn, Fe, Ni, Zn).

Table 1: Experimental details concerning the data collection, indexing of the powder diagrams and the resolution of the structures.

Compound	NiOHtp	FeOHtp/ZnOHtp	MnOHtp
Synchrotron	LURE	ESRF	SLS
Site	Orsay (France)	Grenoble (France)	Villingen (Suisse)
Beamline	DW 22	ID 31	MSX04SA
Waveleng	0,96106 Å 1,0005 Å	0,63248 Å	0,708838 Å
Temp. (K)	300	100	100
Detection details	Si (111) crystal analyser	Nine Si(111) crystals analyser	Multistrip [10]
Indexing	XCell [11]	Isotype/XCell [11]	Isotype
Resolution	FOX [12]	CoOHtp isotype/ EXPO [13]	CoOHtp isotype

Rietveld refinements

The Rietveld method was performed using Fullprop_suite software [14]. The refinement parameters were reported on table 2 and the Rietveld diagrams are presented on figure 1.

Table 2: Structural data and refinement parameters

Compound	MnOHtp	FeOHtp	ZnOHtp	NiOHtp
Formula	$Mn_2(OH)_2tp$	$Fe_2(OH)_2tp$	$Zn_2(OH)_2tp$	$Ni_3(OH)_2(H_2O)_4tp$
Space group	C2/m	C2/m	$P2_1/c$	P-1
a (Å)	19.9174(1)	19.9673(1)	3.48823(2)	10.2025(6)
b (Å)	3.3617(1)	3.3985(1)	5.84648(2)	8.0072(5)
c (Å)	6.3270(1)	6.5231(1)	22.1325(2)	6.3285(4)
α (°)	90.0	90.0	90.0	97.223(5)
β (°)	95.224(1)	95.2063(1)	103.46(1)	97.223(5)
γ (°)	90.0	90.0	90.0	108.770(5)
2-theta range (°)	2.02-67.95	2.51-52.3	5.0-35.0	4.04-50.36
$R_{p\,\%}$	12.2	7.65	11.6	4.9
$R_{wp\,\%}$	15.9	10.6	17.6	6.5
$R_{B\,\%}$	8.15	8.94	10.8	9.7
$R_{F\,\%}$	8.75	14.3	6.7	14.7
χ^2	20.5	5.3	6.0	3.9
Nb. atomic parameters	20	20	30	60

For the ZnOHtp data, the Rietveld refinement was performed using a Thomson-Cox-Hasting function and a microstructural model was applied due to the large anisotropic peaks broadening observed on the pattern.

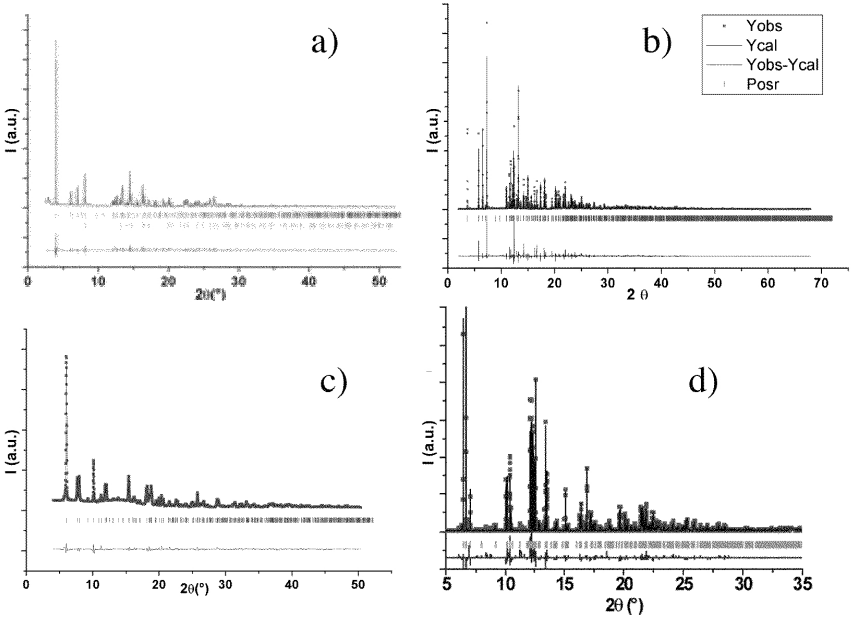

Figure 1: Rietveld diagrams for a) MnOHtp, b) FeOHtp, c) NiOHtp and d) ZnOHtp

Structural descriptions

$M(II)_2(OH)_2tp$ with M = Mn, Fe

The structure of $M(II)_2(OH)_2tp$ (M = Mn, Fe) which is isotypic to $Co_2(OH)_2tp$ [7] is shown on the figure 2. The terephtalate groups are pillared and coordinated to the cobalt hydroxide layers, thus forming a three dimensional network. The structure is characterised by octahedrally coordinated M^{II} ions bearing both triply bridging hydroxyls (μ_3) and carboxylate groups (η^1, η^2). Two crystallographically independent M^{II} ions are present: one bounded to four hydroxyls and two carboxylic oxygen atoms, the other bounded to two hydroxyls and four tp oxygen atoms. Inter atomic distances Mn-O and Fe-O range between 2.17-2.22 and 2.15-2.16 Å respectively. In copper based compound, a triclinic distortion due to Jahn-Teller effect occurs. The regular layer in the Co based compound and the distorted layer in the Cu based compound were presented in the figure 3 of [8].

