Inorg. Chem. **2003**, *42*, 2206–2208

Inorganic Chemistry

Communication

Lanthanide–Transition Heterometallic Extended Structures with Novel Orthogonal Metalloligand as Building Block

Zheng He, Cheng He, En-Qing Gao, Zhe-Ming Wang,* Xiao-Fan Yang, Chun-Sheng Liao, and Chun-Hua Yan*

State Key Lab of Rare Earth Materials Chemistry and Applications and PKU-HKU Joint Lab on Rare Earth Materials and Bioinorganic Chemistry, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received December 15, 2002

One-dimensional lanthanide–transition heterometallic chains of squares, $\{LnNi_2L_3(HL)(DMF)_4(ClO_4)_4{\cdot}S\}_\infty$ (Ln = Gd and Tb; HL is the Schiff base obtained by the condensation of 2-pyridylaldehyde with isonicotinic hydrazide *N*-oxide; S = solvent) and $\{LnNi_2L_4(DMF)_4(ClO_4)_3{\cdot}S\}_\infty$ (Ln = Dy; S = solvent), were synthesized by self-assembly between well-designed orthogonal metalloligands $[Ni(HL)L]^+$ and the Ln(III) ions, which act as the bridging units and nodes, respectively.

The design and synthesis of organized molecular architectures containing lanthanide ions and transition metal ions are currently of great interest in supramolecular chemistry and materials chemistry. The increasing interest in this field is justified not only by the potential applications of these compounds as functional materials[1−4] but also by the particular beauty and the intriguing structural diversity of the architectures.[5] The coordination geometry of the metal ion strongly influences the solid-state architectures. Since the lanthanide ions generally display variable and high coordination numbers with low stereochemical preference,[6] the construction of supramolecular lanthanide complexes, which requires the structural and topological control of the coordination sphere around lanthanide ions, is quite a challenge. Thus, the design of multifunctional ligands containing appropriate coordination sites linked by a spacer with specific positional orientation is especially crucial. To achieve this goal, several research groups have made efforts to design well-tailored ligands for the preparation of functional lanthanide complexes.[5−7] In particular, the group of Piguet has employed elaborately designed N-donor podating ligands to prepare the transition−lanthanide (TM−Ln) heterometallic complexes with specific molecular topologies,[6] while Goodgame et al. used ambidentate “extended reach” ligands for the generation of a family of heterometallic polymeric materials.[5d,e]

Recently, we started a project to design and assemble TM−Ln heterometallic complexes. Our strategy is based on the different coordinative behaviors of transition metal ions and lanthanide ions: the lanthanide cations, as hard acids, prefer oxygen to nitrogen donors, and their large ion sizes and therefore high coordination numbers should favor the construction of extended structures. On the other hand, transition metal ions such as nickel(II) are borderline acids, having a strong tendency to coordinate to N-donors, and adopt predictable coordination geometries as a result of the ligand field influence. From this perspective, we designed a bifunctional ligand HL (Scheme 1) that contains two different coordination sites: lanthanide ions will interact with the

---

* To whom correspondence should be addressed. E-mail: chyan@chem.pku.edu.cn.

(1) For examples, see: (a) Long, D. L.; Blake, A. J.; Champness, N. R.; Schröder, M. *Chem. Commun.* **2000**, 1369. (b) Ma, L.; Evans, O. R.; Foxman, B. M.; Lin, W. B. *Inorg. Chem.* **1999**, *38*, 5837. (c) Su, C. Y.; Kang, B. S.; Liu, H. Q.; Wang, Q. G.; Mak, T. C. W. *Chem. Commun.* **1998**, 1551. (d) Berberich, H.; Roesky, P. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 1569. (e) Aime, S.; Barge, A.; Botta, M.; De Sousa, A. S.; Parker, D. *Angew. Chem., Int. Ed.* **1998**, *37*, 2673. (f) Werts, M. H. V.; Duin, M. A.; Hofstraat, J. W.; Verhoeven, J. W. *Chem. Commun.* **1999**, 799.

(2) Decurtins, S.; Gross, M.; Schmalle, H. W.; Ferlay, S. *Inorg. Chem.* **1998**, *37*, 2443.

(3) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369 and references therein.

(4) Lisowski, J.; Starynowicz, P. *Inorg. Chem.* **1999**, *38*, 1351.

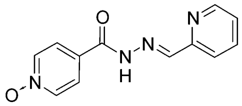
(5) (a) Gheorghe, R.; Andruh, M.; Müller, A.; Schmidtmann, M. *Inorg. Chem.* **2002**, *41*, 5314. (b) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *Inorg. Chem.* **2002**, *41*, 4496. (c) Liang, Y. C.; Cao, R.; Su, W. P.; Hong, M. C.; Zhang, W. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3304. (d) Goodgame, D. M. L.; Menzer, S.; Ross, A. T.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1994**, 2605. (e) Goodgame, D. M. L.; Grachvogel, D. A.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2001**, *40*, 6180

(6) For examples, see: (a) Piguet, C.; Bunzli, J.-C. G.; Bernardinelli, G.; Hopfgartner, G.; Petoud, S.; Schaad, O. *J. Am. Chem. Soc.* **1996**, *118*, 6681. (b) Piguet, C.; Minten, E. R.; Bernardinelli, G.; Bunzli, J.-C. G.; Hopfgartner, G. *J. Chem. Soc., Dalton Trans.* **1997**, 421. (c) Renaud, F.; Piguet, C.; Bernardinelli, G.; Bunzli, J.-C. G.; Hopfgartner, G. *J. Am. Chem. Soc.* **1999**, *121*, 9326.

