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A two-dimensional magnetic hybrid material based on intercalation of a cationic Prussian blue analog in montmorillonite nanoclay

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ABSTRACT

A highly ordered two-dimensional hybrid magnetic nanocomposite has been prepared by synthesizing and intercalating a new cationic aluminum-hydroxy ferric ferrocyanide compound into a cation-adsorbing nanoclay (montmorillonite). Chemical and structural properties were investigated by X-ray diffraction, transmission electron microscopy, thermogravimetric and differential thermal analyses, Fourier transform infrared, X-ray photoemission, and Mössbauer spectroscopies. Elemental analysis was based on proton-induced gamma ray emission and X-ray fluorescence spectroscopy data, N/C elemental ratios, and cation-exchange capacity measurements. Magnetic properties were studied by SQUID magnetometry. The results suggest: (i) that the cationic Prussian blue analog comprises Al-hydroxy cations embedded into a monolayer thick two-dimensional ferric ferrocyanide array; and (ii) that the clay-Prussian blue nanohybrid consists of such arrays stacked between the clay layers. The latter material orders ferromagnetically at ~ 5 K showing a hundred times higher remanence than that of the starting material, soluble Prussian blue (ammonium ferric ferrocyanide).

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1. Introduction

Prussian blue (PB), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, and its analogs have attracted interest in research for almost 300 years since their basic building block, $\text{A}^+\text{B}^{3+}(\text{CN})_6$, serves as a prototype for a large variety of synthetic compounds with remarkable properties. The ions in this block are organized in a face-centered cubic cell, in which alternating A and B atoms occupy the corners of its eight subcubes, while linear cyanide bridges extend along their edges. As the lattice constant is approximately 1 nm, the subcubes are large enough to accommodate neutral molecules or charge compensating cations of size up to about 0.35 nm [1]. Hence, a wide range of PB-based materials can be prepared, including multielemental inorganic coordination compounds [2], hybrid organic-inorganic systems [3,4], and composites with anionic hosts [5].

Due to their diverse applications in electronic devices and sensors, in catalysis and molecular sieving, in photomagnets and high T_c lightweight magnets [6–9], etc., interest in this family of multifunctional molecular assemblies has nowadays revived.

In principle, the physical properties (optical, magnetic, electric) of PB-based materials are strongly dependent on the molecular interaction between their building blocks. This feature enables the rational design of various constructional motifs, thus offering ways not only to mimic conventional solid-state magnets but also to couple magnetism with other properties, such as transduction, sensing, or triggering functions [10]. Yet, the integration of these materials into functional devices requires processing beyond the unit cell constitution, from the nano- through the meso- to the macro-scale into higher-order molecular architectures. Although much work has focused on the relationship between unit-cell structure and magnetic properties, few attempts have been made toward understanding and controlling the growth mechanism of these solids [11]. Templates and organized reaction media have been used for the construction of higher-order assemblies of traditional inorganic solids [12–15]. Through these processes, the control of properties, such as particle size and shape, surface texture,

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and organization, can be integrated directly into the synthesis method. Recently, magnetic thin films consisting of PB and organo-modified clay nanosheets have been prepared using a modified Langmuir–Blodgett method and self-assembly techniques [16–18]. Such films with highly ordered structures have many potential applications in the field of optical devices, microelectronic devices, and sensors [18–22].

Despite the ample literature in the field of Prussian blue and its analogs, no attempt to synthesize inorganic cationic PB-type compounds has been reported so far. Such species are useful building blocks for assembling positively charged nano-multimetallic moieties that open the way for the synthesis at the nano- and meso-scale of hybrid composites thereof, via intercalation into cation-adsorbing hosts, as, e.g., smectites. The present paper gives a comprehensive account of the synthesis and clay intercalation of a cationic ferric ferrocyanide (FFC) compound. The PB compound was prepared by coagulating and repeating an aqueous sol of ammonium ferric ferrocyanide (Monthiers' salt, 1846) on addition of aluminum-hydroxy cations. Intercalation of the PB compound in the interlayer space of a cation-adsorbing clay enabled the synthesis of a highly ordered two-dimensional hybrid magnetic nanocomposite. The structure and properties of the latter were examined via various characterization techniques: X-ray diffraction (XRD), transmission electron microscopy (TEM), thermal analysis techniques (TGA/DTA), Fourier transform infrared (FTIR), X-ray photoemission (XPS), proton-induced gamma ray emission (PIGE), X-ray fluorescence (XRF) spectroscopy, N/C elemental analyses, cation-exchange measurements, Mössbauer spectroscopy, and SQUID measurements.

