

Mössbauer and XRD study of intercalated CaFe-layered double hydroxides

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Abstract N-containing fully saturated (L-prolinate) or aromatic (indole-2-carboxylate) heterocyclic anions were immobilised in CaFe-layered double hydroxide with the dehydration-rehydration method from aqueous ethanol or acetone. The structure

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of the resulting organic-inorganic hybrids was characterised mainly with powder X-ray diffraction and ^{57}Fe Mössbauer spectroscopy, and as supplementary analysis scanning electron microscopy, energy dispersive X-ray spectroscopy with elemental mapping and molecular modelling were also applied. It was found that the solvent mixture used for the synthesis caused enormous difference in the interlayer spacings of the obtained inorganic-organic hybrids.

Keywords CaFe-layered double hydroxide host • L-prolinate and indole carboxylate derivative guests • Effects of synthesis variables • Instrumental characterisation

1 Introduction

The family of layered double hydroxides (LDHs) is a class of (mostly) synthesised anionic layered clays that can be represented by the general formula of $[\text{M}_{1-x}^{\text{II}}\text{M}_x^{\text{III}}(\text{OH})_2]_x^+[\text{X}_m^{-x/m}\cdot n\text{H}_2\text{O}]_x^-$ [1–3]. The partially isomorphous substitution of divalent cations for trivalent ones results in positively charged layers balanced by simply, fully or partially hydrated inorganic anions in the interlayer space. These ions can be exchanged to more complex organic anions forming organic-inorganic functional nanocomposites [4]. These materials can be of many uses like, e.g., immobilised organocatalysts [5–7], protected organic moieties from unwanted transformations (like, e.g., racemisation [8]), targeted delivery of medicine with lengthened effects [9], etc.

Many varieties of LDHs are known, and most of them can be found in nature, however, for applications they are usually synthesised. The most often used preparation method is the co-precipitation of the component salts with the help of a base in solution [10].

There are numerous methods for the introduction of organic anions into the interlayer space as well. One obvious method is anion exchange, but there are frequently used alternative methods as well, like including the organic anion in co-precipitation or using the memory effect of LDHs [11].

The memory effect means that on heat treatment, the LDH gradually dehydrates and at a certain temperature depending on the specific material, the layered structure is lost. However, if the temperature was not too high (again, it depends on the specific LDH), the layered structure can be recovered under humid conditions or simply suspending it in water. If the organic anion is dissolved in water used for rehydrating the dehydrated LDH, intercalation takes place. This method was used in the experimental work leading to this contribution.

In the followings, we describe the syntheses of two organic-inorganic functional nanocomposites using CaFe-LDH as host and L-prolinate or indole-2-carboxylate as anionic guests. The effects of synthesis variables, mostly those of the solvents, are examined and full characterisation of the obtained substances is given. The work was performed with the aim of preparing durable composites that are able to act as catalyst in various organic transformations.

2 Experimental

2.1 Materials used

Concentrated NaOH (~20 M) stock solutions were prepared from Millipore MilliQ water and a.r. grade solid NaOH (VWR International) and their carbonate content was minimised as described previously [12]. The precise concentration was determined through accurate density measurement. The solution was stored in airtight, caustic resistant Pyrex bottle. This solution can be kept carbonate-free easily; therefore, this was used for the making of the 3 M NaOH solution actually used in the synthesis.

CaCl₂, (Molar Chemicals, puriss), iron chloride (FeCl₃·6H₂O, Molar Chemicals, puriss special) were used as received.

Commercially available (Aldrich, purity >98 %) various N-heterocyclic compounds (L-proline and indole-2-carboxylic acid, Fig. 1) were transformed to their sodium salts before intercalation. Acetone and ethanol were also the products of Aldrich Chemical Co.

2.2 Methods of synthesis

CaFe-LDH was prepared by the co-precipitation method, via dropwise addition of 3 M NaOH solution to vigorously stirred and N₂-blanketed CaCl₂/FeCl₃ solution with 3:1 molar ratio [13]. The precipitates formed were rapidly filtered until air dry in a practically CO₂-free atmosphere, with the aid of a caustic resistant vacuum filter unit (Nalgene) equipped with an appropriate membrane (Versapor 129, 0.45 μm). The host materials were calcined before attempting intercalation at 773 K for 5 h in N₂ atmosphere.

