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Intercalation of a nitronyl nitroxide radical into layered inorganic hosts. Preparation and physico-chemical characterization

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Abstract

The synthesis of new intercalation compounds obtained introducing the organic radical 2-(4-carboxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide (NITpBAH) in layered inorganic hosts via topotactic anion exchange reactions or exchange of anionic ligands is presented. Three different inorganic hosts were employed, two LDH-phases (Mg–Al–CO_3 and Zn–Al–Cl) and the butanoxy derivative of λ-zirconium phosphates. In all cases the intercalation procedure was successfully accomplished. The percentage of exchanged anions obtained was 27, 45, 40% for Mg–Al–LDH, Zn–Al–LDH and λ-$ZrPO_4[O(CH_2)_3CH_3]DMSO$, respectively. The magnetic properties of the intercalated compounds were measured with a SQUID magnetometer and compared to those of a polycrystalline powder of the pure radical. The intercalation process does not change the nature of magnetic intermolecular interactions which remain antiferromagnetic but reduces their magnitude.

Keywords: Nitronyl nitroxide radicals; Magnetism; Intercalation compounds

1. Introduction

The ability of many layered solid structures to incorporate guest species in a constrained environment represents a useful tool for materials chemistry. By intercalation procedures it is possible to prepare materials in which a species having peculiar properties is present within the layers of a host in an ordered array that is usually different from that found in a pure phase or a solution. Due to host– and guest–guest interactions, the properties of the material can be modified for specific purposes. Some studies on the effects of intercalation into layered hosts (e.g. double hydroxides and zirconium phosphates and phosphonates) of species of interest in the field of non-linear optics [1], sensing devices [2] and molecular recognition [3] can be found in the recent literature.

From this point of view, we found it of interest to study the change of the properties of magnetic organic molecules when intercalated into lamellar hosts. The guest species selected for this study was a substituted α-nitronyl nitroxide radical. This class of compounds has been extensively investigated since the discovery that some members of the family undergo a transition to a ferromagnetic ordered state at low temperature [4]. The nature and the magnitude of the intermolecular interactions which lead to the magnetic ordering depend on the crystal packing and on the relative orientation of the molecules. For example, the *p*-nitrophenyl nitronyl nitroxide radical crystallizes in four different phases of which only one, the β phase, orders ferromagnetically [4]. The intercalation of these compounds into layered inorganic hosts is expected to change the intermolecular arrangement with respect to those of the pure solid phases therefore affecting the magnetic properties of the

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compounds. Among the different organic radicals which have been synthesized in the last decade, we chose the 2-(4-carboxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide (NITpBAH in the following) [5]. Bearing a carboxylic group, the above compound was expected to be one of the best candidates for intercalation in layered hosts via topotactic anion exchange reactions or exchange of anionic ligands.

Among inorganic layered solids, very few possess anionic exchange capabilities. LDH are the most known and commonly employed inorganic anion exchangers [6]. Their general formula is $M(II)_{1-x}M(III)_x(OH)_2[A^{n-}]_{x/n} \cdot mS$, where M(II) may be Mg, Zn, Co, Ni; M(III) Al, Cr, Fe, V; A^{n-} is the charge compensating anion, $CO_3^{=}$, $SO_4^{=}$, Cl^-, organic anions; *m* the number of co-intercalated solvent S, generally water, per formula weight of compound. The layer–counterion interactions are basically ionic.

Recently, in the Perugia laboratory a new family of anionic ligand exchangers has been developed, that is λ-zirconium phosphates. Although the first synthesized and structurally characterized λ-type compound was $ZrPO_4FDMSO$ [7], the first compound of this class showing anion exchange capabilities is $ZrPO_4ClDMSO$ [8], in which chloride can be easily replaced, by a topotactic anion exchange reaction, with other organic or inorganic monoanionic ligands. In λ-ZrP derivatives the exchangeable anionic ligands are covalently bonded to zirconium atoms, and hence they occupy a specific site in the layer structure.