2. Experimental

2.1. Synthesis

Riedel-de Haën Product-Nr SEC11254 was used as a source for ammonium ferric ferrocyanide (AFFC), $\text{NH}_4\text{Fe}[\text{Fe}(\text{CN})_6]$. This reagent contained 65% w/w of pure AFFC and 35% w/w of anhydrous ammonium chloride. A sol was prepared by adding 13.3 mg of the reagent to 50 ml of distilled-deionized water. Thereafter, the sol was titrated with a 0.01 M AlCl_3 (Aldrich) solution, up to the molar ratio $\text{Al}/\text{X} = 6.5$, where X stands for the $\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]^-$ anion. The titrant was added manually, under continuous stirring, at a rate ranging between 0.5 and 2 mmol/min at the titration start and end, respectively. Throughout the titration the suspension maintained its initial blue color.

The Al-hydroxy ferric ferrocyanide (Al-FFC) compound, formed during titration, was intercalated in a sodium homoionic montmorillonite (Na-STx), prepared from STx-1 clay (Clay Minerals Repository of the University of Missouri, USA) as described elsewhere [23,24]. Clay intercalation was carried out under continuous stirring, by adding 2 ml of the aluminum-titrated AFFC sol ($\text{Al}/\text{X} = 6.5$) to 200 ml of a 0.5% w/w suspension of Na-STx. After 3 h under stirring, the intercalated clay (ST-Al-FFC) was collected from the mixture by centrifugation, washed thoroughly (13 times) with distilled-deionized water, spread on glass plates, and air-dried at room temperature.

2.2. Characterization methods

XRD data of ST-Al-FFC-oriented films, spread over glass plates, were collected on a D8 Advance Bruker diffractometer using Cu $\text{K}\alpha$ (40 kV, 40 mA) radiation and a secondary beam graphite monochromator. The patterns were recorded in the 2-theta (2θ) range from 2° to 80° , in steps of 0.02° with a counting time of 2 s per step.

Transmission electron micrographs were obtained with a JEOL 200CX microscope operating at 200 kV. A few milligrams of the

sample were dispersed in ethanol and one droplet was deposited onto a holey-carbon TEM grid and allowed to dry. The images are typical and representative of the samples under observation.

Thermogravimetric and differential thermal analyses (TGA and DTA, respectively) were performed using a Shimadzu DTG 60 thermal analyzer. Samples of approximately 15 mg were heated in air from 25 to 600 $^\circ\text{C}$, at a rate of 10 $^\circ\text{C}/\text{min}$.

FTIR spectra were recorded between 400 and 4000 cm^{-1} on a Perkin Elmer Spectrum GX infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Each spectrum was the average of 200 scans collected with a 2 cm^{-1} resolution by means of a SpectraTech high-temperature cell attached on a diffuse reflectance accessory (DRIFT). Samples mixed with KBr were heated at different temperatures up to 320 $^\circ\text{C}$.

XPS measurements were carried out using an SSX-100 (Surface Science Instruments) spectrometer with a base pressure of 1×10^{-9} Torr, using a monochromatic Al $\text{K}\alpha$ X-ray source ($h\nu = 1486.6$ eV). The photoelectron take-off angle was 37° and an electron flood gun was used to compensate for sample charging. Evaporated gold films supported on glass served as substrates. All binding energies were referenced to the nitrogen signal at 398 eV (cyanide groups). Spectral analysis included a Shirley–Tougaard background subtraction and peak deconvolution employing Gaussian line shapes.

PIGE and XRF spectroscopy [25] were used to determine the composition—with respect to silicon, aluminum, magnesium, iron, titanium, sodium, and calcium—of Na-STx and of two ST-Al-FFC samples obtained from independent preparations. The carbon and nitrogen content of ST-Al-FFC was determined through duplicate measurements using a CARLO-ERBA CHNS-O EA-1108 elemental analyzer. The chemical formula of the PB compound has been deduced on the basis of the elemental analyses and cation-exchange capacity (CEC) data taken for ST-Al-FFC. In particular, cesium-exchange experiments were carried out by equilibrating batches of this material with ^{137}Cs -labeled, CsCl solutions (10^{-4} – 3×10^{-3} M). Cesium adsorption was deduced by measuring the radioactivity of ^{137}Cs in the liquid, recovered after centrifugation.

Mössbauer measurements were carried out with a conventional, constant acceleration spectrometer equipped with a $^{57}\text{Co}(\text{Rh})$ source. Spectra were obtained at room temperature and fitted with a least-squares minimization procedure assuming Lorentzian line shapes.

The magnetic properties were measured using a Quantum Design Magnetic Property Measurement System (MPMS), known as a superconducting quantum interference device (SQUID) magnetometer. Powder samples were placed inside a gelatin capsule appropriately mounted in a transparent plastic straw (typical diamagnetic contribution: 10^{-5} emu in 1 T). The DC magnetization technique was used, which measures the magnetic moment of the sample. Samples were measured in an external magnetic field after cooling either without applying an external magnetic field (zero-field cooled, ZFC) or in an external magnetic field (field-cooled, FC). These measurements were performed using a magnetic field of 100 Gauss. Typically, the temperature increment used was 0.2 K up to 9 K, 0.5 K/step from 9 to 25 K, and 2 K/step for higher temperatures. Hysteresis loops at various temperatures (from 2 to 5 K) were also investigated.

