

Magnetic Langmuir–Blodgett Films with Metal–Oxalato Complexes

M. Aiai, J. Ramos, C. Mingotaud, J. Amiell, and P. Delhaes*

Centre de Recherche Paul Pascal, CNRS, Avenue A. Schweitzer, F-33600 Pessac, France

A. Jaiswal, R. A. Singh, B. Singh, and B. P. Singh

Department of Chemistry, Faculty of Science, Banaras Hindu University,
221005 Varanasi, India

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Langmuir–Blodgett (LB) films containing various oxalato complexes were prepared using the so-called semiamphiphilic approach where inorganic ions are adsorbed along a charged monolayer. In a first series of experiments, lamellar materials based on monometallic oxalato complexes (with Fe^{III} or Cr^{III}) have been characterized by X-ray diffraction, XPS, FTIR, ESR, and SQUID measurements. The metal complexes are organized either in monolayers or in bilayers within the LB films, depending on the charge density of the organic layer. Within each inorganic layer, the complexes present a particular orientation or distortion. Finally, the magnetic behavior of such LB films is simply described by the Curie law. In a second series of experiments, synthesized heterobimetallic complexes based on a M₁^{III}–M₂^{II}–M₁^{III} trimer have been organized thanks to the LB technique. Magnetization measurements made on these multilayers show a deviation from the Curie law and from that observed in the powder. They emphasize the interest to control perfectly the molecular organization in order to build up specific extended magnetic systems.

Introduction

In the field of research concerning magnetic and electronic organized soft media, a special interest is devoted to organized thin films. To build up molecular layered structures, one of the most powerful tools is the Langmuir–Blodgett technique:¹ the supramolecular architecture associated with such materials could lead to new induced electronic or magnetic properties. Magnetic LB films are currently poorly developed even if specific behaviors of magnetic systems in reduced physical dimensionality can be highly interesting. Indeed, it is well-known that two-dimensional systems are peculiar for the existence of a magnetic long-range order which depends on both the lattice and the spin dimensionalities.² In the lamellar structures built by the LB technique, magnetic interactions can take place between hydrophobic planes or within each layer. They can be modified by careful changes of various parameters such as interlayer spacing, number of nearest neighbors, distance, and position ordering. For example, ferro- and antiferromagnetic interactions mediated by the interlayer organic spacers have been shown recently in lamellar organic/inorganic compounds.³

Concerning the experimental approaches, the few works devoted to magnetic LB films are based upon an ionic association between a metallic (and magnetic)

cation and a long-chain fatty acid or similar molecule. A pioneering work was published by Pomerantz et al.,⁴ who have shown that manganese or iron stearate can form magnetic LB films. These authors have demonstrated that the ESR resonance line presents an anisotropic behavior which is characteristic of 2d dipolar interactions. Using a similar strategy but more recently, Talham and co-workers⁵ have described the realization of manganese octadecylphosphonate LB films with an in-plane structural organization as observed in the solid state. The spin susceptibility temperature dependence of the Mn²⁺ ions (evaluated by the intensity of the ESR signal) follows the expression for a quadratic layer Heisenberg AF.⁶

In the present study, we propose an alternative strategy based on a more sophisticated molecular engineering where magnetic complexes, usually polyanions, are associated with amphiphilic cations. Instead of inducing a direct exchange interaction between transition metals, we plan to use a superexchange mechanism through organic ligands to modulate the magnetic properties of the built-up molecular assemblies. The semiamphiphilic method, which was successfully used in the case of polyoxometalates,⁷ appears to be the easiest way to reach such a goal. Several chemical possibilities are then offered, which must satisfy the two basic requirements at the gas–water

* To whom correspondence should be addressed.

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interface: equilibrium of the electrical charges for this semiamphiphilic association and adjustment of the respective molecular areas. Concerning the amphiphilic cations, insoluble layers can be built from ammonium, sulfonium, or even phosphonium salts. For the magnetic part, the choice is guided by the type of ligands involved. Recent advances in molecular magnetism have shown that magnetic interactions are indeed propagated through some extended bridging networks: the coupling between magnetic moments could then be propagated over relatively large distances.⁸ In particular, new molecular ferro- or ferrimagnets have recently been realized with heterobimetallic compounds using oxalate⁹ and cyanide ligands.¹⁰

In this work, several oxalato complexes with iron or chromium as transition-metal ion have been selected. After interfacial studies with different ionic amphiphiles and transfer of these systems, LB films containing such complexes have been carefully characterized using complementary techniques (infrared spectroscopy, X-ray diffraction, XPS, ESR, etc.). Then for the first time bulk magnetization measurements on LB films have been carried out and analyzed. In a second series of experiments, the properties of synthesized heterobimetallic complexes have been investigated following a similar approach leading to a new lamellar material presenting some magnetic interactions.