This paper reports the preparation and physicochemical characterization of NITpBAH intercalation compounds with both classes of inorganic layered hosts described above; specifically, two LDH-phases (Mg–Al–CO_3 and Zn–Al–Cl LDH), and the butanoxy derivative of λ-zirconium phosphate were employed.

2. Experimental

2.1. Synthesis

The organic radical 2-(4-carboxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl-3-oxide was synthesized according to the procedure previously described [9].

Mg–Al–LDH (NITpBA) derivative (**I**) was prepared as follows: the hydrotalcite $[Mg_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165} \cdot 0.4H_2O$ was calcined in air at 500 °C for 18 h. One gram of the calcined oxides thus obtained was suspended in 80 ml of CO_2-free distilled water at refluxing temperature for 45 min. A solution obtained by dissolving 2.08 g of NITpBAH in 100 ml of ethyl alcohol was added to the above cold suspension of rehydrated oxides. The suspension was stirred for 1 day. After the equilibration the solid was washed once with ethyl alcohol, once whit CO_2-free distilled water and finally dried at room temperature (r.t.) (75% R.H.). Chemical analysis gave the following composition: $[Mg_{0.67}Al_{0.33}(OH)_2](NITpBA)_{0.09}(CO_3)_{0.12} \cdot 0.3H_2O$. TGA: % weight loss at 1000 °C: 54.5 (calc. 54.7, assuming the formation of 0.505 MgO + 0.165 $MgAl_2O_4$ at 1000 °C).

Zn–Al–LDH NITpBA derivative (**II**) was prepared as follows: 1 g of $[Zn_{0.67}Al_{0.33}(OH)_2]Cl_{0.33} \cdot 0.6H_2O$ was equilibrated, for 1 day at r.t., with 180 ml of 0.04 M of hydro-alcoholic (50% v/v) solution of NITpBAH. The pH of this solution was previously set to 8, by NaOH addition. The solid was then separated by centrifugation and washed once with ethyl alcohol, once whit CO_2-free distilled water and finally dried at r.t. (75% R.H.). Chemical analysis gave the following composition: $[Zn_{0.67}Al_{0.33}(OH)_2](NITpBA)_{0.15}(Cl)_{0.18} \cdot 0.5H_2O$. TGA: % weight loss at 1000 °C: 51 (calc. 50.3, assuming the formation of 0.505 ZnO + 0.165 $ZnAl_2O_4$ at 1000 °C).

The hosts, $[Mg_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165} \cdot 0.4H_2O$ and $[Zn_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165} \cdot 0.4H_2O$ were prepared with a procedure accomplished by the thermal hydrolysis of urea [6]. Before NITpBAH intercalation, the carbonate form of Zn–Al–LDH was converted into the chloride form via ion exchange at pH 5. The solid was washed with CO_2-free distilled water and dried at r.t. over P_4O_{10}.

λ-ZrP NITpBA derivative (**III**) was obtained as follows: 0.3 g λ-$ZrPO_4[O(CH_2)_3CH_3]DMSO$ were dispersed in 54 ml of 0.05 M NITpBAH solution and maintained under stirring at 90 °C for 2 days. The solid was then separated by centrifugation and washed twice with 50 ml dioxane each time. The compound obtained presented the same violet color of NITpBAH solution, even after washing. Chemical analysis gave the following composition: $ZrPO_4(NITpBA)_{0.4}(OH)_{0.6}DMSO$. *Anal*. Found (Calc.): C, 23.78 (24.04); N, 2.64 (2.11); H, 3.64% (3.01). TGA: % weight loss at 1000 °C: 49.00 (calc. 48.85, assuming the formation of $(ZrP_2O_7)_{0.5}(ZrO_2)_{0.5}$ at 1000 °C).

