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# Preparation of nanocomposite materials from mercaptoacetate-modified platinum nanoparticles and a layered nickel hydroxyacetate salt

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#### ABSTRACT

Nanocomposites were prepared by a very simple route from preformed platinum particles and a nickel layered hydroxide salt (LHS), these compounds being first synthesized separately by the polyol process. The nanoparticles were treated with mercaptoacetate before being brought into contact with the lamellar compound. XPS and IR spectroscopies give clear evidence for interactions between the platinum nanoparticles and the mercaptoacetate species. XRD, TEM and magnetic characterizations show that the structure of the nickel hydroxide layers is retained and that some of the LHS sheets contain incorporated nanoparticles.

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### 1. Introduction

Layered double hydroxides (LDH) and layered hydroxide salts (LHS) have attracted increasing interest during the last decades. Their properties arise from their foliated structure: they consist of positively charged layers, generally of the brucite type. Anionic species are intercalated in the interlamellar space together with water molecules. This is due, in the case of LDH compounds, to the partial substitution of divalent cations by trivalent cations in octahedral sites, leading to a positive charge on the layers which need to be compensated by intercalated anionic species. In LHS compounds, only divalent cations are present. The insertion of anions has been explained by: (i) the lack of some hydroxyl groups in the sheets, (ii) the partial replacement of hydroxyl groups, or (iii) the protonation of some hydroxyl groups. The large range of compositions possible for the host matrix and the possibility of exchanging the anionic species offer potential for tuning the properties of such materials. Consequently, layered hydroxides are of interest in numerous fields, such as catalysis, electrochemistry, magnetism, environment, medicine, etc. [1-6].

Surprisingly, while several papers discuss of the intercalation of nanoparticles in clays, there are few reports of the introduction of metal nanoparticles in LDH or LHS. However, this would greatly improve the properties of the layered material, or confer additional properties. Noble metals have been introduced either by co-

precipitation of a multicationic lamellar hydroxide, [7] or by impregnation with a metallic complex or salt, followed by in situ reduction [8-9]. However, these routes do not allow the incorporation of much metal, particularly in the case of Pt, [7] and they lead to the precipitation of polydisperse particles. Nanoparticles have also been incorporated by exfoliation and restacking [10]. An alternative method consists in incorporating preformed monodisperse metal nanoparticles. To the best of our knowledge, this method is seldom reported. Recently, Gérardin et al. [11] incorporated preformed  $Ni(C_6H_7O_3)_x(OH)_y$  colloids by anionic exchange into the lamellar space of Mg-Al LDH. However, the reduction of nickel necessitates a further calcination step, followed by reduction at high temperature in dihydrogen, and leads to particles coated by a carbon-rich shell. The present work aims at incorporating directly a large quantity of preformed monodisperse metal nanoparticles into lamellar compounds without any post-synthetic treatment.

Since it is a promising *chimie douce* route, the polyol process was chosen to synthesize the starting compounds. The polyol acts as an amphiprotic solvent, as well as complexant, reductant and surfactant. In the absence of water and at a reasonable temperature, monodisperse nanoparticles of noble metals can be produced [12]. In the presence of water, this route allows the preparation of transition metal layered hydroxyacetate salts [13]. The LHS chosen for this study was a nickel hydroxyacetate (Ni(OH)<sub>1.6</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>0.4</sub>·*n*(H<sub>2</sub>O)) whose synthesis in polyol is now well controlled [13]. The choice of platinum particles was directed by two considerations. The first was the importance of platinum in catalysis applications, the second the ability of our group to obtain

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very small (diameter below 2 nm), monodisperse platinum particles [14].

Our strategy was therefore to first synthesize separately both components by the polyol process, then to make the two systems compatible by grafting a small molecule with a double functionality on the nanoparticle surface, and finally to bring the two components together. The nanocomposites obtained after one and two loading steps are characterized from chemical, morphological, structural and magnetic points of view. The particle concentration in the final composite was chosen on purpose to be higher than required for many applications (for example, catalysis) in order to facilitate characterization. For specific applications the system will need to be optimized.

## 2. Experimental

#### 2.1. Chemicals

Nickel acetate tetrahydrate (Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O 99%), sodium acetate trihydrate (CH<sub>3</sub>COONa·3H<sub>2</sub>O 99%), sodium mercaptoacetate (HSCH<sub>2</sub>COONa 98%, MA) and diethylene glycol (DEG 99%) were purchased from Acros. Potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub> 99.9%) was from Alfa Aesar.