Experimental Section

Metal oxalate complexes ((NH₄)₃(Fe^{III}(Ox)₃)·3H₂O and K₃(Cr^{III}(Ox)₃)·3H₂O) (Aldrich), dimethyldioctadecyl (DODA) ammonium bromide (Kodak) were used without further purification. Chloroform (HPLC grade from Prolabo) was used as spreading solvent. Synthesis of the pyrilium salt (namely, 2,6-thienyl-4-(*N*-hexadecyl-*N*-methylaniline)pyrilium perchlorate (HPYR)) has been already published.¹¹ Molecular structures and purities of the synthesized salts were confirmed by ¹H NMR, IR and elementary analysis: experimental: C 64.12%, H 7.19%, N 2.12%, Cl 5.29%, S 9.59%. Calculated C 64.12%, H 7.17%, N 2.08%, Cl 5.25%, S 9.51%.

Several bimetallic complexes based on a M₁^{III}–M₂^{II}–M₁^{III} trimer, such as (DODA)₄[Fe^{II}(H₂O)₂{Cr^{III}(C₂O₄)₃}₂], (DODA)₄[Mn^{II}(H₂O)₂{Fe^{III}(C₂O₄)₃}₂], and (DODA)₄[Ni^{II}(H₂O)₂{Fe^{III}(C₂O₄)₃}₂], were synthesized following a procedure similar to that of the ref 12. For example, a solution of DODA (4 equiv) in acetonitrile is added to an aqueous solution containing 1 equiv of Fe^{II}SO₄ and 2 equiv of K₃Cr^{III}(C₂O₄)₃. The precipitate is filtered and carefully washed with water and hot ethanol. The elemental analysis and the magnetic behavior are in agreement with the proposed chemical structure: (DODA)₄[Fe^{II}(H₂O)₂{Cr^{III}(C₂O₄)₃}₂]: Experimental C 67.45%, H 11.08%, N 1.91%, Cr 3.39% Fe 2.06%. Calculated C 67.27%, H 11.15%, N 1.91%, Cr 3.55%, Fe 1.91%. (DODA)₄[Mn^{II}(H₂O)₂{Fe^{III}(C₂O₄)₃}₂]: experimental: C 66.37%, H 11.40%, N 1.97%, Mn 1.75%, Fe 3.48%. Calculated C 67.11%, H 11.13%, N 1.90%, Mn 1.87%, Fe 3.80%. (DODA)₄[Ni^{II}(H₂O)₂{Fe^{III}(C₂O₄)₃}₂]: Experimental: C 66.69%, H 11.27%, N 2.05%, Fe 3.18%, Ni 1.91%. Calculated: C 66.21%, H 11.12%, N 1.88%, Fe 3.76%, Ni 1.95%.

Langmuir films have been studied in a thermostated trough already described.¹³ The compression was performed at 20 ± 1 °C using a continuous speed for the barrier motion of ca. 6 Å²/(molecule min). At least two measurements were recorded for each set of experimental conditions. Built-up films have been obtained by the vertical lifting method using a homemade

LB trough working at room temperature under a continuous dried nitrogen flow.¹⁴ For such experiments, compression of the monolayer was performed step-by-step. After each increase of the surface pressure, waiting time allows the system to reach its equilibrium. Steps of 2 mN/m were usually chosen. The water used for the subphase was a Millipore Q-grade water with a resistivity higher than 18 MΩ cm. Films were transferred onto optically polished calcium fluoride for infrared measurements, optically polished glass substrate (treated with dichlorodimethylsilane if needed) for low-angle X-ray experiments and XPS, quartz for ESR, and a thin film of Mylar (75 μm × 5 mm × 18 mm) for SQUID measurements. No difference between the transfers onto these various substrates have been observed.