The carboxylate anions were intercalated into CaFe-LDH with the dehydration-rehydration method, utilising the memory effect of the layered double hydroxide. The heterocyclic compounds were suspended in aqueous ethanol or aqueous acetone. In both solvents, the LDH was stirred for a week. Upon rehydration intercalation occurred. The solid catalyst was filtered and washed with distilled water. The crystals obtained were kept at room temperature in a desiccator over P₂O₅.

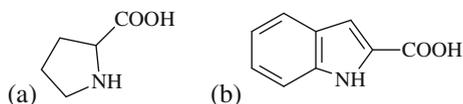
2.3 Characterisation

The key method for studying the structural features of the host as well as the host-guest hybrids were powder X-ray diffraction and ⁵⁷Fe Mössbauer spectroscopy.

The diffractograms were taken in the 3–60° 2θ region with 4°/min scanning rate on a Rigaku Miniflex II instrument using the CuKα radiation (λ = 0.15418 nm). The (003) reflection was used for calculating the basal spacings. The accurate positions of the reflections were determined after fitting Gaussian-type functions.

⁵⁷Fe Mössbauer transmission spectra were measured by conventional constant acceleration type Mössbauer spectrometers (Wissel and Ranger) in transmission geometry in a bath cryostat at 78 K and 295 K. Measurements were performed in two different apparatuses, and the thickness of the layers differed somewhat, leading to

Fig. 1 The intercalated compounds: **a** L-proline and **b** indole-2-carboxylic acid



different line widths at the two temperatures. A $^{57}\text{Co}(\text{Rh})$ source of $\sim 10^9$ Bq activity was used and the spectrometer was calibrated with α -iron at room temperature. Spectrum evaluation was carried out using the MOSSWINN[®] code [14].

The morphologies of the synthesised nanocomposites were studied with a Hitachi S-4700 scanning electron microscope (18 kV acceleration voltage) at various magnifications. The elemental maps of the substances were determined with a Röntec QX2 energy dispersive X-ray spectrometer coupled to the microscope. We were mainly concentrating on verifying the presence of the host anions in the samples *via* detecting the carbon and/or nitrogen of the organic salts and displaying their distribution.

The Fe^{3+} -content of the LDH was determined with a Thermo's IRIS Intrepid II ICP-OES spectrometer, and the quantities of the intercalated carboxylate anions were measured by UV-Vis spectroscopy.

The sizes of the various intercalated carboxylate ions were determined after performing full geometry optimisation with the PM3 [15] semiempirical quantum chemical method included in the Hyperchem 8.0 [16] molecular modelling package.

3 Results and discussion

Powder XRD measurements were performed first on the pristine LDH, the sodium salt of the carboxylic acids, and then, the intercalated samples obtained from both solvent mixtures. The most important parts of the obtained diffractograms are seen in Fig. 2a and b.

Basal spacings were calculated from the (003) reflection. The measured interlayer spacings contain one layer of the host material, which is 0.18 nm thick by high-precision XRD data [17]. Thus, the distance values between the layers are shown in Table 1 along with the dimensions of the anions, optimised by the PM3 semiempirical method.

Huge differences have been observed between the interlayer distances of the intercalated LDHs prepared depending on solvent mixture used during their synthesis. If the rehydration took place in aqueous acetone, the $d(003)$ values became much larger than that of the pristine LDH. However, when the ethanol/water solvent mixture was applied the interlayer distance did not change significantly. The first observation is the obvious sign of the success of the intercalation, while in the second case one may think of its failure. However, it has been found (and it is shown taking indole-2-carboxylate-CaFe-LDH as an example) that both synthesised materials contained organic material (Table 2) in appreciable amounts.

In order to confirm that the organic material is not simply on the outer surface of the LDH but it resides among the layers, the samples were further studied by ^{57}Fe Mössbauer spectroscopy (Fig. 3 and Table 3) and scanning electron microscopy (Fig. 4).

Typical Mössbauer spectra of the samples, recorded at 78 K, are shown in Fig. 3.