#### 2.2. Synthesis procedures

A reaction scheme describing the different steps of the synthesis of the composites and summarizing the products is given in Fig. 1.

The first step consists in synthesizing a layered nickel hydroxyacetate salt (solid noted LHS-Ac) according to a previously described procedure [13]. Nickel acetate (6.222 g, 25 mmol) was



Fig. 1. Reaction scheme for the synthesis of composites.

dissolved in DEG (250 ml) at 100 °C. MilliQ water (110 ml) was added to the cooled solution (hydrolysis ratio,  $n(H_2O)/n(Ni) = 250$ ), which was then heated at 90 °C for one night. A green solid was recovered by centrifugation and washed three times with ethanol.

Platinum nanoparticles were obtained by a method derived from that previously described [14]. It was based on the reduction of a solution containing  $K_2PtCl_4$  (1.2 mmol) and sodium acetate (4.0 mmol) in DEG (200 ml) at 90 °C. To functionalize the nanoparticles, a solution of HSCH<sub>2</sub>CO<sub>2</sub>Na (1.2 mmol) in DEG (100 ml) was then added. Thus, the molar ratio of mercaptoacetate to platinum in the colloidal solution is equal to 1.0. The solution, noted PtMA, was used without centrifugation to make the composites. However, for further characterizations, a volume of the PtMA solution was also centrifuged after addition of ethanol to obtain a powder, noted PtMAp.

A first composite material was obtained by adding the previous colloidal solution, PtMA (150 ml, containing 0.6 mmol of both Pt and MA) to the LHS-Ac dispersion (300 mg, 2.5 mmol) in fresh MilliQ water (300 ml) (molar ratio Pt/Ni = 0.15) and filtering a product, noted LHS-PtMA-1, after 20 h. A second material was made by redispersing this product in MilliQ water (300 ml), adding a second batch of grafted platinum (150 ml) and stirring for another 20 h. This material is noted LHS-PtMA-2.

Finally, LHS-Ac (400 mg, 3.4 mmol) was left with sodium mercaptoacetate (342 mg, 3.0 mmol) in fresh MilliQ water (200 ml) with stirring under nitrogen for 20 h before filtering and washing with water to obtain a solid denoted LHS-MA.

## 2.3. Characterizations

The chemical content of Ni, S and Pt of each sample was checked by using an energy dispersive spectrometer (EDX) EDAX Genesis (SUTW) mounted on a Jeol-JSM 6100 scanning electron microscope operating at 25 kV. The oxygen content was omitted, as it cannot be measured correctly.

X-ray photoelectron spectrometry (XPS) measurements were performed using a Thermo VG Escalab 250 instrument equipped with a monochromatic Al  $K_{\alpha}$  ( $h\nu$  = 1486.6 eV) 200 W X-ray source. The X-ray spot size was 650  $\mu$ m. The pass energy was set at 150 and 40 eV for the survey and the narrow scans, respectively. An electron flood gun was used, under  $2 \times 10^{-8}$  mbar partial pressure of argon, for static charge compensation. These conditions resulted in a negative but uniform static charge. Measurements were carried out on powdered samples mounted on sample holders. Data acquisition and processing were performed with the Avantage software, version 2.20. The surface composition was determined using the integrated peak areas and the corresponding Scofield sensitivity factors corrected for the analyser transmission function. For the majority of the compounds under study, spectra were calibrated by setting the main C(1s) component, assigned to aliphatic carbons, to 285 eV [15]. However, such a peak is not expected in the XPS spectrum of the free mercaptoacetate salt. Consequently, in this case the highest energy component, assigned to carboxylate-type carbons, was set to 289.5 eV.

Fourier transform infra-red (FTIR) spectra were collected on KBr pellets with a PerkinElmer 1750 spectrophotometer in the transmittance mode between 4000 and 600 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>, 64 scans being accumulated.

