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| Beamline: BM01a ID31 | Date of experiment: from: 16 – Sep. – 2007 to: 18 – Sep. – 2007 from: 21 – Apr. – 2008 to: 24 – Apr. – 2008 | Date of report: 29 – Feb. – 2012 |
| Shifts: 6 6 | Local contact(s): Dr. Yaroslav Filinchuk (E-mail: Yaroslav.Filinchuk@uclouvain.be) Dr. Irene Margiolaki (E-mail: irene.margiolaki@esrf.fr) | <i>Received at ESRF:</i> |
| Names and affiliations of applicants (* indicates experimentalists): Dr. Filipe A. Almeida Paz * Dr. Susana S. Braga * Dr. Luís Cunha-Silva * <i>Affiliation:</i> University of Aveiro, CICECO, Department of Chemistry, 3810-193 Aveiro, Portugal. | | |

Why two beam lines?

This report, concerning the approved proposal CH-2533, encompasses the experiments performed at two distinct beam lines at the ESRF: BM01a and ID31. A total of 12 shifts (6 + 6) were given to the submitted proposals. We note at this stage that the collected data sets were highly complementary, particularly concerning the studies on the Metal-Organic Frameworks (MOFs), hence the reason why a global report encompassing all the results was done.

Summary

The samples studied during these two visits to the ESRF span from Metal-Organic Frameworks (MOFs) to biologically-active molecules such as cyclodextrin inclusion compounds and corrole derivative molecules. A total of four (4) publications resulted from the undertaken experiments, all published in relevant international journals in the areas of materials science, crystallography and structural studies on biologically-relevant molecules:

- i) J. Marques, T. M. Braga, F. A. A. Paz, T. M. Santos, M. D. S. Lopes, S. S. Braga, *Biometals* **2009**, 22, 541-556.
- ii) L. Vale, J. F. B. Barata, C. I. M. Santos, M. Neves, M. A. F. Faustino, A. C. Tome, A. M. S. Silva, F. A. A. Paz, J. A. S. Cavaleiro, *J. Porphy. Phthalocyanines* **2009**, 13, 358-368.

- iii) L. Cunha-Silva, D. Ananias, L. D. Carlos, F. A. A. Paz, J. Rocha, *Z. Kristall.* **2009**, *224*, 261-272.
- iv) L. Cunha-Silva, S. Lima, D. Ananias, P. Silva, L. Mafra, L. D. Carlos, M. Pillinger, A. A. Valente, F. A. A. Paz, J. Rocha, *J. Mater. Chem.* **2009**, *19*, 2618-2632.

Summary of the Achieved (and Published) Results:

Cyclodextrin Inclusion Compounds

The inclusion compound TRIMEB·[Ru([9]aneS₃)phenCl]Cl was the subject of data collection at both BM01a and ID31 with the final objective of gathering a pattern with a good signal-to-noise ratio which, eventually, could lead to more detailed investigations. At the BM01a beam line two-dimensional patterns were collected using a MAR image plate (Figure 1 – *top*). Despite the excellent signal-to-noise ratio, the convolution of the reflection lines avoided an unequivocal unit cell indexation. Also, the use of typical unit cell parameters for TRIMEB inclusion compounds did not produce reasonable full pattern decompositions. Line resolution was achieved at the ID31 beam line (Figure 1 – *bottom*), which unequivocally confirmed the presence of more than one crystalline phase. The collected results permitted, however, preliminary global optimization studies in direct space using FOX, leading to a structural model of the supramolecular adduct. This model was found to be very similar to that found for the inclusion compound DIMEB·CpMo(H₂biim)(CO)₂·BF₄.^[1] However, the strongest reflections (at high angle) could not be fully accounted, thus suggesting that most likely a dense material was also co-crystallizing. In short, these results yielded a possible structural model for the inclusion compound TRIMEB·[Ru([9]aneS₃)phenCl]Cl, which was found to exhibit an interesting inhibitory action on the growth of Gram-negative and Gram-positive bacterial strains. These results were published in the specialized journal *Biometals*.^[2]

