

# DESY SUMMER STUDENT PROJECT

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## **Structure determination of novel Metal-Organic Frameworks (MOF)**

Area of research:  
Inorganic chemistry

Time frame:  
July 20 – September 9, 2010

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## 1 Introduction

Capture and separation of carbon dioxide is one of the most challenging tasks of the modern society. To reduce the emissions of greenhouse gases it is important to find new, more efficient sorbents. The second major problem is hydrogen storage as the fuel of the future for motor vehicle. The metal-organic frameworks attracted recently the special attention due to their high carbon dioxide and hydrogen sorption capacity [1]. Metal-Organic Frameworks (MOFs) can be defined as high molecular weight polymers formed by the repetition of monomeric units linked with covalent bonds. Their structure consists of the central atoms (connectors), which are overbridged by organic ligands (linkers).[2]

For the chemists, polymeric coordination networks synthesis could be considered as “construction game”, because the final architecture, design and dimensionality depends on the building modules and their compatibilities [3] (Fig. 1). The coordination number is the main factor determining the dimensionality of the final structure. One-dimensional chains, two-dimensional networks or 3D structures can be created by appropriate selecting of the central atom with suitable coordination number.

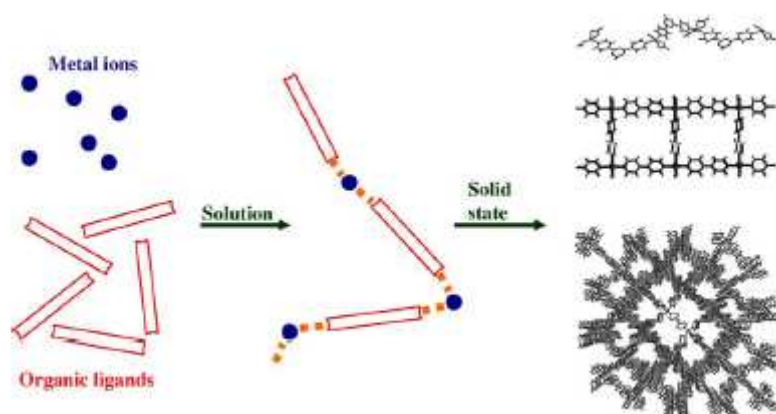


Fig. 1. Construction game used in the synthesis of MOF [2].

MOF like porous materials with large cages and tunnels are increasingly in demand for applications in catalysis, gas storage, separation of gases, sensors, electronics, they can be used as a drug delivery systems or to study spin crossover [4].

## 2 Goals of the research project

## 3 Experimental part

### 3.1 Preparation of the samples $\{\text{Ln}(\text{FOR})_3\}_n$ ( $\text{Ln}^{3+} = \text{La, Ce, Pr, Nd, Sm, Eu}$ )

A mixture of  $\text{H}_3\text{BTC}$  (66mg, 0.3141mmol),  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  ( $x_{(\text{La, Ce, Pr, Nd, Sm})} = 6$ ,  $x_{(\text{Nd})} = 5$ ) (0.7852mmol) in 20 ml  $\text{N,N}'$ -dimethylformamide,  $\text{H}_2\text{O}$  and  $\text{EtOH}$  (v:v:v/1:1:1) was placed in a 25ml Teflon-lined stainless steel vessel. In the first step was the mixture heated at  $80^\circ\text{C}$  for 12 h. In the second step was heated at  $120^\circ\text{C}$  for 36 h, and then cooled to room temperature at a rate of  $0.05^\circ\text{C} \cdot \text{min}^{-1}$ . A small quantity of needle crystals were filtered and washed with 3 x 10 ml ethanol and left to air-dry.

### 3.2 Preparation of the sample $\{[(\text{CH}_3)_2\text{NH}_2] \cdot [\text{Zn}(\text{BTC})_2] \cdot \text{DMF}\}_n$

A mixture of  $\text{H}_3\text{BTC}$  (131mg, 0.6233mmol),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (186mg, 0.6252mmol) and pyrazine (50mg, 0.6243mmol) in 20 ml  $\text{N,N}'$ -dimethylformamide was placed in a Teflon-lined stainless steel vessel and heated a rate  $0,5^\circ\text{C} \cdot \text{min}^{-1}$  at  $200^\circ\text{C}$  for 36 h and then cooled to room temperature at a rate of  $0,05^\circ\text{C} \cdot \text{min}^{-1}$ . Colourless cubic crystals were kept in mother liqueur.