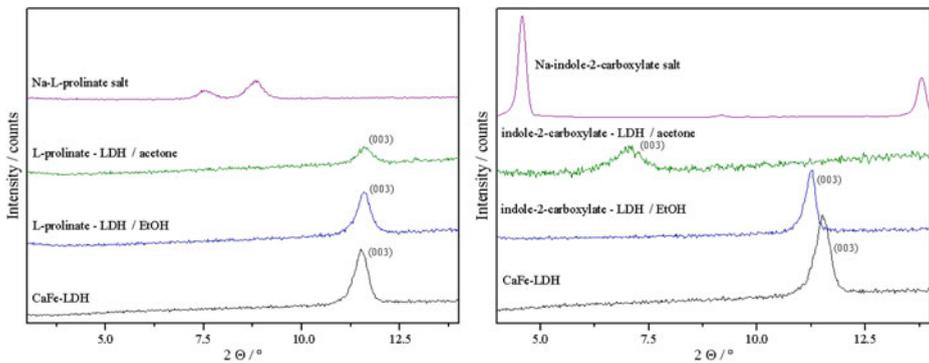


Fig. 2 Powder X-ray diffractograms of the host CaFe-LDH, the N-heterocyclic anion-CaFe-LDH prepared using aqueous ethanol or aqueous acetone and the sodium salts of the N-heterocyclic compounds

Table 1 The $d(003)$ and interlayer distance values for the intercalated LDHs

N-containing heterocycles	$d(003)$	$d(003)$	Dimensions of the anions (nm)*	Interlayer distance EtOH/H ₂ O (nm)**	Interlayer distance acetone/H ₂ O (nm)**
	EtOH/H ₂ O (nm)	acetone/H ₂ O (nm)			
L-prolinate	0.79	0.76	$0.39 \times 0.35 \times 0.53$	0.61	0.58
indole-2-carboxylate	0.79	1.24	$0.50 \times 0.30 \times 0.78$	0.61	1.06

*the edges of a cuboid in which the anion precisely fits, optimised by the PM3 semiempirical method;

**calculated as the experimentally observed $d(003)$ reduced by the layer thickness

Table 2 The quantities of the intercalated indole-2-carboxylate anions between the layers of the CaFe-LDH

	indole-2-carboxylate-LDH EtOH/H ₂ O	indole-2-carboxylate-LDH acetone/H ₂ O
indole-2-carboxylate anion intercalated to the LDH (mol/g)	2.20×10^{-4}	2.75×10^{-4}
$(n_{\text{indole-2-carboxylate}}/n_{\text{Fe}}) \times 100^*$	32 %	40 %

*by ICP-OES measurements the iron-content of the LDH was 6.86×10^{-4} mol/g

The spectra were decomposed into asymmetric doublets, the Mössbauer parameters of which are shown in Table 3. The Mössbauer spectrum of the pristine compound agreed with that reported earlier for CaFe-LDH [18].

The isomer shift is practically the same in these compounds indicating that the electronic density at the site of nucleus remains unchanged upon the intercalation of different anions between the layers of CaFe-LDH and independent from the solvent used for the preparation of the compounds. The isomer shift corresponds well to that what was found to be characteristic of CaFe-LDH materials [18].

However, significant differences have been found in the quadrupole splitting of the pristine and the intercalated substances, both when the Mössbauer spectra were recorded at 78 K and at 293 K. These differences are similar or even higher than those observed between the quadrupole splittings of Ca₂Fe- and Ca₃Fe-LDHs [18].

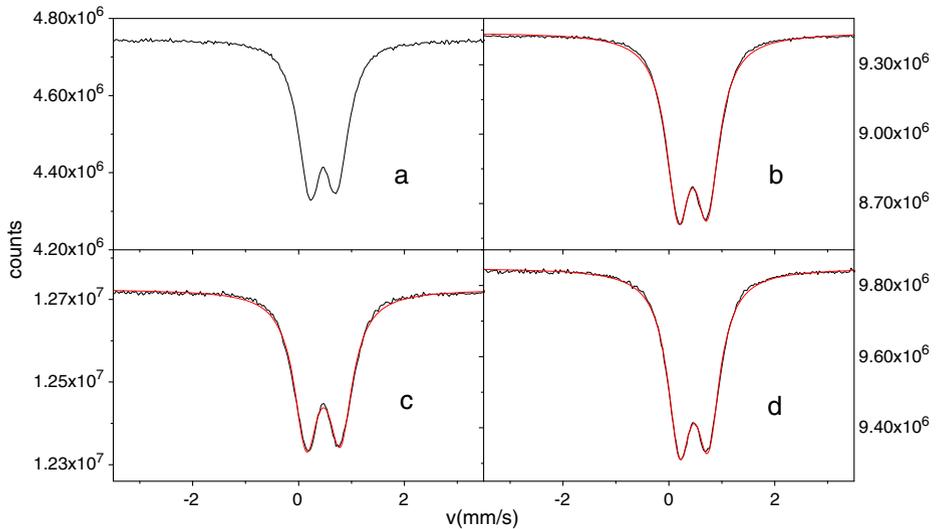


Fig. 3 ^{57}Fe Mössbauer spectra of CaFe-LDH **a** in pristine form and intercalated with **b** L-prolinate or **c** indole-2-carboxylate in ethanol and **d** in acetone recorded at 78 K