Transmission electron microscopy (TEM) images were obtained on a Jeol-100-CX II microscope operating at 100 kV. The samples were dispersed in a solvent (ethanol or toluene); one drop of this solution was deposited on the carbon membrane of the microscope grid and the solvent was left to evaporate at room temperature. Microtomy was used to locate more precisely the nanoparticles in the composite materials. The samples were first embedded in an epoxy resin (from Fluka). They were then sliced with a LEICA ultramicrotome (EM-UC6) to prepare thin specimens (70 nm thick).

Powder X-ray diffraction (XRD) experiments were carried out on a X'Pert Pro Panalytical diffractometer equipped with a Co anode ( $\lambda = 0.17889$  nm) and a multichannel detector (X'Celerator).

The magnetic susceptibility and hysteresis loop measurements were performed on a Quantum Design MPMS-5S SQUID magnetometer. The DC magnetic susceptibility  $\chi(T)$  was measured in the field cooling (FC) mode between 2.5 and 320 K in a magnetic field (H) of 200 Oe. The magnetization curves M(H) were obtained at H = -50 to 50 kOe, after zero-field cooling down to 5 K. All measurements were performed on the as-prepared powders slightly compacted in a plastic sampling tube, in order to prevent their physical movement during the experiments.

## 3. Results and discussion

### 3.1. Formation and chemical analysis of the composite materials

The powder (LHS-PtMA-1) obtained after a first addition of the dark colloidal solution of preformed PtMA (platinum nanoparticles with mercaptoacetate) in DEG to a dispersion of preformed nickel layered hydroxyacetate salt (LHS-Ac) in water was very dark, whereas the supernatant was quasi-colorless. Moreover, it is noteworthy that, in the absence of the layered hydroxyacetate salt, the particles cannot be centrifuged without the addition of a cosolvent. This indicates that all the PtMA particles remain trapped in the powder. EDX analysis was carried out in order to quantify the Pt and S incorporated in the composite (Table 1). The ratio of Pt/Ni found in LHS-PtMA-1 is equal to 0.25 and the sodium counter-ion of the mercaptoacetate salt was absent from the composite material. Finally, the S/Pt ratio was estimated to be approximately 1.0, the same ratio as initially introduced. For comparison, the solution of PtMA alone was also centrifuged after addition of ethanol. The S/Pt ratio obtained for this PtMAp powder is only 0.5. This means that only half of the mercaptoacetate ions are grafted onto the platinum particles, the remaining half staying in solution in the case of PtMAp, while both the mercaptoacetate grafted to platinum and the free mercaptoacetate ions interact with the composite material in LHS-PtMA-1.

In LHS-PtMA-2, obtained after treating LHS-PtMA-1 with a solution of PtMA, the S/Pt ratio is unchanged and no sodium was found either. On the other hand, a great increase in the platinum content is observed: it is twice that obtained after one loading (Pt/ Ni = 0.5 in LHS-PtMA-2). These figures prove the possibility of obtaining a powder containing a large amount of platinum nanoparticles.

#### 3.2. Characterization of the chemical interactions between the elements of the composite material

X-ray photoelectron spectroscopy was used to accurately analyze the chemical interactions in the composite materials. First, PtMAp was compared to the free mercaptoacetate salt (see Fig. 2). The PtMAp spectrum presents additional peaks due to Pt (Pt(4f) at ca. 72 eV and Pt(4d) at ca. 320 eV) whereas the sodium signal disappears. The S(2p) signal for the mercaptoacetate, shown in the inset of Fig. 2, displays an asymmetric peak resulting from the doublets  $S(2p_{3/2})$  (at 164.6 eV) and  $S(2p_{1/2})$ . In the case of the

#### Table 1

Atom percentages of platinum, sulfur and nickel in the composite materials.

Sample	Ni	Pt	S
LHS-PtMA-1	67.1	16.3	16.6
LHS-PtMA-2	50.5	25.0	24.5

Intensity (a.u.) (a) 600 400 200 **Binding Energy (eV)** 

SO

S<sub>2s</sub>

-SH

015

0<sub>1s</sub>

Na<sub>KLL</sub>

(b)

Fig. 2. XPS survey scans of (a) sodium mercaptoacetate, and (b) PtMAp nanoparticles. Insets show the S(2p) high-resolution spectra.

