

In search of 3d/4f-metal single-molecule magnets: Nickel(II)/lanthanide(III) coordination clusters*

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Abstract: The importance of 3d/4f-metal cluster chemistry is outlined, and the employment of 2-pyridyl ketone- and 2-pyridyl oxime-based ligands for the preparation of low-nuclearity Ni^{II}/Ln^{III} complexes (Ln = lanthanide) is reviewed. The synthetic utility of the “metal complexes as ligands” and “one-pot” approaches is critically discussed. The small nuclearity of the products permits the in-depth analysis of their magnetic properties.

Keywords: coordination clusters; magnetic properties; nickel(II)/lanthanide(III) clusters; di-2-pyridyl ketone; 2-pyridyl oximes; single-molecule magnets.

INTRODUCTION

Mixed-metal materials are an important research area for many groups around the world in the fields of condensed-matter physics and solid-state chemistry [1,2]. Molecular chemists have also developed a great scientific interest in mixed-metal compounds during the last 20 years or so. One reason for this is the continuous search for complexes with interesting magnetic properties, such as single-molecule magnets (SMMs) [3,4], single-chain magnets [5], 3D molecule-based magnets [6] and magnetic refrigerants [7,8]. Another reason is the search for models of various heterometallic sites in biology, including the elucidation of the structure, spectroscopic features, and mechanistic aspects of the {CaMnO₅} core of the oxygen evolving center within the photosynthetic apparatus of green plants and cyanobacteria [9,10]. Polynuclear 3d/4f-metal complexes (coordination clusters [11] or simply clusters [12]) occupy a unique place among mixed-metal molecular materials because they provide an alternative [13] to homometallic transition-metal SMMs [14,15].

SMMs are individual molecules (mainly polynuclear) that function as single-domain nanoscale magnets, thus representing a molecular approach to nanomagnetism [16]. They derive their properties [14,15] from a high spin (*S*) in the ground state and easy-axis magnetoanisotropy (negative zero-field

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splitting parameter, D), which result in hysteresis in magnetization vs. applied magnetic field scans below a characteristic blocking temperature, T_B . The upper limit to the relaxation barrier (U) is $S^2|D|$ for integer spins and $(S^2 - 1/4)|D|$ for half-integer spins; quantum tunneling of the magnetization (QTM) [17] makes the effective (true) barrier (U_{eff}) always less than U . The molecular nature of SMMs gives some advantages (synthesis by solution methods, crystallinity, uniform size distribution, facile variation of peripheral ligands, solubility in a variety of organic solvents, sub-nanoscale dimensions, etc.) over traditional magnets. SMMs offer the potential for use in molecule-based information storage of high density and molecular spintronics [18], as well as quantum information processing [19].

Most SMMs are 3d-metal clusters with the majority of them being Mn clusters containing at least some Mn^{III} centers [14,15]. Several groups, including our own, have recently been exploring mixed 3d/4f-metal complexes as attractive routes to new SMMs. The rationale behind such efforts is to take advantage of the lanthanide(III) [Ln^{III}] ion's significant spin and/or its large anisotropy to generate SMMs with properties better than and different from those of the homometallic ones [13]. Indeed, there are now several $\text{Cr}^{\text{III}}/\text{Ln}^{\text{III}}$ [20], $\text{Mn}/\text{Ln}^{\text{III}}$ [4,21–23], $\text{Fe}^{\text{III}}/\text{Ln}^{\text{III}}$ [24–26], $\text{Co}^{\text{II}}/\text{Ln}^{\text{III}}$ [27–29], $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ [30–35], and $\text{Cu}^{\text{II}}/\text{Ln}^{\text{III}}$ [36–39] SMMs, with the majority of them being $\text{Mn}/\text{Ln}^{\text{III}}$ clusters (again containing some Mn^{III} atoms). It should be mentioned at this point that a $\text{Mn}^{\text{III}}_6\text{Tb}^{\text{III}}_2$ cluster possesses the record barrier to magnetization reversal for a 3d- and 3d/4f-metal SMM ($U_{\text{eff}} = 103$ K), providing insights into how the full benefit of the Ln^{III} ions to the mixed-metal SMM area can be realized [40].

We have been targeting synthetic routes that might yield *low-nuclearity* 3d/4f-metal clusters that are amenable to a detailed study of the nature and strength of their magnetic exchange interactions, which would permit a subsequent rationalization of the observed ground-state S value. Such studies are not possible for high-nuclearity clusters because of [41] (i) the resulting large number of pairwise exchange interactions, (ii) spin-orbit coupling effects which preclude magnetic susceptibility fits for large clusters, and (iii) the weak nature of the 3d–4f and 4f–4f exchange interactions.

