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First Ni^{II}–Ln^{III} Coordination Polymers Constructed by Using [Ni(bpca)$_2$] as a Building Block [Hbpca = bis(2-pyridylcarbonyl)amine]: Synthesis, Crystal Structures and Magnetic Properties

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Three new heterobimetallic 1D coordination polymers have been obtained by assembling the [Ni(bpca)$_2$] complex, as a building block, with lanthanide cations: [{Ln(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (Ln Gd **1**; Tb **2**; Dy **3**). The three compounds are isostructural and their structure consists of infinite cationic chains with Ln^{III} ions connected by [Ni(bpca)$_2$] complexes acting as bridging bis-bidentate ligands. The charge of the chains is counterbalanced by uncoordinated nitrate ions. The Ln^{III} ions display a coordination number of nine: four oxygen atoms from the carbonyl groups of the bpca ligands belonging to two {Ni(bpca)$_2$} moieties, two oxygen atoms from a chelating nitrato ion and three water molecules. The magnetic investigation of the gadolinium derivative **1** revealed very weak intrachain Ni^{II}–Gd^{III}-ferromagnetic interactions (θ = +0.15 K). The weak intrachain-exchange interactions, as well as the bad magnetic isolation of the chains in the crystals, preclude the single-chain magnet behaviour of compounds **2** and **3**. The out-of-phase, χ'', signal observed with compounds **2** and **3** can be ascribed to the magnetic slow relaxation of the lanthanide ions (Tb^{III}, Dy^{III}).

Introduction

The interest in the 3d–4f combined coordination chemistry is strongly related to the tremendous development of molecular magnetism.[1] In the early 1990s Cu^{II} and Gd^{III} ions were extensively employed in making heterometallic complexes, because the exchange interaction between the two ions was found to be ferromagnetic in most cases.[2] Numerous Cu^{II}–Ln^{III}-polynuclear complexes, ranging from discrete entities to coordination polymers with various dimensionalities and network topologies, were synthesized.[3] In spite of the large spin carried by the Gd^{III} ion (S 7/2), the critical temperatures for the classical molecule-based magnets were found to be very low.[4] The main reason for this is the rather weak exchange interaction between Cu^{II} and Gd^{III}. More recently, the interest of chemists moved towards lanthanides exhibiting a high anisotropy, as a prerequisite for designing single-molecule magnets (SMMs) and single-chain magnets (SCMs). The best candidates are terbium(III), dysprosium(III) and holmium(III). Indeed, several SMMs based upon 3d and 4f (Tb^{III}, Dy^{III}, Ho^{III}) ions were reported recently.[5] Moreover, it has been shown that even mononuclear Tb^{III} and Dy^{III} complexes fulfil the conditions to exhibit a slow relaxation of the magnetization.[6] Single-chain magnets constructed from anisotropic lanthanides ions are known as well.[7]

Several synthetic strategies are currently employed to obtain 3d–4f complexes:[1,3] (i) self-assembly processes involving metallo-ligands (building-blocks) and assembling Ln^{3+} cations; (ii) the clever use of dissymmetric bi- or tricompartmental ligands, which are able to interact selectively with the two different metal ions; (iii) the employment of preformed 3d–4f complexes as nodes, by connecting them with various spacers; and (iv) one-pot procedures.

The coordination of the bis(2-pyridylcarbonyl)amine anion, pbca$^-$, to various metal ions generates numerous bischelated complexes, [M^{II}(bpca)$_2$] and [M^{III}(bpca)$_2$]$^+$, which can act as ligands towards a second metal ion forming oligonuclear complexes[8] and coordination polymers.[9] Mixed valence Fe^{II}/Fe^{III} chains have also been obtained by assembling low-spin [Fe(bpca)$_2$]$^+$ or similar cations containing methyl-substituted bpca ligands with Fe^{2+} ions. These compounds exhibit single-chain magnetic behaviour.[10]

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Because of their strongly oxophilic character, the lanthanide cations easily interact with the oxygen atoms from the carbonyl groups of the bpca ligands coordinated to the first metal ion to form 3d–4f-heterometallic complexes. In this paper we report on the first one-dimensional coordination polymers constructed from [Ni(bpca)$_2$] building blocks and Ln^{3+} ions.

