ESRF	**Experiment title:** **Cyclodextrin Inclusion of Biomimetic Ruthenium Complexes**	**Experiment number**: CH-2915
Beamline: ID11	**Date of experiment**: from: 24 – Feb. – 2010 to: 26 – Feb. – 2010	**Date of report**: 28 – Feb. – 2012
Shifts: 6	**Local contact(s)**: Dr. Loredana Erra (E-mail: erra@esrf.fr)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Filipe A. Almeida Paz *

Dr. Susana S. Braga *

Dr. Luís Cunha-Silva *

Affiliation:
University of Aveiro, CICECO, Department of Chemistry, 3810-193 Aveiro, Portugal.

Introduction:

Much of our research efforts in the use of cyclodextrin (CD) molecules have been focused at the synthesis, structural characterization and study of the properties of inclusion compounds with organometallic or traditional complexes.[1-3] Cyclodextrins can be envisaged as nanocapsules due to the ability to encapsulate a myriad of functional molecules into their cavities. In this context, these molecules can simultaneously act as a protective second sphere ligand and as a nano-delivery system of, for example, drugs. The purpose of this experiment was to investigate the inclusion of the complexes [Ru([9]aneS3)(aa)]Cl (where [9]aneS3 = trithiacyclononane; aa = glycine (**1**) or tryptophan (**2**)) into native β-CD (**3**) and its derivatives hydroxypropyl-β-CD (**4**), permethylated β-CD (**5**) and CRYSMEB (a β-CD derivative with an average methylation of four residues - compound **6**).

Results and Discussion:

Cyclodextrin Inclusion Compounds

At the moment of the submission of the proposal it was stated that only compounds **1** and **6** were already available for structural studies. These compounds were indeed taken to the ESRF and mounted on Cryoloops for study at the ID11 beam line. As mentioned in the proposal, the crystals were too small to be tested using our in-house single-crystal X-ray diffractometer (a Bruker Kappa APEX II instrument with standard Mo radiation). The two crystals for which a full data set was collected revealed to be difficult to index and to solve. After several attempts it was found that the available crystals in the batches that could indeed be mounted were most likely products of an *in situ* decomposition (ruthenium complexes are known

to undergo such transformations in the presence of water). The results were also of very poor quality and, therefore, unsuitable for publication.

As also stated in the proposal, the remaining materials were synthesized to be taken to the ESRF but, after much efforts trying to find suitable single-crystals to be mounted and studied at ID11, the experimentalists were unable to find any suitable material.

Other structures

Because the leader of the proposal was already anticipating that many of the crystals would be of unsuitable quality, in particular those synthesized after the submission of the proposal, other crystals available in the laboratory were taken for structural studies. In this context, it was collected at ambient temperature an ester derivative of pyrene (Figure 1), which is a valuable intermediate molecule in many of the synthesis that we are carrying at the University of Aveiro at the moment. A large publication orientated towards the organic synthesis of many compounds based on this derivative is being prepared at the moment.

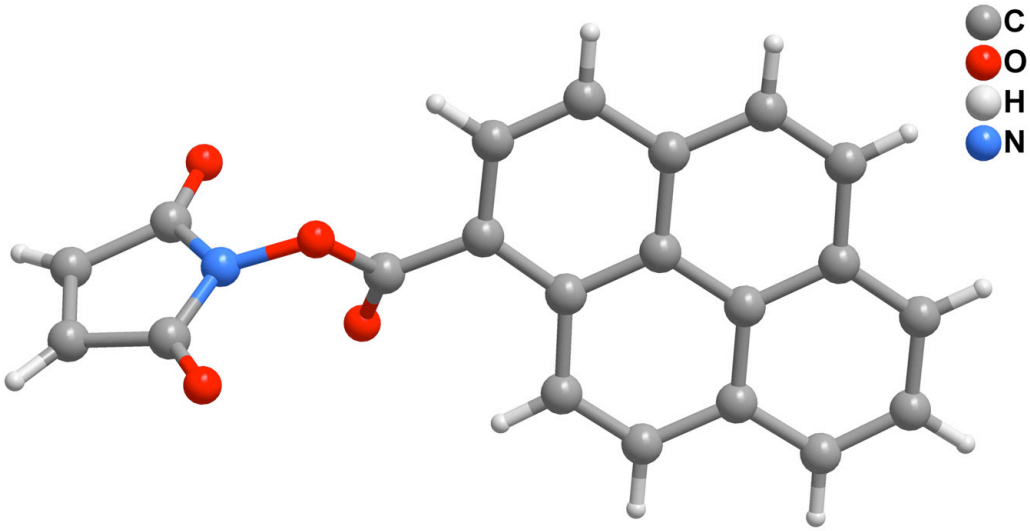

Figure 1. Molecular structure of an intermediate molecule (an ester derivative of pyrene).