This short review will deal with a brief summary of our efforts in the area of $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ cluster chemistry based on two particular ligand families. Emphasis will be given on synthetic, structural, and magnetic aspects of this chemistry. Most of the results presented here have recently been published. A review article on 3d/4f-metal cluster chemistry has never appeared. In the excellent review by Sessoli and Powell [13] entitled “Strategies towards single molecule magnets based on lanthanide ions”, which covers 2p/4f, 3d/4f and pure 4f polynuclear systems, some information is given on 3d/4f-metal clusters based on Schiff bases derived from o-vanillin and tris(hydroxymethyl)aminomethane, bis(2-pyridyl-carbonyl)amine, mixed pivalate/N-substituted diethanolamines ligation, and pivalate/furane-2-carboxylate “blends”.

SYNTHETIC STRATEGIES TOWARD 3d/4f-METAL CLUSTERS

From a synthetic viewpoint, methods must be developed to combine 3d- and 4f-metal ions within a cluster. This is not an easy task because simply mixing the starting materials often leads to pure 3d-metal complexes; the driving force for this is the ligand field stabilization for 3d-metal compounds [13]. We and others have been employing two general approaches for the preparation of 3d/4f-metal clusters. The first approach is the “metal complexes as ligands” strategy [42]. In this approach, mononuclear or dinuclear 3d-metal complexes with uncoordinated O-donor groups are used as reactants; such complexes can be considered as “ligands” (metalloligands) and further react with the oxophilic Ln^{III} centers. The second approach is based on “one-pot” processes; these require a mixture of the appropriate 3d-metal and Ln^{III} salts, and a carefully designed organic ligand featuring distinct coordination compartments for preferential binding of the 3d-metal ion and the Ln^{III} .

Ni(II)/Ln(III) CLUSTERS BASED ON VARIOUS FORMS OF DI-2-PYRIDYL KETONE

The anions of the *gem*-diol, $(\text{py})_2\text{C}(\text{OH})_2$, and hemiketal, $(\text{py})_2\text{C}(\text{OR})(\text{OH})$, forms of di-2-pyridyl ketone, $(\text{py})_2\text{CO}$ (Fig. 1) are excellent sources of 3d homometallic clusters [43–45] and 4f-metal complexes [46,47] with interesting structures and properties. By contrast, with only one exception in $\text{Cu}^{\text{II}}/\text{Ln}^{\text{III}}$ chemistry [48], there was no progress in synthesizing 3d/4f-metal clusters derived from these ligands. The possibility of using $(\text{py})_2\text{CO}$ -based ligands in this area has been encouraging because the relatively soft-donor N atoms tend to bind to 3d-metal ions, whereas the hard-donor O atoms tend to bind to oxophilic Ln^{III} ions.

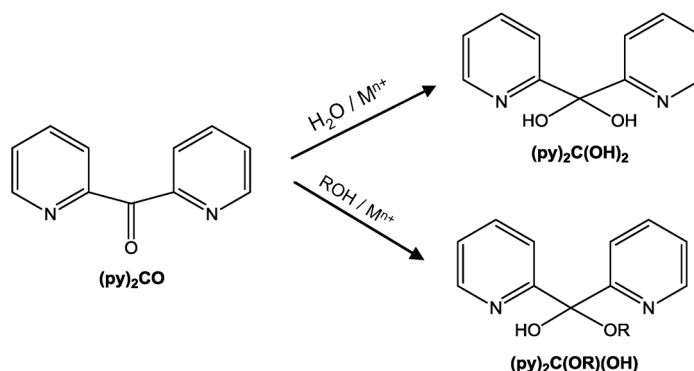


Fig. 1 Di-2-pyridyl ketone-based ligands discussed in this short review. Note that $(\text{py})_2\text{C}(\text{OH})_2$, $(\text{py})_2\text{C}(\text{OR})(\text{OH})$ and their anions do not exist as free species, but they exist only in the presence of metal ions ($\text{M}^{\text{n}+}$ = metal ion; $n = 2$ or 3 ; $\text{R} = \text{Me}, \text{Et}, \dots$).

Complexes $[\text{Ni}_2\text{Ln}\{(\text{py})_2\text{C}(\text{OEt})(\text{O})\}_4(\text{NO}_3)(\text{H}_2\text{O})_2][\text{Ln}(\text{NO}_3)_5](\text{ClO}_4)_2$ ($\text{Ln} = \text{Tb}$, **1**; $\text{Ln} = \text{Dy}$, **2**) and the Y^{III} analogue (**3**) [49,50] were prepared by the 1:1 reaction of the metalloligand $[\text{Ni}(\text{O}_2\text{CMe})\{(\text{py})_2\text{CO}\}\{(\text{py})_2\text{C}(\text{OH})_2\}](\text{ClO}_4)$ (**4**, Fig. 2) [51] and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in EtOH under mild heating in 65–70 % yields.