Results and Discussion

Structures

Three new compounds, with the general formula [{Ln(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O, were obtained by self-assembly processes involving neutral [Ni(bpca)$_2$] building blocks and Ln^{3+} ions (Ln Gd, **1**; Tb, **2**; Dy, **3**). The crystallographic investigation revealed that the three complexes are isostructural (Table 1). Therefore, only the crystal structure of the dysprosium derivative will be described here.

The structure of **3** consists of infinite cationic chains with Dy^{3+} ions connected by [Ni(bpca)$_2$] complexes acting as bridging bis-bidentate ligands (Figure 1). The charge of the chains is counterbalanced by uncoordinated nitrate ions. The nickel ions are hexacoordinated by the two bpca ligands, as in similar complexes.[9] The Ni–N(amide) distances [2.024(3) and 2.027(3) Å] are slightly shorter than the Ni–N(py) ones [2.110(3), 2.106(3), 2.115(3) and 2.131(3) Å]. So the coordination polyhedron of the nickel ion is slightly compressed.

The dysprosium ion displays a coordination number of nine: four oxygen atoms from the carbonyl groups of the bpca ligands belonging to two {Ni(bpca)$_2$} moieties, two oxygens from a chelating nitrato ion and three water molecules. The Dy–O distances vary between 2.336(3) and 2.481(3) Å. The short distances correspond to the dysprosium–aqua bonds. The distance between the metallic centres within a chain is Dy···Ni 5.865 Å. Other relevant bond lengths are collected in Table 2.

The analysis of the packing diagrams shows that all the chains run along the crystallographic *b* axis. At the supramolecular level, the chains interact through graphite-like π–π contacts (3.38–3.62 Å), which are established between the phenyl rings arising from the bpca ligands from neighbouring chains, resulting in a 3D supramolecular array (Figure 2).

The supramolecular interactions between chains are reinforced by hydrogen-bond networks perpendicular to the direction of the chains. The formation of these hydrogen-bond 2D arrays involves all the coordinated and uncoordinated water molecules and nitrate ions. A detailed view of this network is presented in Figure 3. It is interesting to note that some of the crystallization water molecules self-organize by hydrogen bonds into (H$_2$O)$_4$ clusters (O2S···O3S···O2S′···O3S′, Figure 3).

Table 1. Crystallographic data, details of data collection and structure refinement parameters for compounds **1**–**3**.

Compound	**1**	**2**	**3**
Chemical formula	$C_{24}H_{28}GdN_9NiO_{19}$	$C_{24}H_{28}N_9NiO_{19}Tb$	$C_{24}H_{28}DyN_9NiO_{19}$
M [g mol^{-1}]	962.48	964.15	967.73
Temperature [K]	293(2)	293(2)	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [Å]	9.1179(11)	9.1261(10)	9.0747(3)
b [Å]	23.3192(32)	23.287(2)	23.3593(7)
c [Å]	16.4804(15)	16.4972(11)	16.3107(5)
α [°]	90	90	90
β [°]	95.350(10)	95.441(10)	95.177(2)
γ [°]	90	90	90
V [Å^3]	3488.8(6)	3490.1(6)	3443.41(19)
Z	4	4	4
D_c [g cm^{-3}]	1.808	1.812	1.867
F(000)	1868	1872	1924
μ [mm^{-1}]	2.515	2.642	2.795
Goodness-of-fit on F^2	0.995	0.955	1.012
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0719, 0.1413	0.0520, 0.0947	0.0356, 0.0718
R_1, wR_2 (all data)	0.1845, 0.1780	0.1404, 0.1164	0.0647, 0.0810

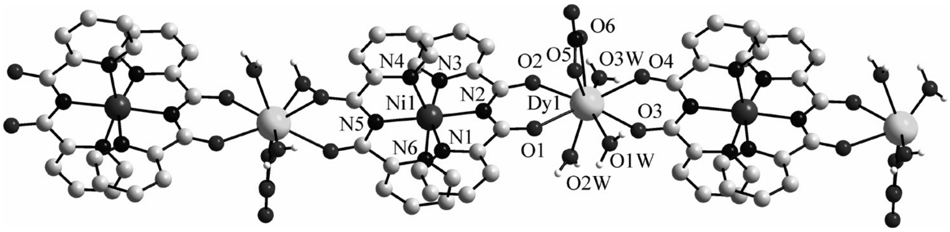

Figure 1. View of a cationic chain in crystal **3**, along with the atom-labelling scheme.

Table 2. Selected bond lengths [Å] and angles for compounds **1**–**3**.