### 3.2 Single crystal X-ray diffraction

The  $\{\text{Ce}(\text{FOR})\}_n$  and  $\{[(\text{CH}_3)_2\text{NH}_2] \cdot [\text{Zn}(\text{BTC})_2] \cdot \text{DMF}\}_n$  complexes crystal structure were measured with a Xcalibur four-circle CCD diffractometer equipped with a graphite monochromator and using MoK $\alpha$  radiation ( $k = 0.71073 \text{ \AA}$ ). The structure was solved using direct methods using SIR92 and refined on F<sup>2</sup> using the SHELXL97 program. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in the calculated positions. The isotropic thermal parameters were fixed to 1.2U<sub>eq</sub> of the parent atom for all H atoms.

Crystal data for  $\{\text{Ce}(\text{FOR})\}_n$ :  $\text{CeC}_3\text{H}_3\text{O}_6$ ,  $M_r = 275.2$ , trigonal, space group R3m with  $a = 10.6891(2) \text{ \AA}$ ,  $c = 4.1116(1) \text{ \AA}$ ,  $V = 406.84 \text{ \AA}^3$ ,  $Z = 3$ ,  $\rho_{\text{calcd}} = 3.369 \text{ mg/m}^3$ ,  $T = 293(2) \text{ K}$ . Of the 6271 total reflections ( $-14 \leq h \leq 14$ ,  $-14 \leq k \leq 14$ ,  $-5 \leq l \leq 5$ ), 288 independent reflections ( $R_{\text{int}} = 0.0288$ ) were used to solve the structure. Based on these data and 23 refined

parameters, final R indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0066$ ,  $wR_2 = 0.015$ ; R indices (all data),  $R_1 = 0.0066$ ,  $wR_2 = 0.015$  and the goodness-of-fit on  $F^2$  is 1.130. Largest diff. peak and hole, 0.258 and  $-0.206 \text{ e } \text{\AA}^{-3}$ .

Crystal data for  $\{[(\text{CH}_3)_2\text{NH}_2] \cdot [\text{Zn}(\text{BTC})_2] \cdot \text{DMF}\}_n$ :  $\text{ZnC}_{14}\text{H}_{18}\text{N}_2\text{O}_7$ ,  $M_r = 387,27$ , monoclinic, space group  $P21/n$  with  $a = 9.500(5) \text{ \AA}$ ,  $b = 16.380(5) \text{ \AA}$ ,  $c = 11.514(5) \text{ \AA}$ ,  $\beta = 97.447(5)^\circ$ ,  $V = 1776,58 \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1,448 \text{ mg/m}^{-3}$ ,  $T = 293(2) \text{ K}$ . Of the 6271 total reflections ( $-12 \leq h \leq 13$ ,  $-19 \leq k \leq 22$ ,  $-15 \leq l \leq 15$ ), 4346 independent reflections ( $R_{\text{int}} = 0.5963$ ) were used to solve the structure. Based on these data and 203 refined parameters, final R indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.2082$ ,  $wR_2 = 0.1631$ ; R indices (all data),  $R_1 = 0.0754$ ,  $wR_2 = 0.1392$  and the goodness-of-fit on  $F^2$  is 0.728. Largest diff. peak and hole, 1.202 and  $-1.104 \text{ e } \text{\AA}^{-3}$ .

### 3.3 High energy X-ray diffraction at BW5

Measurements of room temperature and in-situ heating diffraction pattern carried out on beamline BW5. This wiggler beamline can produce photon beams with energy between 60 to 150 keV. Our experiment was conducted with energy 100 keV and the wavelength was  $0.123984 \text{ \AA}$ . As a source of heating were the halogen lamp and the temperature was measured by thermocouple. Experimental layout with description is on the Fig. 2.