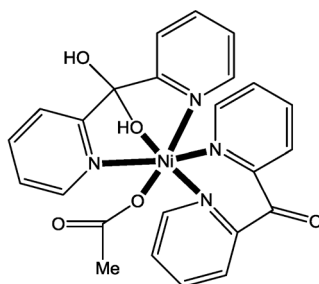


Fig. 2 The octahedral cation $[\text{Ni}(\text{O}_2\text{CMe})\{(\text{py})_2\text{CO}\}\{(\text{py})_2\text{C}(\text{OH})_2\}]^+$ of the metalloligand **4** used in the preparation of **1–3**.

Complexes **1–3** are isomorphous. The fact that **3** is isomorphous with **1** and **2** is not surprising; it is well known that Y has atomic, metallic, and ionic radii that are very close to those of Tb, Dy, Ho, and Er; hence, it resembles the later lanthanides very closely in its chemistry. The molecular structure of **1** consists of $[\text{Ni}_2\text{Tb}\{(\text{py})_2\text{C}(\text{OEt})(\text{O})\}_4(\text{NO}_3)(\text{H}_2\text{O})_2]^{2+}$ cations (Fig. 3, left), $[\text{Tb}(\text{NO}_3)_5]^{2-}$ anions (Fig. 3,

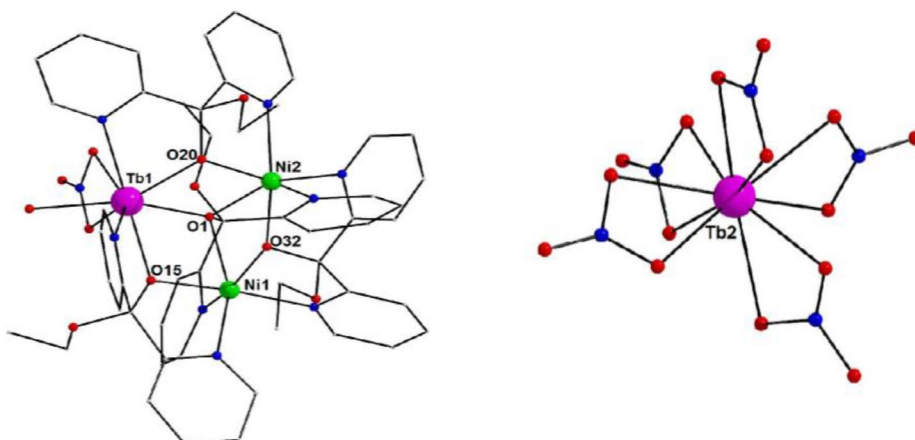


Fig. 3 The structures of one of the two crystallographically independent $[\text{Ni}_2\text{Tb}\{(\text{py})_2\text{C}(\text{OEt})(\text{O})\}_4(\text{NO}_3)(\text{H}_2\text{O})\}^{2+}$ cations (left) and the 10-coordinate $[\text{Tb}(\text{NO}_3)_5]^{2-}$ anion (right) that are present in the crystal structure of **1**.

right), and ClO_4^- anions in a 2:1:2 ratio. The Tb^{III} atom in $[\text{Tb}(\text{NO}_3)_5]^{2-}$ is coordinated by five bidentate chelating nitrate groups and has a sphenocorona coordination geometry [52,53]. The cation contains one Tb^{III} and two Ni^{II} atoms in a triangular arrangement capped by a central $\mu_3\text{-O}^-$ atom (O1) of a unique 3.3011 (Harris notation [54]) $(\text{py})_2\text{C}(\text{OEt})(\text{O})^-$ ligand (Fig. 4). The triangular unit is essentially isosceles with atom O1 ~ 1.2 Å out of the Ni_2Tb plane. Each metal–metal edge is bridged by the deprotonated, alkoxido O atom of one 2.2011 $(\text{py})_2\text{C}(\text{OEt})(\text{O})^-$ ligand (Fig. 4). The core is $\{\text{Ni}_2\text{Tb}(\mu_3\text{-OR}')(\mu_2\text{-OR}'')\}_3^{3+}$. The 8-coordinate Tb^{III} atoms of the two cations create a distorted coordination polyhedron close to a biaugmented trigonal prism. An alternative way of describing the structure of the cations is as a distorted defective cubane in which the fourth metal site is missing; three O atoms (O15, O20, O32) are therefore only doubly bridging (instead of triply in a normal cubane).