1		**2**		**3**	
Ni1–N1	2.118(8)	Ni1–N1	2.113(4)	Ni1–N1	2.110(3)
Ni1–N2	2.025(7)	Ni1–N2	2.023(3)	Ni1–N2	2.024(3)
Ni1–N3	2.110(7)	Ni1–N3	2.102(4)	Ni1–N3	2.106(3)
Ni1–N4	2.125(7)	Ni1–N4	2.117(4)	Ni1–N4	2.115(3)
Ni1–N5	2.024(7)	Ni1–N5	2.028(3)	Ni1–N5	2.027(3)
Ni1–N6	2.126(7)	Ni1–N6	2.128(4)	Ni1–N6	2.131(3)
Gd1–O1	2.436(6)	Tb1–O1	2.429(3)	Dy1–O1	2.406(2)
Gd1–O2	2.407(6)	Tb1–O2	2.398(3)	Dy1–O2	2.397(2)
Gd1–O3	2.429(6)	Tb1–O3	2.428(3)	Dy1–O3	2.422(2)
Gd1–O4	2.424(6)	Tb1–O4	2.419(3)	Dy1–O4	2.404(2)
Gd1–O5	2.472(8)	Tb1–O5	2.460(5)	Dy1–O5	2.473(3)
Gd1–O6	2.494(8)	Tb1–O6	2.491(4)	Dy1–O6	2.481(3)
Gd1–O1W	2.403(6)	Tb1–O1W	2.389(3)	Dy1–O1W	2.349(3)
Gd1–O2W	2.398(7)	Tb1–O2W	2.386(4)	Dy1–O2W	2.336(3)
Gd1–O3W	2.394(7)	Tb1–O3W	2.363(4)	Dy1–O3W	2.341(3)

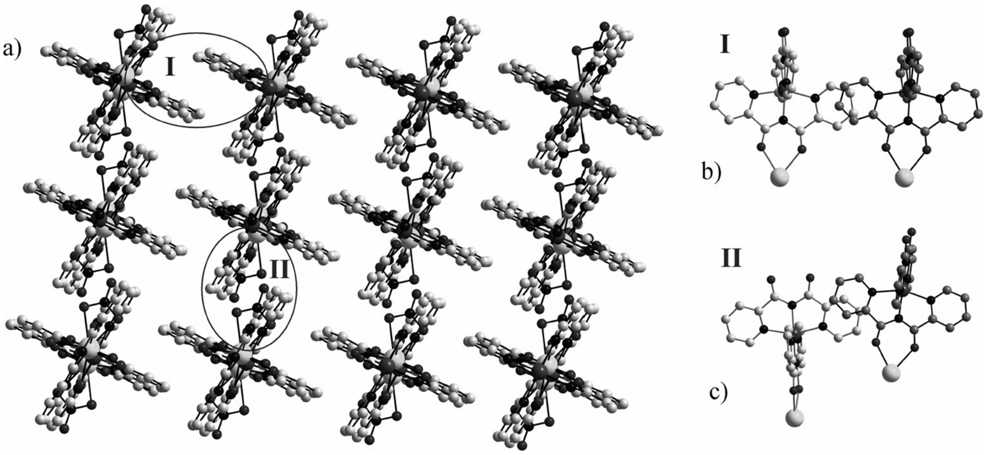

Figure 2. View of the packing diagram in crystal **3** along the *b* axis [(a) the uncoordinated nitrate ions and water molecules were omitted for clarity], and details of the π–π stacking interactions established between the phenyl rings arising from the bpca ligands from neighbouring chains [(b) and (c)].