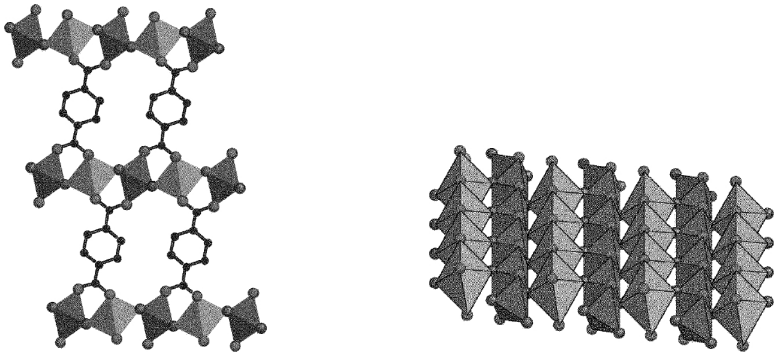

Figure2: Structure of $M_2(OH)_2(C_8H_4O_4)$ and representation of a layer

$Zn_2(OH)_2tp$

A general view of the structure of $Zn_2(OH)_2tp$ is represented on the figure 3a. It can be compared to that of figure 2. Similarly, the tp molecules have a bridging character and are bidentate, i.e. connect two adjacent Zn^{2+} cations. Two different orientations, leading to two distinct interlayer regions, were observed for tp molecules in ZnOHtp compound while all the tp molecules have the same orientation in the MOHtp (M = Mn, Fe, Co, Cu) analogues. The layers represented on the figure 3b are formed of infinite 'ZnO_5' pentahedra connected by corners via μ_3OH. Pentahedra can be described as triangular bipyramids, which is more or less an unusual coordination for Zn^{2+}. Three distances Zn-OH range from 1.969(8) to 2.119(9) Å and two Zn-Otp are of 2.048(9) and 2.005(8) Å. It must be emphasised that a second phase with composition $Zn_3(OH)_4tp$ have been found. It structure have been refined from single crystal X-ray diffraction data [9]. This structure presents zinc atoms in three different O-coordinations (tetra, penta and octa).

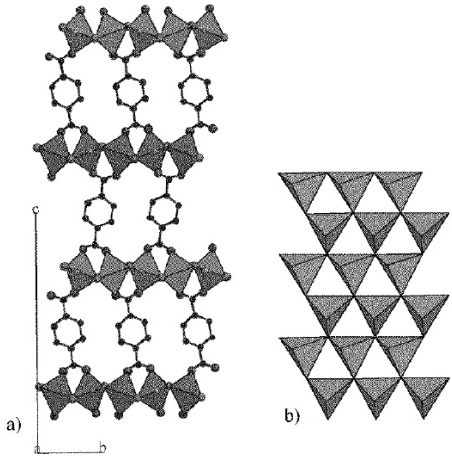

Figure 3. a) $Zn_2(OH)_2(tp)$, b) layer

$[Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_4].2H_2O$

The structure of $[Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_4].2H_2O$ is shown on the figure 4a. It is formed by infinite layers parallel to the (010) planes. Each layer is build from 1D chains of nickel octahedra, parallel to the c axis, connected by bridging and bidentate tp anions. An isolated chain is represented on the figure 4b. These layers are themselves connected by hydrogen bonding between Ni-coordinated water molecules. There is two different crystallographic positions for the Ni atoms : Ni(1) and Ni(2). The structural unit of the nickel oxide chains is $[Ni(1)O_6]_2Ni(2)O_6$, consisting of two edges sharing octahedra related to the symmetry center linked via μ_3-OH to a vertex of Ni(2) octahedron. The Ni(1) coordination is ensured by two oxygen from two water molecules, two OH and two oxygen from carboxylates groups. The interatomic distances Ni-O are ranging between 2.03 to 2.16 Å as it is usually encountered for Ni-O iono-covalent bonding.

It is interesting to compare the structural properties of $[Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_4].2H_2O$ with that of the parent fumarate compound $[Ni_3(OH)_2\ (C_4H_2O_4)_2(H_2O)_4].2H_2O$ [15] for which the structure as been redrawn in the figure 4c. Both structures are formed by the same structural unit, ie the trimeric octahedra forming the link of the chains, but in the latter, the pillar fumarate anion form a 3D framework.