Table 3 The ^{57}Fe Mössbauer parameters of the pristine and the intercalated LDH samples at 78 K

	CaFe-LDH	L-prolinate-LDH	Indole-2-carboxylate-LDH	
			EtOH/H ₂ O	acetone/H ₂ O
δ (mm/s)	0.47 ± 0.005	0.46 ± 0.005	0.47 ± 0.005	0.47 ± 0.005
Δ (mm/s)	0.45 ± 0.009	0.51 ± 0.009	0.64 ± 0.009	0.54 ± 0.009

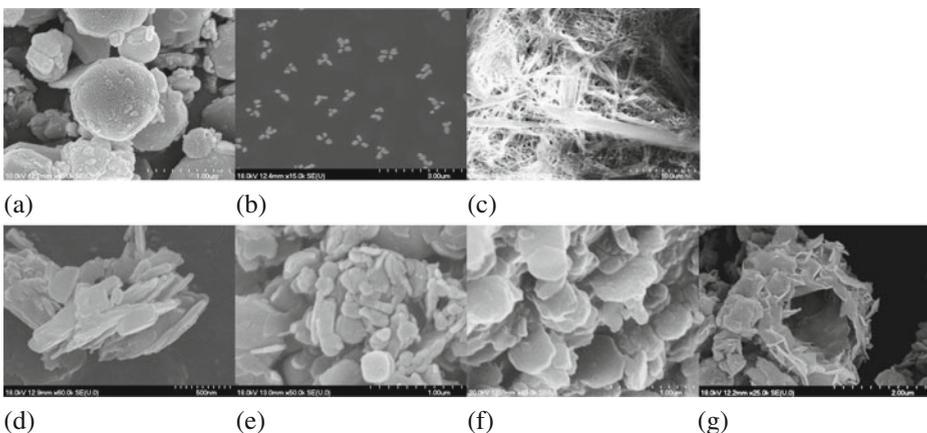


Fig. 4 SEM images of the pristine CaFe-LDH **(a)**, the sodium salts of L-proline **(b)** and indole-2-carboxylic acid **(c)**, the L-prolinate-CaFe-LDHs prepared using aqueous ethanol **(d)**, aqueous acetone **(e)** and the indole-2-carboxylate-CaFe-LDH prepared using aqueous ethanol **(f)**, aqueous acetone **(g)**

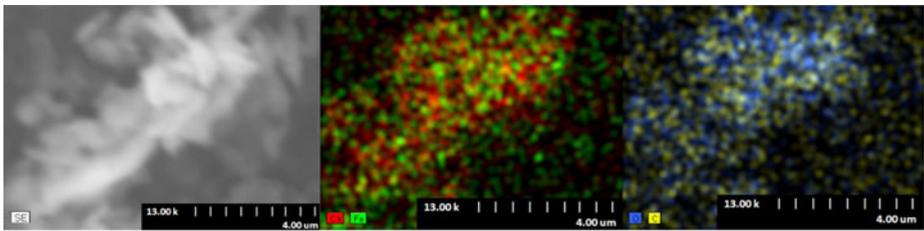
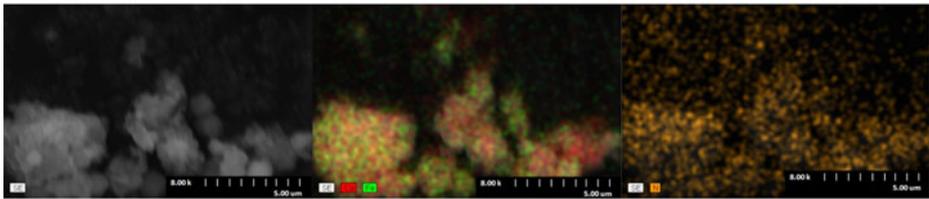
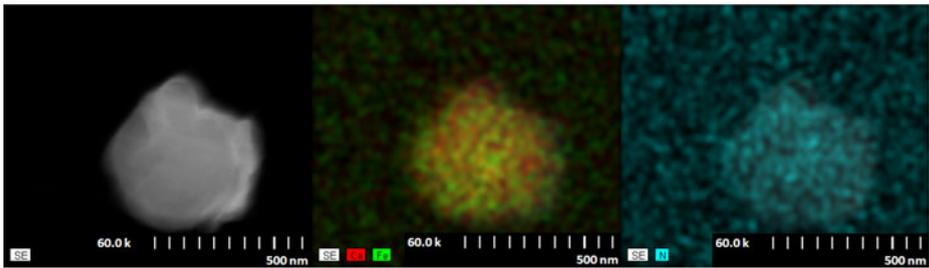
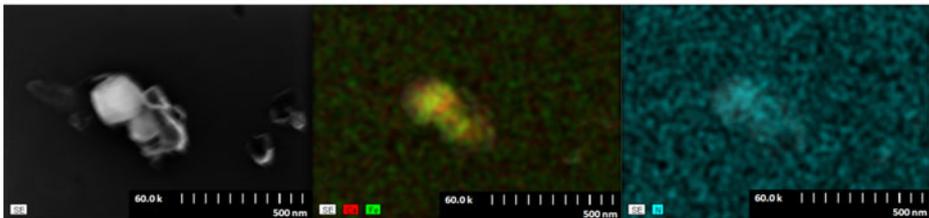
L-prolinate–CaFe-LDH from EtOH/H₂OL-prolinate–CaFe-LDH from acetone/H₂Oindole-2-carboxylate–CaFe-LDH from EtOH/H₂Oindole-2-carboxylate–CaFe-LDH from acetone/H₂O