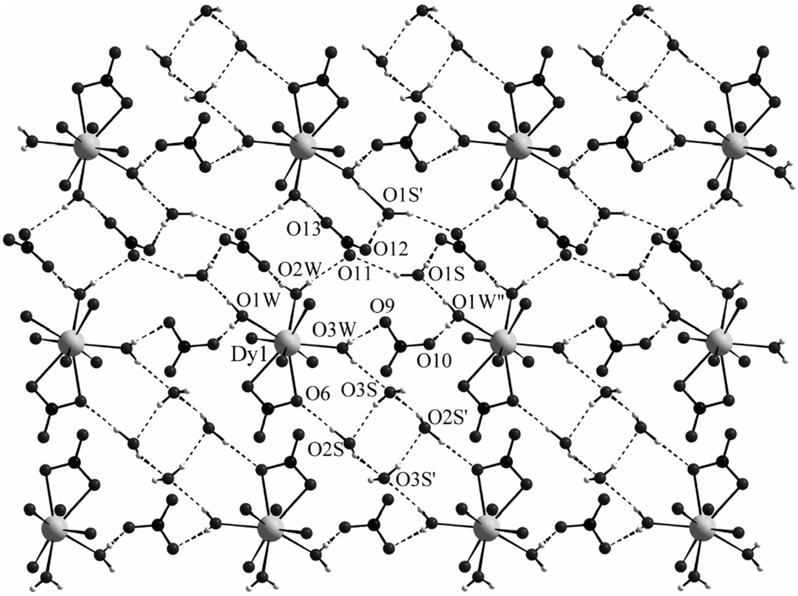

Figure 3. View of the hydrogen-bond network in crystal **3**: O1W–H2W···O1S 1.77(5) Å (*x*, *y*, *z*); O1W–H1W···O10 1.90(5) Å (–1 + *x*, *y*, *z*); O1S–H2S···O11 2.18(5) Å (–1 + *x*, *y*, *z*); O1S–H1S···O12 1.95(6) Å (1 – *x*, 1 – *y*, –*z*); O2W–H3W···O11 2.06(4) Å (*x*, *y*, *z*); O2W–H4W···O13 1.94(5) Å (1 – *x*, 1 – *y*, –*z*); O3W–H6W···O9 2.10(7) Å (*x*, *y*, *z*); O3W–H5W···O3S 2.07(6) Å (*x*, *y*, *z*); O3S–H5S···O2S 1.97(8) Å (*x*, *y*, *z*); O2S–H3S···O6 2.01(8) Å (*x*, *y*, *z*); O2S–H4S···O3S 2.13(4) Å (2 – *x*, 1 – *y*, 1 – *z*).

The collective effect of the supramolecular interactions plays a certain role in the magnetic properties of these compounds (vide infra).

Magnetic Properties

In the present study we focused on the following lanthanides as partners for the nickel(II) ion: gadolinium, terbium, dysprosium. The reasons for this are the following: (i) the nature and magnitude of the Ni^{II}–Gd^{III}-exchange interaction can, in principle, be easily determined since Gd^{III}, with an $^8S_{7/2}$ ground term, has no orbital contribution to the magnetic moment and the Heisenberg–Dirac–Van Vleck Hamiltonian can be employed;[11] and (ii) terbium(III) and dysprosium(III) are expected to bring a strong anisotropy to the magnetic moment and, consequently, one important condition to eventually observe the slow relaxation of the magnetization is fulfilled. The nickel(II) ion itself exhibits an anisotropy as a consequence of the zero-field splitting effects.

These compounds are also potentially very appealing from a dynamic point of view. In fact monodimensional compounds based on both 3d and 4f ions are quite recent[12] and to the best of our knowledge none of these display single-chain magnet (SCM) behaviour. As reminded in the introduction, SCMs based either on 3d or 4f ions are already known, but each of these categories of chains has its own drawbacks.

On the one hand, transition ions are obviously good candidates to build SCMs as they generally give rise to strong magnetic-exchange interactions in the system. Hence Co^{II}, Ni^{II}, Mn^{III}, Fe^{III} based SCMs are known.[13] But these ions are slightly anisotropic and this precludes more spectacular slow relaxation. On the other hand, some of the lanthanide cations such as the Tb^{III} and Dy^{III} are highly anisotropic. As the $g_{//}$ values are very large and the $g_{\perp}$ almost vanished, they can be considered as almost perfect Ising ions. However, the magnetic interaction between the 4f ions is rather weak as their magnetic orbitals are highly shielded by the 5s, 5p and 6s ones. In fact, reported 4f-based SCMs also involve organic radicals providing the required strong intrachain-magnetic interaction. Hence these chains are not strictly based on 4f ions but have to be considered as 2p–4f magnetic chains.[7] Finally, a huge amount of work reports quite strong magnetic-exchange interactions between transition and lanthanide ions in molecular complexes.[1–3] Therefore, combining 3d or 4f ions in the same one-dimensional edifice could offer the possibility to enhance the magnetic slow relaxation process in SCMs.

