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| | Experiment title: Cyclodextrin Inclusion Compounds with Europeium(III) Beta-Diketonates | Experiment number: CH-2414 |
| Beamline: ID31 | Date of experiment: from: 25 – Apr. – 2007 to: 27 – Apr. – 2007 | Date of report: 27 – Feb. – 2012 |
| Shifts: 6 | Local contact(s): Dr. Irene Margiolaki (E-mail: irene.margiolaki@esrf.fr) | <i>Received at ESRF:</i> |
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Introduction and Summary of the Results:

During the last decade or so our research group has been particularly active in the field of supramolecular chemistry while studying the inclusion of metallic and organometallic complexes into the cavities of cyclodextrin molecules.^[1-15] These organic molecular capsules are particularly useful as they provide a second-sphere environment for functional complexes: capsules may either act as a protective shell or even to, for example, fine-tune the observed photoluminescent properties. In this context, the general aim of this experiment was to study a couple of novel inclusion compounds of cyclodextrins with europium(III)-based photoluminescent compounds. The collection of high-resolution powder X-ray diffraction patterns was expected to greatly help the development of structural models for these inclusion compounds using the strategy we have employed in the past for laboratory data.^[8, 11] Towards the end of the experiment we also collected high-resolution data for layered double hydroxides intercalated by oxomolybdenum catecholate complexes, which ultimately resulted in a publication in *Inorganic Chemistry*.^[16]

Results and Discussion:

During the first morning of the experiment researchers had very fruitful discussions with the local contact, Dr Irene Margiolaki, so to explain the aims, expected objectives and results and also the problematic of collecting poorly crystalline cyclodextrin inclusion compounds. It was decided that a wavelength of about 0.9337 Å would be suitable for the materials in study (it would, for example, permit a very good discrimination of the overlapped reflections, which is a typical feature of cyclodextrin inclusion compounds). Due to the large amount of water molecules that were expected to be present in the compound, it was also decided that low temperature data acquisitions would be preferable. It was strategically planned to use the

two nights for the collection of data sets for layered double hydroxides intercalated by oxomolybdenum catecholate complexes that were also brought to the ESRF for the experiment. For this system, the robot at ID31 was used to facilitate the sample change and permit the experimentalists to rest during the night (for safety reasons).

Cyclodextrin Inclusion Compounds

A significant portion of the shifts allocated to the execution of this experiment (CH-2414) was dedicated to the data acquisition of high signal-to-noise powder patterns for a number of cyclodextrin inclusion compounds. Figure 1 summarizes some of the collected powder patterns. Besides the presence of a large amount of amorphous material, a typical feature of these inclusion compounds, the improved resolution of the patterns collected at ID31 were clear showing the presence of mixtures of crystalline phases: the patterns have reflections with very distinct half-widths-at-half-maximum values, which is a clear indication of a mixture of phases. We note that this feature was completely unexpected: our laboratory data, of poor resolution, indicated *a priori* the presence of single phases and only once the reflections were discriminated we were able to unequivocally conclude on the presence of physical mixtures.