3. Results and discussion

3.1. Synthesis and clay intercalation of the cationic PB compound

The titration curve of the AFFC sol is shown in Fig. 1, wherein the sequence of different flocculation patterns is highlighted and X stands for the $\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]^-$ anion. During the first titration

Fig. 1. Potentiometric titration of the AFFC sol and of deionized water (blank) with an aqueous AlCl_3 titrant.

steps and up to an Al/X molar ratio less than ~ 0.4 , no turbidity is discernible across the blue-colored sol. At subsequent steps, flocculation starts appearing due to neutralization of X anions by aluminum-hydroxy cations, which are the predominant Al species at $\text{pH} \sim 4$. As the titration proceeds, turbidity increases and at a ratio of $\text{Al}/\text{X} \sim 1.1$ extended flocculation occurs. Peptization of the flocks sets on as Al/X exceeds ~ 1.5 , while for $\text{Al}/\text{X} > \sim 6.5$ a completely clear blue sol is obtained again. The overall picture hints at the formation of a cationic complex compound between X and Al-hydroxy cationic species through the gradual neutralization and charge reversal of the negative colloidal particles initially present in the AFFC sol. Direct evidence that the Al-hydroxy-titrated sol ($\text{Al}/$

$\text{X} > 6.5$) contained positively charged FFC species was provided by a qualitative electrophoretic test. Application of a DC voltage of a few volts caused the blue sol to move toward the cathode leaving a clear and colorless liquid to build up near the anode.

On contacting the Al-hydroxy-titrated AFFC sol ($\text{Al}/\text{X} = 6.5$) with the cationic Na-STx clay suspension, quick clay flocculation was observed, leaving a clear and colorless supernatant. This fact demonstrated that the positive Al-hydroxy-FFC species contained in the intercalant replaced the interlayer Na^+ cations according to the following reaction scheme:

The horizontal bars symbolise the ~ 0.96 -nm-thick clay layers of montmorillonite. The successful exchange of the interlayer cations with the positively charged FFC compound was further indicated by the absence of sodium peak in the XPS spectrum of ST-Al-FFC (not shown here) and by PIGE elemental analysis.

3.2. X-ray diffraction patterns

Fig. 2 shows XRD diagrams for ST-Al-FFC films spread over glass plates, initially dried at room temperature (20°C) and then heated in air to successively higher temperatures up to 320°C . The prominent peak moving from $2\theta \sim 6.1^\circ$ to $\sim 8.4^\circ$ as the temperature increases is associated with the d_{001} basal reflection of the intercalated clay. From the line width of this peak one estimates via the Scherrer equation that the examined ST-Al-FFC clay composite consists of aggregates of ~ 7 clay layers each. The 20°C pattern gives an interlayer spacing $d_{001} \sim 1.4$ nm, i.e., an interlayer gallery height of about $1.40 - 0.96 = 0.44$ nm. However, at 320°C the d_{001} spacing drops to ~ 1.06 nm. As this variation of the interlayer gallery height furnishes information about the thermal stability of the intercalated compound, it has been followed more closely by monitoring also the d_{001} reflections up to 320°C . Note that the reflection at

Fig. 2. X-ray diffraction patterns of ST-Al-FFC-oriented films taken at several temperatures from 20°C up to 320°C . The intensities of the peaks at $2\theta < 12^\circ$ are drawn reduced either by a factor of 10 (20°C), 5 (60 – 240°C), or 3 (280 and 320°C); inset: temperature variation of the d_{001} interlayer spacing.

$\sim 21.8^\circ$ is due to cristobalite, i.e., a SiO_2 clay impurity stable up to at least 500°C . More specifically, going from room temperature to $\sim 115^\circ\text{C}$, the interlayer gallery height decreases steadily from 0.44 to ~ 0.27 nm (Fig. 2, inset). A further decrease is observed at temperatures above 240°C and the gallery height finally reduces to ~ 0.1 nm at about 320°C , indicating that at these temperatures the intercalated structure has essentially broken down, leaving in the interlayer residues like, e.g., $\text{Fe}(\text{CN})_2$ [26–28]. This trend is in qualitative agreement with XRD results by Miyata and Hirose [29] showing that the interlayer gallery of a $\text{Mg-Al-}[\text{Fe}(\text{CN})_6]^{4-}$ hydrotalcite has drastically decreased at 250°C . In line with the XRD findings, the DTA-TGA data discussed hereafter show that at $\sim 115^\circ\text{C}$ dehydration of ST-Al-FFC has been completed, while at $\sim 320^\circ\text{C}$ the intercalated ferric ferrocyanide moieties are decomposed.