Infrared (IR) spectra were recorded on a FTIR 750 Nicolet spectrometer. IR linear dichroism was performed to calculate the usual dichroic ratio *R*:

$$R = A(i=60^\circ)/A(i=0^\circ)$$

where *A*(*i*) is the absorption coefficient and *i* the angle between the plane of the LB film and the IR light electric vector. This ratio *R* is related to the degree of anisotropy out of the substrate plane and enables the evaluation of the ϕ angle between the normal to the substrate and the dipole moment of a particular vibration.¹⁵

X-ray diffraction experiments (θ - 2θ scans) were performed with an INEL curve detector associated with an IBM computer for peak assignments.¹⁶

Photoelectron spectroscopy (XPS) on LB films was done with an ESCALAB 220 i-XL under high vacuum at room temperature. The signals associated with each type of atoms enable to estimate the various relative atomic concentrations within the multilayers. The calibration of energy was made versus the C 1s peak (at 285 eV). Peaks associated to nitrogen (N 1s), sulfur (S 2p), iron (Fe 2p_{3/2}), and chromium (Cr 2p_{3/2}) were located respectively at 401.7, 163.8, 711, and 576.6 eV. The peak intensities are corrected by the instrumental factor and by the atomic sensitivity factors of Scofield.¹⁷

ESR experiments were realized with a Bruker ESP 300 E system working at 10 GHz (X-band) equipped with an Oxford Liquid He⁴ temperature accessory. The magnetic susceptibility of LB films has been measured with a SQUID magnetometer Quantum Design MPMS-5 between 1.7 and 300 K. Two experiments (substrate and LB film then substrate alone) are carried out successively under the same experimental conditions (applied magnetic field from 1 to 5 T, parallel to the substrate). By difference, the intrinsic LB film magnetization is obtained. However, the experimental procedure adopted for such a measurement does not allow the evaluation of the susceptibility anisotropy of these LB films. For powders, the molar paramagnetic susceptibilities were calculated taking into account the usual diamagnetic core corrections.

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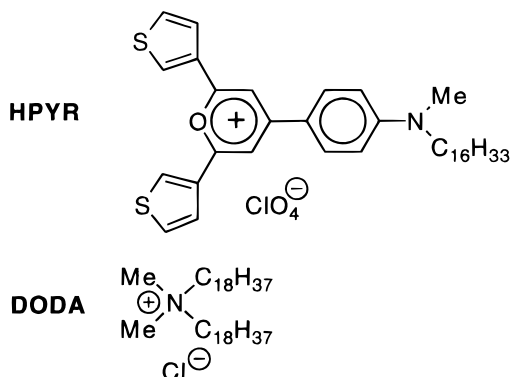


Figure 1. Molecular structure of the compounds used in this work

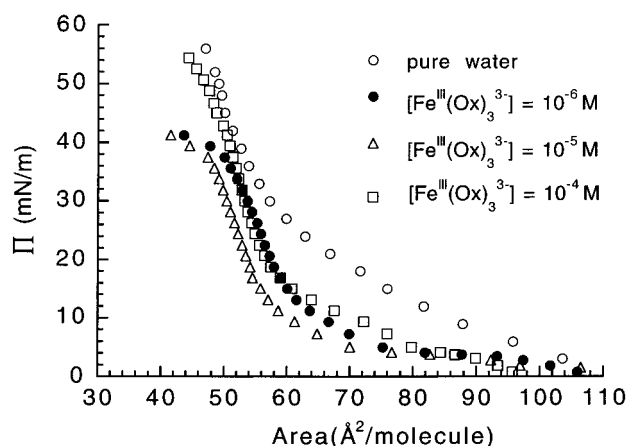


Figure 2. Compression isotherm of DODA monolayer on various subphases at 20 °C.

Results and Discussion

A. Monometallic Oxalato Complexes. (1) *Langmuir Films.* Two positively charged lipids (see Figure 1) were used as template to organize the metal complexes in monolayer. In the case of DODA and as already described in the literature,^{14,18} the isotherm (see Figure 2) on pure water suggests that the DODA monolayer is in an expanded state at the interface because of the high repulsion between the charged polar heads. Figure 2 demonstrates that the compression isotherm of DODA is progressively modified when oxalato complexes are dissolved in the subphase. In a first stage, the Π - A curve is shifted toward the smaller areas per molecule and at the same time the curve is steeper at the end of the compression. When the concentration in ions reaches ca. 10^{-5} M, maximum density is found for the Langmuir film at a given surface pressure. Then, any further increase in the complex concentration induced an increase in the molecular areas. Such type of behavior has been already reported for some other inorganic ions.¹⁴ Adsorption of the negatively charged complexes along the positively charged monolayer easily explains that higher molecular density than on pure water can be achieved for a given surface pressure. When the concentration continues to increase, a double layer of adsorbed ions could be built at the gas-water interface, inducing new changes in the isotherms. Similar adsorption process takes place when using the chromium oxalato complex instead of the iron one.