Static Magnetic Properties

$\{[\{Gd(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}](NO_3)_2\cdot 3H_2O\}_n$ (1)

The thermal variation of the $\chi_M T$ product is shown in Figure 4. It has a constant value equal to 8.99 $cm^3\,K\,mol^{-1}$ from 300 to about 70 K and then it increases slightly. Below 25 K, the $\chi_M T$ product decreases rapidly to reach a value of 7.40 $cm^3\,K\,mol^{-1}$ at 3 K. The value of $\chi_M T$ at room temperature (8.99 $cm^3\,K\,mol^{-1}$) is close to the expected value of 8.96 $cm^3\,K\,mol^{-1}$ for the two isolated Gd^{III} (S 7/2, g 2.00) and Ni^{II} (S 1, g 2.08) complexes. The experimental and calculated magnetizations from 0–6 T are shown in Figure 5. The value of the magnetization at 6 T is 8.6 μ_B, close to the expected saturated value of 9 μ_B for one Gd^{III} and one Ni^{II} ion; even if the curve is not flat. The calculated magnetization is obtained from a classical Brillouin function for two magnetically isolated Gd^{III} (S 7/2, g 2.00) and Ni^{II} (S 1, g 2.08)[9b] ions.

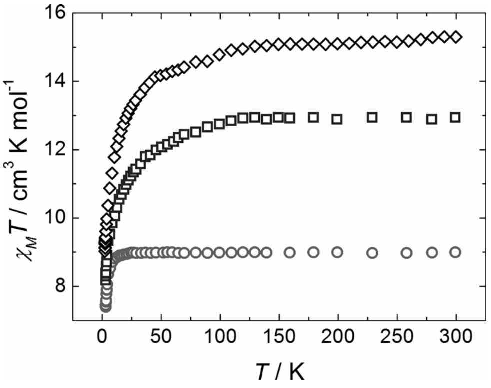

Figure 4. Thermal variation of the $\chi_M T$ product in the temperature range 3–300 K for **1** (gray circles), **2** (dark-gray squares) and **3** (diamonds).

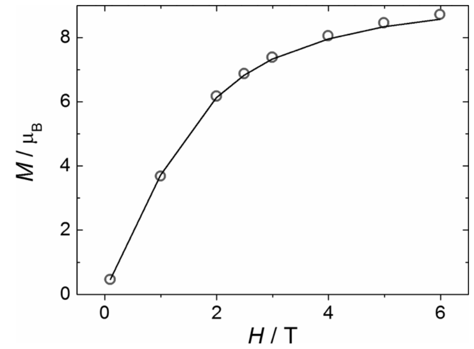

Figure 5. Experimental (gray circles) and calculated Brillouin-function (full black line) magnetizations of **1** over the field range 0–6 T.

The experimental and calculated magnetizations are quasi-superimposed (Figure 5), the magnetic-exchange interaction is indeed supposed to be very weak between the Ni^{II} and Gd^{III} ions through the $bpca^-$ ligand. At high field the calculated magnetization is lower than the experimental one leading to a possible very weak ferromagnetic interaction. The Gd^{III} ion is the only truly isotropic lanthanide ion (g 2.00) and can thus be easily modelled. The ferromagnetic-exchange interaction is confirmed by the weak but positive Curie–Weiss constant θ +0.15 K, extracted from the fit of the high temperature region of the χ^{-1} vs. T curve (Figure S1). On the other hand the decrease at low temperatures, out of the fitted region, can be attributed to two phenomena: (i) antiferromagnetic-intermolecular-exchange interactions from the short contacts between two nearest nitrate anions bonded to a Gd^{III} ion leading to the formation of a hydrogen-bond network (Figure 3) and π–π interactions between the phenyl rings of the $bpca^-$ ligands (Figure 2); and (ii) zero-field splitting of the Ni^{II} ions.

$\{[\{Tb(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}](NO_3)_2\cdot 3H_2O\}_n$ (2) and $\{[\{Dy(O_2NO)(H_2O)_3\}\{Ni(bpca)_2\}](NO_3)_2\cdot 3H_2O\}_n$ (3)