Informative about the nature of these moieties are the peaks at $2\theta \sim 17.5^\circ$, 24.9° , and 35.4° which correspond to the (2, 0, 0), (2, 2, 0), and (4, 0, 0) reflections of the ~ 1 nm face-centered cubic unit cell of PB [30]. Such PB reflection can be the result of small amounts of nonintercalated PB on the outer surface of the clay. This possibility has been reduced by washing the sample thoroughly with water (13 times) in order to remove the possible aggregates on the outer surface. If the diffraction intensity originates from intercalated PB, this means that these reflections arise from clay nanoplatelets perpendicular to the scattering plane. It requires a coherent structure of the PB blocks across the clay platelets, and a coherence within the layers of ~ 5 nm. This estimated network linear dimension of ~ 5 nm complies also with the FTIR results and the ST-Al-FFC chemical analysis discussed further below. The association of the characteristic PB reflections shown in Fig. 2 to intercalated Al-hydroxy FFC moieties is further strengthened by the fact that the reflections are still present above the decomposition temperature of PB ($\sim 200^\circ\text{C}$) and that similar reflections appear also in the XRD patterns of a clay–organic hybrid PB film made of 25 montmorillonite layers built layer-by-layer by the Langmuir–Blodgett method [16].

Consequently, the XRD data and the TEM results presented below hint at the formation of a monolayer of $\text{Fe}^{3+}[\text{Fe}^{2+}(\text{CN})_6]$ building blocks arranged along the (*a*, *b*) plane of the ST-Al-FFC clay interlayer. In such a monolayer arrangement, four CN ligands expand along this plane and establish links among the iron atoms which are about 0.5 nm apart and form the nodes of a square array. The remaining two CN ligands are directed toward the upper and lower clay nanoplatelets without, however, linking to iron atoms. Moreover, these terminal CN ligands are not perpendicular to the clay platelets because the distance between the nitrogen and the iron atoms in the FFC octahedra is about 0.3 nm, while the gallery height was less than ~ 0.44 nm at all temperatures. Therefore, cavities are formed between the iron nodes of the aforementioned square array and the clay layers. Each of these cavities extends to ~ 0.5 nm along the *a* and *b* axes, while its height varies from ~ 0.44 to ~ 0.27 nm in the temperature range 20 – 210°C . Hence, in this temperature range the cavities can accommodate molecules as large as water, hydroxyl, or ammonium. As presented further below, the elemental composition of the interlayer moieties in ST-Al-FFC suggests by itself the existence of such roomy cavities.

3.3. HRTEM images

Strong evidence for the successful clay intercalation of an Al-FFC monolayer was provided via high resolution transmission electron microscopy (HRTEM). Fig. 3 shows the HRTEM image of the ST-Al-FFC nanohybrid, in which the linear array of dark spots reveals the Al-FFC monolayer intercalated between the clay nanoplatelets. The clay interlayer separation estimated from this image is in agreement with the XRD findings.

Fig. 3. HRTEM image of ST-Al-FFC.

Fig. 4. DTA and TGA curves of Na-STx (bottom), AFFC (middle), and ST-Al-FFC (top).

3.4. Thermal analysis

Fig. 4 shows the DTA-TGA traces for ST-Al-FFC in comparison with those for the starting materials AFFC and Na-STx. The pronounced endothermic peaks around 80°C observed for Na-STx and ST-Al-FFC reveal clay dehydration, while the exothermic features around 300°C are due to the $[\text{Fe}^{2+}(\text{CN})_6]$ -anion thermal decomposition in AFFC and ST-Al-FFC. The endothermic peak at $\sim 275^\circ\text{C}$ displayed in the AFFC DTA curve is due to NH_4Cl , which is a significant admixture in the reagent used as AFFC source. Of particular significance is the dissimilarity of the AFFC and ST-Al-FFC traces in the 300 – 500°C region, since it indicates that the thermal decomposition of the ferric ferrocyanide structure in these two materials goes through different rearrangement and recrystallization modes. More specifically, the processes known to unfold during the thermal decomposition of ferric ferrocyanides [26–28] suggest that the aforementioned differences are probably caused by the presence of Al-hydroxy cations in ST-Al-FFC (see below). In a simplified way, these processes can be depicted as follows: the onset of CN liberation around 300°C leads to reduction of trivalent iron and subsequent disruption of the $\text{Fe}^{2+}\text{--CN--Fe}^{3+}$ network. If during thermal decomposition oxidation is possible, some divalent iron may become trivalent; evidently such an oxidative process imposes additional constraints in the development of the various intermediate phases. Moreover, for maintaining electro-neutrality during these changes, the extent of reduction is continuously controlled by the extent of oxidation. Hence, before terminating in the formation of metal oxides, the thermal decom-

position of the material in air passes through a series of intermediate mixed-valence structures having a varying number of broken CN linkages, as well as different amounts of divalent and trivalent iron distributed rather at random between the C and N holes. Within this simplified picture, Al-hydroxy cations present in ST-Al-FFC cannot only balance the positive charge deficit created by the reduction of trivalent iron due to CN losses but may also reestablish at least some of the missing Fe-to-Fe links in the disrupted CN skeleton. As a result, the thermal decomposition of ST-Al-FFC may proceed without the need for major rearrangements, in contrast to the AFFC case. Therefore, the data in Fig. 4 provide clear evidence that in ST-Al-FFC, aluminum-hydroxy cations and FFC anions have formed a molecular complex; i.e., ST-Al-FFC does not consist of a mechanical mixture of FFC anions and Al-hydroxy cations.