Over the last two decades we have also been highly active in the synthesis, structural characterization and study of the photoluminescent properties of lanthanide silicates, many of which exhibit unusual features.[4-20] In this context, we also collected at ambient single-crystal data for a dense europium silicate material whose crystals were too small to be collected using our in-house instrument. The material (Figure 2), with empirical formula $Na_2[Eu_2Si_2O_9]$, crystallizes in the tetragonal *I*-4 space group, and the structure was solved with good *R*-factors (*R*1 = 0.0219 and w*R*2 = 0.0573). The photoluminescent properties are being compiled at the moment for a publication in an international journal.

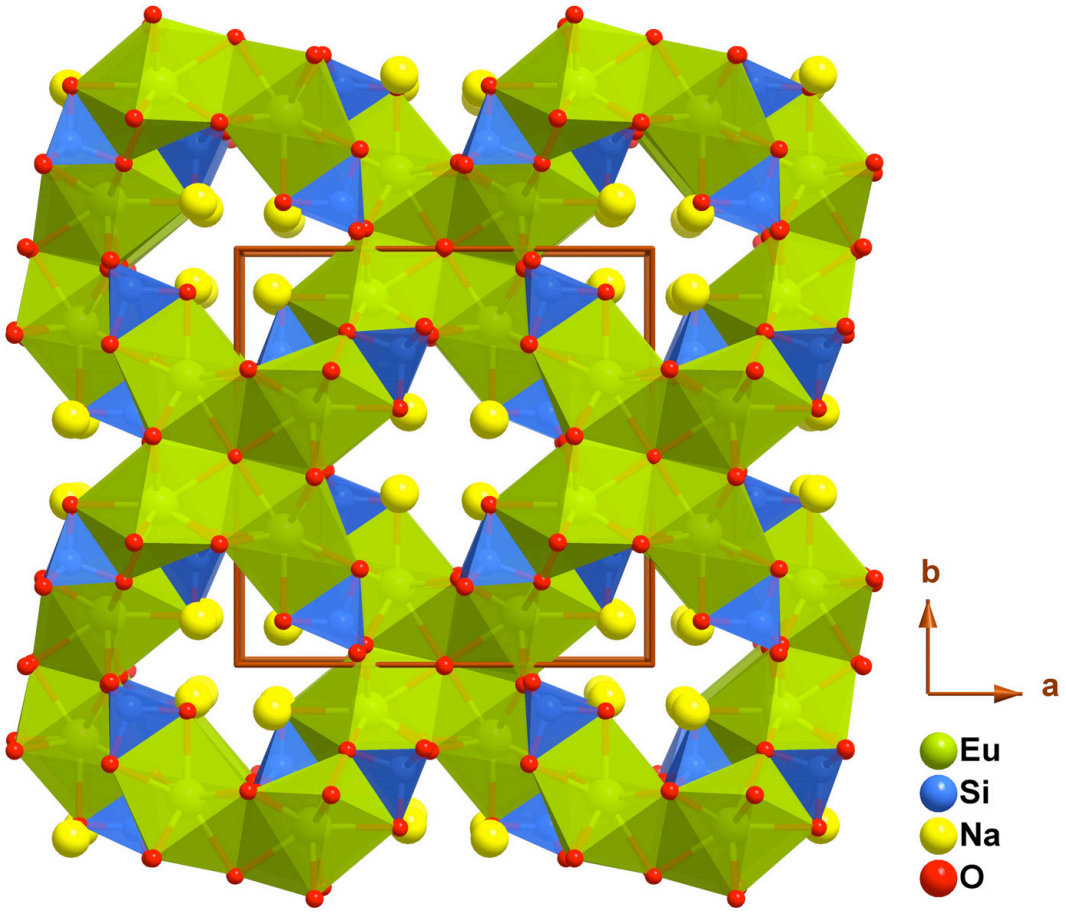

Figure 2. Crystal packing of $Na_2[Eu_2Si_2O_9]$ viewed in perspective along the [001] direction of the unit cell.

Conclusions:

Due to the poor quality of the crystals with ruthenium complexes, it was not possible to collect useful data sets that could solve our demands in terms of structural elucidation of their cyclodextrin inclusion compounds. During this experiment (CH-2915) the experimentalists were, however, able to optimize the available beam time so to collect two data sets for materials which will be published shortly: one is an organic intermediate and the other is a photoluminescent europium(III) dense silicate exhibiting interesting photoluminescent properties. We expect to be able to publish these structures in international journals with good impact factor.