PtMAp nanoparticles, the  $S(2p_{3/2})$  signal is shifted down to 163.9 eV, indicating charge transfer and the presence of  $S^{\delta_{-}}$ species [16]. An additional contribution is detected at ca. 169.1 eV, originating from very oxidized sulfur species such as sulfonates. By peak fitting they are estimated to represent 57% of the total sulfur species. They correspond to mercaptoacetate molecules not bound by their mercapto extremity, oxidized after centrifugation in contact with air. This phenomenon of the oxidation of thiol groups on exposure to air is classically observed after a few days [16–18]. The Pt(4f) signal observed for PtMAp particles is also split into two components,  $Pt(4f_{7/2})$  and  $Pt(4f_{5/2})$ , at 72.2 and 76.0 eV, respectively. These figures are significantly higher than those obtained for a Pt(0) compound (70.9 and 74.2 eV). Moreover, the contributions of two Pt species can be evidenced. Their proportion has been estimated by fitting the whole Pt(4f) signal, considering two oxidation states for Pt and, for each species, two peaks ( $Pt(4f_{7/2})$ ) and  $Pt(4f_{5/2})$ ). In order to account for the multiplet splitting, asymmetric peaks were used. On the basis of this analysis the main component can be assigned to neutral Pt (Pt( $4f_{7/2}$ ) peak at 71.8 eV), while the other corresponds to  $Pt^{\delta+}$  species (72.7 eV). In conclusion, the XPS experiments carried out on PtMAp show clearly an interaction between the surface Pt of the nanoparticles and the thiol extremity of mercaptoacetate, with the formation of a  $Pt^{o+}$ - $S^{\delta-}$  bond.

XPS was then carried out on LHS-Ac and LHS-PtMA-2 (Fig. 3a and b, respectively). Clear modifications are observed after addition of the colloidal PtMA solution: the nickel and oxygen signals are attenuated compared to bare LHS, while new peaks appear at *ca*. 72 and 320 eV due to Pt(4f) and Pt(4d), respectively. Although almost indistinguishable on the survey spectrum, a signal originating from sulfur core electrons also appears, at *ca.* 163 eV. The S(2p) high-resolution spectrum (inset of Fig. 3) reveals the presence of two types of sulfur species, as previously observed for PtMAp nanoparticles, with a sulfonate-type contribution at 168.3 eV and a sulfide-type one at 163.4 eV. The proportion of oxidized species is between 45% and 60% depending on the sample (LHSPtMA-1 or 2). The Pt(4f) signal also resembles that of PtMAp samples with a broad peak with binding energy of ca. 72 eV for Pt( $4f_{7/2}$ ). It contains the two components Pt<sup>0</sup> and Pt<sup> $\delta$ +</sup>. These observations confirm that mercaptoacetate ions are still in interaction with the Pt particles. Finally, the nickel signal is unchanged after PtMA loading, with a Ni(2p) spectrum (Ni( $2p_{3/2}$ ) at *ca.* 857.2 eV) characteristic of Ni<sup>2+</sup> species, indicating that the sheets of the LHS are preserved.





**Fig. 3.** XPS survey scans of (a) LHS-Ac, and (b) LHS-PtMA-2. Insets show the S(2p) and Ni(2p) high-resolution spectra.

The system was further characterized by FTIR analysis. The bands were mainly attributed using reference [19]. As previously, the sodium mercaptoacetate and the centrifuged PtMAp particles were first analyzed (Fig. 4a and b, respectively).

The spectrum of mercaptoacetate (Fig. 4a) presents the typical antisymmetric and symmetric stretching vibrations of  $(CO_2^{-})$  of a sodium acetate salt at 1588 and 1400 cm<sup>-1</sup>, respectively. The spectrum of PtMAp (Fig. 4b) is quite different. The first striking observation is the appearance of a band at  $1734 \text{ cm}^{-1}$ , which can be assigned to the C=O stretching vibration of a carboxylic acid. The second difference is the appearance of two intense bands at 1139 and 1052 cm<sup>-1</sup>. These can be assigned to SO<sub>3</sub><sup>-1</sup> antisymmetric and symmetric stretching vibrations of a  $RSO_3^-H_3O^+$  type compound [20]. Consequently, it can be concluded that the mercaptoacetate ions are present in the PtMAp sample but have undergone several changes: (i) some of the thiol extremities have been oxidized to hydrated sulfonic acid after centrifugation in contact with air, in agreement with XPS conclusions and other studies [16-18]; (ii) some acetate extremities have been protonated, explaining the absence of sodium, established by XPS. The protons gained by the acetate groups probably come from the thiol extremities. This coexistence of both the carboxylic acid and the carboxylate form has already been observed when sodium mercaptoacetate was used to coat gold nanoparticles [20].