3.5. FTIR spectroscopy

In order to gain a better insight into the chemical structure of the Al-hydroxy-FFC compound, FTIR spectra were taken for Na-STx, AFFC, and ST-Al-FFC heated to several temperatures up to 320 °C. For simplifying the presentation and discussion of the FTIR results, Fig. 5 shows only the 1500–2300 cm^{-1} region of the spectra taken for AFFC and ST-Al-FFC heated to 150 and 320 °C. The regions below 1200 cm^{-1} and above 2800 cm^{-1} , containing bands of the montmorillonite lattice and the associated water vibrations [3,31] are omitted for clarity. In Fig. 5, one observes that the 150 °C spectra of both materials exhibit the strong $\text{C}\equiv\text{N}$ stretching band at $\sim 2085 \text{ cm}^{-1}$, which is characteristic of the $\text{Fe}^{2+}\text{-CN-Fe}^{3+}$ group [27,32,33]. In the 320 °C spectrum of AFFC, the $\text{C}\equiv\text{N}$ peak has split into a doublet with wavenumbers ~ 2027 and 2072 cm^{-1} , indicating the presence of $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ anions [33] formed on decomposition of the FFC structure. The 320 °C spectrum of ST-Al-FFC does not, however, show such a doublet, a fact that hints at a superior thermal stability of the FFC structure

in this material. This feature implies that the aluminum-hydroxy cations in ST-Al-FFC probably provide additional linkages across the CN network. Around 1860 cm^{-1} , one notices another difference between the AFFC and the ST-Al-FFC spectra, namely that this rather broad peak appears in both spectra of the latter material only and is possibly due either to a CO or to a NO vibration of a NCO moiety [33,34]. A second indication for such a moiety may emerge from the $1550\text{--}1750 \text{ cm}^{-1}$ band shown in Fig. 5. More specifically, AFFC spectra vary rather randomly in this region, while this band is present in ST-Al-FFC spectra at all measured temperatures up to 320 °C (see inset (a)). Furthermore, it was possible to consistently fit all these spectra with Lorentzian peaks centered at ~ 1585 , ~ 1630 , and $\sim 1660 \text{ cm}^{-1}$ (see inset (b) for an example of such a fit). The peak at $\sim 1630 \text{ cm}^{-1}$ is characteristic for the bending $\delta(\text{H-O-H})$ vibration of zeolitic water [3,31,33], i.e., of water molecules adsorbed by the silica network, and therefore appears also in the Na-STx spectra (not shown here). As expected, the intensity of this peak diminishes with increasing temperature in the spectra of Na-STx and ST-Al-FFC. The peaks centered around 1585 and 1660 cm^{-1} could be assigned to a C=N stretching vibration [35–40], providing evidence for an Al-O-N=C bridge in the Al-OH-FFC compound within ST-Al-FFC.

The aforementioned assignments are strengthened by theoretical calculations, carried out by means of the density functional theory-based DMol³ program [41,42]. The considered unit cell for the Al-hydroxy-FFC compound was based on a cubic lattice belonging to the P1 symmetry group, with lattice lengths a , b , and c equal to 10 Å and angles α , β , and γ equal to 90°. In this lattice, iron atoms occupied the edges, cyanide groups were placed along the cube sides, while interstitial cubic sites accommodated the aluminum-hydroxyl species, according to the experimental evidence. Subsequently, this cell was optimized by utilizing the Becke exchange plus Lee–Yang–Parr correlation functional, namely BLYP [43], in the spin-restricted approach. The double numerical plus d -polarization function on all nonhydrogen atoms, namely DND, basis set

Fig. 5. Fourier transform infrared spectra of AFFC and ST-Al-FFC samples at 150 and 320 °C. Insets: (a) Spectra of ST-Al-FFC measured at different temperatures up to 320 °C, and (b) representative example of deconvolution of the $1550\text{--}1750 \text{ cm}^{-1}$ band for ST-Al-FFC (150 °C spectrum).

was used and the calculation was performed under fine DMol³ convergence criteria. The optimized geometry was further investigated by means of frequency analysis at the same BLYP/DND level of theory. These calculations revealed three, characteristic for the unit cell, vibrations: (i) one at 1591 cm⁻¹ belonging mainly to the C≡N site of a bidentate C≡N–O–Al–O–N≡C bridge; (ii) one at 1682 cm⁻¹ belonging to the monodentate Al–O–N≡C; and (iii) another one at 1862 cm⁻¹ belonging to a CO vibration of a NCO moiety. The resulting FFC structure with embedded Al–OH molecules is depicted in Fig. 6.