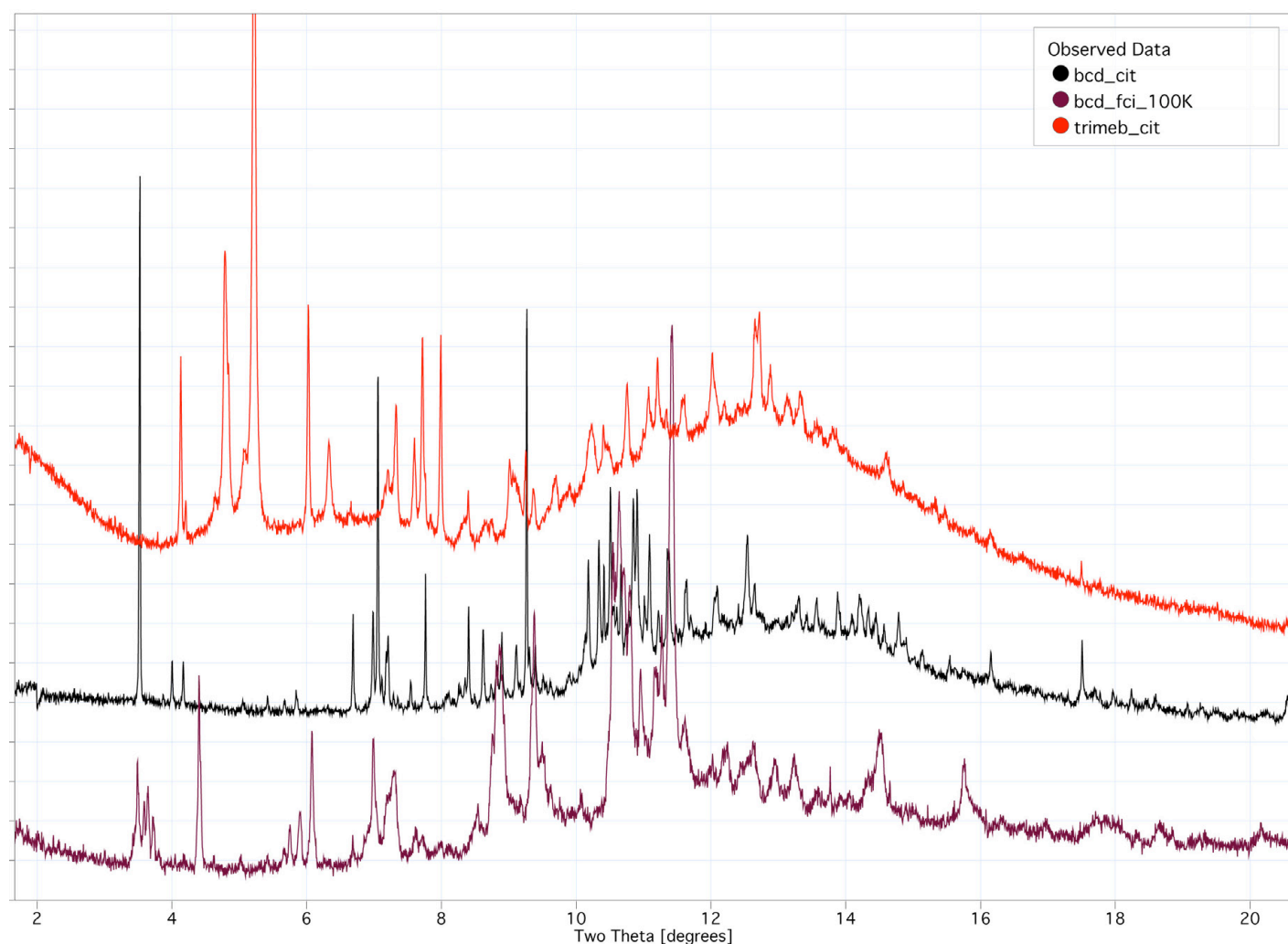


Figure 1. Powder X-ray diffraction patterns collected at ID31 for three cyclodextrin (beta-cyclodextrin and TRIMEB) inclusion compounds.

The powder patterns for the cyclodextrin inclusion compounds selected for this experiment were, nevertheless, studied using the methods we have been using in the past for related compounds: i) as expected, direct indexing of the patterns failed to provide a reliable unit cell for the materials (most certainly due to

the presence of at least two crystalline phases); ii) comparison of the patterns with the study by Caira also failed to, at least, indicate what type of inclusion compound could be present in the physical mixture.

Layered double hydroxides intercalated by oxomolybdenum catecholate complexes

Oxomolybdenum(VI) complexes of 3,4-dihydroxybenzoic acid (3,4-H₂dhb) incorporated into layered double hydroxides (LDHs) by treatment of the LDH-nitrate (Zn-Al, Mg-Al) or LDH-chloride (Li-Al) precursors with aqueous or water/ethanol solutions of the complex (NMe₄)₂[MoO₂(3,4-dhb)₂]·2H₂O at 50 or 100 °C, have also been studied during this visit to the ESRF. As mentioned in the introduction section, various data sets for this family of compounds were collected during the night, at ambient temperature, using the automatic system present at ID31. The results, which are very briefly summarized in the following, were published in a full paper in *Inorganic Chemistry*.^[16] We note that not all the collected data sets reached the final publication.

