

This article was downloaded by:

On: 30 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

Spectroscopic Properties of Co-Fe Hydrotalcites

M. del Arco^a; R. Trujillano^a; St. Kassabov^b; V. Rives^a

^a Dpto. de Química Inorgánica, Universidad de Salamanca, Salamanca, Spain ^b Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

To cite this Article Arco, M. del , Trujillano, R. , Kassabov, St. and Rives, V.(1998) 'Spectroscopic Properties of Co-Fe Hydrotalcites', *Spectroscopy Letters*, 31: 4, 859 — 869

To link to this Article: DOI: 10.1080/00387019808007404

URL: <http://dx.doi.org/10.1080/00387019808007404>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPIC PROPERTIES OF Co-Fe HYDROTALCITES

Key words: hydrotalcite, hydroxycarbonate, Co-Fe hydrotalcite, anionic clays, Mössbauer, FT-IR

M. del Arco¹, R. Trujillano¹, St. Kassabov² and V. Rives^{1*}

¹Dpto. de Química Inorgánica, Universidad de Salamanca, Salamanca,
Spain

²Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113-Sofia, Bulgaria.

ABSTRACT

The spectroscopic properties of hydrotalcite-like compounds, containing Co(II) and Fe(III) in the layers, have been studied. In these materials, depending on the experimental conditions during synthesis, Co(II) becomes partially oxidized to Co(III). Although the environment of the cations is close to octahedral in all cases, Mössbauer data indicate a more symmetric environment for Fe(III) ions in samples not submitted to hydrothermal treatment. The FT-IR spectra show some distortion of the carbonate anions in the interlayer space.

INTRODUCTION

The use of multicomponent catalysts in different processes is limited because of a lack in the structural homogeneity and/or chemical segregation during preparation, that generally lead to lower catalytic activity and changes in selectivity. An alternative to overcome

this problem is to use different precursors, and the so-called "anionic clays" seem to be good precursors to prepare these catalysts. Among these anionic clays, the most widely systems have the hydrotalcite structure, and so they are usually known as "hydrotalcite-like" compounds (HT). These are layered double hydroxides with the general formula $[M_{1-x}M'_x(OH)_2]^{x+} (X)_{x/m} \cdot nH_2O$, where M=divalent cation (Mg, Zn, Ni, ...), M'=trivalent cation (Al, Fe, Cr, ...) and X=anion (carbonate, sulphate, nitrate, chloride, ...). The structure consists of brucite layers positively charged because of partial substitution by trivalent cations, with the interlayer space filled with anions (to balance the positive charge of the layers) and water molecules. The number of natural and synthetic anionic clays containing different metallic cations (divalent: Mg, Mn, Fe, Co, Ni, Cu, Zn, Ca; trivalent ones: Al, Cr, Mn, Fe, Co, La and V) studied so far is very large; the same structure is also shown by compounds containing monovalent/trivalent cations (Li, Al) and even divalent/tetravalent (Co, Ti). These materials exhibit anion-exchange properties and their properties have been recently reviewed.¹⁻³ Upon thermal decomposition they lead to mixed oxides.^{1,4,5} The mechanism of the thermal decomposition of such precursors makes possible preservation of structural elements from the initial phase in the final products, so making possible recovering of the layered structure upon rehydration.⁶

In the present paper we report on the spectroscopic (Visible-ultraviolet, infrared and Mössbauer) properties of layered double hydroxides with the hydrotalcite structure containing Co(II) and Fe(III) as layer cations, prepared by coprecipitation. Hansen et al. have recently reported⁷ the synthesis of these materials; in our case, the use of different experimental conditions during synthesis has led to partial oxidation of Co(II) to Co(III).

EXPERIMENTAL

The samples have been prepared by precipitation, adding an aqueous solution of Co(II) and Fe(III) nitrates on an aqueous solution of sodium carbonate, obtaining a brown suspension. This suspension was

submitted to three different treatments: (i) washing until total removal of NO_3^- and Na^+ ,⁸ filtering and drying in air at 343 K; this sample will be named I; (ii) hydrothermal treatment at 370 K during 5 days in a stainless steel digestion bomb lined with teflon; the solid was washed until total removal of NO_3^- and Na^+ , filtered and dried at room temperature in open air, leading to sample H. In order to avoid partial oxidation of Co(II) species to Co(III), presumably taking places during these treatments and already reported for other Co-containing hydrotalcites,^{9,10} a third sample, named as II, was prepared similarly to sample I, but in this case the solid was dried in open air at room temperature.