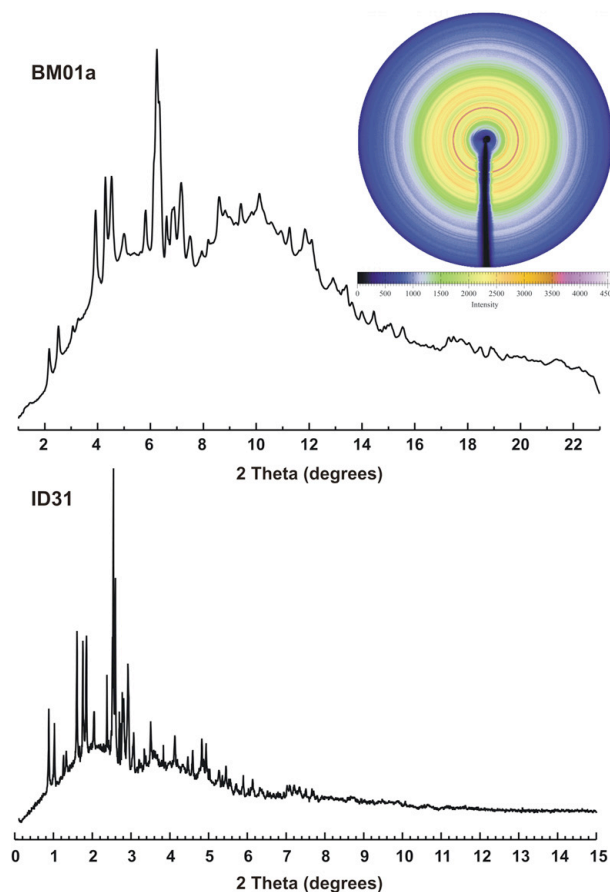


Figure 1. Synchrotron (BM01a and ID31) powder X-ray diffraction patterns of the inclusion compound TRIMEB·[Ru([9]aneS₃)phenCl]Cl.

Corrole Derivatives

A very small single-crystal of the gallium(III)(pyridine) complex of 3-[3,4-bis(methoxycarbonyl)-1-methyl-2,3,4,5-tetrahydropyrrol-2-yl]-5,10,15-tris(pentafluorophenyl)corrole was studied at the Swiss-Norwegian Beam Line BM01a using conventional synchrotron optics, a MAR345 Research imaging plate and a fixed monochromated wavelength of $\lambda = 0.7173 \text{ \AA}$. A full data set was collected at low temperature (100K) which allowed the unequivocal structural elucidation of the compound in the $I2/a$ space group. At this temperature the asymmetric unit of the compound was found to be composed of two identical, but crystallographically independent, molecular units with one of them being represented in Figure 2a for illustrative purposes. Nevertheless, the corrole cores of the two molecular units are almost identical as depicted in the structure overlay provided in Figure 2b. These results were published in *Journal of Porphyrins and Phthalocyanines*.^[3]