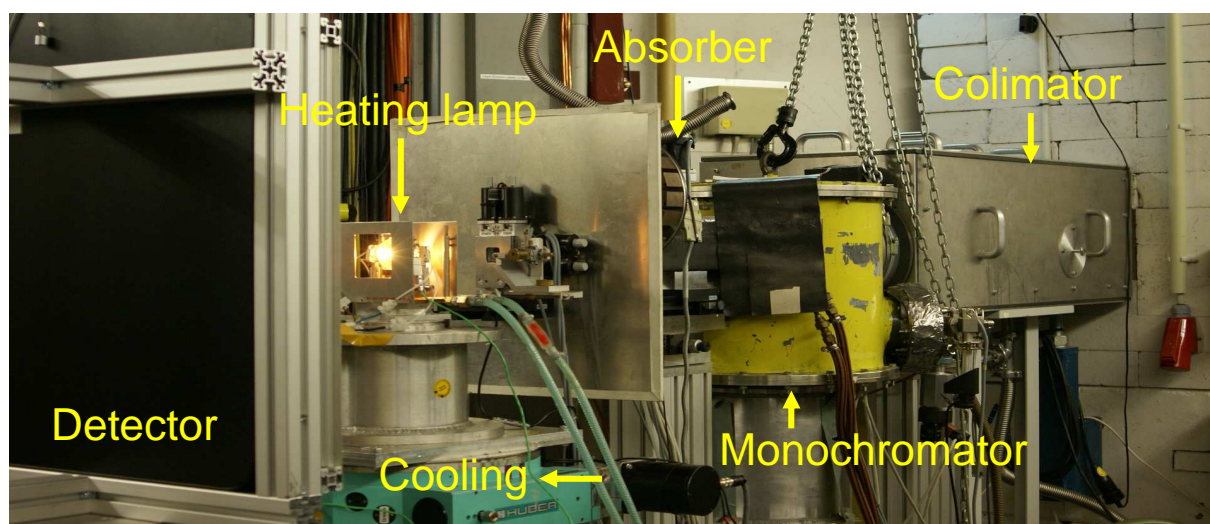


Fig. 2 Component arrangement at beamline BW5.

Generate a high energy polychromatic radiation from accelerated positrons entering the first collimator. The purpose of the collimator is profile of entering beam. During our experiments we used square-shaped opening with  $1 \times 1 \text{ mm}^2$  size. Polychromatic radiation is

passed to the monochromator, where the single crystal Ge-Si (111) monochromatize the polychromatic beam. Beam transmit through absorber that reduce the intensity and impact of the sample. High intensity may in fact damage the detector. Diffracted photons from the sample are collected using 2D square detector Perkin-Elmer. Obtained diffractograms were then processed by using program FID2D. Sample distance from detector was determined by LaB<sub>6</sub> calibrant and calculated distance is 1438.8cm. This large distance was necessary for us to increase the resolution of the resulting diffraction pattern.

## 4 Results and Discussion

### Complex $\{[(\text{CH}_3)_2\text{NH}_2][(\text{Zn}(\text{BTC})_2)\cdot\text{DMF}]\}_n$

The complex  $\{[(\text{CH}_3)_2\text{NH}_2][(\text{Zn}(\text{BTC})_2)\cdot\text{DMF}]\}_n$  crystallises in the monoclinic crystal system in space group P21/n with cell parameters with  $a = 9.500(5) \text{ \AA}$ ,  $b = 16.380(5) \text{ \AA}$ ,  $c = 11.514(5) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 97.447(5)^\circ$ ,  $\gamma = 90^\circ$ . The zinc(II) is tetrahedrally surrounded by four oxygen atoms from four different trimesate ligands. One carboxylate group is bidentate and the other two are monodentate. The connectivity between dinuclear zinc units and trimesate gives rise to a 3-D anionic framework featuring parallelogrammic channels encapsulating hydrogen bond supported dimethylammonia cations ( $(\text{CH}_3)_2\text{NH}_2^+$ ) and dimethylformamide (DMF) molecules (Fig. 3).