The thermal variation of the $\chi_M T$ product and the magnetization curves are shown for the two compounds in Figure 4 and S2, respectively. The values at 300 K are 12.94 $cm^3\,K\,mol^{-1}$ for **2** and 15.30 $cm^3\,K\,mol^{-1}$ for **3**. These experimental values are close to the expected values of 12.90 $cm^3\,K\,mol^{-1}$ and 15.25 $cm^3\,K\,mol^{-1}$, respectively, calculated from the equation $\chi_M T$ $(Ng^2_{Ni}\beta/3k)[S_{Ni}(S_{Ni} + 1)] + (Ng^2_{Ln}\beta^2/3k)[J_{Ln}(J_{Ln} + 1)]$, with one Ln Tb^{III} (J 6, g_J 3/2) or one Ln Dy^{III} (J 15/2, g_J 4/3)[1a] associated with one Ni^{II} ion (S 1, g 2.08). Both curves show a plateau on cooling until 150 K and then decrease in a monotonous manner. At 3 K the $\chi_M T$ product has a value of 8.30 $cm^3\,K\,mol^{-1}$ and 9.60 $cm^3\,K\,mol^{-1}$ for the Tb^{III} and Dy^{III} derivatives, respectively.

The Tb^{III} ion is a non-Kramer ion having a $^7F_6$ ground state whereas the Dy^{III} ion is a Kramer ion with a $^6H_{15/2}$ ground state.[11] Including them in a one-dimensional compound is of interest as it brings great anisotropy to the system and can give rise to SCM behaviour.[7] However, the fitting of the magnetic data of such a sample is complicated by the strong spin-orbit coupling affecting the lanthanide ions. In particular, the ground state is split into Stark sublevels under the influence of the crystal field.[1b] The crystal-field effects are of the order of 100 cm^{-1} for lanthanides. Consequently when the temperature decreases, the depopulation of these sublevels leads to a deviation from the Curie law leading to a variation of the $\chi_M T$ product even in the absence of any exchange interaction. One can consider that at low temperature only the non-Kramers ground state (for Tb^{III} ion) or Kramers doublet (for Dy^{III} ion) are populated because the energy state separation between the ground state and the first exited state is greater than 1500 cm^{-1}.[11] The magnetic properties can thus be modelled using an effective spin S_{eff} 1 (for Tb^{III} ion) and S_{eff} 1/2 (for Dy^{III} ion) with a very anisotropic g_{eff} value. Below 150 K, the decrease of the $\chi_M T$ product for both compounds is therefore attributed to the depopulation of the Stark sublevels of the Ln^{III} ions and not to a magnetic-exchange interaction. This phenomenon hampers the observation of an eventual magnetic-exchange interaction between the Ni^{II} and the Ln^{III} ions. However, some of us, in a previous work on a trinuclear compound of formula $\{[Ni(bpca)_2][Dy(hfac)_3](CHCl_3)\}$ (noted **4**),[8c] have demonstrated that a weak ferromagnetic-exchange interaction between the Ni^{II} and the Dy^{III} ions through the $bpca^-$ ligand can occur. Moreover previous investigations on similar compounds have shown that with these types of compounds Dy^{III}- and Tb^{III}-based complexes display magnetic-exchange interactions of the same nature.[1a]

The magnetic analysis of the Gd^{III} derivative gives us evidence of a weak ferromagnetic exchange interaction with the Ni^{II} ion, and hence we found it reasonable to consider that the Ln^{III} and the Ni^{II} ions are weakly ferromagnetically coupled in **2** and **3**. Given the structural configuration of these compounds, we believe that the interchain interactions should be considered as the principal cause of the low temperature decrease of $\chi_M T$. The low value of the intrachain-magnetic interaction, together with the numerous pathways expected to alter the good isolation of the chain, do not allow for a fit of the $\chi_M T$ vs. T curve with a ferromagnetic-chain model.

Dynamic Magnetic Properties

For the reasons stated above we focus our *ac* analysis on the Tb^{III} (Figure S3) and Dy^{III} (Figure 6) derivatives. In the absence of an external field a small frequency dependence is visible on either the in or out-of-phase signals (χ' and χ'', respectively). Even if weak, these signals differ notably from the noise of the susceptometer. However, both derivatives display a low χ''/χ' ratio, with most of the susceptibility coming from the in-phase component of the magnetization. We thus found it unreasonable to attribute this frequency dependence to a magnetic slow relaxation.

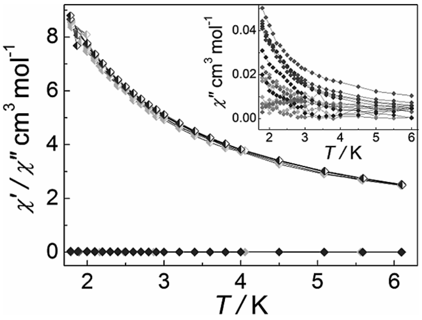

Figure 6. Temperature dependence of the in-phase (half filled symbols) and out-of-phase (filled symbols) susceptibility for **2** (from 100 to 20000 Hz). In the inset the out-of-phase susceptibility is enlarged.