In the light of theoretical predictions, peak deconvolution of the temperature-dependent FTIR spectra suggests that: (i) the number of the bidentate bridges (~1591 cm⁻¹) is smaller than the number of the monodentate ones (~1682 cm⁻¹); (ii) their areas sum up to ~20% with respect to the area of the main C≡N vibration; and (iii) both these bridge types persist up to higher temperatures compared with the C≡N groups. Summarizing the FTIR results, one may infer that the thermal resilience shown by the 1585, ~1660, and 1860 cm⁻¹ vibrations constitutes a strong indication that the CN network in ST-Al-FFC is reinforced by Al–O–N≡C bridges.

3.6. X-ray photoemission spectroscopy

Additional support for the creation of Al–O–CN bridges comes from the N 1s core level photoemission spectrum of ST-Al-FFC, shown in Fig. 7, which contains three components at 398.0, 399.9, and 402.9 eV, respectively. The peak at 398.0 eV binding energy is assigned to the nitrogen of the cyanide ligands, while the peak at 402.9 eV arises from the ammonium groups (NH₄⁺) originating from the starting AFFC [44–48]. The peak at 399.9 eV binding energy is shifted by ~1.9 eV relative to the cyanide nitrogen peak and indicates that a new chemical environment has been created around this nitrogen by the oxygen of the aluminum-hydroxy species attached to the FFC structure. Therefore, the 399.9 eV peak is probably due to –CNO groups. Compared to the 398.0 eV peak area, the percentage of the 399.9 eV peak area is 18%, i.e., about one-fifth of the CN ligands form –CNO bridges between the FFC skeleton and the Al-hydroxy moieties attached to it. This percentage agrees well with the percentage of Al–O–NC bridges with respect to the CN ligands estimated from the FTIR results. Moreover, this percentage complies well also with the constitution of the cationic complex as derived from the elemental analysis presented below.

In the Fe 2p core level photoemission spectra (Fig. 8) of AFFC and ST-Al-FFC, two principal peaks are observed at 708.6 and 712.8 eV binding energy, assigned to Fe²⁺(CN)₆ and Fe³⁺(NC)₆, respectively [49,50]. In the AFFC spectrum, the area ratio of these

Fig. 7. Nitrogen 1s core level photoelectron emission spectrum of ST-Al-FFC. The background was modeled by the Shirley function.

two peaks is 1:1, as expected. Moreover, the peak at 712.8 eV is asymmetric due to the multiplet splitting effect [46]. Comparing now the ST-Al-FFC spectrum with that of AFFC, one pinpoints two differences. The first is a broadening of the aforementioned principal peaks due to contributions from the Fe 2p signal of the clay (see Na-STx spectrum in Fig. 8). The second difference concerns the increase of the Fe²⁺:Fe³⁺ area ratio from 1:1 to about 1:1.3, a value in close agreement with that deduced from the Mössbauer results presented below (see Table 2). This increase can be understood from the titration curves shown in Fig. 1. More specifically, the fact that the AFFC titration curve lies systematically lower than the curve of an identical titration of deionized water (see blank solution, Fig. 1) reveals that the pH during the for-

Fig. 8. X-ray photoemission Fe 2p spectra of AFFC, ST-Al-FFC, and Na-STx. In the two former spectra, Tougaard background curves are also drawn, while the thick arrows indicate the positions of Fe²⁺ and Fe³⁺ contributions due to the FFC moieties.

Fig. 6. Schematic presentation of a FFC structure with embedded Al–OH species. The ions shown are not to scale with respect to their actual atomic sizes.

Table 1Chemical analysis (wt.% oxides) based on PIGE and XRF.^a

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	CaO	Na ₂ O	LOI ^b
Na-STx	68	14.7	1.05	3.0	0.24	0.17	2.49	10.5
ST-Al-FFC	58.3	14.31	6.12	2.62	0.22	0.22	0.19	18.0

^a All values are quoted so that their most probable error is comparable to their last significant digit.^b Loss on ignition in wt.% on calcining the samples at 800 °C.

mer titration—especially during its first steps—is controlled by a small amount of Fe³⁺ ions which are more acidic than Al³⁺ ions. These iron ions get into the aqueous solution by dissolution of Fe²⁺ and Fe³⁺ ions located in the centers of broken CN octahedra at the surface of FFC sol particles. As, however, Fe²⁺ is readily oxidized in the acidic aqueous solution, Fe³⁺ ions become the predominant species and therefore determine the solution pH. Due to a concomitant process, some of the Fe²⁺ ions left within the broken CN octahedra may also get oxidized. This will thus lead to an increase of the Fe²⁺:Fe³⁺ area ratio.