Fig. 4. FTIR spectra of (a) sodium mercaptoacetate, and (b) PtMAp nanoparticles.



Fig. 5. FTIR spectra of (a) LHS-Ac, (b) LHS-PtMA-1, (c) LHS-PtMA-2, (d) LHS-MA.

The spectra of LHS-Ac, LHS-MA, LHS-PtMA-1 and LHS-PtMA-2 are displayed in Fig. 5. The most striking feature is the presence in all the spectra of the stretching vibrations of acetate groups. The first one,  $v_{as}(COO^{-})$ , is observed at 1610 cm<sup>-1</sup> for LHS-Ac and LHS-MA and 1600 cm<sup>-1</sup> for LHS-PtMA-2. The second,  $v_s(COO^-)$ , is observed at  $1374 \text{ cm}^{-1}$  for LHS-Ac,  $1350 \text{ cm}^{-1}$  for LHS-MA,  $1355 \text{ cm}^{-1}$  for LHS-PtMA-2. In each case, the difference  $\Delta v = v_{as} - v_s$  is between 220 and 260 cm<sup>-1</sup>, suggesting that the acetate ions are coordinated to nickel as unidentate species [21]. In no sample is a band characteristic of C=O stretching vibration near  $1740-1700 \text{ cm}^{-1}$  detected. This means that all the acetate and mercaptoacetate terminal groups are in the ionic form rather than the acid form, -COOH, contrary to the case of the PtMAp powder. The second point is the presence of intense bands at 1125 and 1028 cm<sup>-1</sup> for the three samples LHS-MA, LHS-PtMA-1 and 2. They were already present in PtMAp and assigned to SO<sub>3</sub><sup>-</sup> antisymmetric and symmetric stretching vibrations of a  $RSO_3^-H_3O^+$  type compound. These observations lead to the conclusion that the sulfur-containing extremity of mercaptoacetate is not much modified during the adsorption on LHS, whereas the other extremity, -COOH in the PtMAp sample, is deprotonated during the adsorption process even though the experiment is carried out in water. This point, together with the absence of sodium, suggests that some mercaptoacetate ions interact with the LHS sheets through their carboxylate extremities. This can be related to the chemical analysis previously reported: the amount of mercaptoacetate in LHS-PtMA-1 and 2 (S/Pt = 1) is twice that in PtMAp (S/ Pt = 0.5). This means that 0.5 mercaptoacetate per Pt, and thus 0.125 and 0.25 mercaptoacetate per Ni (=S/Pt × Pt/Ni, see Table 1), respectively, have replaced acetate ions in LHS-PtMA-1 and 2 to assure the neutrality of the LHS sheets.

#### 3.3. Morphological characterization

A TEM image of the platinum particles is presented in Fig. 6. Very small, almost isotropic, monodisperse and non-agglomerated objects with a mean diameter of  $1.7 \pm 0.3$  nm are observed. These features are the result of a very rapid precipitation (high heating rate and quenching just after the appearance of the particles) and of the interaction with acetate ions which limit particle growth and prevent aggregation.

TEM images of LHS-Ac, LHS-MA, LHS-PtMA-1 and LHS-PtMA-2 materials are reported in Fig. 7a–f. The particles of LHS-Ac appear as thin sheets forming aggregates (Fig. 7a). No significant evolution of the morphology is noticed after 20 h in a mercaptoacetate solution (Fig. 7b).



Fig. 6. TEM images of as-synthesized platinum particles.

The composite obtained after one contact with the solution of PtMA presents nearly the same sheet morphology without well defined shape and arrangement (Fig. 7c). However, the LHS particles are less aggregated and they seem very thin, as the contrast between the layers and the carbon grid is very low (Fig. 7d). The Pt particles adsorb preferentially on some sheets, while other sheets remain free from particles, resulting in an inhomogeneous material. Finally, very few particles are detected beside the LHS sheets, confirming the strong interaction with the LHS sheets. After a second contact with the PtMA solution, mainly