In bulk, exchange of the chloride ion in the DODA molecule by the metaloxalato complex is easily achieved leading to the compound of formula $(\text{DODA})_3\text{M}(\text{Ox})_3$. Such compound gives a Langmuir film characterized by an isotherm which is found between the one of DODA on pure water and on a subphase containing 10^{-5} M of the oxalato complex. A part of the $\text{M}(\text{Ox})_3$ complex associated initially to the DODA monolayer is then exchanged with ions of the water subphase. Dissolution of the metal-oxalato complex is then needed in order to achieve complete adsorption along the interface.

Other experiments performed using the other positively charged molecule (namely HPYR) lead to similar results: the effect of the $\text{M}(\text{Ox})_3$ concentration is again a decrease of the molecular area for a given surface pressure. However, the areas per molecule are smaller for this compound containing only a single alkyl chain than for DODA.

(2) *Langmuir-Blodgett Films.* Attempts to transfer onto solid substrate the stable Langmuir films spread on metaloxalato complex solution and described above were made using the Langmuir-Blodgett technique. Monolayers of HPYR or DODA lead to very good multilayers when the concentration of $\text{M}(\text{Ox})_3$ corresponds to the one where the compression isotherm of the monolayer is shifted to the minimum value for the areas per lipid (i.e., where the Langmuir film is the most packed). The transfer ratio was found close to 0.95 for both compounds with a dipping speed of 1 cm/min.

These LB films were characterized by complementary techniques such as infrared spectroscopy, X-ray diffraction, XPS, ESR, and magnetic susceptibility measurements.

Infrared Linear Dichroism. Besides the bands at ca. 2918, 2850, and 1468 cm^{-1} assigned to the CH_2 stretching or scissoring vibrations of DODA alkyl chains, strong bands associated to the oxalato group are clearly visible in the IR spectra of the LB films. Compared to values in KBr pellet, these absorption bands in LB films are narrower and somewhat shifted (see Table 2). Furthermore, when the infrared electrical field is not parallel to the plane of the substrate, a splitting of $\text{C}=\text{O}$ bands around 1700 cm^{-1} is observed (see Figure 3 and Table 1) in the DODA LB film. This dichroism demonstrates that the oxalato groups and then the $\text{M}(\text{Ox})_3$ complexes have a particular organization within the LB films. The electrostatic interactions with the charged lipids are certainly responsible for such orientation or/and distortion of the complexes in the multilayers. The exact orientation of the complexes is however difficult to evaluate because of the somewhat imprecise knowledge of the IR band assignments. In the case of HPYR LB films, the dichroic experiments do not show strong features as for DODA films: the inorganic ions appear to be less organized. Finally, the dichroism of the absorption bands associated with the CH_2 groups allows the evaluation of the angle between the substrate normal and the alkyl chains (which are supposed to adopt a fully extended all-trans conformation). Table 2 gives the tilt angle values found close to 20° for DODA films and 30° for HPYR multilayers, respectively.

X-ray Diffraction. Layer thicknesses of the LB films were evaluated from X-ray diffraction data. One to two Bragg peaks were generally observed in the diffract-

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Table 1. Infrared Spectra of LB Films and Powder of Metal–Oxalato Complexes (Wavenumbers Given in cm^{-1})

$(\text{NH}_4)_3\text{Fe}^{\text{III}}(\text{Ox})_3$ in KBr	$\text{K}_3\text{Cr}^{\text{III}}(\text{Ox})_3$ in KBr	$\text{Fe}^{\text{III}}(\text{Ox})_3$ in DODA LB film	$\text{Cr}^{\text{III}}(\text{Ox})_3$ in DODA LB film	$\text{Fe}^{\text{III}}(\text{Ox})_3$ in HPYR LB film	assignments ^a
1712 vs ^b 1682 vs, 1649 vs	1713 vs 1688 vs, 1650 vs	1710 w 1676 ^c s, 1664 s	1708 w 1683 ^c s, 1673 s, 1650 ep	1708 w 1660 s, 1642 ep	$\nu_a(\text{C}=\text{O})$ $\nu_a(\text{C}=\text{O})$
1397 s 1271 m, 1254 m	1393 s 1258 m	1361 m 1248 w	1363 m 1240 w		$\nu_s(\text{CO}) + \nu(\text{CC})$ $\nu_s(\text{CO}) + \delta(\text{O}=\text{C}=\text{O})$

^a From ref 24. ^b vs = very strong, s = strong, m = mean, w = weak, sh = shoulder. ^c Infrared band appearing when the angle between the plane of the substrate and the electric field is set to 60° .