The Fourier Transform Infrared spectra (FT-IR) were recorded in a FT-IR 1730 Perkin Instrument using the KBr pellet technique; one hundred scans were averaged, with a nominal resolution of 4 cm^{-1} . Mössbauer spectra were recorded in the constant acceleration mode, using Co in a Pd matrix as source; fitting of the spectra was achieved assuming Lorentzian-shaped lines. The Vis-UV spectra were recorded by the diffuse reflectance (DR) technique in a Shimadzu UV-240 instrument, using MgO as reference and a slit of 10 nm.

RESULTS AND DISCUSSION

Synthesis and characterization of the samples have been described elsewhere.¹¹ Briefly, the Co:Fe atomic ratio was close to 2.5 in all three cases, and X-ray powder diffraction showed well crystallized materials; the XRD peaks for sample H were rather more intense and sharp than for the other two samples, probably indicating a larger crystallinity. Temperature programmed reduction data suggested the presence of Co(III) species in sample H, probably because of partial oxidation during synthesis.

Visible-Ultraviolet/Diffuse Reflectance Spectra

The Vis-UV/DR spectra of the samples are shown in Fig. 1. Bands expected would be due to $d-d$ Laporte-forbidden transitions, as well as to charge transfer processes. In the hydrotalcites, the cations are located in octahedral holes in the brucite-like layers.¹⁻³

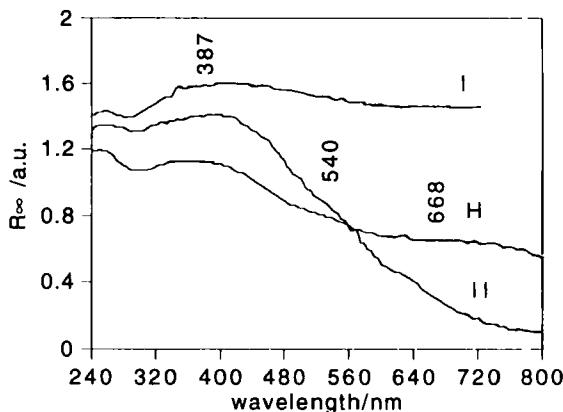


FIG. 1. Visible-Ultraviolet spectra, recorded following the Diffuse Reflectance technique, of samples I, II, and H.

For sample II a broad band is recorded, with maximum at 387 nm and shoulders at 540 and 668 nm. In addition, an absorption is observed from *ca.* 300 nm towards lower wavelength; this last band should be undoubtedly due to a charge transfer process. For octahedrally coordinated Co(II), three spin-allowed *d-d* transitions are expected, corresponding to transitions $^4T_1(F) \rightarrow ^4T_{2g}(F)$, $^4T_1(F) \rightarrow ^4A_{2g}(F)$ and $^4T_1(F) \rightarrow ^4T_{1g}(P)$. However, for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ only the band due to transition $^4T_1(F) \rightarrow ^4T_{1g}(P)$ is observed close to 540 nm, as transition $^4T_1(F) \rightarrow ^4T_{2g}(F)$ is expected in the near infrared region, close to 1200 nm (outside the range of the spectrophotometer used), and transition $^4T_1(F) \rightarrow ^4A_{2g}(F)$ is essentially a two-electron transfer process, so being very weak.¹² Actually, all these bands are rather weak, and so, in our samples, they are obscured by the charge transfer transitions involving the Fe(III), which are much more intense.

The spectrum for sample H is rather similar to that described for sample II, although the shoulders are less evident and the absorption in the large wavelength region is sensibly larger.

The spectrum is absolutely different for sample I. An almost continuous absorption is observed in all the spectral range studied, with the maximum close to 400 nm. This spectrum is rather similar to that recorded for bulk Co_3O_4 ,¹³ although X-ray diffraction data for this sample does not show any evidence of the presence of this compound in its crystalline form.

