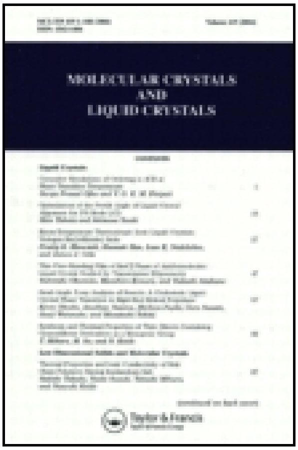

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[Zn-Cr-X] and [Zn-Al-X] LDHs containing electroactive interlamellar anions. Chemical and structural characterization

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[Zn-Cr-X] and [Zn-Al-X] LDHs containing electroactive interlamellar anions. Chemical and structural characterization

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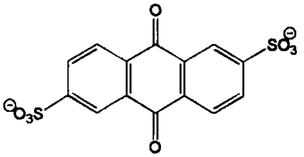
Intercalation of electroactive organic sulfonate anions, such as aromatic and organo-metallic derivatives, into LDH anion exchanger.

Keywords : LDH, intercalation, organic sulfonate electroactive anions

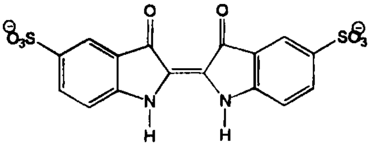
INTRODUCTION

Research arose focusing on the preparation of electrodes modified with inorganic structured materials such as zeolites and clays. In both cases, a three-dimensional architecture is built on the electrode surface allowing study of molecular recognition effects in the design of electrocatalysts. The anion exchange property of Layered Double Hydroxides (LDH) has been used to insert organic electroactive anions. We have studied different kind of modified electrodes with these organic-inorganic hybrid materials in the aim of electrocatalysis, specially for applications with systems such as metallo-porphyrins[1,2].

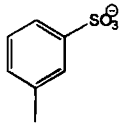
In this paper, we report the synthesis and the characterization of LDH [Zn-Cr-X] and [Zn-Al-X] containing eleven different organic electroactive anions bearing one to four sulfonate groups to assure electrostatic interactions with the hydroxide layers. See for example :



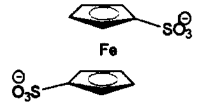
Anthraquinone : AQDS-2,6



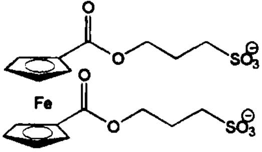
Indigo carmine : IC



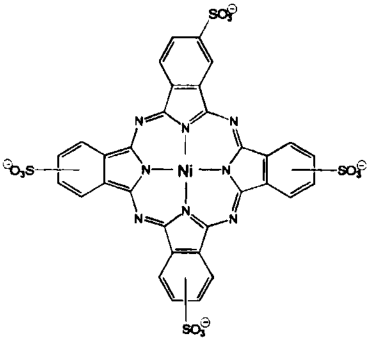
Nitrobenzene : NBS



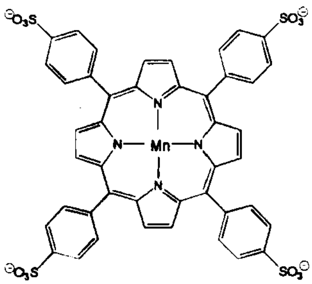
Ferrocenes : FcDS



FcDPS



Phthalocyanine : NiPcTS



Porphyrin :MnTSPP

RESULTS AND DISCUSSION

All organic anions are commercial except the ferrocene derivatives (FcMS, FcDS, FcPS and FcDPS) which we have synthesized[3,4]. The [Zn-Cr-X] and [Zn-Al-X] LDH with M^{II}/M^{III} ratio near to 2 or 3 and intercalated with these organic sulfonate anions have been prepared either by a direct coprecipitation (method A)[2] or by an exchange reaction method (method B) using a [Zn-Cr-Cl] LDH previously prepared by a coprecipitation method[1] (Table I).

Under anionic exchange, the M^{II}/M^{III} ratio of the precursor was maintained while using the coprecipitation method the desired ratio was always obtained.