Table 2. Characterization of the LB Films Containing $\text{M}^{\text{III}}(\text{Ox})_3$

technique	parameter	DODA (M = Fe^{III})	DODA (M = Cr^{III})	HPYR (M = Fe^{III})
IR spectroscopy	Φ (deg) ^a	20	21	31
X-ray diffraction	d (\AA) ^b	61	59	64
XPS	ratio	3.5 ± 0.5	4.5 ± 0.5	2.5 ± 0.5
magnetization	ratio	3.0 ± 0.5	4.5 ± 0.5	3.5 ± 0.5

^a Tilt angle ($\pm 5^\circ$) of the alkyl chains. ^b Periodicity ($\pm 2 \text{\AA}$) of the layers.

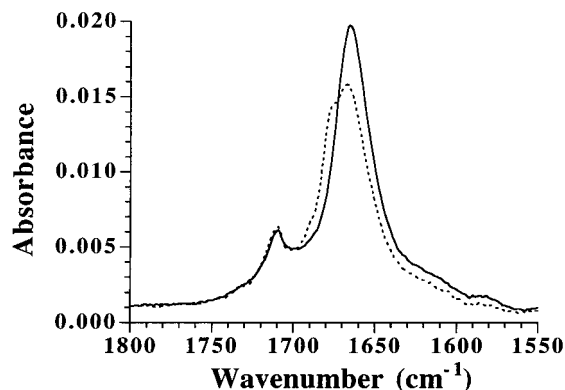


Figure 3. Infrared spectra of a DODA/ $\text{Fe}(\text{Ox})_3$ LB film (19 layers) on CaF_2 . The angle between the plane of the substrate and the electric field is either 0° (solid line) or 60° (dashed line).

gram leading to a spacing value close to 60\AA for the DODA system and 64\AA for the HPYR multilayers (see Table 2). Taking into account the tilt angle of the alkyl chains and the length of the lipid (extracted from ref 19 for the DODA and calculated using a space filling molecular model for HPYR), thickness of each inorganic layer in LB can be estimated to respectively ca. 17.5 and 8\AA for DODA and HPYR systems. From crystallographic data, the radius of such metaloxalato complex could be evaluated to 4.5\AA .²⁰ Then, bilayers of $\text{M}(\text{Ox})_3$ should be built with the DODA when only a monolayer of complexes can be found in HPYR multilayers. Formation of these monolayers instead of the expected bilayers implies that large reorganizations are occurring during the upper stroke transfer. Such behavior has been already observed for other polyanions¹⁴ and is mainly related to the surface charge density of the Langmuir film.

ESR. ESR signals of LB films are observed at low temperature (4.2 K) without any detectable anisotropy. They get broader when the temperature increases and are undetectable above nitrogen temperature. They are characterized by two lines respectively at $g = 4.28$ and $g \approx 2$ for a DODA/ $\text{Fe}^{\text{III}}(\text{Ox})_3$ ($S = 5/2$) LB film and one line at $g = 3.66$ with a bump around $g \approx 2$ for a DODA/ $\text{Cr}^{\text{III}}(\text{Ox})_3$ ($S = 3/2$) multilayer.²¹ The spectra of LB films show the same structure as that of oxalato metal complexes in powder. This demonstrates that the metal has still an octahedral environment within the LB film.

These experiments prove that the metal complex is indeed transferred together with the Langmuir film and that its structure (perhaps slightly distorted) is maintained within the LB film and organized in inorganic mono- or bilayer depending on the type of cationic surfactant. However, the amount of ions trapped in the LB films or the ratio DODA/ion cannot be determined with the techniques used above. To obtain such information, XPS analysis and magnetic susceptibility on LB films were performed.

XPS. XPS experiments on LB films demonstrate easily the presence of the metal complex within the LB film. Moreover, quantitative evaluation of the atomic ratio between nitrogen and iron was made: this ratio was found close to 3.5 ± 0.5 in the DODA/ $\text{Fe}(\text{Ox})_3$ multilayers (see Table 2). A similar procedure was used for DODA/ $\text{Cr}(\text{Ox})_3$ LB films leading to a value ca. 4.5 . For the pyrilium systems, the atomic ratio between sulfur and iron was used to evaluate the ratio HPYR/ $\text{M}(\text{Ox})_3$. These analyses confirm within the experimental accuracy the expected stoichiometries deduced from the electroneutrality.