The host, λ-$ZrPO_4[O(CH_2)_3CH_3]DMSO$, was prepared as follows: 1 g of λ-$ZrPO_4ClDMSO$ (prepared as previously reported [8]) was suspended in 85 ml of a 0.1 M n-Bu_3N in BuOH as solvent for 5 days at 80 °C. The solid was washed with BuOH and dried at 70 °C.

2.2. Analytical and instrumental procedures

C, N and H elemental analysis was obtained by a C. Erba 1106 Analyzer.

Mg(II), Zn(II) and Al(III) content was determined as follows. Weighed amounts of the samples (approximately 100 mg) were dissolved in a few drops of concd. HCl and diluted with water to 50 ml. These solutions were then titrated with standard EDTA.

TGA measurements were performed with a Stanton Redcroft STA780 thermoanalyzer. Ion Chromatography was carried out with a Dionex 2000 i/sp instrument, AS4A column and 1.7×10^{-3} M $NaHCO_3$/1.8×10^{-3} M Na_2CO_3 solution as eluent.

X-ray powder diffraction (XRD) measurements were used for phase identification and for monitoring the evolution of topotactic reactions of insertion of NITpBAH into the hosts. It was accomplished by evaluating the change of the interlayer distance, determined from the first strong reflection of the XRD patterns, recorded with a Philips X'PERT diffractometer using the Cu Kα radiation.

J-modulated ^{13}C liquid NMR spectra were taken with a Bruker DPX 200: about 50 mg of solid sample were dissolved in 1 ml of 6 M HF using a proper deuterated solvent.

Static magnetic susceptibilities were measured with a Metronique Ingeniérie MS02 SQUID magnetometer with an applied field of 1 T. Magnetic data were corrected for diamagnetic contributions which were directly measured on the non-intercalated inorganic hosts.

EPR spectra were recorded on a Varian E-9 spectrometer working at X-band (9.25 GHz) and equipped with an He flux cryostat ESR9 built by Oxford Instruments, which allows temperature variation from 4 K to r.t.

3. Results and discussion

Fig. 1 shows the structure formula and the approximate dimensions of NITpBAH. In Fig. 2 the temperature dependence of the χT product of the pure radical is shown. A continuous decrease of χT upon decreasing temperature is observed indicating the presence of intermolecular antiferromagnetic interactions. The magnetic properties of the compound were previously discussed by some authors which reported different behaviors and used different models to reproduce experimental data (dimer model [5], chain model [9] and 2D square lattice model [10]). We found the best model to fit our data was the Bonner and Fisher model for antiferromagnetic chains of $S = 1/2$ Heisenberg spins [11]:

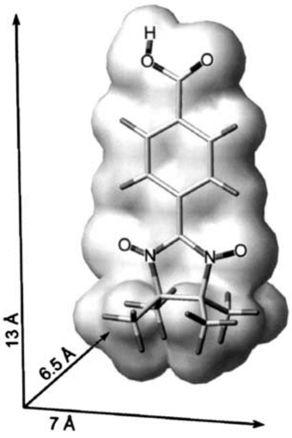

Fig. 1. Structure formula of NITpBAH. Van der Waals dimensions are also shown.

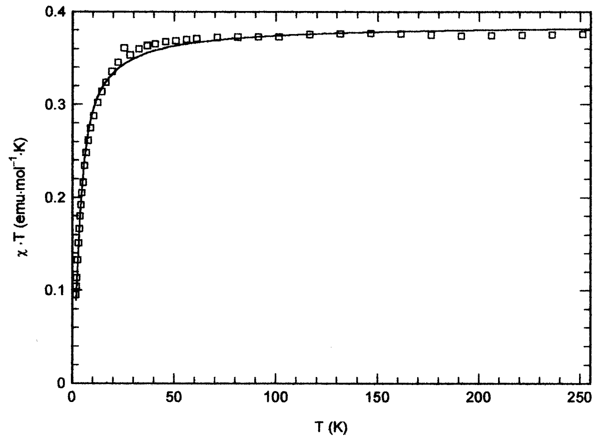

Fig. 2. Temperature dependence of χT measured at 1 T on a polycrystalline sample of NITpBAH. The full line represents the fit to Eq. (1).