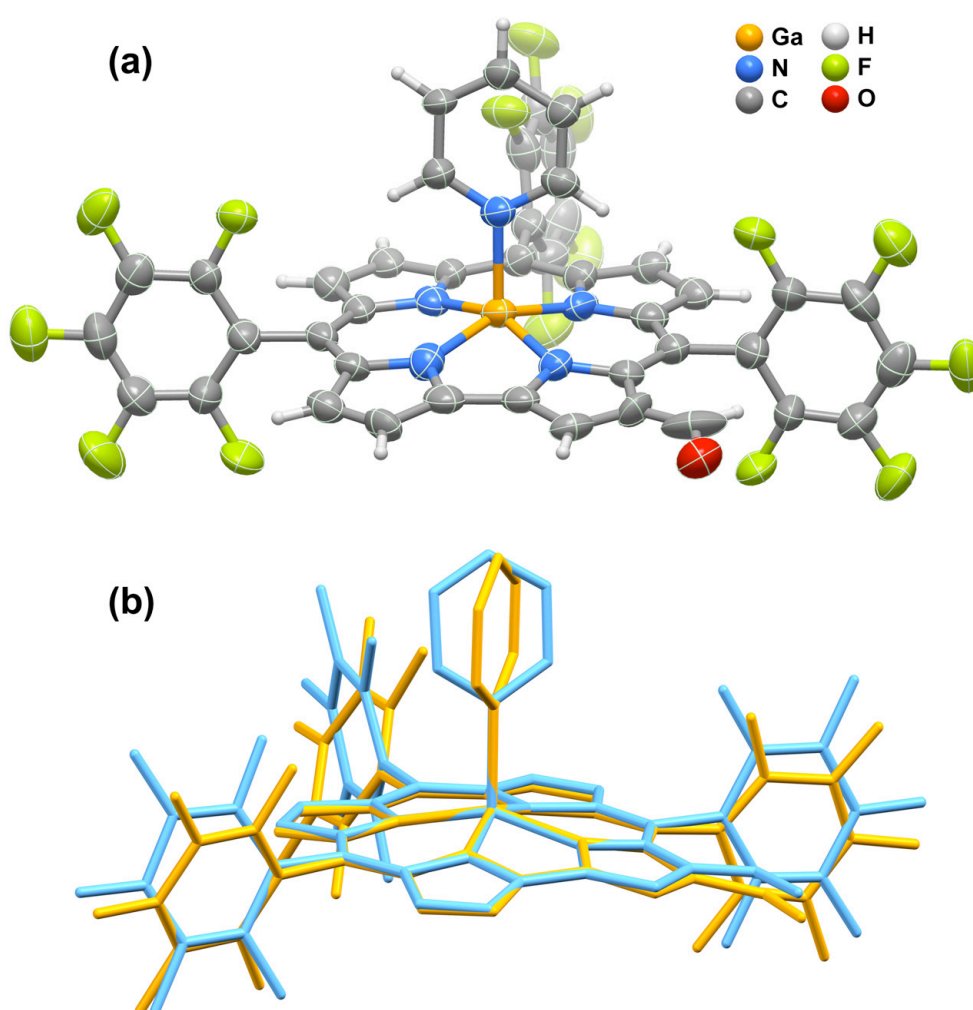


Figure 2. (a) Schematic representation of one $C_{43}H_{13}F_{15}GaN_5O$ molecular unit composing the asymmetric unit. Non-hydrogen atoms are represented as thermal ellipsoids drawn at the 30% probability level and hydrogen atoms as spheres with arbitrary radii. (b) Structure overlay of the two crystallographically independent $C_{43}H_{13}F_{15}GaN_5O$ molecular units composing the asymmetric unit (hydrogen atoms have been omitted for clarity), emphasizing the distinct rotations associated with the pyridine and $-C_6F_5$ substituent groups.

Metal-Organic Frameworks

A new family of photoluminescent layered materials, ultimately formulated as $[\text{Ln}(\text{H}_2\text{cmp})]\cdot x\text{H}_2\text{O}$ [where H_5cmp stands for (carboxymethyl)iminodi(methylphosphonic acid) and $x < 1$; $\text{Ln}^{3+} = \text{Nd}^{3+}$ and Eu^{3+}], were systematically isolated as microcrystalline powders.^[4] A full structural elucidation from powder X-ray diffraction could only be achieved by using powder synchrotron X-ray diffraction data. First, the high-resolution diffractometer installed at the Swiss-Norwegian beam line was used to collect a high signal-to-noise ratio pattern for *ab initio* crystal solution (Figure 3). In parallel, to unequivocally find the systematic absences a further high signal-to-noise powder synchrotron X-ray diffraction pattern was then collected at 298K at the BM01a station (Figure 4). The combination of these two data sets (from the two stations) allowed a full elucidation of the structural details of the $[\text{Nd}(\text{H}_2\text{cmp})]\cdot 0.75\text{H}_2\text{O}$ material. These results permitted the study of the photoluminescent properties of isotypical Eu^{3+} compounds, with all the information being published in a special issue of the international journals *Zeitschrift Fur Kristallographie*.^[4]