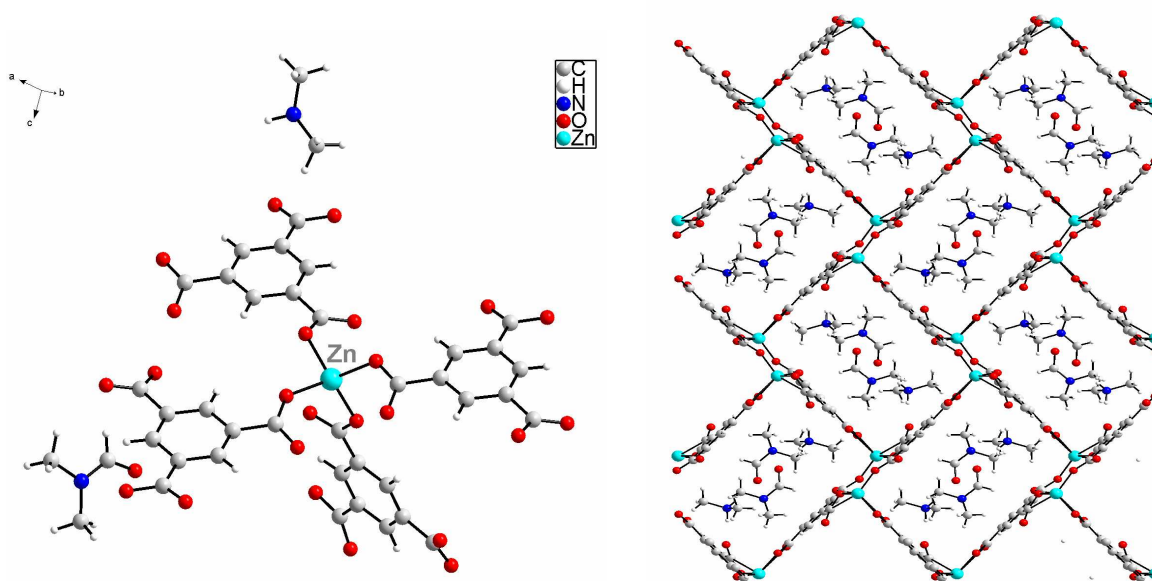
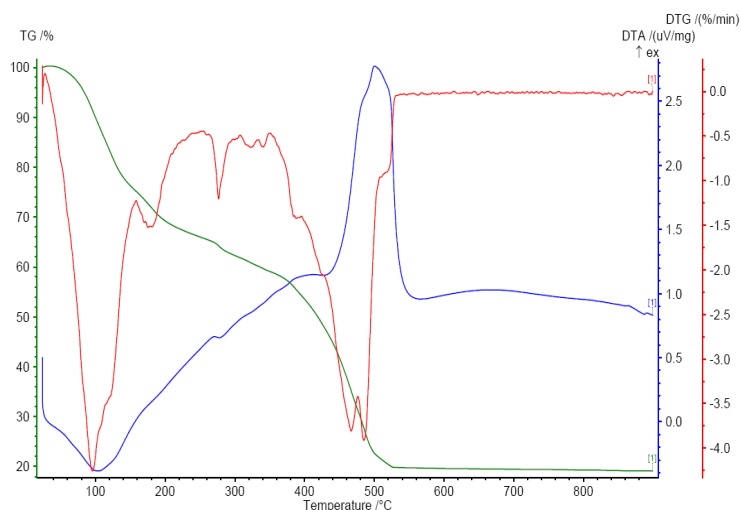


Fig. 3 Zinc atom geometry and 3D structure viewed along the a axis.



The aim of our research was to determine whether it is possible to remove the guest molecules situated in the cavity. As is evident from the thermogravimetric analysis (TGA) these molecules can be removed by thermal heating to a temperature 200-300°C. And then the cavities are open for sorption

of gases. Therefore we decided to measure in situ heating powder x-ray diffraction. Obtained diffraction patterns were then processed by using program FID2D. Measured diffractograms show that at higher temperature are lost Bragg peaks. Gradually increasing temperature disappears a fraction of the crystalline phase and the structure collapses (Fig 5). Measurement results show that the guest molecules located in the channel of the structure have a significant stabilizing effect for the structure.

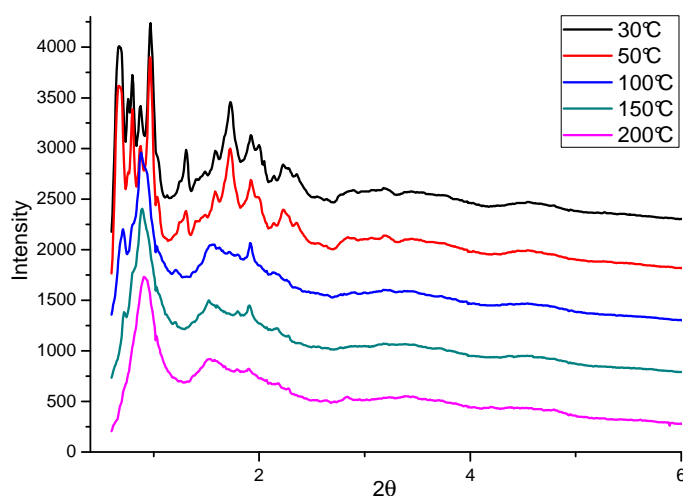


Fig. 4 Diffraction pattern measured at different temperature.