Fourier Transform Infrared Spectra

The technique is most valuable to identify the nature of the interlayer anions existing in these samples. This cannot be straightforward concluded from X-ray diffraction analysis, as some anion, i.e., carbonate and hydroxyl, can give rise to similar (coincident, within experimental error) basal spacings.¹

The spectra for the three samples are given in Fig. 2. The band close to 3400 cm^{-1} , recorded in all samples, is due to the hydroxyl stretching mode, and appears very broad because of the presence of multiple strength hydrogen bondings in the structure, among the interlayer water molecules, and among these and the layer hydroxyl groups. The shoulder recorded close to 3050 cm^{-1} has been ascribed^{14,15} to OH stretching modes involving interlayer carbonate anions. The medium intensity band at $1600\text{--}1640\text{ cm}^{-1}$ is due to the bending mode of interlayer molecular water molecules. The most intense band is recorded close to 1350 cm^{-1} , and corresponds to mode ν_3 of interlayer carbonate anions. Although this position is quite apart from that corresponding to free carbonate,¹⁶ the restricted symmetry in the interlayer space of the hydrotalcite would account for this apparently abnormal behaviour.

Mössbauer Spectra

The Mössbauer spectra of the three samples are shown in Fig. 3. The best fit obtained assuming two quadrupolar doublets (A and B) are also shown in the figure; analysis assuming three doublets (A, B, and C) did not improve sensibly the fit, as this third component would require an extremely high quadrupolar splitting constant Δ , only compatible

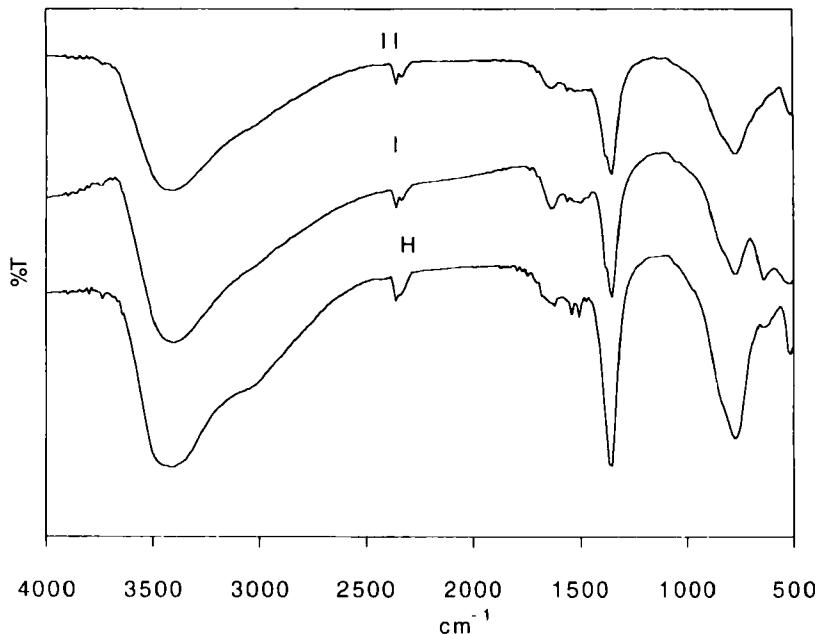


FIG. 2. FT-IR spectra of samples I, II, and H.

with a heavily distorted environment for the Fe(III) ions, such as pentacoordinated moieties, hardly to be expected in hydrotalcites, where the metal cations are located in octahedral holes of the brucite-like structure; moreover, this third component would only account for a mere 10% of the signal recorded.

Results of the two-components fit analysis are summarized in Table 1. Isomer shifts (δ) and quadrupole splittings (Δ) are given, together with the fraction of each component for each spectrum. All δ values are close to 0.6 mm s^{-1} , characteristic of Fe(III) cations, $3d^5$ configuration, in $^6S_{5/2}$ fundamental state. The existence of two quadrupoles should be taken as indicative of the presence of Fe(III) cations in two environments with different symmetries. The lower Δ