The high-resolution synchrotron PXRD patterns of Li-Al-Mo(50)A (Figure 2) and Li-Al-Mo(100)A were unequivocally indexed with an expanded hexagonal unit cell (space group *P*6₃/m) for which, as in the original Li-Al-Cl material, the length of the *c*-axis (*ca.* 30.7 Å) encompasses two interlayer voids. Fourier maps showed that: (1) the mixed Li-Al hydroxide layers retain their structural integrity and two-dimensional ordering after intercalation; (2) within each layer, the structural disorder between lithium and aluminium sites was minimal; (3) statistically-disordered electron density is located in the interlayer spaces and periodically distributed; (4) the highest intensities for the interlayer electron density are found close to the Li-Al hydroxide layers. These results were fully compatible with structural models based on the intercalation of dimeric bis(catecholate) complexes.

The material Zn-Al-Mo(50) also showed an expanded structure. However, the (*00l*) reflections envelope of the collected powder pattern could not be matched with analogous patterns for other materials, which suggested a longer *c*-axis. Indeed, the pattern could be unequivocally indexed with a hexagonal unit cell with a *c*-axis of 45.932(2) Å. Analysis of the systematic absences revealed that the overall symmetry of this intercalated material is better described in the *P*6₄ space group (see Figure 3). Fourier maps for Zn-Al-Mo(50) led to the same geometrical conclusions for the intercalation mode of dimeric species as those described above for the two Li-Al compounds, with the average gallery height being *ca.* 10.6 Å.