non-aggregated thin platelets interacting with densely packed platinum particles are observed all over the grid (Fig. 7e and f). In the two samples, LHS-PtMA-1 and 2, guasi-parallel lines of particles are observed at the edges of the LHS platelets, which are probably bent up (Fig. 7d–f). In order to be sure that these lines cannot be attributed to artefacts and to determine whether the platinum particles are incorporated within the interlamellar space of the LHS, powders were embedded in a resin and TEM was performed after microtomy. The aspects of the particles of LHS-Ac (Fig. 8a) and LHS-PtMA-2 (Fig. 8b and c) are very different. For the composite, alignments of particles are seen all over the grid. The distance between two adjacent particles in one interslab is estimated to be ca. 3.0 nm and that between two lines ca. 4.0 nm. The fact that the lines are parallel and that the distance between two lines is more or less constant argues in favor of an intercalation of the particles.

#### 3.4. Structural characterization

The X-ray powder pattern of the LHS-Ac phase (Fig. 9a) can be indexed in the hexagonal system and is characteristic of a stacking of brucite-like sheets, as previously described by Poul et al. [13] and Taibi et al. [22] The first three peaks correspond to  $(0\ 0\ 1)$ reflections with an interlayer spacing c = 0.96 nm. The fourth peak corresponds to the  $(1\ 0\ 0)$  reflection with the in-plane parameter a = 0.31 nm. The asymmetry of the in-plane reflections is due to the turbostratic character. The structural parameter a is the same as that previously reported by Poul and Taibi, but c is slightly lower (reported interlayer spacing of 1.06 nm). This variation can be explained on the basis of different water contents and/or a change



Fig. 7. TEM images of (a) LHS-Ac, (b) LHS-MA, (c-d) LHS-PtMA-1, (e-f) LHS-PtMA-2.



Fig. 8. TEM images after microtomy of (a) LHS-Ac, and (b) and (c) LHS-PtMA-2.

in their arrangement in the interlayer spacing. For comparison, if the LHS is left for 20 h in a mercaptoacetate solution to produce the LHS-MA phase, the structure is maintained, with the same in-plane parameter (XRD pattern not given). However, the distance between layers shrinks (c = 0.89 nm) owing to hydrogen bonding between the salt and the layers.

After the first contact of LHS-Ac with the PtMA particles, the characteristic peaks of the LHS structure are still visible, even if less intense (Fig. 9b). The structural parameter *a* remains constant as compared to LHS-Ac and *c* is increased to 1.06 nm, the value found for the LHS-Ac phase by Poul et al. [13]. The relative intensities of the peaks are modified: the ratio between the intensities of the (0 0 1) and (1 0 0) peaks (I(0 0 1)/I(1 0 0)) decreases when the LHS is loaded with nanoparticles. This observation is also true for the ratio I(0 0 1)/I(1 1 0). This suggests that the order within the sheets is retained whereas the correlation length between two sheets is not always the same in the whole sample.

Besides the LHS structure peaks, a very broad peak appears on the XRD pattern near  $2\theta = 46^{\circ}$  corresponding to the most intense reflection of platinum, the (1 1 1) peak. The width of the peak can be related to the size of the platinum particles using the Scherrer



**Fig. 9.** XRD patterns of (a) the LHS-Ac, (b) the LHS-PtMA-1, and (c) LHS-PtMA-2. Low angles are presented in the insets.

formula with a shape factor for spheres (K = 0.89). The particle size evaluated in this way is about 1.5 nm, which is in good agreement with the TEM measurements.

Finally, a fast increase in intensity is visible as the angle becomes very small. Consequently, a new diagram was recorded at  $2\theta$  from 2° to 15° with narrower slits in order to detect the peaks which could be present in this interval (see inset of Fig. 9). Besides the (0 0 1) peak of the LHS structure near 10.6°, a broad peak which does not exist in the pristine LHS sample (XRD pattern not given at low angles) appears at *d* = 2.2 nm. It cannot be attributed to the distance between two particles adsorbed on a same LHS sheet, as this distance was estimated by TEM to be *ca.* 3.0 nm.