The percentages of exchange were calculated from sulfur contents, the amount of remaining Cl^- anion was also determined by elemental analysis (Table I). These compositions were verified in some cases by XED analyses. For exchange reactions (method B), the average exchange percentage is about 60%. It can be increased to 80% if the exchange reaction was performed under reflux conditions. In the case of coprecipitation (method A), the percentage of organic anions in the interlayer compensating the positive charge is generally 100%. When organic anions and chlorides do not counterbalance the positive charge of the inorganic matrix, carbonate anions insure the overall neutrality.

TABLE I : [Zn-Cr-X] and [Zn-Al-X] characterizations

LDH-X	Method	M^{II}/M^{III}	% anion	% Cl	a (Å)	d (Å)
[Zn-Cr-Cl]	A	1.8	-	100	3.11	7.7
[Zn-Al-Cl]	A	3.0	-	100	3.06	7.8
[Zn-Cr-NBS]	B	1.8	60	<5	3.11	15.6
[Zn-Cr-AQS2]	B	1.9	64	36	3.09	19.9
[Zn-Cr-AQDS15]	B	1.9	58	3	3.10	15.9
[Zn-Cr-AQDS26]	B	1.8	55	12	3.10	18.9
[Zn-Cr-AQDS26]	B_{reflux}	1.8	70	3	3.10	18.9
[Zn-Cr-IC]	B_{reflux}	2.2	80	0	3.10	21.8
[Zn-Cr-FcMS]	A	2.1	100	5	3.10	20.0
[Zn-Cr-FcDS]	A	2.2	100	0	3.10	15.0
[Zn-Cr-FcPS]*	A	2.1	93	1	3.10	22.2
[Zn-Cr-FcPDS]*	A	1.6	78	0	3.10	17.1
[Zn-Al-NiPcTS]*	A	3.2	100	0	3.06	23.0
[Zn-Al-MnTSPP]*	A	3.2	100	0	3.06	23.3

* **d** is calculated from the mean positions of the third first lines (00l) et **a** is calculated as **a** = $2d_{(110)}$

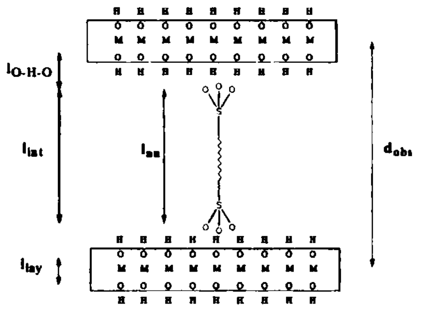
With all LDH containing ferrocene derivatives, we have observed, by elemental analysis, XPS and Mössbauer spectroscopies, a partial decomplexation of the Fc derivatives during their incorporation into the LDH network leading to the precipitation of nanoparticles of $Fe(OH)_3$ onto the LDH layers.

The presence of high spin Fe^{III} excess in the inorganic matrix affects strongly the magnetic properties of the LDH [3].

__The XRPD data__ (Table I) confirm the presence of organic anions in the LDH structure. The basal spacing values are calculated from the *c* cell parameters ($d = c/3$), obtained from a unit cell refinement in the classical $R\bar{3}m$ hexagonal indexation. The basal spacings of the [Zn-Cr-Cl] and [Zn-Al-Cl] precursors are 7.71 Å and 7.80 Å, respectively. The presence of organic sulfonate expands the interlayer space of the LDH to basal spacings between 15 Å and 23 Å depending on the size of the guest molecules and their arrangement in the internal galleries (l_{an}).

The d spacings of aromatic disulfonate-pillared LDH phase are calculated taking into account that the sulfonate groups are oriented with an optimal interaction with the hydroxyl leading to strong hydrogen bondings ($l_{O\text{-}H\text{-}O} = 2.7 \pm 0.1$ Å) as determined for SO_4^- containing LDH[11].

This involves the contribution, to the overall basal spacings, of a constrained value $L_{cons} = l_{lay} + 2\ l_{O\text{-}H\text{-}O} = 2.1 + 2\ (2.7 \pm 0.1) = 7.5 \pm 0.2$ Å. (l_{an} is calculated using Alchemy software).