Fig. 5 The SEM-EDX elemental maps of N-heterocyclic carboxylate–CaFe-LDH samples prepared in different solvent mixtures

The changes in quadrupole splitting can be associated with changes in the electric field gradient (EFG) due to changes in the charge distribution around the iron atom that can be caused by change in the molecule symmetry (spatial arrangement of ligands) [19]. In our case, the increase in quadrupole splitting, observed upon the intercalation, compared to that characteristic of pristine can be explained by lowering the symmetry of charge distribution in the compound. Furthermore, the intercalation of different anions into the layers of CaFe-LDH can modify the charge distribution differently, producing different ligand contributions to the EFG, consequently

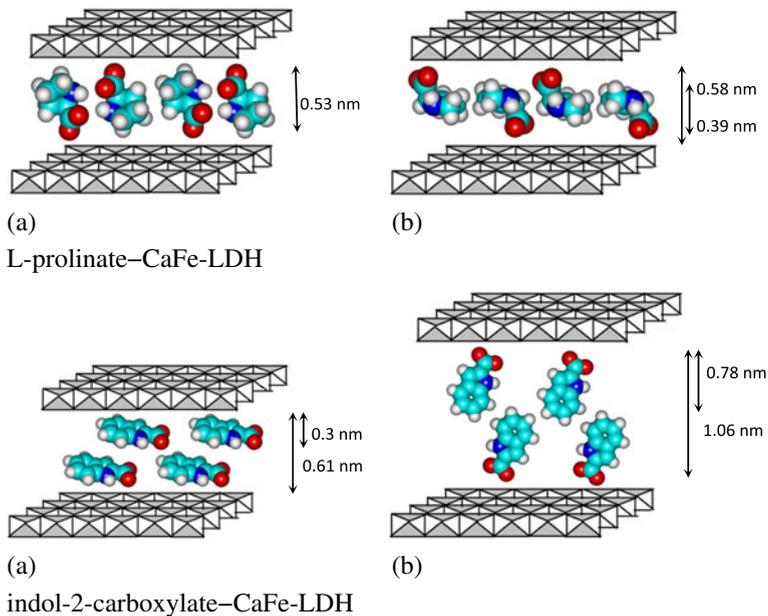


Fig. 6 The possible arrangement of N-heterocyclic anions between the layers depending on the solvent mixture used during the synthesis, **a** ethanol/water, **b** acetone/water

resulting in different quadrupole splitting values. On the other hand, the different values of quadrupole splitting, when the same anion (indol-2-carboxylate) was used but the solvent mixture was different, indicate the different spatial arrangement of the anions between the layers of LDH, also shown by XRD, SEM and EDX methods (Figs. 2, 4 and 5). Mössbauer results support the model for arrangement of N-heterocyclic anions between the layers shown in Fig. 6, since smaller EFG can be expected for the arrangement with acetone/H₂O solvent (Fig. 6b) than for that with EtOH/H₂O (Fig. 6a).