Different reasons may explain the absence of a divergence of the $\chi_M T$ product at low temperature, together with the non-relevant χ'' signal. The first and obvious one is the very weak intrachain-magnetic interaction. As described thanks to the study of **1**, the interaction is very low (Curie–Weiss constant θ +0.15 K) in these chains. However, no 3D ordering is visible here. This is in contrast with what has been observed in other reported chains.[12] Another reason is the bad magnetic isolation of the chains. The π-stacking interactions (Figure 2) between the chains and the extended network created by the hydrogen bonds (Figure 3) strongly alter the ratio between the intra- and interchain interactions. This hampers the apparition of a single-chain magnetic behaviour.

In order to further explain the properties of these two chains we want to compare them to the previously cited {[Ni(bpca)$_2$][Dy(hfac)$_3$](CHCl$_3$)} (**4**) compound. This complex is a field dependant SMM, in the sense that its slow relaxation is switched on by a small external field. It thus displays a field dependence at the maximum of the χ'' values. In fact it exhibits a low χ''/χ' ratio in the zero-external field, which is a consequence of a fast zero-field tunnelling of the magnetization. Recent results on phthalocyaninate derivatives of lanthanide[6] have shown that this fast tunnelling can be suppressed by applying a small static field. Surprisingly it was found that **2** and **3** do not behave in the same way and do not show any field dependence of the out-of-phase susceptibility.

A last consideration can be made thanks to a close analysis of the molecular structure of **3** and **4**. This latter complex is very similar to the chain. Its inner core formed by the [Ni(bpca)$_2$] moiety is highly similar to that of the chain. The major deviations in the Ni^{II}–N$_x$ distances and angles are about 0.02 Å and 2°, respectively. From the magnetic point of view the similarity in the compression of the octahedron around the nickel ion allows us to assume that the anisotropy is equal in **3** and **4**. The main differences between the two compounds are obviously in the environment of the Dy^{III} ions. The {[Ni(bpca)$_2$][Dy(hfac)$_3$](CHCl$_3$)} complex is made up of Dy^{III} coordinated to three hfac$^-$ entities and two oxygen atoms from the bpca$^-$ ligand, which can be considered to be in a *cis* position. This arrangement gives a coordination polyhedron with two quasi-quadrilateral faces composed of four oxygen atoms [torsion angle (O10–O9–O15–O13) 176.6°, (O14–O16–O11–O12) 11.43°]. The coordination polyhedron is close to a square antiprism, a D_{4d} site symmetry.

On the contrary the coordination polyhedron of Dy^{III} in **3** has a different symmetry. Indeed the torsion angle between the four oxygen atoms sharing the possible quadrilateral face is (O2–O1–O6–O5) 165.7°, which is now quite far from the expected 180°. Hence the coordination polyhedron, even if slightly distorted, is close to a 4-capped square antiprism, having a C_{4v} site symmetry.[14]

Ishikawa and coworkers have shown how the magnetic slow relaxation of 4f systems is strongly related to the symmetry of the lanthanide polyhedron.[15] Unfortunately quantitative analyses were only performed for the D_{3h} symmetry. But by the same manner, it seems reasonable to consider that in our case the passage from a D_{4d} to a D_{2d} symmetry affects the dynamic properties of the Dy(hfac)$_3$ moiety. In fact, the crystal field potentials for these two site symmetries are quite different.[16] This may be, together with the above hypotheses, an explanation for the absence of a slow relaxation in **2** and **3**. Over the investigated temperature range we are not able to assign unambiguously the origin of the out-of-phase signal. Given the very low interaction between the magnetic centres along the chain, it seems reasonable to think that the magnetic slow relaxation of the lanthanide ion is one of the origins of the χ'' signal.

Conclusions

Compounds **1**, **2** and **3** are examples of 3d–4f molecular chains in which the magnetic intrachain interactions are quite weak. This, together with their bad magnetic isolation, hampers the apparition of a magnetic slow relaxation in **2** and **3**. However, we can learn something from these compounds. On comparing them with **4**, the absence of any field dependence of the out-of-phase susceptibility in **2** and **3** may highlight the role played by the symmetry of the lanthanide polyhedron. The use of the lanthanide precursor in an appropriate symmetry environment may be an additional key to favour the slow relaxation of the lanthanide ion in 4f-based compounds. To the best of our knowledge, compounds **1**–**3** are the first coordination polymers constructed by using [M(bpca)$_2$] complexes as building blocks.