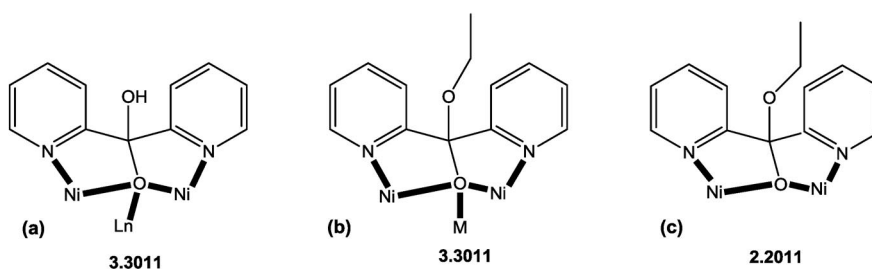


Fig. 4 The coordination modes of $(\text{py})_2\text{C}(\text{OH})(\text{O})^-$ (a) and $(\text{py})_2\text{C}(\text{OEt})(\text{O})^-$ (b and c) in complexes **1–3**, **5** and **6**, and the Harris notation that describes these modes ($\text{Ln} = \text{Gd}, \text{Tb}$; $\text{M} = \text{Y}, \text{Tb}, \text{Dy}$; $\text{M}' = \text{Y}, \text{Gd}, \text{Tb}, \text{Dy}$).

It is obvious that the “metal complexes as ligands” strategy is not effective in the $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}/(\text{py})_2\text{CO}$ chemistry in the sense that the metalloligand **4** has not been incorporated as a structural component in **1–3**.

Reaction systems involving $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $(\text{py})_2\text{CO}$, and $\text{NaO}_2\text{CMe} \cdot 3\text{H}_2\text{O}$ in warm EtOH, i.e., “one-pot procedures”, gave complexes $[\text{Ni}_2\text{Ln}\{(\text{py})_2\text{C}(\text{OEt})(\text{O})\}_3\{(\text{py})_2\text{C}(\text{OH})(\text{O})\}(\text{NO}_3)(\text{H}_2\text{O})(\text{ClO}_4)_2]$ in very good yields ($>70\%$), e.g., for $\text{Ln} = \text{Gd}$ (**5**) and $\text{Ln} = \text{Tb}$ (**6**). The $[\text{Ln}(\text{NO}_3)_5]^{2-}$ ions are absent in the structures of **5** and **6**, while their dications are structurally similar to those of **1–3**, the only differences being the replacement of the 3.3011 $(\text{py})_2\text{C}(\text{OEt})(\text{O})^-$ of

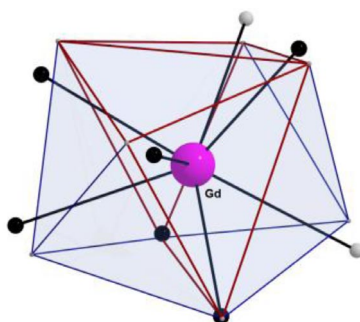


Fig. 5 The triangular dodecahedral coordination sphere of Gd^{III} in the structure of **5**. The very small spheres define the vertices of the ideal polyhedron.

the latter by the unique 3.3011 (py)₂C(OH)(O)⁻ ligand (Fig. 4) in the former, and the coordination polyhedron for Gd^{III} and Tb^{III}, which is close to a triangular dodecahedron (Fig. 5) [52,53].

Complexes **1**, **2**, **5**, and **6** are characterized by ferromagnetic Ni^{II}...Ni^{II} and Ni^{II}...Ln^{III} exchange interactions. The ferromagnetic behavior of the Ni^{II}₂ unit is independently supported by the study of **3**, which contains the diamagnetic Y^{III} atom. Complex **3** is ferromagnetic with a J value of +8.0(2) cm⁻¹ (based on the $H = -J\hat{S}_1 \cdot \hat{S}_2$ formalism). The presence of strong spin-orbit coupling effects in **1**, **2**, and **6** makes the fitting of the dc magnetic susceptibility data to obtain Ni^{II}...Ni^{II} and Ni^{II}...Ln^{III} exchange parameters far from straightforward. Such an analysis benefits greatly from the availability and parallel study of the Gd^{III} ($S = 7/2$, $L = 0$) complex **5**. The best set of parameters obtained using the analytical equation derived from the Hamiltonian $H = -J_1(\hat{S}_{\text{Gd}} \cdot \hat{S}_{\text{Ni1}} + \hat{S}_{\text{Gd}} \cdot \hat{S}_{\text{Ni2}}) - J_2(\hat{S}_{\text{Ni1}} \cdot \hat{S}_{\text{Ni2}})$ are $J_1 = +1.03(8)$ cm⁻¹, $J_2 = +0.9(2)$ cm⁻¹ and $g = 2.25$. Magnetization data at 2 K reveal a saturation under 5 T at 12.7 μ_B, indicating an $S = 11/2$ ground state. Most of the studied Ni^{II}...Gd^{III} interactions are weakly ferromagnetic [31,55–58], although antiferromagnetic ones have also been reported [32,59,60].