Comparison of the distance $l_{int} = d_{obs} - l_{cons}$ and l_{an} allows to discuss the arrangement of the organic anions in the interlayer (Table II). Generally, l_{an} and l_{int} are of the same magnitude, in agreement with the anionic functions sticked to the layers and with a perpendicular orientation of the aromatic ring to the sheets. In particular, the ferrocene guest anions have their metal-ring centroid axes parallel to the host layers as reported for various organometallic sandwich compounds in SnS_2 layered structure[12]. For NiPcTS and MnTSPP, our data confirmed the perpendicular arrangement of the para substituted macrocycles between the LDH layers previously reported in the literature[13]. As all samples were dried at room temperature, slight deviations are often due to internal hydration of LDH, as for example the [Zn-Al-MnTSPP].

TABLE II : Basal spacings of LDH containing disulfonate aromatic compounds and organometallic compounds

Compound	d_{obs} (Å)	l_{an} (Å)	l_{int} (Å)	Ref
2,5-dihydroxybenzene-1,4-disulfonate	14.7	7.5	7.0-7.4	5
Naphtalene-1,5-disulfonate	15.2	7.5	7.5-7.9	6
Naphtalene-2,7-disulfonate	16.5	9.3	8.8-9.2	7
Naphtalene-2,6-disulfonate	15.4	9.8	7.7-8.1	7
AQDS26	18.9 (18.8)	11.5	11.2-11.6	*this work* (8)
AQDS15	15.9	7.5	8.2-8.6	*this work*
IC	21.8 (21.2)	14.4	13.5-14.5	*this work* (9)
FcDS	15.0	7.5	7.3-7.7	*this work*
NiPcTS	23.0	15.8	15.3-15.7	*this work*
MnTSPP	23.3	14.6	15.6-16.0	*this work*
MnTSPP (heated at 150°c)	22.2	14.6	14.5-14.9	*this work*

By comparison with data obtained with disulfonate aromatic anions, we can assume the same perpendicular orientation of monosulfonate anions (Table III). This assumption is made on the basis of the constant increase (2 Å) in the observed d values for the sequence of benzene sulfonate, naphtalene-2-sulfonate and anthracene-2-sulfonate (AQS2), value corresponding to the molecular size increases in the series. The higher values observed for l_{int} compared to the anion size l_{an} (Δ) are in agreement with a intertwined single layer arrangement. In these cases, the dehydration does not affect the basal spacings.

The fact that the d spacings obtained with monosulfonate anions are systematically higher than that measured with the disulfonate is confirmed from the data obtained with BHMBS which can be introduced into the interlayer region of LDH as either a monovalent or divalent counter-ion [10] and with all ferrocene derivatives ($\delta = d_{mono}-d_{di} \cong 5$ Å) (Table I and III).

TABLE III : Basal spacings of LDH containing monosulfonate aromatic compounds

Compound	d_{obs} (Å)	l_{an}(Å)	l_{int}±0.2 (Å)	Δ (Å)	Ref
Benzene sulfonate	15.7	6.0	8.2	2.2	5
NBS	15.6	6.2	8.1	1.9	*this work*
p-Toluene sulfonate	17.5	6.8	10.0	3.2	6
Naphtalene-1-sulfonate	16.5	6.0	9.0	3.0	6
Naphtalene-2-sulfonate	17.9	8.1	10.4	2.3	6
AQS2	19.9	10.2	12.4	2.2	*this work*
BHMBSm*	20.0	8.5	12.5	4.0	10
BHMBSd*	13.8	7.5	6.3	1.2	10

***BHMBS** = 5-benzoyl-4-hydroxy-2-methoxybenzene sulfonate

CONCLUSION

The perpendicular arrangement of the sulfonate electroactive guest molecules in the LDH interlayer domains is a great advantage for heterogeneous catalysis and electrocatalysis applications, in particular with the macrocycles compounds. Preliminary results obtained with the [Zn-Al-MnTSPP] LDH allow to consider applications for electroassisted oxydations with molecular oxygen.

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