The decrease in the intensity of the (001) peak of the LHS-Ac structure together with the appearance of a new broad peak at 2.2 nm could be more likely attributed to the co-existence of two phases: the initial one (LHS-Ac) and a new one (poorly organized, as only one peak is observed). The new phase which is formed cannot be a lamellar phase in which the acetate is replaced by mercaptoacetate (and/or sulfonate) anions. Indeed, the (001) peak should appear at 0.89 nm in this case. TEM images show parallel lines of particles spaced out by 4.0 nm. This distance corresponds approximately to the diameter of one particle and the length of two mercaptoacetate ions and two LHS wall thickness. Consequently, the new phase could correspond to the LHS in which one out of two (most of the time) interslabs of LHS is filled with nanoparticles. Such compounds are known as second-stage intercalation compounds, whose formation has been described by Daumas and Hérold [23] and which have been observed in several LDH compounds [24-26]. For these materials containing alternate layers with two different basal spacings,  $d_1$  and  $d_2$ , then the basal reflections expected in XRD are  $(d_1 + d_2)/n$ , with n = 2 usually the most intense. In the present case, this reflection can be expected at a spacing of *ca*. 2 nm. Consequently, the peak at low angles can be due to this phase. The other reflection peaks should be less intense and could contribute to the width of the peaks. However, the structure is clearly not so well organized, and has filling defects and medium-range disorder.

Finally, LHS-PtMA-2 was also characterized. For this sample, the peaks characteristic of the LHS structure continue to decrease in intensity compared to the broad peak due to platinum nanoparticles at 0.23 nm and that at 2.2 nm (Fig. 9c), in agreement with the EDX results. The intensity ratios  $(I(0 \ 0 \ 1))/I(1 \ 0 \ 0)$  and  $I(0 \ 0 \ 1)/I(1 \ 0)$  continue to decrease compared to their values in LHS-

#### Table 2

Curie temperature ( $T_c$ ), coercivity ( $H_c$ ), saturation magnetization per gram of sample ( $M_{sat}$ ) and remanence to saturation ratio ( $M_r/M_{sat}$ ) of LHS salts before and after loading with platinum particles.

Sample	$T_{\rm c}$ (K)	$H_{\rm c}$ (Oe)	$M_{\rm sat}~({ m emu}~{ m g}^{-1})$	$M_{\rm r}/M_{\rm sat}$ (%)
LHS-Ac	14	750	97.8	39
LHS-MA	14	745	96.0	38
LHS-PtMA-1	10	285	50.0	26
LHS-PtMA-2	10	285	39.0	19

PtMA-1 and LHS-Ac. This correlates well with the TEM images, which show that more LHS particles contain PtMA particles.

#### 3.5. Magnetic measurements

The temperature dependence of the mass magnetic susceptibility  $\chi_m$  (per gram of product) and the  $\chi_m T$  product are plotted in Fig. 10. The variation of the mass magnetization (*M*), when the magnetic field (*H*) is cycled at 5 K, is plotted in Fig. 11 for the reference LHS-Ac, LHS-MA and PtMAp compounds and for the two composites, LHS-PtMA-1 and LHS-PtMA-2.

Apart from PtMAp, which exhibits a Pauli-like paramagnetic behavior characterized by a magnetic susceptibility temperatureindependent, all samples exhibit ferromagnetic behavior: (i) at high temperature, the  $\chi_m T$  product increases when the temperature decreases, suggesting the occurrence of short-range ferromagnetic interactions, namely ferromagnetic in-layer nickel hydroxide plane interactions, (ii) at lower temperature  $\chi_m$ increases to reach a kind of plateau when the temperature decreases, a phenomenon which can be related to the occurrence of 3D ferromagnetic correlations and (iii) the variation of M versus H presents an hysteresis loop. The Curie temperature,  $T_c$ , is determined at the maximum (not shown) of the curve of  $\chi_m T$  as a function of T. The values obtained are summarized in Table 2.  $T_c$  is equal to ca. 14 K for LHS-Ac and LHS-MA. and 10 K for LHS-PtMA-1 and 2. This variation is probably due to modifications of the interactions between the layers with the introduction of Pt particles. The maximum value of  $\chi_m T$  as a function of T decreases from  $1.016 \text{ cm}^3 \text{ K g}^{-1}$  of product  $(121 \text{ cm}^3 \text{ K mol}^{-1} \text{ of } \text{Ni}^{2+})$  to  $0.773 \text{ cm}^3 \text{ K}$  (101 cm<sup>3</sup> K mol<sup>-1</sup>) as the basal spacing decreases from 0.96 to 0.89 nm on going from LHS-Ac to LHS-MA. This interesting behavior is related to the influence of the weakening of the demagnetization field when the interlayer distance increases [22]. The maximum value of  $\chi_m T$  falls to 0.428 (79 cm<sup>3</sup> K mol<sup>-1</sup>



**Fig. 10.** Variation of the susceptibility (per gram of product) vs. temperature measured at H = 200 Oe for: (a) LHS-Ac, (b) LHS-PtMA-1, (c) LHS-PtMA-2, (d) PtMAp, (e) LHS-MA. The variations of  $\chi_m T$  as a function of T are presented in the inset.