The room temperature $\chi_M T$ value of 17.4 cm³ K mol⁻¹ for **6** (χ_M is the molar magnetic susceptibility and T is the absolute temperature) is larger than the ~14.2 cm³ K mol⁻¹ value expected for one Tb^{III} (⁷F₆ free ion, $S = 3$, $L = 3$, $g_J = 3/2$) and two Ni^{II} ($S = 1$, $g = 2.2$) non-interacting ions, probably from the spin-orbit effects of the Tb^{III} center in a distorted crystal field. The product decreases gradually to a well-defined minimum of 16.5 cm³ K mol⁻¹ at 30 K, most likely to the depopulation of the Stark sublevels of Tb^{III}, before increasing to 18.2 cm³ K mol⁻¹ (Fig. 6); the latter increase clearly indicates ferromagnetic exchange interactions and the presence of a high-spin state for this cluster. Magnetization measurements indicated a small anisotropy for the triangular unit and as a consequence no SMM behavior was observed.

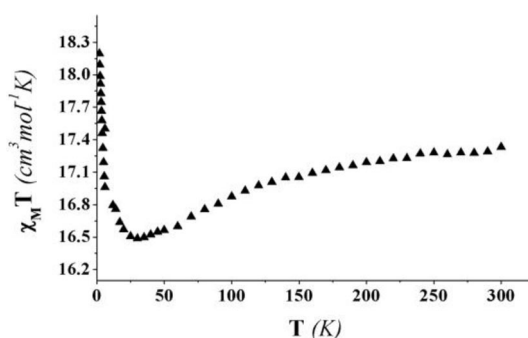


Fig. 6 Plot of $\chi_M T$ vs. T for complex **6**.

The $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}/(\text{py})_2\text{CO}$ chemistry under solvothermal conditions has resulted in novel “star”-shaped $\{\text{Ni}_3\text{Ln}\}$ clusters and SMMs containing an in situ reduced form of the ligand (di-2-pyridyl methanol) [32].

Ni(II)/Ln(III) CLUSTERS BASED ON 2-PYRIDYL OXIMES

2-Pyridyl oximes $[(\text{py})\text{C}(\text{R})\text{NOH}]$; $\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{NH}_2, \text{CN}, \dots$; Fig. 7a) are currently popular ligands in coordination chemistry [61]. Their anions (2-pyridyloximate ligands) are particularly versatile in that they possess simultaneously chelating and bridging (μ_2 – μ_4) capabilities. Such ligands have been key “players” in several areas of single-molecule [62] and single-chain magnetism [63]. The activation of 2-pyridyl oximes by transition-metal ions toward further reactions is also becoming a fertile area of synthetic chemistry [64]. Although many interesting 3d- and mixed 3d/3d'-metal clusters with anionic 2-pyridyl oximes have been prepared and studied [61,62,64–72] (refs. [64–72] describe recent work from our groups), no 3d/4f-metal clusters were known prior to our involvement in this project. The $(\text{py})\text{C}(\text{R})\text{NO}^-$ ions are attractive ligands for 3d/4f-metal chemistry when the 3d metal is divalent, because the softer (HSAB model) N atoms will prefer the 3d M^{II} atom, whereas the hard, deprotonated oximate O atom will favour binding to oxophilic Ln^{III} atoms (Fig. 7b). Because of space limitation, we shall briefly describe below the use of methyl 2-pyridyl ketoxime $[(\text{py})\text{C}(\text{Me})\text{NOH}]$, i.e., $\text{R} = \text{Me}$ in Fig. 7) in mixed $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ chemistry.

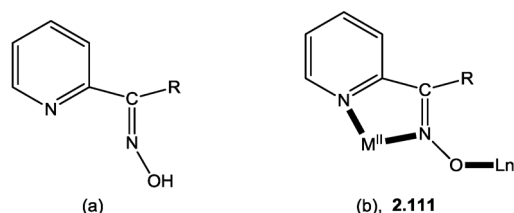


Fig. 7 General structural formula of simple 2-pyridyl oximes ($\text{R} = \text{H}, \text{Me}, \text{Ph}, \text{NH}_2, \text{CN}, \dots$) (a) and the common coordination mode of 2-pyridyloximate ligands in 3d/4f-metal chemistry ($\text{M}^{\text{II}} = \text{divalent 3d metal}$).

The metalloligand chosen is the mononuclear octahedral complex $[\text{Ni}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2\{(\text{py})\text{C}(\text{Me})\text{NOH}\}]$ (7) illustrated in Fig. 8. This precursor possesses three free O atoms, two from the deprotonated oximate groups and one from the neutral oxime group, in a *cis-cis-cis* or *fac* configuration. It can thus be considered as a tridentate chelating “ligand”.

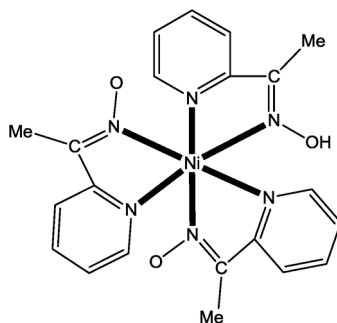


Fig. 8 Schematic representation of the metalloligand $[\text{Ni}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2\{(\text{py})\text{C}(\text{Me})\text{NOH}\}]$ (7).