Magnetization Measurements. Figure 4 gives a typical result concerning the magnetization of the LB film of DODA/ $\text{M}(\text{Ox})_3$. These films follow the Curie law until low temperature (ca. 20 K). Such behavior is clearly demonstrated by the linear relationship between the inverse of the magnetization and the temperature. Interactions between metal complexes should then be negligible within the LB film. This was expected taking into account the average large distance (see below) and the lack of superexchange pathways between the magnetic centers. Furthermore, the decrease in the χT product at low temperatures (which is associated with a zero field splitting⁸) is similar in the LB film and in powder. This proves that the metal complex structure is not strongly modified within the multilayer architecture. Finally, the average of the χT product for temperatures higher than 30 K should be proportional to the quantity of metal complexes trapped in the LB films. Comparing this mean value together with the results

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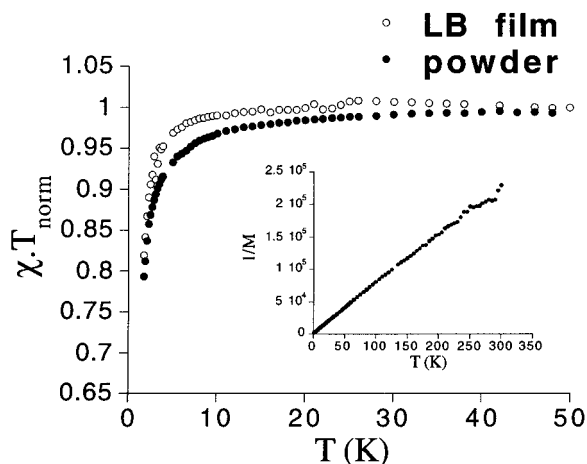


Figure 4. Plot of χT (normalized value) versus temperature for $K_3Cr(Ox)_3$ in powder (full circle) and for a DODA/ $Cr(Ox)_3$ LB film of 379 layers (open circle). Inset: inverse of the magnetization M (in emu) of the DODA/ $Cr(Ox)_3$ LB film versus temperature. All data concerning the LB films are corrected from the substrate and diamagnetisms.

in powder, an estimation of the amount of magnetic ions was made. Knowing the number of layers deposited onto the substrate, the transfer ratio, and the area per molecule at the transfer surface pressure, calculation of the number of lipid molecules is straightforward. Then, the ratio between the metal complexes and the positively charged lipids was easily evaluated (see Table 2). Taking into account the relatively poor accuracy for such measurements, all these values appear somewhat similar. The XPS and magnetic measurements demonstrate that the concentration of metal complexes found in the LB films is close to that expected for the electroneutrality between the complexes and the positively charged lipids.

The careful adjustments of the parameters controlling the fabrication of the LB and the full characterizations of the multilayers using complementary techniques lead then to information concerning the amphiphilic or inorganic part of these new materials. Figure 5 schematically describes the structure of the DODA/ $M(Ox)_3$ LB films deduced from these experiments: a bilayer of complexes between layers of DODA where the alkyl tails are slightly tilted. In such a material, the average distance between two complexes in the same inorganic sheet can be estimated to be ca. 13 Å taking into account the number of DODA per $M(Ox)_3$ (Table 2) in the LB film and the area per DODA in the monolayer during transfer (see Figure 2). Such a large distance when compared to the size of the complex made negligible the possible (magnetic) interactions between ions: the magnetization of the DODA/ $M(Ox)_3$ LB films follows then the Curie law. To build magnetic multilayers with interacting spins, one possible way is to use clusters in which intramolecular interactions take place.

