ESRF	**Experiment title: Structural Determination of zinc carboxylates with long aliphatic chains by HRPD**	**Experiment number**: CH-2017
Beamline: ID31	**Date of experiment**: From: 14 Dec 2005 to: 16 Dec 2005	**Date of report**: 18 Sep 2006
Shifts: 6	**Local contact(s)**: Dr Irene MARGIOLAKI	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Adel MESBAH*

Anne CARTON*

Michel FRANCOIS*

***Laboratoire de Chimie du Solide Minéral UMR 7775, BP 239,Faculté des Sciences et Techniques, Vandoeuvre les Nancy, 54506 France**

Report:

REPORT OF THE ESRF-CH1017 EXPERIMENT

1- INTRODUCTION

This experiment was a contribution to a program offering an environmentally friendly alternative to the zinc and magnesium protection conversion process. The project number CH1017, proposed to determine the crystallographic structures of the corrosion inhibitors with general formula $M((C_nH_{2n-1})O_2)_2\ (H_2O)_x$ with n ≥10 (code MCn with M= Zn,Mg) using ab-initio methods of resolution. We measured also same well structured mixing compound as ZnCn-ZnCn'. Among the nine samples measured (see the table after), three new structures have been fully determined. Some results are presented in the following.

2- EXPERIMENTAL

X-ray powder diffraction data were collected by using the synchrotron radiation at the Europeen Synchrotron Radiation Facilities (ESRF), on the very high resolution powder diffractometer installed on the beam line ID31. A primary double crystal monochromator Si(111) is used for selecting the wave length. The detection is ensured by nine consecutive crystals Ge(111) analyser. The sample constituted of a fine powder is introduced in a Lindeman tube (Φ = 1 mm). The sample was contained in spinning on the axis of the diffractometer. The capillary was translated along the axis to give a fresh region of sample every 15 mn to avoid radiation damage. Data were recorded by using a wave length of 0.851243(4) Å, at 100 K with an interval of 0.003° and a total counting time of 2 h.

3- CRYSTALLOGRAPHIC RESULTS

3-1- Mixed compounds

$Zn(C_{10}H_{19}O_2)(C_{14}H_{27}O_2)$ (ZnC10C14)

The diffraction pattern of the mixed compound ZnC10 C14 could be indexed in a triclinic lattice P1 with the parameters: a = 4.311 (1) Å, b = 4.997(1) Å, c = 28.999 (1) Å, α = 94.80 (1) °, β = 93.16 (1) ° = and γ = 64.57(1) °). Rietveld refinement is presented on figure 1 (Rp = 15.1, Rwp = 21.9, Chi2 = 26.8, R_B = 14.8, R_F = 12.7). Structural model showing the structure with adjacent ZnC10 and ZnC14 slabs is shown on Figure 1. Atomic coordinates for ZnC10C14 are reported in Table 1

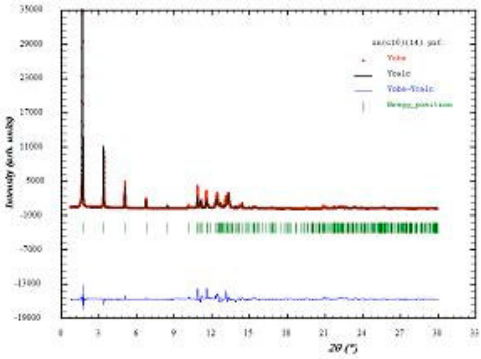

Figure1 : Rietveld refinement for Zn(C10-C14)

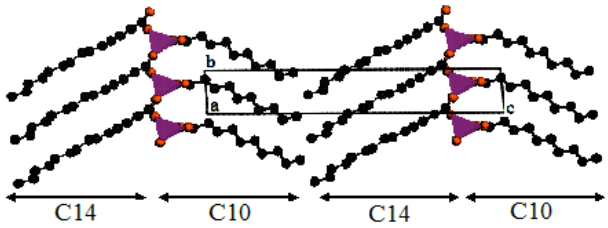

Figure 2: projection along [100] of the structure of $Zn(C_{10}H_{19}O_2)(C_{14}H_{27}O_2)$

Table1 : Final fractional coordinates for non-hydrogen atoms for $Zn(C_{10}H_{19}O_2)(C_{14}H_{27}O_2)$.