### Complex $\{[\text{Ln}(\text{FOR})_3]\}_n$

The complex  $\{[\text{Ce}(\text{FOR})_3]\}_n$  crystallises in the hexagonal crystal system in space group R3m with cell parameters with  $a = 10.6891(2) \text{ \AA}$ ,  $b = 10.6891(2) \text{ \AA}$ ,  $c = 4.1116(1) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ . This compound was prepared by solvothermal technique. Structure of complex is formed by three-dimensional framework, containing cerium cations which are overbridged by the formate ligand. The cerium atoms lie on a site of 3m symmetry and is

coordinated by nine oxygen atoms in typical coordination geometry. The formate ligands lie on mirror planes. Each carbon atom makes three C-O- cerium linkages through one  $\mu_1$ -bound O atom and one  $\mu_2$  bridging O atom, as show on Fig. 5. Three Ce atoms and three formate anions are connected , formig six-membered rings, which are connected by futher formate anions, generating a trhee-dimensional network (Fig 6). The distance between adjacent Ce atoms is 4.112 Å.

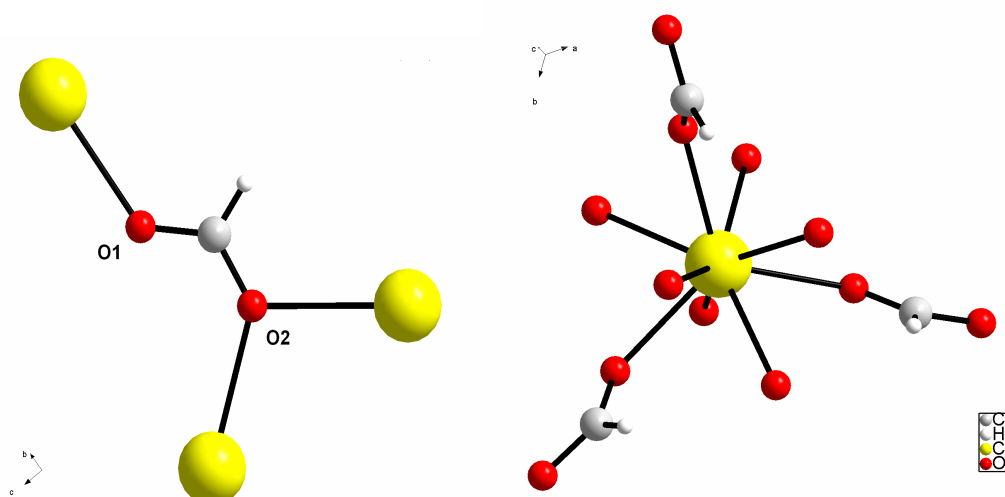


Fig. 5 Binding of ligands in the crystal structure of complex  $\{[\text{Ce}(\text{FOR})_3]\}_n$ .

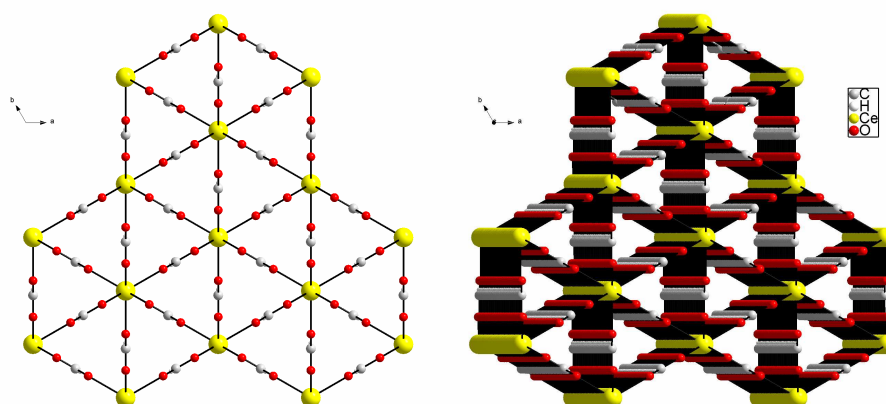


Fig. 6 Packing diagram viewed down the c axis.