The 1:1 reactions of **7** and $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in various solvents gave complexes $[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2(\text{NO}_3)_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}]$ in good yields. The molecular structure [73] of the Tb^{III} member of this family (**8**) is shown in Fig. 9. The three O atoms that were free in **7** are indeed coordinated to the Tb^{III} atom in **8**, as anticipated. The *fac* disposition of the oxime/oximate groups is preserved in the product. Three chelating nitrate groups complete a capped square antiprismatic geometry [74] around the lanthanide.

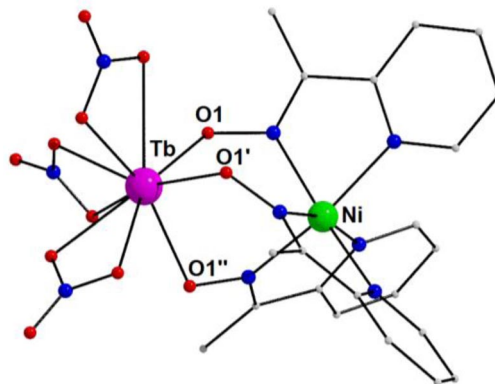


Fig. 9 The molecular structure of **8**. The 3-fold crystallographic axis, which connects the two metal ions, is likely masking the presence of a proton statically disordered among the three ligand groups [73].

Since the coordination sphere of the Ln^{III} atom in the dinuclear complexes is completed by three terminal groups, we suspected that using a 2:1 metalloligand to Ln^{III} reaction ratio would lead to trinuclear Ni_2Ln clusters. The reactions of $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with 2 equiv of **7** and 2 equiv of Et_3N in MeOH gave complexes $[\text{Ni}_2\text{Ln}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_6(\text{NO}_3)]$ in moderate yields. The molecular structure [73] of the Tb^{III} member (**9**) of this family of trinuclear species is shown in Fig. 10. The cation can be considered as a “mononuclear” octahedral Tb^{III} complex featuring two deprotonated, tridentate chelating metalloligands. As expected, **9** can also be prepared by the reaction of **8** with 1 equiv of **7** in the presence of a base.

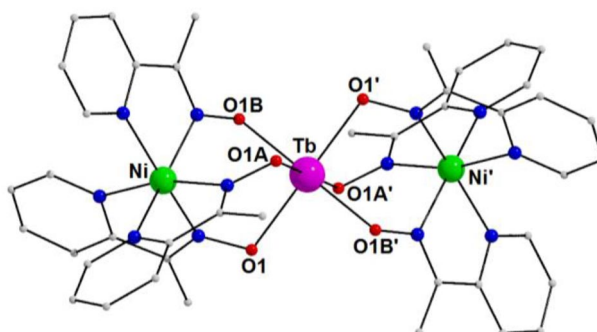


Fig. 10 The molecular structure of centrosymmetric **9**.

In the starting metalloligand **7** and the dinuclear complex **8**, one of the three organic ligands is neutral. We suspected that the presence of a base (while keeping the $\text{Ni}^{\text{II}}:\text{Ln}^{\text{III}}$ ratio 1:1) could affect the product identity and this has, indeed, turned out to be the case. Repeating the process that led to

$[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2(\text{NO}_3)_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}]$, but in the presence of 1 equiv of base (e.g., Et_3N) per **7**, gave tetranuclear clusters of the general formula $[\text{Ni}_2\text{Ln}_2\{(\text{py})\text{C}(\text{Me})\text{NO}\}_6(\text{NO}_3)_4]$ in good yields. The molecular structure [73] of the Dy^{III} (**10**) member of this family of tetranuclear species is shown in Fig. 11. The centrosymmetric molecule consists of two dinuclear $\text{NiDy}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2(\text{NO}_3)_2$ units which have a structural resemblance to the Dy^{III} analogue of **8**. The formerly neutral oxime group is now deprotonated and bridging providing the interdimer linkage. Thus, four $(\text{py})\text{C}(\text{Me})\text{NO}^-$ anions behave as 2.111 ligands (Fig. 7b) and two as 3.211 ligands. The coordination polyhedron of Dy1 (and its symmetry equivalent) is best described as triangular dodecahedron. As expected, treatment of **8** with base leads to $[\text{Ni}_2\text{Tb}_2\{(\text{py})\text{C}(\text{Me})\text{NO}\}_6(\text{NO}_3)_4]$ (**11**) [73].