B. Bimetallic Oxalato Complex. All the synthesized bimetallic complexes are especially interesting because of their magnetic behavior. For example, the derivative (noted CrFeCr) formulated as $(DODA)_4[Fe^{II}(H_2O)_2\{Cr^{III}(C_2O_4)_3\}_2]$ exhibits (see Figure 7) below room temperature a Curie constant corresponding to magnetically diluted $Cr^{III}-Fe^{II}-Cr^{III}$ trimers ($C_{app} \approx 6.1$). Below ca. 75 K, its magnetic moment increases continu-

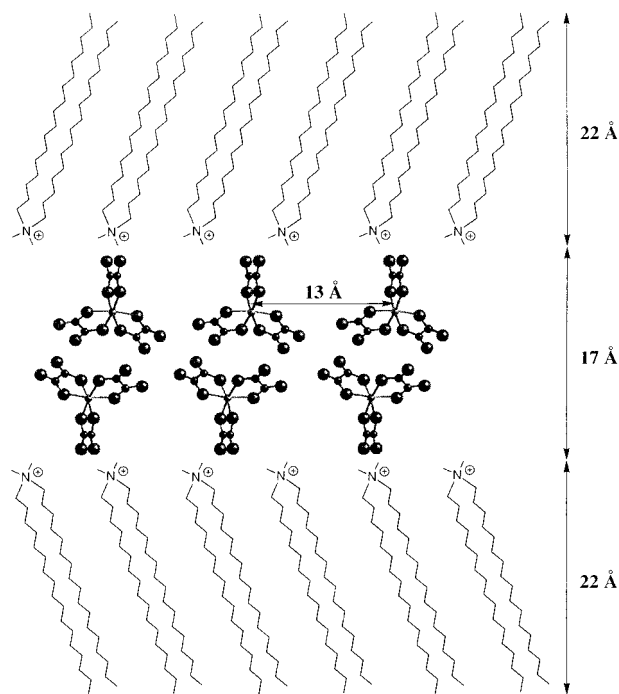


Figure 5. Schematic organization of a DODA/ $M(Ox)_3$ LB film.

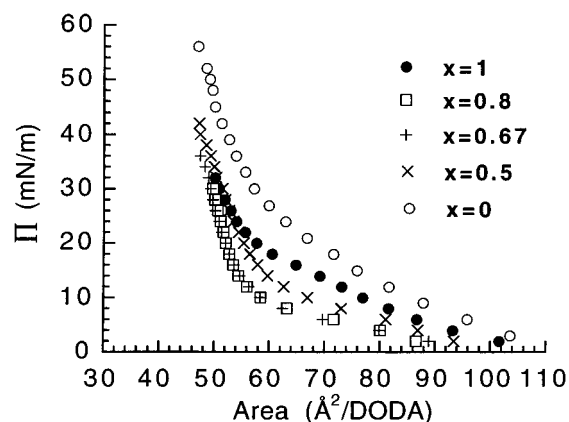


Figure 6. Compression isotherm of CrFeCr complex/DODA mixtures on pure water for various mole fraction x of DODA coming from the complex.

ously upon cooling, indicating a ferromagnetic exchange coupling between the chromium and iron: the fit corresponding to a linear trimer gives an exchange parameter J close to 1.2 cm^{-1} similar to those already reported.²²

(1) *Langmuir Films.* The bimetallic complexes form stable monolayers at the gas–water interface but only the CrFeCr compound can be transferred onto solid substrates. The compression isotherm of such a complex on pure water lies between that of pure DODA on water and on a metal–oxalato complex dissolved in the subphase (see Figures 2 and 6). The CrFeCr complex interacts with the organic monolayer inducing a higher density of the alkyl chains when compared to the pure DODA Langmuir film spread on pure water. However, densities of the hydrophobic tails comparable to that obtained for DODA on a metal–oxalato complex subphase cannot be reached except near the collapse pressure of the CrFeCr monolayer. Nevertheless, higher

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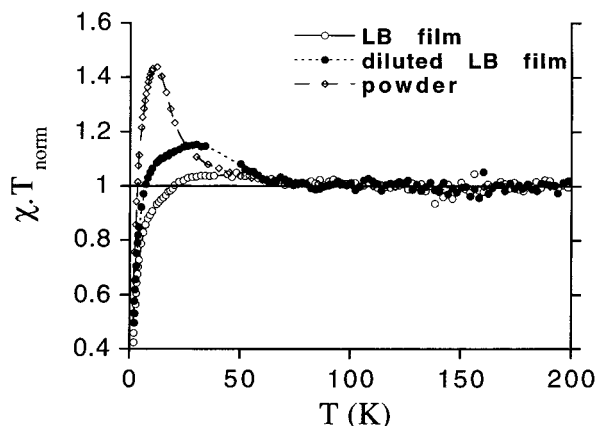


Figure 7. Plot of χT (normalized value) versus temperature for the CrFeCr complex in powder (open diamond), in pure LB film of ca. 1000 layers (open circle) and in a mixed CrFeCr/DODA LB film (see text) (full circle). All data concerning the LB films are corrected from the substrate diamagnetism.

