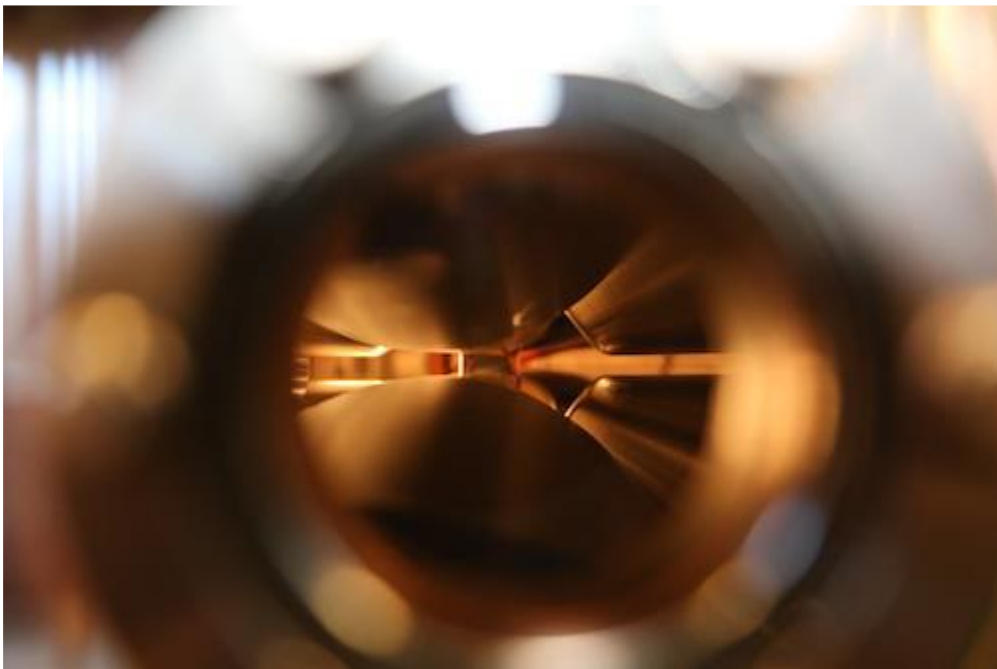


Max IV Lab Activity Report 2014-15



Editors: Johansson, U., Nyberg, A., Nyholm, R.

Lund University 2016

Structural features of metal-amino acid complexes intercalated in layered double hydroxide

G. Varga^a, Z. Csendes^a, É.G. Bajnóczi^b, S. Carlson^c, P. Sipos^b and I. Pálinkó^a

^a*Department of Organic Chemistry, University of Szeged, Szeged, Hungary*

^b*Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary*

^c*Max IV Lab, Lund University, Lund, Sweden*

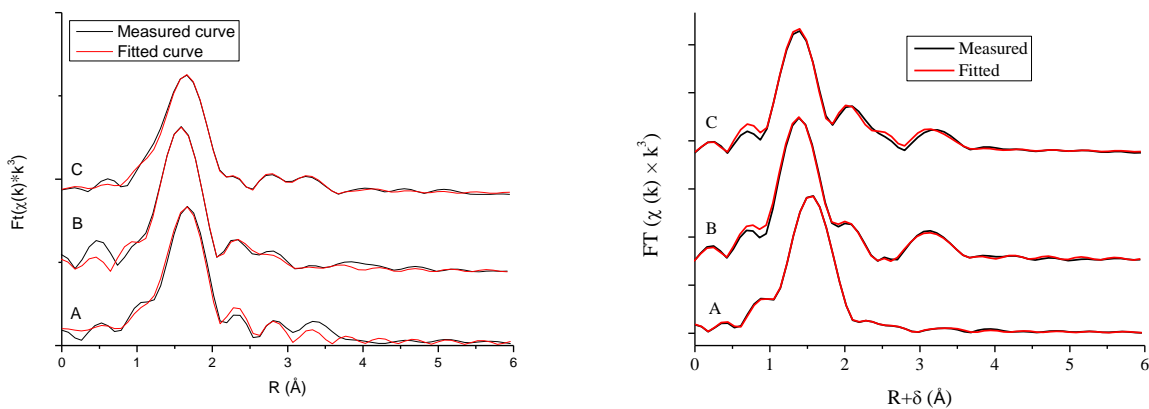
The main goal of the experiments was to determine the structure of the Mn(II)-, Ni(II)- or Cu(II)-amino acid (L-cysteine, L-tyrosine and L-histidine) complexes intercalated in Ca₂Al-layered double hydroxide (LDH) with two different methods, applying XANES/EXAFS spectroscopies. Before these experiments, we have already used FT-IR spectroscopy, and have learnt that the organic ligands were present in/on the LDH, while SEM-EDX measurements indicated that the metal ions were also there. The shift of the most relevant 001 reflection in the X-ray diffractogram verified that the components of the complex were among the layers of the LDH host, meaning that complexation occurred, and the complex was intercalated, indeed. However, these pieces of information said nothing about actual structure of the intercalated complex. XANES/EXAFS measurements were thought to provide with the missing structural data complemented with far IR and in some cases EPR spectra as well.