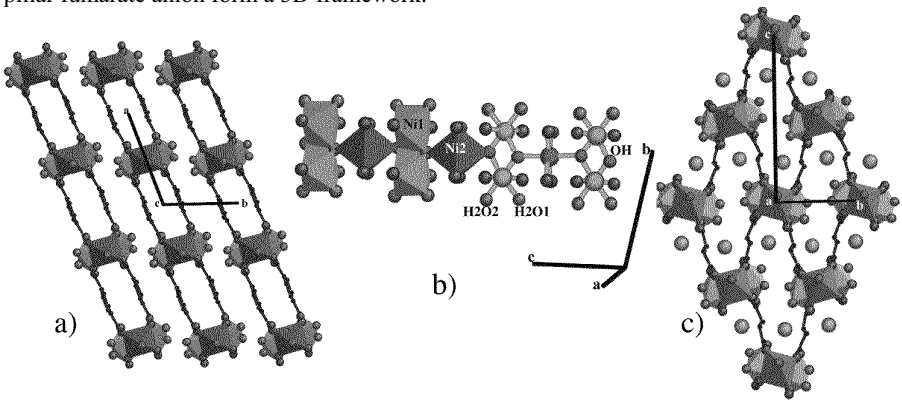

Figure 4: a) NiOHtp 2D structure b) isolated chain of octahedra c) NiOH-fumarate 3D structure [15]

Conclusion

We have presented here a structural study from synchrotron powder diffraction data for transition metal hydroxyterephthalates. The compositions and the structures are metal dependent. Three structures are reported of which two are new: those adopted by Zn and Ni based compounds that have been solved by ab initio methods.

In summary, in the $M_2(OH)_2$tp structural series, symmetry is C2/m for M = Mn, Fe, Co, P-1 for M = Cu and $P2_1/c$ for M = Zn. Magnetic divalent cations are in a relatively regular octahedron for M = Mn, Fe, Co and in a distorted one for M = Cu. The Zn^{2+} cations are found to be in a relatively unusual triangular bipyramidal coordination.

The nickel based compound crystallises with its own formula unit $[Ni_3(OH)_2(C_8H_4O_4)_2(H_2O)_4].2H_2O$ but which is similar to the fumarate based compound $[Ni_3(OH)_2(C_4H_2O_4)_2(H_2O)_4].2H_2O$ previously reported [15]. Both the structures contain chains (1D), but the linking of the organic species is different and leads to a 3D structure in the fumarate ($C_4H_2O_4^{2-}$) and a 2D structure in the terephthalate ($C_8H_4O_4^{2-}$).
Relationship between magnetic and structural properties for M = Mn, Fe and Ni based compound will be published elsewhere.

References

1. Laget, V., Rouba, S., Rabu, P., Hornick, C. & Drillon, M ., 1996, *J. of Magnetism and Magnetic Materials*, **154**, L1-L7.
2. Drillon, M. & Panissod, P., 1998, *J. of Magnetism and Magnetic Materials*, **188**, 93-99.
3. Rabu, P., Hornick, C. & Drillon M., 1998, *Lettre des Sciences Physiques*, **68**, 31-34.
4. Hornick, C., Rabu, P. & Drillon, M., 2000, *Polyhedron*, **19**, 259-266.
5. Rabu, P., Huang, Z.-L., Hornick, C. & Drillon, M., 2001, *Synthetic Metals*, **122**, 509-515.
6. Clément, R., Lacroix, P.G., O'Hare, D. & Evans, J., 1994, *Adv. Mater.*, **10**, 794-797.
7. Huang, Z.-L., Drillon, M., Masciocchi, N., Sironi, A., Zhao, J.-T., Rabu, P. & Panissod, P., 2000, *Chem. Mater.*, **12**, 2805-2812.
8. Abdelouhab, S., François, M., Elkaim, E.& Rabu, P., 2005, *Solid State Sciences*, **7**, 227-232.
9. Carton, A., Abdelouhab, S., Renaudin, G., Rabu, P. & François, M., 2006, *Solid State Sciences*, **8**, 958-963.
10. Schmitt, P., 2003, B. Mythen detector system. *NuclearIinstruments and Methods in Physics Research*, section **A 501**, 267.
11. Neumann, M., 2003, *J. Appl. Cryst*., **36**, 356-365.
12. Favre-Nicolin, V. & Černý, R., 2004, *Z. Kristallogr.*, **219**, 847–856.
13. Altomare, A., Burla, M. C., Camalli, M., Carrozzini, B., Giacovazzo, C., Guaguiardi, A., Moliterni, A.G.G., Polidori, G. & Rizzi, R., 1999, *J. Appl. Cryst.*, **32**, 339-340.
14. Rodriguez-Carvajal, J., FULLPROF version June 2005, ILL (unpublished).
15. Guillou, N., Pastre, S., Livage, C. & Férey, G., 2002, *Chem. Commun.*, 2358-2359.

Acknowledgements. The authors would like to thank Eric Elkaim from 'Laboratoire pour l'Utilisation du Rayonnement Synchrotron (LURE)' in Orsay, France, Bern Schmitt from 'Swiss Light Source (SLS)' in Villigen, Switzerland, and Irena Margiolaki from 'European Synchrotron Radiation Facilities (ESRF)' in Grenoble, France, for helping us in ours experiments.