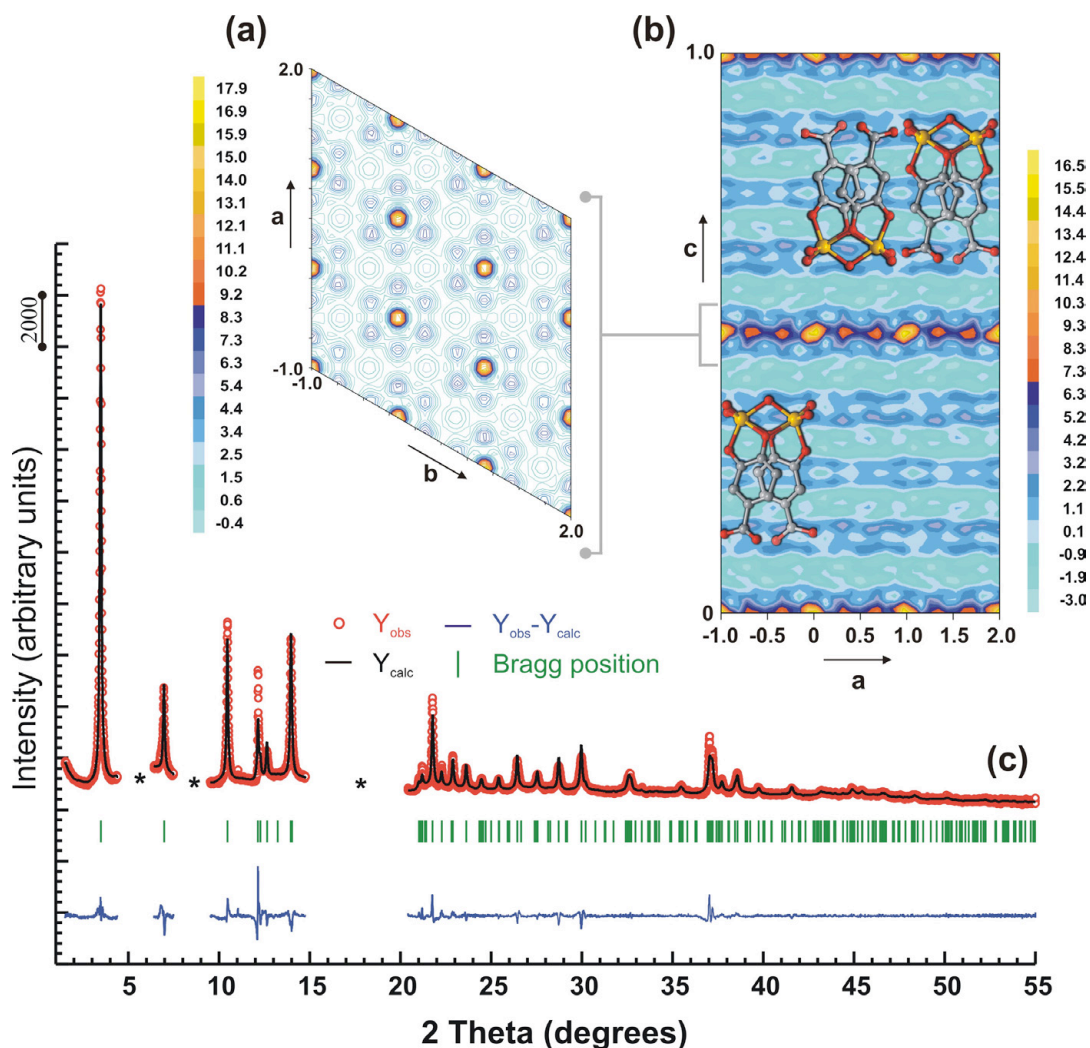


Figure 2. Fourier maps calculated by GFourier and by employing the F_{obs} extracted from a Le Bail whole-powder-diffraction-pattern decomposition of Li-Al-Mo(50)A summed from: (a) -0.43 to 0.57 along the c -axis, showing the typical hexagonal distribution of $\{\text{AlO}_6\}$ and $\{\text{LiO}_6\}$ octahedra in the ab plane; (b) 0 to 1 along the a -axis, emphasizing the electron density in the interlayer spaces attributed to the presence of disordered $[\text{Mo}_2\text{O}_5(3,4\text{-dhb})_2]^{4-}$ species (represented in ball-and-stick mode). (c) Experimental data (red circles), Le Bail whole-powder-diffraction-pattern profile fitting (upper solid black line) and difference (lower solid blue line) XRPD pattern. Vertical bars indicate the angular positions of the allowed Bragg reflections for space group $P6_3/m$ (hexagonal crystal system). The asterisks depict three regions which were not considered for refinement due to the presence of a trace amount of an impurity. Refined unit cell parameters (after Le Bail profile fitting with FullProf.2k): $a = b = 5.0934(2)$ Å, $c = 30.725(2)$ Å. Zero point = $0.0201(8)^\circ$. Pearson profile function with $M = 0.999(1)$. Caglioti halfwidth parameters: $U = 0.283(15)$, $V = -0.053(4)$ and $W = 0.0125(1)$. Asymmetry parameters = $0.0074(6)$. Independent reflections = 264. Global refined parameters = 1. Profile refined parameters = 8. $R_{\text{Bragg}} = 0.24\%$ and $\chi^2 = 6.62$.