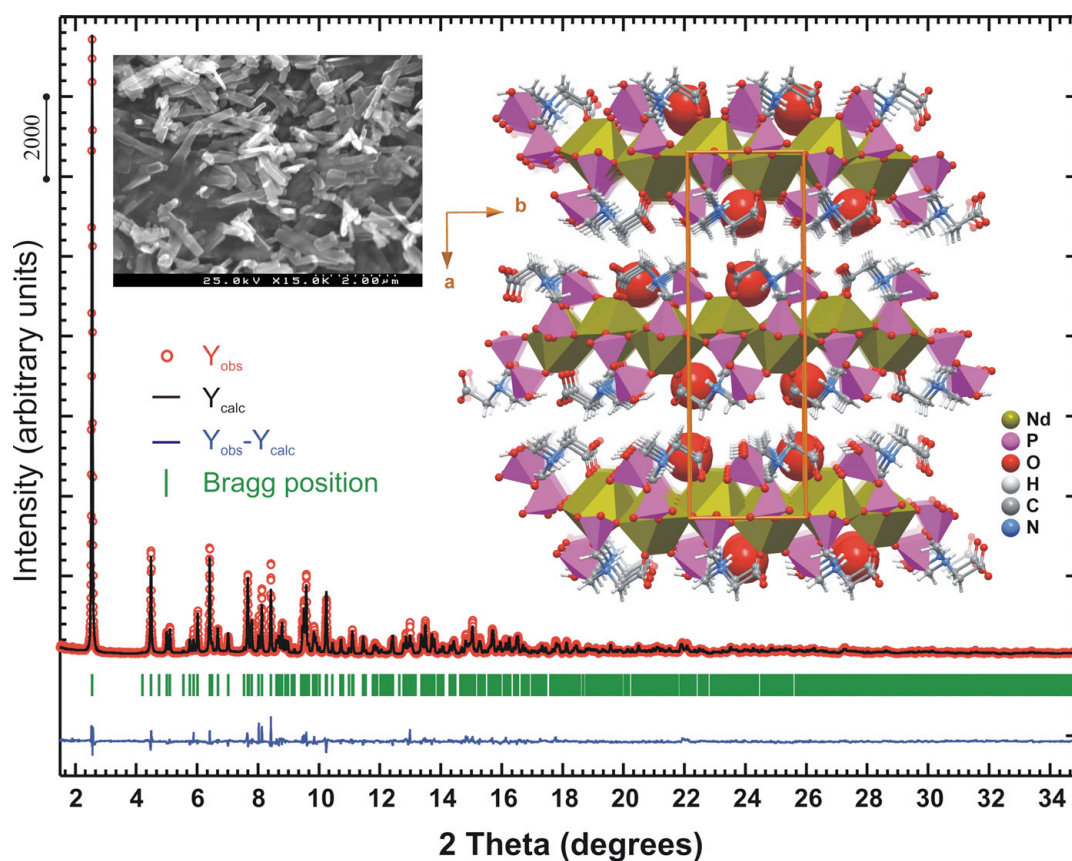


Figure 3. Final Rietveld plot (powder synchrotron X-ray diffraction data) of $[\text{Nd}(\text{H}_2\text{cmp})]\cdot 0.75\text{H}_2\text{O}$. Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. A SEM picture of the bulk material and the crystal structure viewed down $[001]$ are provided as insets (water molecules of crystallization are drawn in red in space-filling mode; phosphonate tetrahedra are represented in purple).

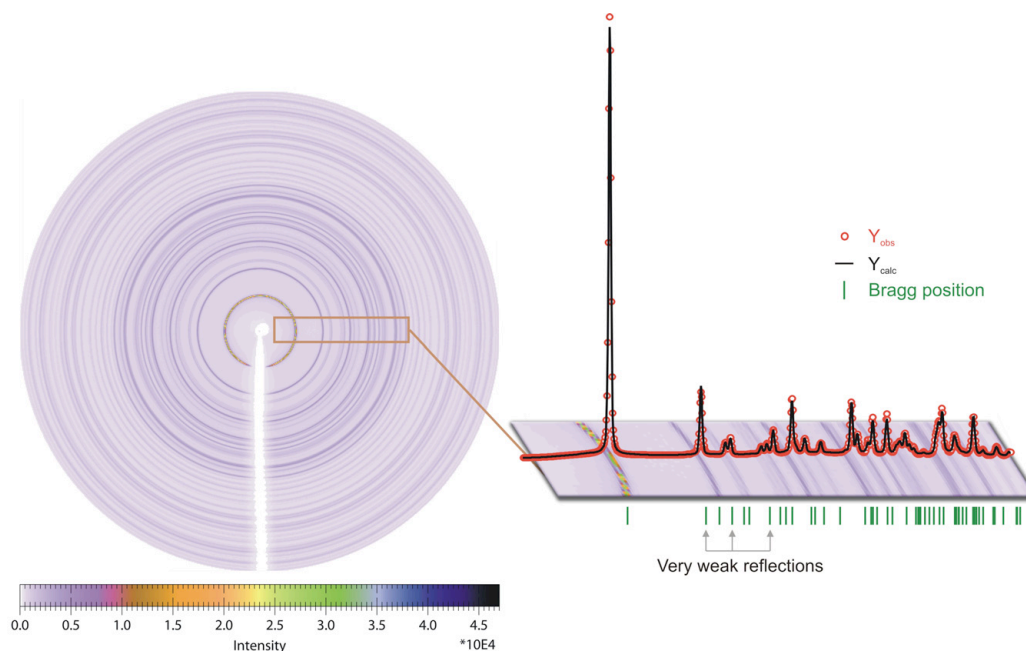


Figure 4. Two-dimensional powder pattern of $[\text{Nd}(\text{H}_2\text{cmp})]\cdot 0.75\text{H}_2\text{O}$ collected using the MAR imaging plate assembled at the BM01a beam line at the ESRF (Grenoble, France). On the right a magnification of the pattern is overlaid with a whole-powder-diffraction-pattern-decomposition (Le Bail extraction) in $P2_12_12_1$ aof the integrated pattern.