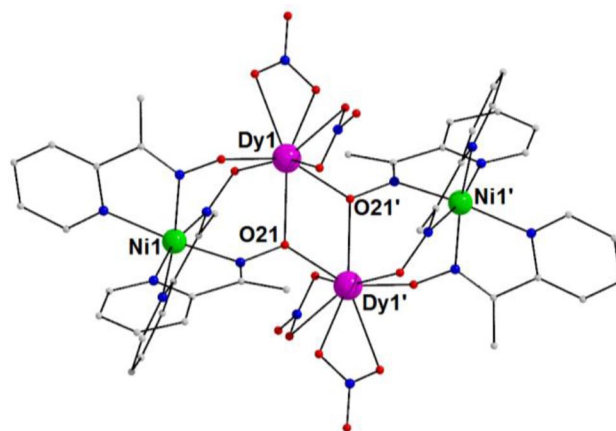


Fig. 11 The molecular structure of **10**.

Variable-temperature magnetic susceptibility studies on **8** and **9** indicate depopulation of the Stark sublevels of Tb^{III} and weak antiferromagnetic $\text{Ni}^{\text{II}}\cdots\text{Tb}^{\text{III}}$ exchange interactions [73]; these conclusions are supported by the magnetic study of the Gd^{III} analogues of **8** and **9** (complexes **12** and **13**, respectively).

As in the case of $(\text{py})_2\text{CO}$ -based ligands (vide supra), “one-pot procedures” lead to different products [75]. Despite our efforts, only dinuclear $\text{Ni}^{\text{II}}\text{Ln}^{\text{III}}$ complexes could be isolated. Reactions of $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$, $\text{Ln}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ and $(\text{py})\text{C}(\text{Me})\text{NOH}$ in a 1:2:6 molar ratio in MeOH afforded complexes $[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3](\text{ClO}_4)_2$ in moderate yields. The molecular structure of the Dy^{III} (**14**) member of this family is shown in Fig. 12. The metal ions are bridged by the three oximate groups of the 2.111 $(\text{py})\text{C}(\text{Me})\text{NO}^-$ ligands (Fig. 7b). The Ni^{II} atom is facially coordinated by six nitrogen atoms belonging to the “chelating” part of these anionic ligands. The Dy^{III} atom is bound to an O_3N_6 set of donor atoms. The O atoms belong to the deprotonated oximate groups of the $\{[\text{Ni}(\text{mpko})_3]^-$ unit, while six nitrogen atoms belonging to three bidentate chelating $(\text{py})\text{C}(\text{Me})\text{NOH}$ (1.011) ligands complete a trigonal prismatic coordination (Fig. 13) around the lanthanide.

The presence of three organic ligands per Ni^{II} in the starting metalloligand **7** seems to restrict the number of the organic ligands that are present in $[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_2(\text{NO}_3)_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}]$ (exemplified by **8**; Fig. 9) to three, and thus the coordination sphere of the Ln^{III} atom is completed by three bidentate chelating nitrate groups, resulting in neutral complexes. By contrast with these complexes, the coordination sphere of the Ln^{III} atom in $[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3](\text{ClO}_4)_2$ (exemplified by **14**; Fig. 12), which were prepared using a 6:1 ligand:Ni ratio, is completed by three bidentate chelating, neutral $(\text{py})\text{C}(\text{Me})\text{NOH}$ groups resulting in cationic complexes. The preference of the oxophilic Ln^{III} atoms for the nitrate ligands is compensated for by the formation of three strong intramolecular $\text{O}\{(\text{py})\text{C}(\text{Me})\text{NOH}\}-\text{H}\cdots\text{O}\{(\text{py})\text{C}(\text{Me})\text{NO}^-\}$ hydrogen bonds in the structures of

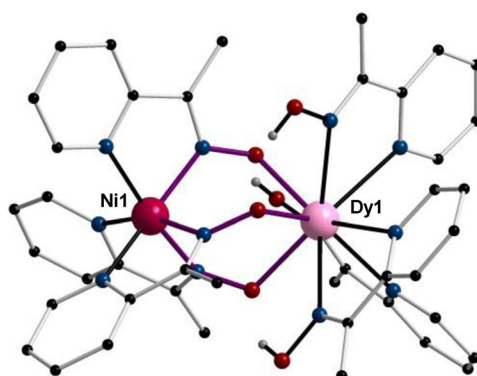


Fig. 12 The molecular structure of one of the two crystallographically independent cations $[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3]^{2+}$ that are present in **14**.

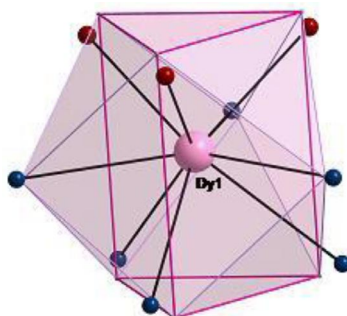


Fig. 13 The tricapped trigonal prismatic coordination sphere of Dy1 in the structure of **14**. The very small spheres define the vertices of the ideal polyhedron.