It is further noted that in Fig. 8 the background curves shown were calculated via Tougaard analysis [51,52], which takes into account the inelastic mean free path λ of the photoelectrons. This quantity corresponds to the average distance travelled by the photoelectrons between successive inelastic collisions while moving from the photoemitting atom to the surface. The resulting λ is 2 nm for ST-Al-FFC and 2.25 nm for AFFC. The lower λ value for ST-Al-FFC gives an additional indication that the Al-hydroxy-FFC cations are situated in the interlayer space, since in such a composite photoelectrons must pass through the clay nanoplatelets before reaching the surface.

3.7. Elemental composition

Analysis of the PIGE and XRF data for Na-STx and ST-Al-FFC yielded the oxides wt.% shown in Table 1. Under the reasonable assumptions that only silicon fills up the tetrahedral clay sites [31] and that FFC anions maintain their structure, one obtains the following clay unit cell formulae [53]:

- (a) For Na-STx: [Si₈]{Al_{3.00} Fe_{0.14} Mg_{0.78} Ti_{0.03}}O₂₀(OH)₄ (Ca_{0.03} Na_{0.84}) + 3.8SiO₂ + 4.0H₂O, where square brackets denote tetrahedral sites, curly brackets octahedral sites, and inequality brackets exchangeable cations in the interlayer space.
- (b) For ST-Al-FFC: [Si₈]{Al_{3.00} Fe_{0.14} Mg_{0.78} Ti_{0.03}}O₂₀(OH)₄ (Ca_{0.05} Na_{0.08}) [Al_{0.34} (OH)_{0.34} X_{0.39} (NH₄⁺)_{0.42}]^{+0.72} + 3.6SiO₂ + 5.1H₂O. The vertical double lines denote the intercalated Al-hydroxy-FFC compound, while X stands for the {Fe³⁺[Fe²⁺(CN)₆]} anion. In the derivation of the above formula, ammonium ions were also considered, since the experimentally determined N/C

molar ratio in ST-Al-FFC was found equal to 1.18, i.e., larger than the theoretical value of 1.00 for hexacyanometallates. To verify whether the ammonium ions do actually take part in the constitution of the PB compound, cesium-exchange experiments were carried out on ST-Al-FFC. The adsorption isotherm followed a Langmuir-type equation from which the CEC of ST-Al-FFC was determined to be 0.40 meq/g. However, according to the above formula (b), the expected CEC due to the interlayer Ca and Na cations is equal to ~0.17 meq/g-clay. This discrepancy may be resolved by assuming that out of the 0.42 mol of NH₄⁺ given in formula (b) about 0.23 mol is in the clay interlayer space as exchangeable cations. In such a case, the exchangeable cations shown in formula (b) would be: (Ca_{0.05} Na_{0.08} NH₄⁺)_{0.23}. Nevertheless, the fact that the CEC determined for ST-Al-FFC is undoubtedly less than 0.87 meq/g-clay, which is the value resulting from the Na-STx unit cell formula (a), provides a clear testimony that the Al-hydroxy-FFC compound is actually intercalated as an entire chemical entity and not as a sum of separated charged species that simply balance the difference between 0.87 and 0.40 meq/g-clay.

In view of the above, one deduces from formula (b) the following composition for the intercalated Al-FFC compound: [Al_{0.34} (OH)_{0.34} X_{0.39} (NH₄⁺)_{0.19}]^{+0.50}. The lateral extent of the PB compound in the interlayer can be estimated by taking into account: (i) that the surface of the clay unit cell is $\sigma \sim 0.5$ nm², with a and b parameters amounting to approximately 0.5 and 1 nm, respectively [54] and (ii) that the charge deficiency of the clay unit cell is $\varphi \sim 0.9$ electrons. Therefore, a moiety carrying a positive charge $q \sim 0.5$ occupies an area $\alpha \sim 0.28$ nm² ($=\sigma \times q/\varphi$) once projected on the clay nanolayer. Moreover, for expressing the stoichiometry of the intercalated PB compound in integers, 25 or more clay unit cells should be envisaged; i.e., each cationic moiety occupies at least an interlayer area of about 7 ($=25\alpha$) nm².