This definitive crystal structure was resolved only compound containing cerium. If we used other lanthanides cations (La(III), Pr(III), Nd(III), Sm(III), Eu(III)) in the synthesis the resulting products were powders, no single crystal. But the measured infrared spectra of powder compounds were similar to complex containing cerium. Our idea was. Are these compounds isostructural? This means that the structure of compounds is the same and change only the metal atom. This question can anwer the powder diffraction. Measured diffraction patterns are similar (Fig. 7) implying that these compounds have the same structure. Exception are compounds containing neodymium and samarium in which during synthesis create second phase. And the second picture shows the zoom on pattern in twotheta angle of

about  $3.3^\circ$ . Where are shown peak shift to right side. This means that with increasing atomic number of central atom occurs to reduce the cell parameter. This phenomenon can be explained by lanthanides contraction. This term is used in chemistry to describe the decrease in ionic radii of elements in the lanthanide series. In short, the effect results from poor shielding of nuclear charge by 4f electrons. The shielding effect exerted by the inner electrons decreases in the order  $s > p > d > f$ . Usually, as a particular subshell is filled in a period, atomic radius decreases. This effect is particularly pronounced in the case of lanthanide, as the 4f subshell which is filled across these elements is not very effective at shielding the outer shell electrons. Thus the shielding effect is less able to counter the decrease in radius caused by increasing nuclear charge.