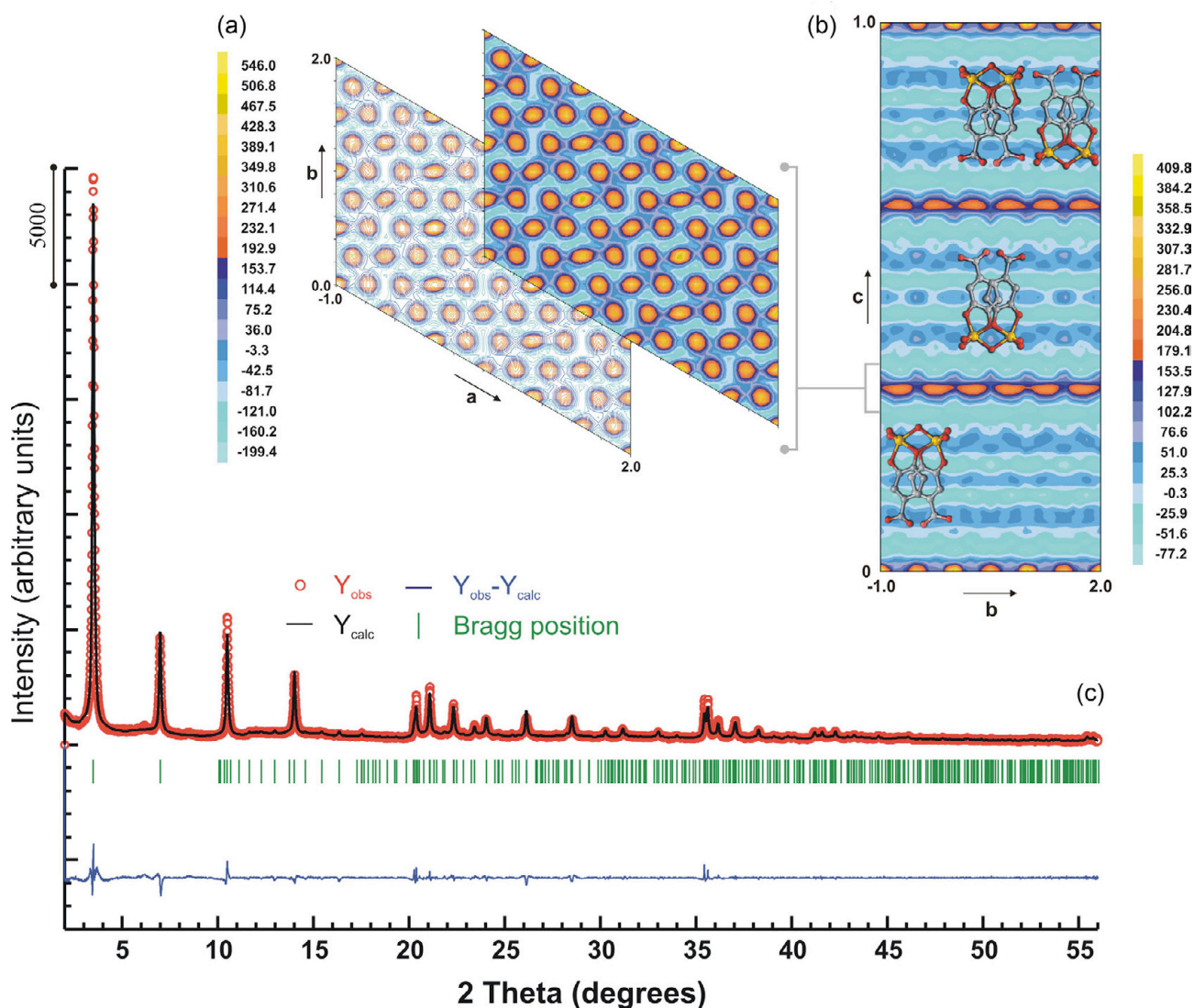


Figure 3. Fourier maps calculated by GFourier and by employing the F_{obs} extracted from a Le Bail whole-powder-diffraction-pattern decomposition of Zn-Al-Mo(50) summed from: (a) -0.1 to 0.1 along the c -axis, showing the typical hexagonal distribution of $\{\text{AlO}_6\}$ and $\{\text{ZnO}_6\}$ octahedra in the ab plane; (b) 0 to 1 along the a -axis, emphasizing the electron density in the interlayer spaces attributed to the presence of disordered $[\text{Mo}_2\text{O}_5(3,4\text{-d}hb)_2]^{4-}$ species (represented in ball-and-stick mode). (c) Experimental data (red circles), Le Bail whole-powder-diffraction-pattern profile fitting (upper solid black line) and difference (lower solid blue line) XRPD pattern. Vertical bars indicate the angular positions of the allowed Bragg reflections for space group $P6_4$ (hexagonal crystal system). Refined unit cell parameters (after Le Bail profile fitting with FullProf.2k): $a = b = 6.1372(1)$ Å, $c = 45.932(2)$ Å. Zero point = $0.0017(7)^\circ$. $M(16) = 43.5$ and $F(16) = 44.2$. Pearson profile function with $M = 1.158(5)$. Caglioti halfwidth parameters: $U = -0.021(7)$, $V = 0.003(2)$ and $W = 0.0133(2)$. Asymmetry parameters = $-0.0042(5)$ and $-0.0015(1)$. Independent reflections = 603. Global refined parameters = 1. Profile refined parameters = 8. $R_{\text{Bragg}} = 0.07\%$ and $\chi^2 = 3.99$.

Conclusions:

During this experiment we came to the conclusion that, unfortunately, screening cyclodextrin inclusion compounds using conventional powder X-ray diffraction may lead to erroneous conclusion with respect to the presence of single crystalline phases *versus* physical mixtures. This was, in fact, the main limiting factor that promoted the data collection of unsuitable samples. Only the high resolution of patterns from the ID31

beam line was able to clearly show the existence of physical mixtures. However, we can also conclude that if a pure cyclodextrin compound were to be analyzed at ID31, the collected powder data would be most useful as the improved resolution could indeed point to a correct structural model.

This experiment (CH-2414) was, nevertheless, still quite fruitful as we were able to during the nights collect data sets for a large family of layered double hydroxides intercalated by oxomolybdenum catecholate complexes. These data sets allowed us to unequivocally prove the intercalation of these complexes and, from different Fourier maps, also show how they could be orientated in the interlamellar space. These results were published in *Inorganic Chemistry*.

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