$[\text{NiLn}\{(\text{py})\text{C}(\text{Me})\text{NO}\}_3\{(\text{py})\text{C}(\text{Me})\text{NOH}\}_3](\text{ClO}_4)_2$. Preliminary results show that use of external bases in the 1:2:6 $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}/\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}/(\text{py})\text{C}(\text{Me})\text{NOH}$ general reaction system lead to the above-mentioned $[\text{Ni}_2\text{Ln}_2\{(\text{py})\text{C}(\text{Me})\text{NO}\}_6(\text{NO}_3)_4]$ clusters and higher-nuclearity Ni_xLn_y complexes ($x, y > 2$) [76].

Variable-temperature, solid-state dc magnetic susceptibility studies (Fig. 14) have been carried out on **14** and its Pr^{III} (**15**), Gd^{III} (**16**), and Tb^{III} (**17**) analogues [75]. The data for **16** in the 2–300 K range have been fit to a model with one J value revealing an antiferromagnetic $\text{Ni}^{\text{II}} \cdots \text{Gd}^{\text{III}}$ exchange interaction [$J = -1.1 \text{ cm}^{-1}$ based on $H = -J(\hat{S}_{\text{Ni}} \cdot \hat{S}_{\text{Gd}})$]. Antiferromagnetic $\text{Ni}^{\text{II}} \cdots \text{Dy}^{\text{III}}$, $\text{Ni}^{\text{II}} \cdots \text{Pr}^{\text{III}}$, and $\text{Ni}^{\text{II}} \cdots \text{Tb}^{\text{III}}$ exchange interactions have also been suggested for **14**, **15**, and **17**, respectively.

The chemistry described above is highly dependent on the 2-pyridyl oxime that is used for the preparation of heterometallic complexes. For example, use of 2-pyridinealdoxime ($\text{R} = \text{H}$ in Fig. 7a) leads to Ni_8Ln_8 [33] and Ni_4Ln_4 [76] clusters.

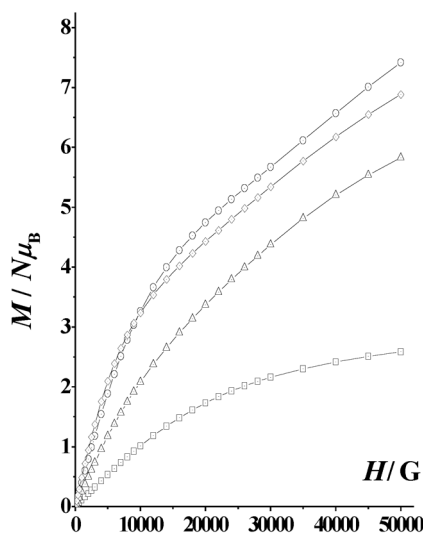


Fig. 14 Experimental plots of $\chi_M T$ vs. T for compounds **14** (\diamond), **15** (\square), **16** (\circ), and **17** (\triangle). The solid line for **16** represents the best fit of the data to the theoretical model.

CONCLUDING REMARKS

We hope that this article has convinced the readers that 3d/4f-metal cluster chemistry is interesting, and that 2-pyridyl ketone- and 2-pyridyl oxime-based ligands are basic “players” in this area. Two are the main synthetic conclusions from our efforts: (1) The two ligand families can indeed lead to low-nuclearity $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes (amenable to detailed magnetic studies) with beautiful structures, without requiring the copresence of ancillary organic groups (e.g., carboxylates), and (2) the “metal complexes as ligands” and “one-pot reaction” approaches give, in general, different products, and thus both should be used. From the magnetism viewpoint, the main points are also two: (a) Although complexes **1**, **2**, and **6** are ferromagnetic, these are not SMMs probably due to their angular topology, which leads to a small anisotropy, and (b) the deprotonated oximate group seems to propagate antiferromagnetic $\text{Ni}^{\text{II}}\cdots\text{Ln}^{\text{III}}$ exchange interactions which do not favor SMM behavior. However, we note that $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ clusters based on a reduced form of $(\text{py})_2\text{CO}$ [32] and higher-nuclearity $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ complexes based on $(\text{py})\text{C}(\text{H})\text{NOH}$ [33] do exhibit SMM behavior.

Continuing efforts in our laboratories reveal that we have seen only the tip of the iceberg in 3d/4f-metal cluster chemistry based on the ligands shown in Figs. 1 and 7a. We have prepared, structurally characterized, and studied hundreds of Mn^{II} and/or $\text{Mn}^{\text{III}}/\text{Ln}^{\text{III}}$, Fe^{II} or $\text{Fe}^{\text{III}}/\text{Ln}^{\text{III}}$, Co^{II} and/or $\text{Co}^{\text{III}}/\text{Ln}^{\text{III}}$, and $\text{Cu}^{\text{II}}/\text{Ln}^{\text{III}}$ clusters with new topologies and interesting magnetic properties. We have also discovered that replacement of nitrates with simple carboxylates (HCO_2^- , MeCO_2^- , PhCO_2^-) or β -diketonates (e.g., acac^- , hfac^- , ...) in the reaction systems leads to structurally novel giant clusters.

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