Experimental Section

Syntheses: The [Ni(bpca)$_2$] complex was obtained according to ref.[9b] The compounds [{Gd(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (**1**), [{Tb(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (**2**) and [{Dy(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (**3**) were obtained by the same manner: [Ni(bpca)$_2$] (0.05 mmol) was dissolved in a mixture of CHCl$_3$/CH$_3$OH (1:1, 5 mL) and added to a methanolic solution (3 mL) containing Gd(NO$_3$)$_3$·6H$_2$O (0.05 mmol) for **1**, Tb(NO$_3$)$_3$·6H$_2$O (0.05 mmol) for **2** and Dy(NO$_3$)$_3$·5H$_2$O (0.05 mmol) for **3**, respectively. After 2–3 min the combination of the components produced very fine needle-like light-brown crystals. These same solutions, containing the crystalline precipitates, were allowed to stand at room temp. for 1–2 d, which resulted in the dissolution of the precipitates, and further standing for 2 d led to the occurrence of the prismatic light-brown crystals of **1**, **2** and **3**, by slow evaporation.

Gd(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (1): Yield 82%. IR data (KBr): ṽ = 3375 (s, broad), 1675 (s), 1596 (m), 1563 (m), 1470 (w), 1447 (w), 1382 (vs), 1345 (s), 1283 (m), 1114 (w), 1090 (w), 1043 (w), 1018 (w), 833 (vw), 799 (w), 757 (m), 713 (w), 628 (m), 544 (vw), 517 (w), 418 (w) cm^{-1}. C$_{24}$H$_{28}$GdN$_9$NiO$_9$ (962.48): calcd. C 29.92, H 2.91, N 13.09; found C 30.4, H 2.7, N 12.9.

[{Tb(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (2): Yield 85%. IR data (KBr): ṽ = 3367 (s, broad), 1675 (s), 1597 (m), 1563 (m), 1471 (w), 1449 (w), 1384 (vs), 1347 (s), 1291 (m), 1150 (w), 1093 (w), 1044 (w), 1018 (w), 833 (vw), 811 (vw), 758 (m), 718 (w), 633 (m), 519 (w), 420 (w) cm^{-1}. C$_{24}$H$_{28}$N$_9$NiO$_9$Tb (964.15): calcd. C 29.87, H 2.90, N 13.07; found C 29.3, H 3.1, N 12.8.

[{Dy(O$_2$NO)(H$_2$O)$_3$}{Ni(bpca)$_2$}](NO$_3$)$_2$·3H$_2$O (3): Yield 91%. IR data (KBr): ṽ = 3356 (s, broad), 1674 (s), 1597 (m), 1561 (m), 1473 (m), 1451 (m), 1384 (vs), 1297 (m), 1150 (vw), 1094 (w), 1046 (w), 1017 (w), 833 (vw), 811 (vw), 759 (m), 720 (w), 634 (m), 519 (w), 420 (w) cm^{-1}. C$_{24}$H$_{28}$DyN$_9$NiO$_9$ (967.73): calcd. C 29.76, H 2.89, N 13.02; found C 29.3, H 2.9, N 13.1.

X-ray Structure Determinations: X-ray diffraction measurements were performed with a Bruker-Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. Calculations were performed using the SHELX-97 crystallographic software package.

CCDC-653381 -653383 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements: All magnetic measurements were performed using pellets in order to avoid orientation of these very anisotropic materials. The *dc*-magnetic susceptibility measurements were performed with a Cryogenic S600 SQUID magnetometer between 2 and 300 K in an applied magnetic field of 0.1 T for temperatures in the range 2–50 K and 1 T for temperatures between 50 and 300 K. These measurements were all corrected for the diamagnetic contribution as calculated with Pascal's constants. The *ac*-magnetic susceptibility measurements were performed on the same samples using a homemade *ac*-probe operating in the range 100–25000 Hz.[17]

Supporting Information (see also the footnote on the first page of this article): Temperature dependence of χ^{-1} for compound **1** (Figure S1), magnetization versus field curves for compounds **2** and **3** (Figure S2), Temperature dependence of the in- and out-of-phase susceptibilities for compound **3** (Figure S3).

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