Atom	*x*	*y*	*z*
Zn1	-0.876	-0.306	-0.127
O11	-0.623	-0.297	-0.068
O12	-0.275	-0.297	-0.095
O21	-0.080	-0.043	-0.179
O22	-0.574	-0.644	-0.168
C11	-0.327	-0.320	-0.052
C12	-0.351	-0.204	-0.000
C13	-1.036	-0.407	0.028
C14	-1.112	-0.351	0.080
C15	-0.982	-0.652	0.103
C16	-1.141	-0.611	0.151
C17	-1.027	-0.911	0.173
C18	-1.049	-0.856	0.226
C19	0.178	-1.139	0.251
C110	0.005	-1.062	0.298
C21	-0.394	0.115	-0.196
C22	-0.539	-0.031	-0.235
C23	-0.281	-0.191	-0.275
C24	-0.495	-0.309	-0.308
C25	-0.168	-0.419	-0.337
C26	-0.277	-0.548	-0.382

C27	0.042	0.414	-0.408
C28	0.106	0.193	-0.453
C29	-0.549	0.131	-0.473
C210	0.447	-0.005	-0.527
C211	0.822	-0.148	-0.546
C212	0.819	0.721	-0.596
C213	1.210	0.539	-0.604
C214	1.232	0.431	-0.656

$Zn(C_{10}H_{19}O_2)(C_{16}H_{31}O_2)$ Zn C10 C16

The diffraction pattern of the mixed compound ZnC10 C16 could be indexed in a triclinic lattice P1 with the parameters: a = 4.762 (1) Å, b = 4.779 (1) Å, c = 30.960 (2) Å, α = 90.39 (1) °, β = 85.81 (1) ° = and γ = 70.88 (1) °). Rietveld refinement is presented on Figure 3 (Rp = 14.5%, Rwp = 21.7%, Chi2 = 28.9, R_B = 24.8, R_F = 26.6). Structural model showing the superstructure with adjacent ZnC10 and ZnC16 slabs is shown on figure 4. Atomic coordinates for ZnC10C16 are reported in Table 2

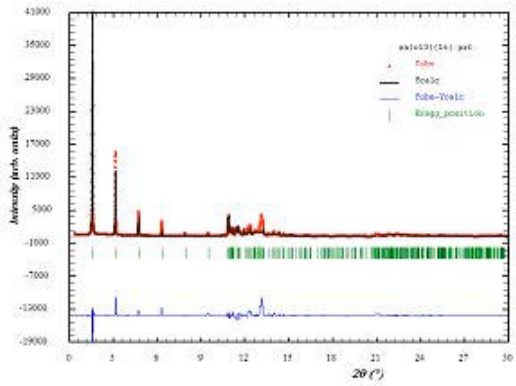

Figure 3 : Rietveld refinement for Zn(C10-C16)

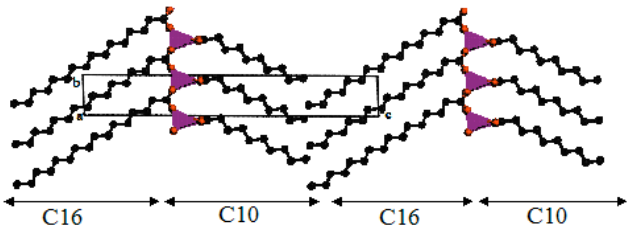

Figure 4: projection along [100] of the structure of $Zn(C_{10}H_{19}O_2)(C_{16}H_{31}O_2)$

Table 2: Final fractional coordinates for non-hydrogen atoms for Zn $(C_{10}H_{19}O_2)(C_{16}H_{31}O_2)$.

Atom	x	y	y
Zn1	-0.199	-1.021	-0.649
O11	0.505	-1.135	-0.604
O12	0.067	-1.157	-0.603
C1	0.269	-1.124	-0.583
C2	0.227	-1.070	-0.534
C3	0.372	-1.362	-0.513
C4	0.319	-1.317	-0.464
C5	0.463	-1.609	-0.442
C6	0.410	-1.564	-0.393
C7	0.554	-1.857	-0.371
C8	0.501	-1.812	-0.322
C9	0.645	-2.104	-0.300
C10	0.592	-2.059	-0.251

O21	-0.262	-0.792	0.294
O22	-0.189	-0.314	0.311
C21	-0.155	-0.605	0.281
C22	-0.102	-0.619	0.232
C23	-0.154	-0.896	0.214
C24	-0.095	-0.919	0.165
C25	-0.146	-1.196	0.147
C26	-0.087	-1.219	0.098
C27	-0.139	-1.496	0.080
C28	-0.080	-1.519	0.031
C29	-0.132	-1.796	0.014
C210	-0.073	-1.819	-0.034
C211	-0.124	-2.095	-0.052
C212	-0.065	-2.118	-0.101
C213	-0.116	-2.395	-0.119
C214	-0.058	-2.418	-0.168
C215	-0.109	-2.695	-0.185
C216	-0.051	-2.718	-0.235

$Mg(C_{10}H_{19}0_2)_2(H_2O)_3$ (MgC10)

Magnesium carboxylates contain water molecules. The structure of $Mg(C_{10}H_{19}O_2)_2(H_2O)_3$ determined from synchrotron data is similar to that of heptanoate equivalent. No evidence for existence of polytypes is observed. Rietveld refinement (see Figure 5) of the powder pattern leads to satisfactory R factors (R_B = 7.7%, R_{wp} = 6.3%, χ^2= 2.71). The structure is presented in Figure 6. The magnesium atoms are in a octahedron constituted by three oxygen atoms coming from carboxylate groups and by three oxygen atoms coming from water molecules. The layer thus consists of two half-layers connected by hydrogen bonds.