$$\chi T = \frac{Ng^2\mu_B^2}{k_B} \times \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \quad (1)$$

where $x = |J|/k_B T$. The best fit parameters we found were $g = 2.03(1)$ and $J = 3.38(8)$ cm^{-1} with $R = 6.9 \times 10^{-3}$. The data are in good agreement with those reported in Ref. [9] (the g value is larger than 2 due to an experimental artifact) and can be explained on the basis of a magnetic interaction operating through the chain-like structure formed by hydrogen bonds between the oxygen atom of the nitronyl nitroxide groups and the carboxylic groups, where a small amount of spin density is expected to be delocalized.

The procedures used to intercalate NITpBAH and the products obtained for the different hosts, together with their magnetic properties, will be discussed separately in the following.

3.1. LDH-NITpBA derivatives

A powerful synthetic route for inserting inorganic and organic anions into LDH is the so-called memory effect, that is the ability of Mg–Al–CO_3–LDH calcined at 500 °C to reconstruct its layered structure in the presence of water and anions [12].

NITpBA$^-$ was first intercalated into Mg–Al–LDH using this effect. The mixture of magnesium aluminium oxides formed after heat treatment was regenerated in

CO_2-free distilled water, obtaining the following compound: $[Mg_{0.67}Al_{0.33}(OH)_2](OH)_{0.33} \cdot nH_2O$, in which the balancing anions are hydroxyl groups. In the presence of NITpBAH an acid–base reaction takes place and lead to **I** where 27% of OH groups where exchanged by NITpBA anions. The residual hydroxyl groups were spontaneously converted into carbonate anions by CO_2 from air. Owing to the high reactivity of LDH in OH form and to its strong selectivity towards carbonate, all our attempts to increase the amount of intercalated NITpBA were unsuccessful.

XRD patterns showed an interlayer distance of 20.7 Å, and the typical reflection of the carbonate form (7.6 Å).

To obtain an increased amount of $NITpBA^-$ in the interlayer region we used a direct anionic exchange reaction path. In this case the host used was Zn–Al–LDH in chloride form, and the following reaction was carried out:

$$[Zn_{0.67}Al_{0.33}(OH)_2]Cl_{0.33}0.6H_2O + 0.15\ NITpBA^- \rightarrow Zn_{0.67}Al_{0.33}(OH)_2](NITpBA)_{0.15}(Cl)_{0.18}0.5H_2O + 0.15\ Cl^- + 0.1\ H_2O$$

As indicated from the composition of **II** about 45% of the chloride anions were exchanged with $NITpBA^-$. The interlayer distance was 19.7 Å, very close to that observed for **I**.

3.1.1. *Magnetic properties*

The temperature dependence of the χT product per mol of radical of the Mg–Al–LDH and Zn–Al–LDH intercalated compounds are shown in Fig. 4(a and b), respectively. For both compounds χT slowly decreases on lowering temperature indicating that weak antiferromagnetic intermolecular interactions are still present in both compounds. The data can be fit to a Curie–Weiss law with $C = 0.376$ emu K mol^{-1} and $\theta = -2.3$ K for Mg–Al–LDH and $C = 0.356$ emu K mol^{-1} and $\theta = -3.0$ K for Zn–Al–LDH. For both compounds at low temperature a small deviation from this law is observed, which indicates that low dimensional interactions are operating, as it should be expected. An analysis of magnetic data considering a dimer, an antiferromagnetic chain and a 2D square lattice models was attempted but none of the models could satisfactory reproduce the experimental data. The failure of the above models can be the consequence of the incompleteness of the radical intercalation into the layered structure or of a not fully ordered packing of the radical which can make the interpretation of the magnetic behavior more complex.