DODA surface density is easily obtained by mixing the CrFeCr compound with pure DODA as it can be seen in Figure 6 where x is the mole fraction of DODA coming from the trimer ($x = 1$ for pure CrFeCr complex and $x = 0$ for pure DODA). When the mole fraction x is larger than 0.5, the recorded isotherm is similar to that of pure DODA spread on a $M(\text{Ox})_3$ subphase. Increasing the number of alkyl tails per bimetallic complex (i.e., decreasing x) seems to induce a higher compacity of the alkyl tails when compared to the pure complex. Finally, when the mole fraction x is lower than 0.5, a new shift of the isotherm is observed toward that of pure DODA.

(2) *Langmuir–Blodgett Films.* Transfer of the pure CrFeCr monolayer (Y type) can be easily performed. The transfer ratio is found close to 0.8 for a dipping speed of 0.5 cm/min. For the mixed films, transfer can be achieved only for a ratio CrFeCr cluster/pure DODA larger than $1/4$ (i.e., for a mole fraction x larger than 0.5) and with a very low dipping speed close to 0.2 cm/min. The infrared spectrum of the LB film is similar to that of DODA/Cr(Ox)₃. However, the tilt angle of the alkyl chains is found to be close to 30°, a value larger than in DODA/M(Ox)₃ suggesting that the hydrophobic tails are slightly less packed in the CrFeCr multilayers than in the monometallic complex films. This is somewhat confirmed by the dichroism experiments made on a mixed CrFeCr complex/pure DODA LB film, for which a tilt angle for the alkyl chains is found between 15° and 25° depending on the mole ratio of pure DODA. X-ray diffraction experiments give only one Bragg peak which corresponds to a spacing of ca. 62 Å (63 Å for the mixed $1/2$ LB film). Then, the organization of the CrFeCr LB film should be similar to that of the LB films built from monometallic oxalato complexes. The ESR signal of the multilayer at very low temperature is reminiscent to that of Cr(Ox)₃ salt in powder (it should be ESR silent in view of the integer spin states). Furthermore, XPS analysis of the LB film gives a DODA/Cr ratio of about 5 and a Cr/Fe ratio around 7. Even if the iron signal is difficult to integrate taking into account the background noise, clearly some iron ions are lacking in the CrFeCr LB film when compared to the expected ratio equal to 2. Such EPR and XPS results could be a hint of a chemical instability of the

spread bimetallic complex. Indeed, the weak trimer could be in equilibrium at the gas–water interface with the stable Cr(Ox)₃ complex. Because infrared spectra and ESR signals of Cr(Ox)₃ and CrFeCr complexes are very close both in the solid state and in LB films, no clear demonstration can be made concerning such chemical instability. However, the SQUID measurements prove that the LB films do not contain only the chromium complex (see Figure 7). Indeed, the χT product slightly increases around 75 K and strongly decreases when the temperature goes below 25 K. This drop cannot correspond to the zero field splitting of pure trisoxalatochromium III complex which is found only below 10 K (see Figure 4). Furthermore, when a mixed Langmuir film is used ($1/2$ in CrFeCr complex/pure DODA), the magnetization of the LB films (ca. 1000 layers deposited) presents a clear increase of the χT product below 75 K. This demonstrates that some interactions still occur between magnetic centers within this LB film. The difference between pure and mixed multilayers can be linked to the chemical stability of the complex at the gas–water interface which is perhaps increased when diluting the CrFeCr complex with pure DODA. These experiments demonstrate the limit of the semiamphiphilic approach based on inorganic complexes which are too weak chemically to be fully stable at the gas–water interface.

Conclusion

We have demonstrated that metaloxalato complexes can be organized by the LB technique leading to new hybrid materials. In such multilayers, the monometallic compounds are organized in stable monolayer or bilayer depending on the positively charged lipid used as template. Because of the large distances between ions, the magnetic behavior of these LB films is perfectly described by the Curie law. However, synthesized heterobimetallic clusters enable the fabrication of multilayers in which some local magnetic interactions occur even if the suspected chemical instability of the trimers in Langmuir films is a clear limit to the understanding of the magnetic multilayer behavior.

Careful choice of the chemical structure of metal complexes can then give rise to new magnetic materials. One other complementary way which we plan to use is based on interfacial manipulations and chemistry in order to get in-situ synthesized complexes forming an extended network as the 2D polymers already described in bulk.²³

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