The hydrothermal reaction of rare-earth (RE) chloride salts with *N*-(carboxymethyl)iminodi(methylphosphonic acid) (H_5cmp) led to the isolation of a series of layered networks formulated as $[\text{RE}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$ [$\text{RE}^{3+} = \text{Y}^{3+}, \text{La}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}$ and Er^{3+}]. All compounds were usually obtained as micro-crystalline powders. Full structural elucidation was attained by the combination of synchrotron radiation (micro-crystal and powder diffraction data).^[5]

In a first stage, very thin fragments of $[\text{La}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$ were inspected under the synchrotron radiation beam at the BM01a beamline until the collected diffraction patterns resembled that of a typical single-crystal and for which the collected frames could also be unequivocally indexed. A complete micro-crystal data set was collected at 100(2) K for the best diffracting crystal, and the crystal structure solved though with very poor *R*-factors.

Powder synchrotron X-ray diffraction patterns with a high signal-to-noise ratio for several bulk materials were collected at ambient temperature (298K) at the multi-purpose powder station assembled at the BM01a beam line. Rietveld structural refinements using as starting premise the atomic coordinates of the single-crystal structural model were performed (Figure 5).

The compound consists of $\infty^2[\text{La}(\text{H}_2\text{cmp})(\text{H}_2\text{O})]$ layers in the *ab* plane of the unit cell, constructed from a single La^{3+} centre (in a highly distorted dodecahedral coordination environment with one water molecule in the first coordination sphere) and one $\text{H}_2\text{cmp}^{3-}$ ligand present in a zwitterionic form. Connections between layers along the *c*-axis are assured by strong and highly directional O–H \cdots O hydrogen bonds involving the protonated phosphonate group (donor) of one layer and one oxygen atom (acceptor) of the carboxylate group in the adjacent layer. We note that the same structural features have been observed for the remaining members of the series. The structural details and catalytic and optical properties of these materials have been published in *Journal of Materials Chemistry*.^[5]