The intercalation of the organic radical in the inorganic host destroys the main path for exchange along the hydrogen bond between the carboxylic group and the nitronyl nitroxide oxygen. However, the intermolecular interactions arising from the different packing of the radical in the interlayer are of the same nature and not as strong as those observed in the free radicals. The EPR spectrum of the two compounds were recorded at 30 K. The two spectra consist of a single line centered at $g = 2.00$ for both samples. The linewidths are 10.5 and 12.5 G for Mg–Al–LDH and Zn–Al–LDH, respectively. Within the resolution limit of our instrument no significant differences were observed with the spectrum of the pure radical where a single line with linewidth 12.5 G is present.

3.2. *λ-ZrP NITpBA derivative*

Preliminary experiments to intercalate NITpBAH directly into λ-$ZrPO_4ClDMSO$ were unsuccessful, probably due to the high steric hindrance of the guest species.

To facilitate the topotactic reaction, it was therefore used, as host, the λ-butanoxy derivative, of formula λ-$ZrPO_4[O(CH_2)_3CH_3]DMSO$. This derivative has a larger interlayer distance than the chloride one (15.7 vs. 10.2 Å) and it is more reactive towards the anion exchange reactions, because of the high basic character of the alkoxy anions [13]. Using this phase, the intercalation of $NITpBA^-$ was easier than with the λ-$ZrPO_4ClDMSO$ phase, following the scheme:

$$ZrPO_4[O(CH_2)_3CH_3]DMSO + 0.4\ NITpBAH + 0.6\ H_2O \rightarrow ZrPO_4(NITpBA)_{0.4}(OH)_{0.6}DMSO + CH_3(CH_2)_3OH$$

Note that only 40% of anions were exchanged by NITpBA anions, and all our attempts to increase this amount were unsuccessful. Owing to the presence of four methyl terminal groups, the cross section of NITpBAH was evaluated to be roughly 45 $Å^2$, a value close to the free cross section per site available in the interlayer region of a λ-derivative (43.5 $Å^2$). Furthermore, the cross section of NITpBA groups is not uniform, the terminal part being larger than the body; the extra free room in the interlayer space hence created, is probably occupied by NITpBA groups coming from adjacent layers, in an interdigitated arrangement as depicted in the hypothetical model of Fig. 3. The interlayer distance derived from this model is consistent with the experimental interlayer distance for sample **III** (18.7 Å), when the organic group is tilted by an angle of 74° with respect to the layers plane.

The butanoxy groups not exchanged by NITpBA anions were not found in the final compound, as detected by ^{13}C NMR measurements. Preliminary experiments carried out in pure λ-butanoxy derivative have shown that butanoxy groups can be easily replaced by hydroxyl groups, because of the strong basic character of butanoxy anions. Therefore, it is presumable that the butanoxy groups not exchanged by

NITpBA were replaced by OH groups coming from water vapour. Chemical and thermogravimetric analysis are in agreement with this assumption.

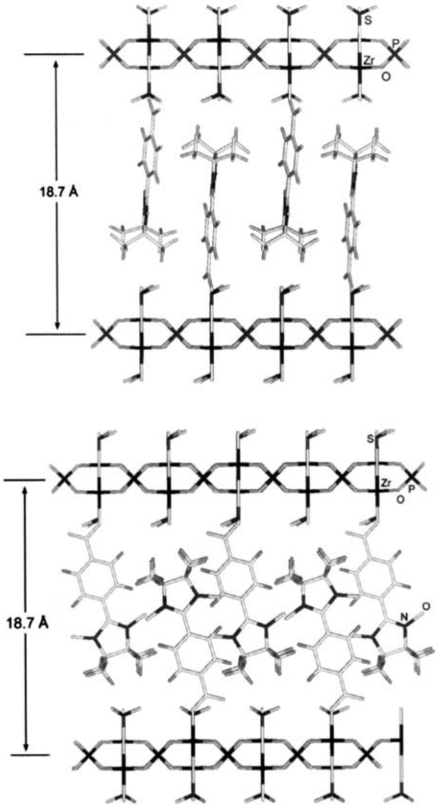

Fig. 3. Structural model, viewed along two directions perpendicular to each other, showing the hypothetical arrangement of NITpBAH in the interlayer region of λ-ZrP.