The lamellar morphologies of the LDHs are reflected in the images both for the pristine LDH and for those containing the organic anion, hopefully in-between the layers. Note, that the SEM images of the carboxylate salts are different from those of the organic material treated LDH samples. This finding and the results of the organic content analysis prove that intercalation also occurred when aqueous ethanol was used for the syntheses.

Further verification could be obtained when the elemental maps made on the basis of SEM-EDX measurements are examined. The almost uniform distribution of the ions on the Ca-Fe elemental map indicated that double hydroxides were formed, indeed. The N or C elemental maps revealed that the organic material was present and again in almost uniform distribution (Fig. 5).

After verifying that the organic anions were intercalated indeed, whichever solvent mixture was used, one can take the interlayer distance values and size data of the organic anions from Table 1 and attempt to visualise the possible arrangement of the anions between the layers. It can be envisaged that when aqueous ethanol was used during preparation both the L-prolinate and the indole-2-carboxylate fit between

the layers in a horizontal arrangement. On using aqueous acetone, the anions can be accommodated in an orientation perpendicular to the layers (Fig. 6a and b, respectively).

The change in the geometry of the arrangement of the anions must be due to the influence of the solvent molecules by either a direct interaction with the LDH layers (therefore with the ligand sphere of iron, built in the LDH layers) or by water withdrawing effect. This has yet to be explored through more detailed research.

4 Conclusions

N-containing heterocyclic anions could be introduced in between the layers of CaFe-LDH. The success of intercalation was verified by several instrumental methods. The interlayer distance values from XRD measurements and size data of the anions from molecular modelling calculations allowed to give an approximate picture on the arrangement of the anions among the layers.

Most importantly, it was shown that the choice of solvent mixture used during the intercalation dramatically influenced the interlayer distance in the hybrids, thus significantly influencing the geometry of the intercalation.

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References

1. Cavani, F., Trifirò, F., Vaccari, A.: *Catal. Today* **11**, 173 (1991)
2. Vaccari, A.: *Catal. Today* **41**, 53 (1998)
3. Evans, D.G., Slade, R.C.T.: *Struct. Bond.* **119**, 1 (2006)
4. Pálkó I.: *Nanopages* **1**, 295 (2006)
5. Choudary, B.M., Kavita, B., Chowdari, N.S., Sreedhar, B., Kantam, M.L.: *Catal. Lett.* **78**, 373 (2002)
6. An, Z., Zhang, W., Shi, H., He, J.: *J. Catal.* **241**, 319 (2006)
7. Shi, H., He, J.: *J. Catal.* **279**, 155 (2011)
8. Aisawa, S., Takahashi, S., Ogasawara, W.: *J. Solid State Chem.* **162**, 52 (2001)
9. Ambrogi, V., Fardella, G., Grandolini, G., Perioli, L.: *Int. J. Pharm.* **220**, 23 (2001)
10. Duan, X., Lu, J., Evans, G.D.: *Assembly chemistry of anion-intercalated layered materials*. In: Xu R., Pang W., Huo Q. (eds.) *Modern Synthetic Inorganic Chemistry*, pp. 375–404. Elsevier B.V., Amsterdam (2011)
11. Miyata, S.: *Clays Clay Miner.* **28**, 50 (1980)
12. Sipos, P., Heftler, G.T., May, P.M.: *The Analyst* **129**, 955 (2000)
13. Srankó, D., Pallagi, A., Kuzmann, E., Canton, S.E., Walczak, M., Sági, A., Kukovecz, Á., Kónya, Z., Sipos, P., Pálkó, I.: *Appl. Clay Sci.* **48**, 214 (2010)
14. Klencsár, Z.: *MossWinn 4.0Pre*, A Software for Mössbauer Spectrum Analysis. Budapest, Hungary
15. Stewart, J.J.P.: *J. Comput. Chem.* **10**, 209–220 (1989) (see also **10**, 221 (1989))
16. Hyperchem 8.0, Hypercube, Inc., Gainesville, Florida (2007)
17. Rousselot, I., Taviot-Guého, C., Leroux, F., Léone, P., Palvadeu, P., Besse, J.-P.: *J. Solid State Chem.* **167**, 137 (2002)
18. Sipiczki, M., Kuzmann, E., Homonnay, Z., Megyeri, J., Pálkó, I., Sipos, J.: *Mol. Struct.* **1044**, 116 (2013)
19. Gütllich, P., Bill, E., Trautwein, A.: *Mössbauer Spectroscopy and Transition Metal Chemistry*. Springer-Verlag GmbH, Berlin, Heidelberg, New York (2011)