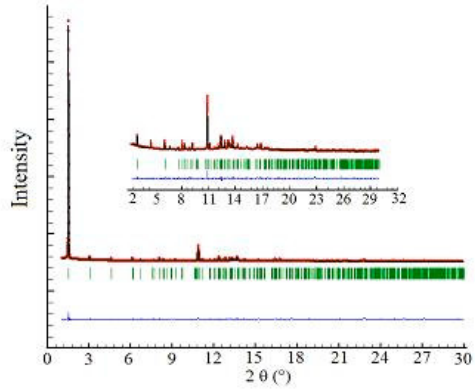

Figure 5 : Affinement Rietveld de MgC10 (groupe C2)

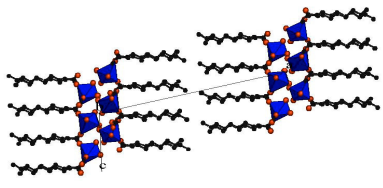

Figure 6: projection along [010] of the $Mg(C_{10}H_{19}0_2)_2(H_2O)_3$.

Table 3: Final fractional coordinates for non-hydrogen atoms for $Mg(C_{10}H_{19}0_2)_2(H_2O)_3$.

Atom	*x*	*y*	*Z*
Mg	1.1316(4)	0.6529(4)	0.93603(11)
O1	1.0740(30)	0.9046(9)	0.9388(10)
O2	0.9850(2)	0.6570(30)	0.9814(6)
O2	1.2145(4)	0.6350(30)	1.00126(17)
O1	0.9455(16)	0.5901(10)	0.8934(7)
O12	0.8005(17)	0.8021(19)	0.9024(7)
C11	0.8500(30)	0.6970(30)	0.87885(14)
C12	0.8100(50)	0.7203(11)	0.83229(18)
C13	0.810(40)	0.5662(19)	0.8063(5)
C14	0.7180(30)	0.5810(4)	0.7634(3)
C15	0.7710(40)	0.4760(4)	0.7297(3)
C16	0.6860(40)	0.5080(5)	0.6872(3)
C17	0.7390(20)	0.4120(4)	0.6529(4)
C18	0.6300(30)	0.4100(4)	0.6129(6)
C19	0.6600(30)	0.2770(4)	0.5824(6)
C110	0.5550(30)	0.2780(5)	0.5408(6)
O21	0.6930(3)	0.1092(1)	0.9242(10)
O22	0.7870(2)	0.3587(1)	0.9324(7)
C21	0.7628(16)	0.2318(1)	0.9109(4)
C22	0.8761(12)	0.2160(4)	0.8811(2)
C23	0.8220(4)	0.2598(2)	0.83501(18)
C24	0.8450(4)	0.1220(3)	0.8043(4)
C25	0.7600(4)	0.1330(3)	0.7589(4)
C26	0.7990(3)	0.0020(4)	0.7280(6)
C27	0.6965(11)	-0.0120(6)	0.6855(3)
C28	0.7712(7)	-0.0610(5)	0.6476(4)
C29	0.6641(15)	-0.1100(5)	0.6082(7)
C210	0.7300(3)	-0.2170(4)	0.5769(9)

4- **CONCLUSION**

At present time we have established structural models for the compounds ZnC10C14, ZnC10C16 and MgC10. The indexation of the remaining pattern is in progress. Nevertheless, we have to emphasis that some patterns are relatively difficult to analyze. Indeed, some apparent 'pure' pattern can in fact be due to melt of polytypes with very narrow lattices. This is probably due to the various ways for stacking these lamellar structures. An other crucial problem in this kind of compound is the preferred orientation. It seems it remains relatively high although the facts the compound were measured in capillaries.

The results have been presented to EPDIC-10 in geneva (Suisse) [1] and to MATERIAUX-2006 in Dijon (France) [2].

[1] A. Mesbah, C Juers, M François, E. Rocca and J Steinmetz, "Magnesium And Zinc Long Aliphatic Chains Carboxylates", EPDIC-10, 1-4 septembre 2006, Genève

[2] A. Mesbah, C Juers, F. Lacouture, S. Mathieu, M. François, E. Rocca Et J. Steinmetz « Structures cristallines de carboxylates métalliques assurant la protection du zinc et du magnésium contre la corrosion, Matériaux 2006, 132-17 Novembre 2006, Dijon