Acknowledgements

We are very grateful to Dr Loredana Erra for assistance with data collection and treatment, and also for fruitful discussions. We also would like to thank Fundação para a Ciência e a Tecnologia (FCT, Portugal), FEDER and COMPETE for financial support.

References

[1] J. Marques, T. M. Braga, F. A. A. Paz, T. M. Santos, M. D. S. Lopes, S. S. Braga, *Biometals* **2009**, *22*, 541-556.

[2] J. Marques, L. Anjo, M. P. M. Marques, T. M. Santos, F. A. A. Paz, S. S. Braga, *J. Organomet. Chem.* **2008**, *693*, 3021-3028.

[3] C. C. L. Pereira, M. Nolasco, S. S. Braga, F. A. Almeida Paz, P. Ribeiro-Claro, M. Pillinger, I. S. Goncalves, *Organometallics* **2007**, *26*, 4220-4228.
[4] D. Ananias, M. Kostova, F. A. A. Paz, A. N. C. Neto, R. T. De Moura, O. L. Malta, L. D. Carlos, J. Rocha, *J. Am. Chem. Soc.* **2009**, *131*, 8620-8626.
[5] C. M. Kowalchuk, F. A. A. Paz, D. Ananias, P. Pattison, L. D. Carlos, J. Rocha, *Chem.-Eur. J.* **2008**, *14*, 8157-8168.
[6] M. H. Kostova, D. Ananias, L. D. Carlos, J. Rocha, *J. Alloy. Compd.* **2008**, *451*, 624-626.
[7] M. H. Kostova, D. Ananias, F. A. A. Paz, A. Ferreira, J. Rocha, L. D. Carlos, *J. Phys. Chem. B* **2007**, *111*, 3576-3582.
[8] M. H. Kostova, R. A. S. Ferreira, D. Ananias, L. D. Carlos, J. Rocha, *J. Phys. Chem. B* **2006**, *110*, 15312-15316.
[9] D. Ananias, F. A. A. Paz, L. D. Carlos, C. Geraldes, J. Rocha, *Angew. Chem.-Int. Edit.* **2006**, *45*, 7938-7942.
[10] D. Ananias, L. D. Carlos, J. Rocha, *Opt. Mater.* **2006**, *28*, 582-586.
[11] G. A. Pereira, D. Ananias, J. Rocha, V. S. Amaral, R. N. Muller, L. V. Elst, E. Toth, J. A. Peters, C. Geraldes, *J. Mater. Chem.* **2005**, *15*, 3832-3837.
[12] J. Rocha, L. D. Carlos, F. A. A. Paz, D. Ananias, J. Klinowski, in *Recent Advances in the Science and Technology of Zeolites and Related Materials, Pts a - C, Vol. 154* (Eds.: E. VanSteen, M. Claeys, L. H. Callanan), Elsevier Science Bv, Amsterdam, **2004**, pp. 3028-3035.
[13] J. Rocha, L. D. Carlos, A. Ferreira, J. Rainho, D. Ananias, Z. Lin, in *Advanced Materials Forum Ii, Vol. 455-456* (Eds.: R. Martins, E. Fortunato, I. Ferreira, C. Dias), Trans Tech Publications Ltd, Zurich-Uetikon, **2004**, pp. 527-531.
[14] J. P. Rainho, D. Ananias, Z. Lin, A. Ferreira, L. D. Carlos, J. Rocha, *J. Alloy. Compd.* **2004**, *374*, 185-189.
[15] D. Ananias, J. P. Rainho, A. Ferreira, J. Rocha, L. D. Carlos, *J. Alloy. Compd.* **2004**, *374*, 219-222.
[16] D. Ananias, M. Kostova, F. A. A. Paz, A. Ferreira, L. D. Carlos, J. Klinowski, J. Rocha, *J. Am. Chem. Soc.* **2004**, *126*, 10410-10417.
[17] A. Ferreira, D. Ananias, L. D. Carlos, C. M. Morais, J. Rocha, *J. Am. Chem. Soc.* **2003**, *125*, 14573-14579.
[18] D. Ananias, A. Ferreira, L. D. Carlos, J. Rocha, *Adv. Mater.* **2003**, *15*, 980-+.
[19] D. Ananias, J. P. Rainho, A. Ferreira, M. Lopes, C. M. Morais, J. Rocha, L. D. Carlos, *Chem. Mat.* **2002**, *14*, 1767-1772.
[20] D. Ananias, A. Ferreira, J. Rocha, P. Ferreira, J. P. Rainho, C. Morais, L. D. Carlos, *J. Am. Chem. Soc.* **2001**, *123*, 5735-5742.