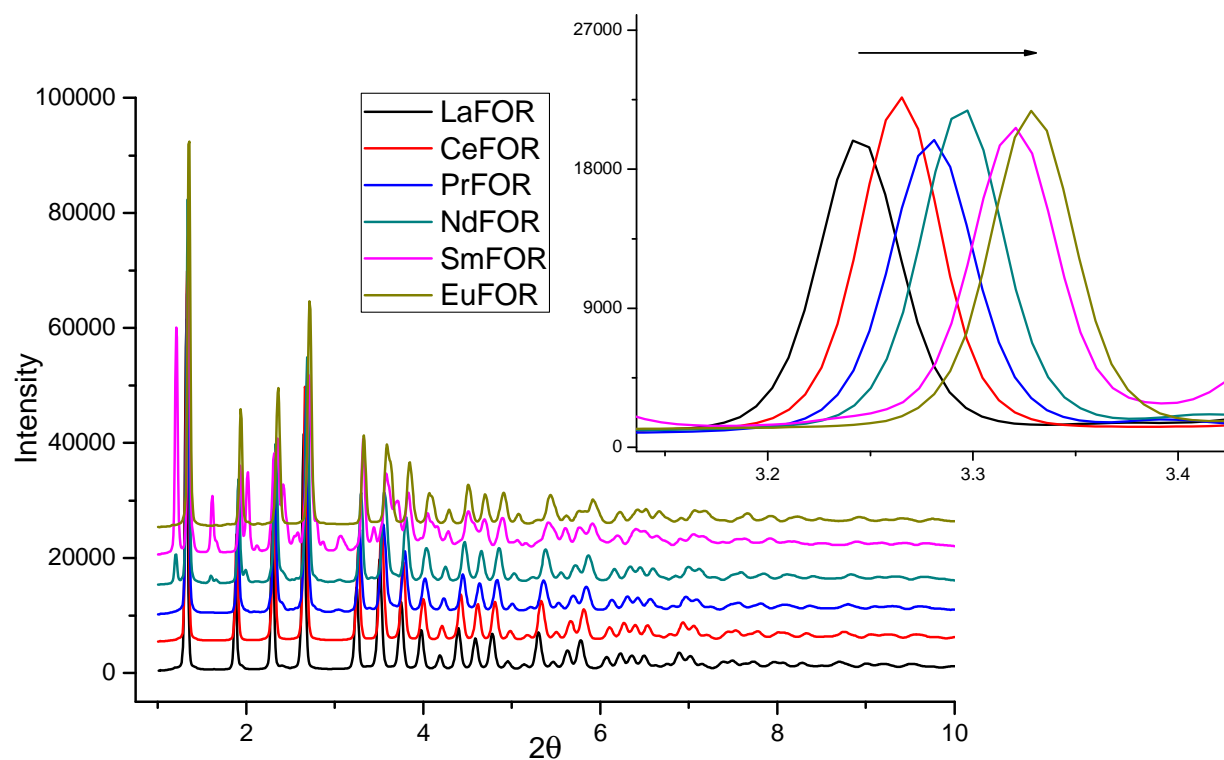


Fig. 7 Comparison of diffraction patterns of complexes  $\{Ln(OR)_3\}_n$ .

Finally we calculate the cell parameters for individual compounds using program TOPAS (Fig. X) and FITTIK. First was created a calculate diffraction pattern from resolved crystal structure contains cerium cation. Based on this pattern it was possible to indexing of peaks of pattern by other isostructural compounds. Then using mathematical term (1.1 and 1.2) and values of known h k l indexes was calculated the cell parameters of the compounds. Values are given in table below (Tab. 1).

$$n\lambda = 2d \sin \Theta \quad (1.1)$$



$$\frac{1}{d_{hkl}} = \frac{4}{3} \cdot \frac{h^2 + hk + l^2}{a^2} + \frac{l^2}{c^2} \quad (1.2)$$

Tab. 1 Calculated cell parameters for compounds  $\{[\text{Ln}(\text{FOR})_3]\}_n$ .

Central atom	Ionic radii [pm]	a [Å]	c [Å]	V [Å <sup>3</sup> ]
La <sup>3+</sup>	117.2	10.7255	4.1480	413.249
Ce <sup>3+</sup>	115	10.6658	4.1211	406.007
Pr <sup>3+</sup>	113	10.6042	4.0960	398.885
Nd <sup>3+</sup>	112.3	10.5766	4.0786	395.127
Sm <sup>3+</sup>	109.8	10.4983	4.0450	386.089
Eu <sup>3+</sup>	108.7	10.4584	4.0378	382.475