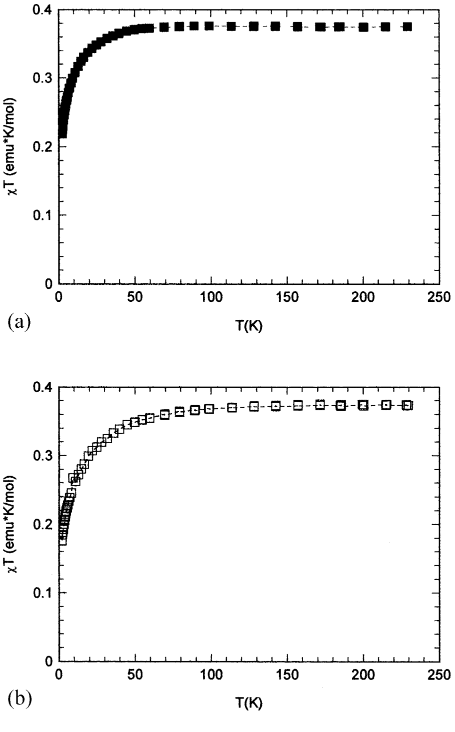

Fig. 4. Temperature dependence of the χT product of NITpBA–Mg–Al–LDH (a) and NITpBA–Zn–Al–LDH (b).

3.2.1. Magnetic properties

The χT versus T curve of the compound is shown in Fig. 5. If compared to the other two compounds a smaller decrease of χT on lowering temperature is observed, suggesting even weaker antiferromagnetic intermolecular interactions. The data could be satisfactory fit either to a Curie–Weiss law with $C = 0.38$ emu K mol^{-1}and $\theta = -1.1$ K, by a 2D square lattice model with $J = 0.63$ cm^{-1} or by the AF chain model with $J =$ 1.2 cm^{-1}, the best R value ($R = 0.0025$) being obtained for the last model. However, due to the small value of involved magnetic interactions no conclusions on their dimensionality can be drawn from the data fit. Anyway the data confirm that the different radical arrangement in this host results in weaker intermolecular interactions.

The EPR spectrum of this compound recorded at 30 K is similar to that of the other intercalated compounds and consists of a single line at $g = 2.00$ with linewidth 13.5 G.

4. Conclusions

The intercalation of the organic radical NITpBAH into inorganic hosts was successfully accomplished. In all the investigated compounds intermolecular interactions are still antiferromagnetic but are weaker than those observed in the free radical. Despite the results obtained with this radical are on the opposite directions than that we hoped for, the proposed method has shown to provide an effective route to modify magnetic interactions in organic radicals.

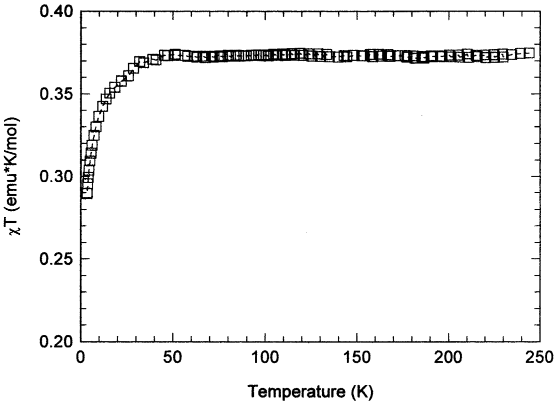

Fig. 5. Temperature dependence of the χT product of λ-ZrP NITpBA derivative.

Acknowledgements

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