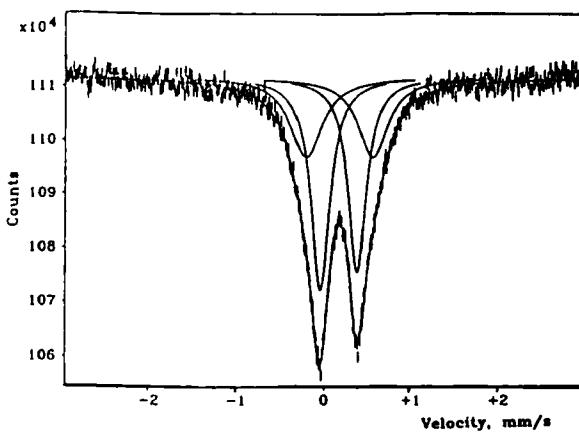
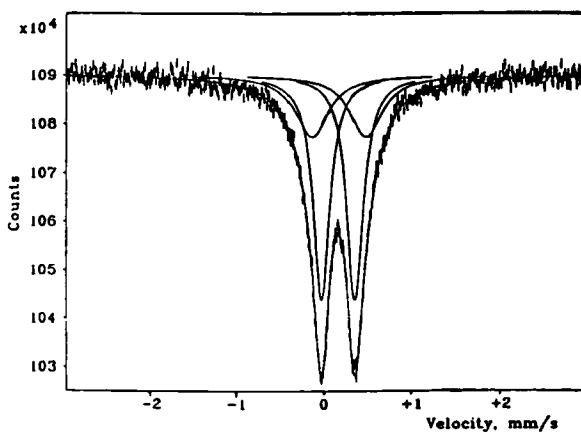
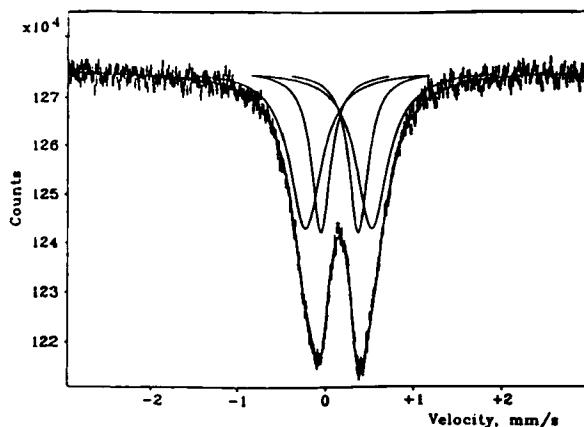


Fig. 3. Mössbauer spectra of samples I, H, and II (from top to bottom).

TABLE 1
Best fit of the Mössbauer spectra of samples I, H and II

Sample	Components					
	A			B		
	δ	Δ	%	δ	Δ	%
I	0.604	0.390	65	0.611	0.624	35
H	0.595	0.434	38	0.584	0.762	62
II	0.602	0.416	60	0.614	0.755	40

δ =isomer shift; Δ =quadrupole splitting; both in mm/s

value for component A is consistent with a more symmetric environment for the Fe(III) cations responsible for this signal; on the contrary, the higher Δ value for signal B indicates a more distorted symmetry from ideal octahedral symmetry. On the other hand, the rather large width of component B suggests the presence of hyperfine quadrupole structure.

Overall, the results indicate a more symmetric environment for the Fe(III) cations in samples II and I (60-65% component A) than for sample H (38% component B). However, one would expect more crystalline samples after hydrothermal treatment, as already found by PXRD. Quite surprisingly, it is the sample submitted to hydrothermal treatment that one where the local environment of the Fe(III) cations in the brucite-like layers appears to be more distorted. This apparent controversy is overcome taking into account that in all samples, $[\text{CoO}_6]$ and $[\text{FeO}_6]$ octahedra with different sizes (ionic radii for high spin Co(II) and Fe(III) are 0.885 and 0.785 Å, respectively¹⁷) should coexist. In small crystals (i.e., those existing in samples I and II), the lower size would

permit a better *integration* of the octahedra in the crystallites, so the octahedra retaining its almost regular structure. On the contrary, for sample H, submitted to hydrothermal treatment, formation of larger crystals would require to locate the octahedra in a larger crystal, where distortions would not be so easily *absorbed* by the crystal.

CONCLUSIONS

Control of experimental conditions during synthesis is of paramount importance on determining the oxidation state of cobalt in the final hydrotalcites. A partial oxidation has been observed in sample I by Vis-UV spectroscopy. Mössbauer spectra indicate that the local environment around the the Fe(III) ions is more symmetric in samples I and II due to the differences in the ionic radii and to the distortion of the octahedra.