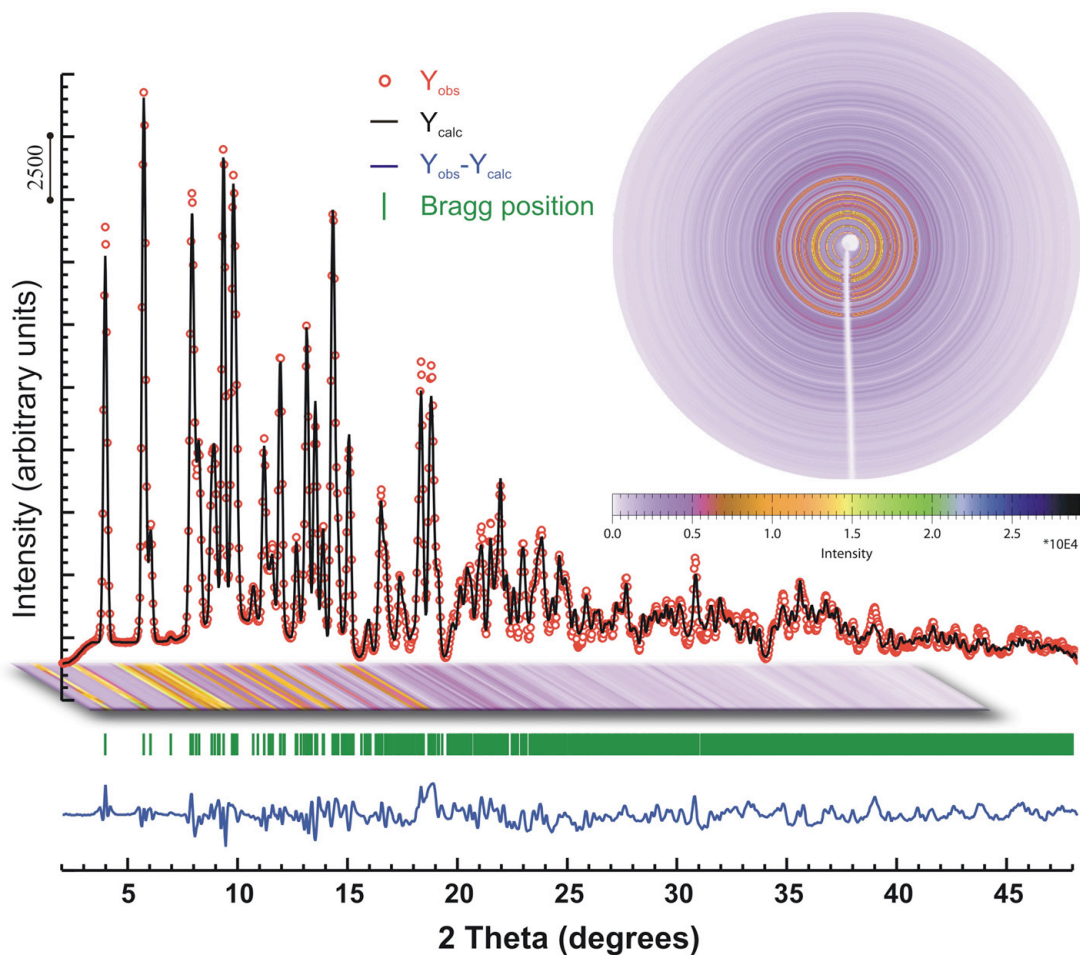


Figure 5. Final Rietveld plot (powder synchrotron X-ray diffraction data) of the bulk [La(H₂cmp)(H₂O)] material. Observed data points are indicated as red circles, the best-fit profile (upper trace) and the difference pattern (lower trace) are drawn as solid black and blue lines, respectively. Green vertical bars indicate the angular positions of the allowed Bragg reflections. The inset depicts the 2D powder pattern collected with the MAR345 imaging plate at the BM01a beam line.

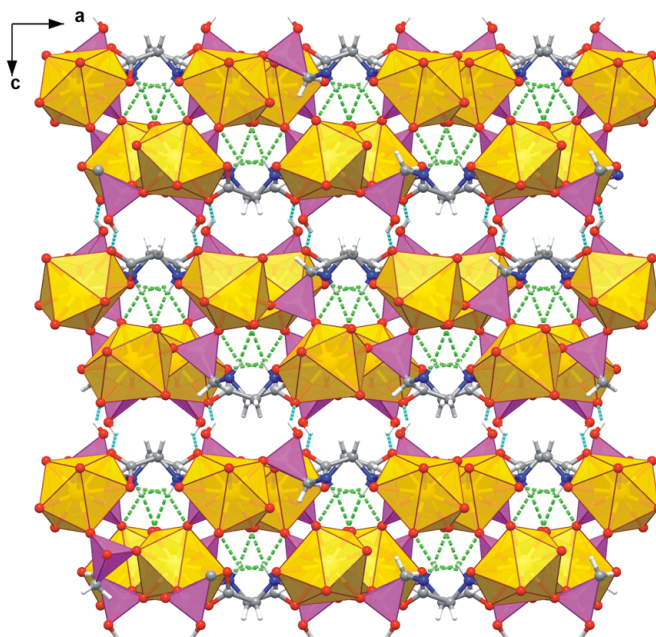


Figure 6. Mixed ball-and-stick and polyhedral representation of the crystal packing of [La(H₂cmp)(H₂O)] viewed along the [010] of the unit cell. Intra- and inter-layer hydrogen bonds are represented as green and blue dashed lines, respectively.

Conclusions:

The two trips to the ESRF to collect data at the ID31 and BM01a beam lines proved to be highly prolific with the collected data sets allowing us to report interesting results in four (4) distinct scientific publications.

Acknowledgements

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- [3] L. Vale, J. F. B. Barata, C. I. M. Santos, M. Neves, M. A. F. Faustino, A. C. Tome, A. M. S. Silva, F. A. A. Paz, J. A. S. Cavaleiro, *J. Porphyr. Phthalocyanines* **2009**, *13*, 358-368.
- [4] L. Cunha-Silva, D. Ananias, L. D. Carlos, F. A. A. Paz, J. Rocha, *Z. Kristall.* **2009**, *224*, 261-272.
- [5] L. Cunha-Silva, S. Lima, D. Ananias, P. Silva, L. Mafra, L. D. Carlos, M. Pillinger, A. A. Valente, F. A. A. Paz, J. Rocha, *J. Mater. Chem.* **2009**, *19*, 2618-2632.