ESRF	**Experiment title: Extended Supramolecular Grid-Like Coordination Arrays**	**Experiment number**: CH-1124
Beamline: ID-11	**Date of experiment**: from: 16.09.2001 to: 22.09.2001	**Date of report**: 27.02.2002
Shifts: 15	**Local contact(s)**: Dr. Gavin Vaughan	*Received at ESRF:*

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Report:

22 catagories of samples were taken to Grenoble and of those, 12 crystals were mounted for study. X-ray diffraction measurements at normal temperature and also at variable temperatures (in the case of the magnetical switchable spin crossover Fe^{II} compounds) were carried out. Finally, nine data sets could be collected. The refinemet of most of the data sets is either almost finished or in course. Some of the most important data sets are discussed below.

1. **Intermediate compounds in self-assembly process of [4x4] Pb(II)-grid architectures**

The previous experiments CH 832, CH 918 and CH 1026 succeeded finally in determining the structure of the **[4x4] Pb(II)-grid**. Because this is an outstanding example for extended supramolecular architectures, the formation process was studied in more detail by X-ray investigations at the beamline ID 11. Variation of the stochimetric ratio of ligand and metal gave different compounds which could be elucidated by the X-ray investigations. Thus, the structure of a crossbar like compound was determined. Furthermore, using the identical ligand system but in a different composition, a helical compound was structurally revealed.

This variability in structure formation using the same bricks in different ratio opens up new views into the self-assembly of large supramolecular architectures.

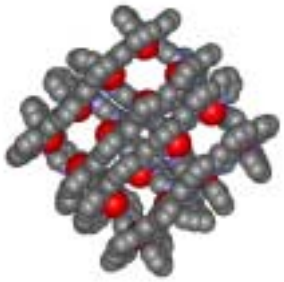

Figure 1: Final X-ray structure of the [4x4] Pb^{II}_{16}-grid architecture

2. New hydrazone-based [2x2] M^{II} complexes

A new type of ligand systems was introduced for the first time and the structures of five derived [2x2] M^{II} -complexes were elucidated (M= Co, Zn, Mn). As a first important result, this new ligand system seems to avoid the strains in the molecular architectures (Figure 2). This finding might be important for the construction of high-nuclear grid-compounds in future.

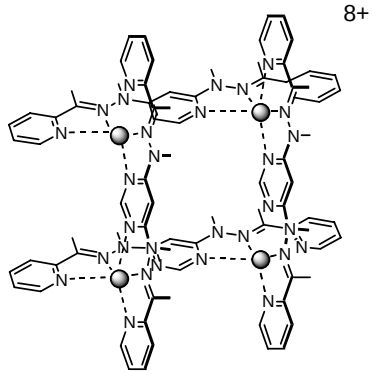

Figure 2: [2x2] M^{II}-complexes based on new Hydrazone-based ligand systems

3. 1D-SC-[2x2] Fe^{II} compounds

Once more, we persisted also in succeeding a good data set of aligned 1D wire of spin crossover [2x2] Fe^{II} units. Although we were able to collect one data set at two different temperatures of that compounds, we couldn´t solve the structure of this important compound. Obviously, the compound was destroyed in X-ray beam and only attenuation of the beam ensured the necessary life-time for measuring. However, the obtained structure has not been the expected 1D-polymer, in contrary, we detected only the unconnected SC-Fe_4-units. In a forthcoming experiment we should persist in solving this example of a hierarchical coordination.

4. A new class of helical $[M_2L_2]^{4+}$ -complexes

Based on the ligand system depicted in Figure 3 a new class of helical coordination compounds was synthesized and structurally elucidated. Different metals like Cu^{2+}, Pb^{2+} and Zn^{2+} were investigated.

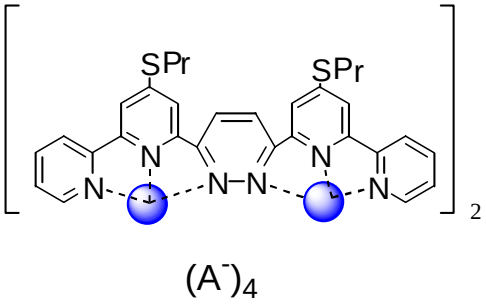

Figure 3 : New class of dinuclear coordination helices

Publications

1. The utilization of persistent H-bonding motifs in the self-assembly of supramolecular architectures

M. J. Krische, J.-M. Lehn, *STRUCT BOND*, 96, **2000**, 3-29 .

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Ulrich Ziener, Esther Breuning, Jean-Marie Lehn, Elina Wegelius, Kari Rissanen, Gerhard Baum, Dieter Fenske, Gavin Vaughan, *Chemistry*, 6, **2000**, 4132-4139

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R.W. Saalfrank, I. Bernt, M.M. Chowdhry, F. Hampel, G.B.M. Vaughan, *Chemistry*, 7, **2001,** 2765-2769.

4. Helical molecular programming: Folding of oligopyridine-dicarboxamides into molecular single helices

V. Berl, I. Huc, R.G. Khoury, J.-M. Lehn, *Chemistry*, 7, **2001,** 2798-2809.

5. Self-assembly of tetrahedral and trigonal antiprismatic clusters $[Fe_4L_4]$ and $[Fe_6L_6]$ on the basis of trigonal tris-bidentate chelators

R.W. Saalfrank, H. Glaser, B. Demleitner, F. Hampel, M.M. Chowdhry, V. schunemann, A.X. Trautwein, G.B.M. Vaughan, R. Yeh, A.V. Davis, K.N. Raymond, *Chemistry*, 8, **2002,** 493-497.

6. Ionic modulation, toward helical (H)-linear (L) or double helical (DH) and extension/contraction motions

M. Barboiu, J.-M Lehn, *Proc. Nat. Acad. Sci*., **2002**, in press