ACKNOWLEDGEMENTS

Authors thank financial support from DGICYT (grant PB96-1307-C03-01) and Junta de Castilla y Leon (Consejería de Educación y Cultura, ref. SA45/96).

REFERENCES

- 1 Cavani F., Trifiro F., Vaccari A. Hydrotalcite-type Anionic Clays: Preparations, Properties and Applications. *Catal. Today* 1991; 11: 173-301.
- 2 De Roy A., Forano C., El Malki K., Besse J. P. Anionic Clays: Trends in Pillaring Chemistry. In: Occelli, M. L.; Robson, H. E. Eds. *Expanded Clays and Other Microporous Solids*, New York: Van Nostrand Reinhold 1992: 108-169.
- 3 Trifiró F., Vaccari A. Hydrotalcite-like Anionic Clays (Layered Double Hydroxides). In: Atwood J. L., Davies J. E. D., MacNicol D. D., Vögtle F., Lehn J. M. eds. *Comprehensive Supramolecular Chemistry*. Oxford: Pergamon Press 1996, vol. 7: 251-291.

4 Uzunova E., Klissurski D., Kassabov S. Nickel-iron Hydroxide Carbonate Precursors in the Synthesis of High-dispersed. *J. Materials Chem.* 1994; 4: 153-159.

5 Uzunova E., Klissurski D., Mitov I., Stefanov P. Cobalt-iron Hydroxide Carbonate as a Precursor for the Synthesis of High-dispersity Spinel Mixed Oxides. *Chem. Materials* 1993; 5: 576-582.

6 Chibwe K., Jones W. Synthesis of Polyoxometalate-pillared Layered Double Hydroxides via Calcined Precursors. *Chem. Materials* 1989; 1: 489-490.

7 Hansen H. C. B., Koch C. B., Taylor R. M. Synthesis and Characterization of Cobalt(II)-Iron(III) Hydroxide Carbonate, a Layered Double Hydroxide Belonging to the Pyroaurite Gruop. *J. Solid State Chem.* 1994; 113: 46-53.

8 Burriel F., Lucena F., Arribas S., Hernández J. *Química Analítica Cuantitativa*, 13th ed. Madrid: Paraninfo, 1989.

9 Ulibarri M. A., Hernández J. M., Labajos F. M., Rives V. Anionic Clays with Variable Valence Cations: Synthesis and Characterization of $[Co_{(1-x)}Al_x(OH)_2](CO_3)_{x/2} \cdot n H_2O$. *Chem. Materials* 1991; 3: 626-630.

10 Del Arco M., Galiano M. V. G., Rives V., Trujillano R., Malet P. Preparation and Study of Decavanadate-Pillared Hydrotalcite-like Anionic Clays Containing Cobalt and Chromium. *Inorg. Chem.* 1996; 35: 6362-6372.

11 Del Arco M., Trujillano R., Rives V. Cobalt-iron Hydroxycarbonates and their Evolution to Mixed Oxides with the Spinel Structure. *J. Materials Chem.* submitted for publication.

12 Sutton D. *Espectros Electrónicos de los Complejos de los Metales de Transición*, Barcelona: Reverté, 1975.

13 Del Arco M., Rives V. Interactions with the Support in Co/TiO₂ and Co₃O₄/TiO₂ Systems. *J. Materials Sci.* 1986; 21: 2938-2940.

14 Kruissink E. C., Van Reijen L. L., Ross J. R. H. Coprecipitated Nickel-Alumina Catalysts for Methanation at High Temperature. Part 1. Chemical Composition and Structure of the Precipitates. *J. Chem. Soc. Faraday Trans. 1*, 1981; 77: 649-663.

15 Labajos F. M., Rives V., Ulibarri M. A. Effect of Hydrothermal and Thermal Treatments on the Physicochemical Properties of Mg-Al Hydrotalcite-like Materials. *J. Materials Sci.* 1992; 27: 1546-1552.

16 Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th. ed. New York: John Wiley & Sons, 1986.

17 Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed., Harper Collins: New York, 1993.

Date Received: December 12, 1997
Date Accepted: January 28, 1998