3.8. Mössbauer spectroscopy

Room temperature Mössbauer spectra obtained for AFFC and ST-Al-FFC (Fig. 9 and Table 2) provide additional evidence for the Al-hydroxy-FFC compound. More specifically, analysis by a singlet for Fe²⁺ and a doublet for Fe³⁺ showed that, going from AFFC to ST-Al-FFC, the Fe³⁺ quadrupole splitting (QS) increased from 0.22 to 0.49 mm/s, while the isomer shift (δ) decreased from 0.41 to 0.37 mm/s. These changes are ascribed to a higher anisotropy of the Fe³⁺ environment [32], and to a lower 3d electron density in the Fe³⁺ core. Hence, the ST-Al-FFC Mössbauer data suggest that additional ions, as, e.g., aluminum-hydroxy, distort the original Fe³⁺ octahedral environment created by its six NC ligands. This idea is further supported by room temperature Mössbauer spectra of AFFC and ST-Al-FFC samples heated in air from 50 to 350 °C for 1 h (not shown here). Analysis of these data reveals [55,56] that the end phases are: (i) in AFFC, pure haematite undergoing the Morin transition; and (ii) in ST-Al-FFC about 50% pure haematite with the same hyperfine parameters as in AFFC and 50% aluminous haematite. Evidently, these results corroborate the aforementioned suggestion that in ST-Al-FFC, aluminum ions are located near trivalent iron ions.

3.9. Magnetic measurements

Considering the magnetic results shown in Fig. 10, it is first noted that the low T_c ferromagnetism of PB is due to the high spin Fe³⁺ ions only, since the divalent iron ions have a low spin configuration. Hence, as the Fe³⁺ ions are too far apart (~1 nm), their magnetic interaction is made possible via superexchange paths

Table 2

Mössbauer parameters resulting from least-square fits of the RT spectra of AFFC and ST-Al-FFC.

Sample	$\Gamma/2^a$	δ^b	QS ^c	Area (%)
AFFC	0.15	−0.13	0.00	49
	0.23	0.41	0.22	51
ST-Al-FFC	0.18	−0.13	0.00	42
	0.26	0.37	0.49	55
	0.50	0.35	0.72	3 ^d

^a Half line width, $\Gamma/2$ (in mm/s).^b Isomer shift, δ (mm/s), relative to α -Fe at RT.^c Quadrupole splitting, QS (mm/s), denotes the splitting of the doublet.^d Parameters for the structural iron of the STx-1 clay lattice. The most probable errors for the hyperfine parameters are ± 0.01 mm/s and for the area $\pm 3\%$.

Fig. 9. Room temperature ^{57}Fe -Mössbauer spectra of AFFC and ST-Al-FFC.

over the $-\text{NC}-\text{Fe}^{2+}-\text{CN}$ bridges due to minute electron delocalization in the low-spin Fe^{2+} ions [7,57,58]. Fig. 10 shows field-cooled magnetization (M) versus temperature (T) at 100 Oe for AFFC and ST-Al-FFC. The steep increase in M below ~ 5 K reveals that both materials order ferromagnetically with Curie temperatures of 5.2 K, as deduced where the order parameter extrapolates to zero. These findings are typical for soluble PB systems, as, e.g., AFCF [59]. From the curves of Fig. 10 it is clear that both samples show the

same type of fluctuations near T_c and thus the dimensionality in these materials is similar. This behavior could be due to small amount of unreacted FFC moieties attached on the outer surfaces of the clay platelets which dominate the signal. However, the same magnetic behavior could also arise from the monolayer thick Al-hydroxy-FFC networks intercalated between the clay layers which are rather extended. This has already been inferred from the chemical composition of ST-Al-FFC and is further strengthened by the presence of magnetic hysteresis in this material too (Fig. 10, inset), since this hysteresis rules out superparamagnetic phenomena which turn up when a network has a small number of magnetic nodes [60]. It is finally noted that the higher remanence of ST-Al-FFC relative to that of AFFC (see Fig. 10, insets) hints at an increased spin anisotropy in the former material. This finding is not only concomitant to the low-dimensional character of the FFC moieties intercalated or attached on the outer surfaces of the clay mineral, but it may also hint at a considerable extra Fe^{3+} spin anisotropy caused by the $\text{Al}-\text{O}-\text{N}=\text{C}$ and $\text{C}=\text{N}-\text{O}-\text{Al}-\text{O}-\text{N}=\text{C}$ bridges in ST-Al-FFC.

4. Conclusions

In conclusion, the present study describes the synthesis of a hybrid consisting of nanometer-size FFC monolayers incorporating aluminum-hydroxy cations, and of micrometer-long clay nanoplatelets. The characterization techniques employed allowed estimation of the constitution and structural motif of the intercalated cationic nano-moieties. These appear to consist of aluminum-hydroxy-modified Prussian blue-type monolayers extending over a few nanometers square. Thus, the synthetic route presented here opens the way to build hybrid multimetallic nanocomposites comprising hexacyanometallates and cations of different metals. In view of a variety of applications, this work provides therefore the possibility to tune the physicochemical properties of such cationic moieties, on one hand, by varying the constituting metals, and of their clay derivatives, on the other hand, through the way of assembling them.

Fig. 10. Magnetic susceptibility (χ) vs. temperature curves at 100 Oe field for AFFC and ST-Al-FFC. Insets: hysteresis curves at 2 K.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.04.068. The data contain Cartesian coordinates of the Al-hydroxy-FFC structure used in the simulations.

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