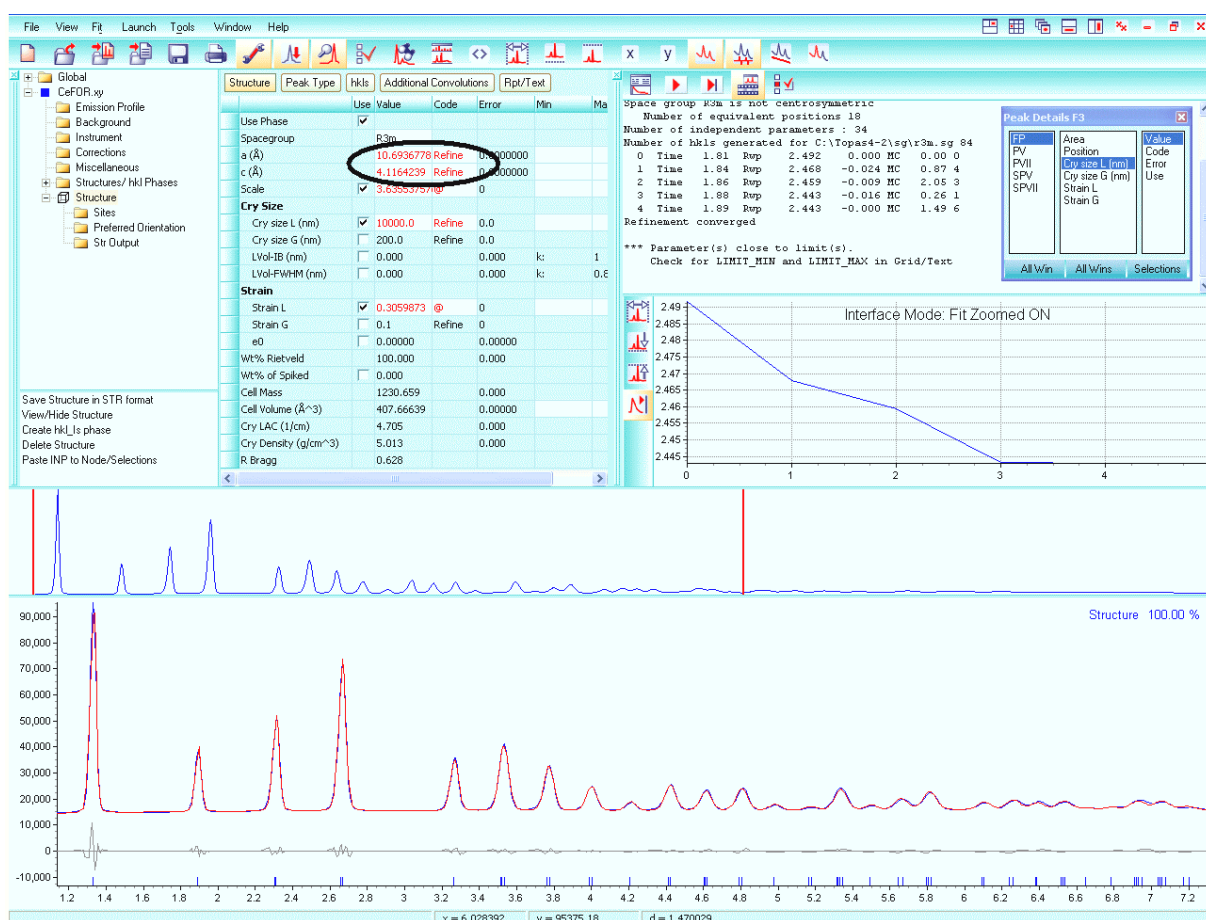


Fig. 8 Print screen of resolved cell parameter of compound  $\text{Pr}(\text{FOR})_3$  using program TOPAS (Le Bail fitting).

And at the end were calculated the volume cell via mathematical term (1.3). We tried to find a relationship between cell volume and ionic radii of lanthanide cations. On the graph (Fig. 9) below is very good linear correlation between the two variables.

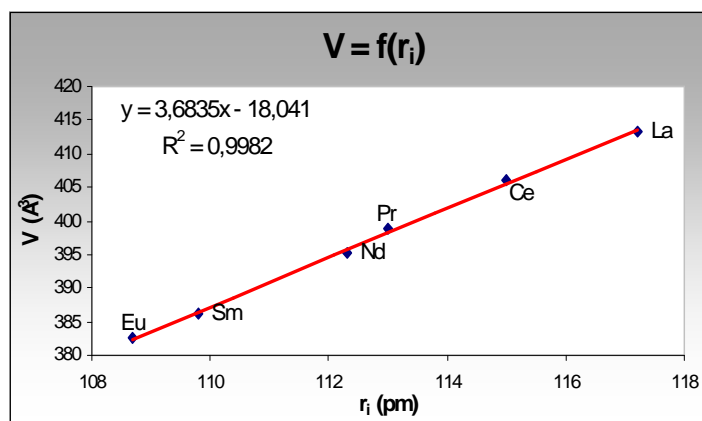


Fig. 9 Linear relationship between cell volume and ionic radii.

## 5 Conclusions

Fig. 4 shows that guest molecules of dimethylformamide and dimethylammonia are not possible to remove the compound with formula  $\{[(\text{CH}_3)_2\text{NH}_2].[\text{Zn}(\text{BTC})_2].\text{DMF}]_n$ . Because if these guest molecules are removed through heating the structure collapses. Measurement results show, that the host molecules located in the channel of structure have a significant stabilizing effect for the structure.

Measured diffraction patterns show that compounds with composition  $\{[\text{Ln}(\text{FOR})_3]\}_n$  (where  $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu}$ ) are isostructural. In the case of compounds containing neodymium and samarium on the pattern can be observed parasite peaks. This means that during synthesis another unidentified phase is created. In these compounds were also calculated lattice parameters, which are listed in the table Tab. 1. Finally we tried to find the relationship between ionic radii of lanthanide cations and cell volume. On the picture Fig. 9 is a very good linear correlation.

## Acknowledgement

I would like to render thanks to all people and colleagues from Hasylab who helped me during my stay here at DESY. I want to thank my two supervisors Dr. Hanns-Peter Liermann

and Dr. Ann-Christin Dippel and especially Dr. Jozef Bednarcik, who helped me. Big thanks belong to DESY allowing me to participate at the DESY Summer Student Program 2010.

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