It is a general aim of modern catalysis to develop substances that are able to act as highly active and, more importantly, highly selective catalysts. One promising way to meet these requirements is attempting to construct biomimetic structures resembling the active site of, e.g., metalloenzymes. These materials should provide similar activities and selectivities to the real enzymes, and they should be less sensitive to harsher experimental conditions, i.e. they should withstand higher temperatures and pressures, and should work in various solvents not only in water under physiological conditions. Increasing the durability of these biomimetic metal-amino acid complexes may be achieved in several ways, like their immobilization on various supports or intercalate them in LDHs. These substances were found or thought to be capable of working under more rigorous conditions, and they could be or expected to be easily recovered and recycled. Metal complexes intercalated in confined environment, like e.g., the interlamellar space of LDHs, are thought to offer additional advantage through shape selectivity, thus increasing the overall selectivity of the transformations.

In order to develop new heterogeneous bioinspired electron-transfer catalysts Mn(II)-, Ni(II)- or Cu(II)-histidine, cysteine and tyrosine complexes were intercalated applying two methods (intercalating the amino acid anions first, then building the complex inside the LDH or constructing the complex separately, and then intercalating it in anionic form) in Ca₂Al-LDH. Several instrumental characterization methods (XRD, SEM, SEM-EDX, mid IR) were applied to verify that host-guest systems were constructed indeed, but detailed structural information could not be obtained. Through applying sophisticated IR measurements (ATR-IR – a surface-sensitive technique and P(hoto)A(coustic)-IR – a bulk-sensitive method of detection) samples could be selected having the complexes among the layers of the LDH exclusively. XANES/EXAFS measurements were used for determining the coordination number of the intercalated metal ion, giving strong hints of the coordinating atoms as well as providing with numerical data for the metal ion-coordinating atom distances. These data complemented with information obtained from far

IR and EPR (for the intercalated manganese and copper complexes) measurements, common chemical sense as well as molecular modeling made possible to envisage the arrangement of complexes among the layers.

Generally speaking, XAS measurements (Fig. 1) indicated octahedral coordination environment.



(a) (b)
Fig. 1. The Fourier-transformed X-ray absorption spectra of the (a) Mn(II)-amino acid–CaAl-LDH composites – A: Mn(II)-tyrosinate–CaAl-LDH, B: CaAl–Mn(II)-histidinate–LDH and (C) Mn(II)-cysteinate–CaAl-LDH; (b) Cu(II)-amino acid–CaAl-LDH composites – A: CaAl–Cu(II)-cysteinate–LDH, B: Cu(II)-histidinate–CaAl-LDH and C: Cu(II)-tyrosinate–CaAl-LDH.

Moreover, it was also revealed that the thiolate sulfur in the cysteinate ligand was coordination site. The amino nitrogens in all the composites and the phenolate oxygen in the metal(II)-tyrosinate–CaAl-LDH were also coordinated. The histidine nitrogen was also a sure coordination site. The carboxylate oxygens were probably used in the intercalation process; nevertheless, they might have taken part in the metal ion coordination, too.

The proposed models for the structural arrangements of the intercalated manganese complexes are displayed in Fig. 2.

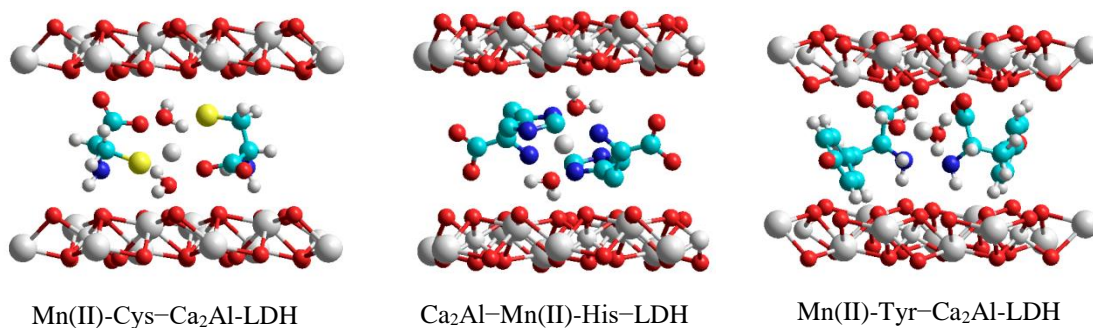


Fig. 2. The proposed steric arrangement of the intercalated complexes between the layers of CaAl-LDH, based on XRD, mid and far IR, EPR and XAS measurements.

Acknowledgment: This work was also supported by the NKFI 106234 grant. The financial help is highly appreciated.