**Fig. 11.** Hysteresis loops (per gram of product) measured at *T* = 5 K for: (a) LHS-Ac, (b) LHS-PtMA-1, (c) LHS-PtMA-2, (d) PtMAp, (e) LHS-MA.

with respect to  $Ni^{2+}$ ) and 0.412 cm<sup>3</sup> g<sup>-1</sup> K (89 cm<sup>3</sup> K mol<sup>-1</sup>) for LHS-PtMA-1 and 2 respectively. Similarly, the 5 K saturation magnetization  $(M_{sat})$  of the two reference compounds, LHS-Ac and LHS-MA, obtained by extrapolating the curve of *M vs.* 1/*H* to zero, is found to be ca. 97 emu g<sup>-1</sup>, corresponding to 1.9  $\mu_B$  mol<sup>-1</sup> of Ni<sup>2+</sup>. This value is very close to that expected  $(2 \mu_B/Ni)$  for an oxygencoordinated Ni<sup>2+</sup> ion. The values obtained for LHS-PtMA-1 and 2 (Table 2) are significantly lower due to the very weak magnetic contribution of Pt. When expressed per mol of Ni<sup>2+</sup>, M<sub>sat</sub> is equal to 1.6 and 1.5  $\mu_B$  for LHS-PtMA-1 and 2, respectively. The weakening of the magnetization when Pt is intercalated in the interslabs contributes also to a decrease in the coercitive field  $(H_c)$  from LHS-Ac and LHS-MA to LHS-PtMA-1 and 2. These net modifications of the characteristic magnetic values after loading indicate modifications of the interlayer interactions and agree well with the intercalation of platinum nanoparticles within the interlamellar space.

#### 4. Conclusions

In this paper we report the formation of nanocomposites made from platinum nanoparticles and a lamellar nickel hydroxyacetate salt by the mediation of a short organic molecule: a mercaptoacetate salt. The two starting blocks of the nanocomposite were made separately by the polyol process, a simple and rapid method which assures very good control of the particle morphology. The platinum particles are very small, monodisperse objects (1.7 nm in diameter). The acetate ions adsorbed at their surface were exchanged for mercaptoacetate species which are compatible with both the metal particles and the LHS compound. This functionalization of the platinum particles by mercaptoacetate species was followed by XPS and IR spectroscopies. The shift of the surface platinum binding energy in the XPS spectra indicates that strong bonds are formed with the salt. Infrared spectra indicate that the grafted molecules are in the acid rather than the acetate form. This probably results from proton release by the thiol group when it bonds to platinum. This is confirmed by the absence of a Na signal in the XPS spectra. Moreover, an oxidation of some thiol extremities is observed. The contact between a colloidal solution of grafted platinum particles and a layered hydroxyacetate nickel salt leads to the formation of a composite with a high particle content. Structural study and magnetic characterizations show that the structure of the nickel hydroxide layers is retained in the composite materials. Mercaptoacetate ions are in this case in their basic form, as attested by IR spectroscopy. TEM images show the incorporation of the platinum nanoparticles within the layers of some lamellar sheets. XRD and magnetic measurements are in

agreement with this incorporation. The composites obtained can be described as a mixture of two phases: the LHS-Ac starting materials and a LHS containing nanoparticles incorporated with only short-range coherence.

This work opens large perspectives for synthesizing composite materials with tunable multifunctional properties. Indeed, the nature of the particles does not play any role in the intercalation process and they can be replaced by other metals or semiconductors. In the same way, other metal LHS can be used. Consequently, composites with mixed magnetic, catalytic, optical properties can be designed. One key point to consider will be the interaction between the host matrix and the incorporated nanoparticles, and the interest of using a mediating molecule, such as mercaptoacetate ion.

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