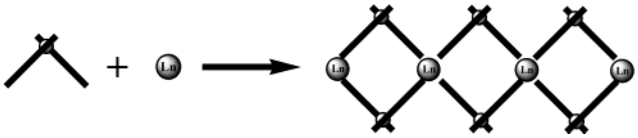
(7) (a) Reeves, Z. R.; Mann, K. L. V.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D.; Barigelletti, F.; Armaroli, N. *J. Chem. Soc., Dalton Trans.* **1999**, 349. (b) Reineke, T. M.; Eddaoudi, M.; Fehr, M.; Kelley, D.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 1651. (c) Reineke, T. M.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 2590. (d) Alexander, V. *Chem. Rev.* **1995**, *95*, 273. (e) Guerriero, P.; Tamburini, S.; Vigato, P. A. *Coord. Chem. Rev.* **1995**, *139*, 17. (f) Setyawati, I. A.; Liu, S.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **2000**, *39*, 496.

10.1021/ic026271n CCC: $25.00

Scheme 1



Scheme 2



pyridine-*N*-oxide, as has been well established,[1a,8] while the nickel(II) ion will bind to the tridentate chelating site to form an octahedral geometry.

While focusing our attention primarily on the structural aspects of the extended heterometallic complexes, it is noteworthy that the magnetic behaviors of TM−Ln complexes are also an active subject of research currently.[3,9] Here we report the synthesis and the novel crystal structures of one-dimensional (1D) Ni(II)−Ln(III) heterometallic coordination polymers, along with the preliminary magnetic investigation on the Ni−Gd compound, which behaves as a ferrimagnetic chain.

The metalloligand Ni(HL)LClO$_4$ (**1**) was first obtained by the reaction of Ni(ClO$_4$)$_2$·6H$_2$O with the ligand HL. X-ray single-crystal structure analysis revealed the formation of the orthogonal building unit as expected.[10] Figure 1 shows the perspective drawing of the orthogonal unit in **1**. Each Ni(II) center resides in a slightly distorted octahedral environment coordinated by the carbonyl oxygen atoms, pyridine nitrogen atoms, and imine nitrogen atoms from two L species in a chelating fashion. The two ligands bond to Ni(II) in the mer configuration. The dihedral angle between the two coordination planes is ca. 87°, and the pyridine-*N*-oxide sites are free. Thus, metalloligand **1** can be utilized as a versatile building block[11] with the two pyridine-*N*-oxide sites predetermined to coordinate to lanthanide ions (Scheme 2).

To the brownish red solution of **1** was added Ln(ClO$_4$)$_3$·6H$_2$O. Brownish red crystals of compounds {LnNi$_2$L$_3$(HL)(DMF)$_4$(ClO$_4$)$_4$·S}$_\infty$ (**2** and **3** for Ln = Gd and Tb, respectively; S = solvent) and {LnNi$_2$L$_4$(DMF)$_4$(ClO$_4$)$_3$·S}$_\infty$ (**4** for Ln = Dy; S = solvent) suitable for X-ray analysis were prepared by the diffusion of benzene/acetonitrile into the mother liquor.[12] The crystals of **2**, **3**, and **4** lost crystallinity quickly upon exposure to air, indicating a loss of solvent. Compounds **2** and **3** are isomorphous, and only the structure of **2** will be described here. The single-crystal structure analysis of compound **2** revealed an extended 1D chain of corner-sharing squares composed of a {[GdNi$_2$(HL)L$_3$(DMF)$_4$]$^{4+}$}$_\infty$ cation, ClO$_4^-$ anions, and solvent molecules, illustrated in Figure 2. The central Gd(III) ion displays a slightly distorted square antiprism coordination geometry. Each Gd(III) is bonded to four oxygen atoms of pyridine-*N*-oxide groups from four metalloligands (the Gd−O distances are 2.342(5) and 2.356(5) Å, respectively, which are slightly shorter than those observed for europium[13a] and gadolinium[13b] complexes of pyridine-*N*-oxides; the N−O−Gd angles are 132.3° and 132.5°, respectively) and four oxygen atoms from four DMF molecules (the Gd−O distances are 2.433(5) and 2.361(6) Å, respectively). The oxygen atoms of the pyridine-*N*-oxide groups and the oxygen atoms of the DMF molecules occupy the top and bottom corners of the square antiprism, respectively.

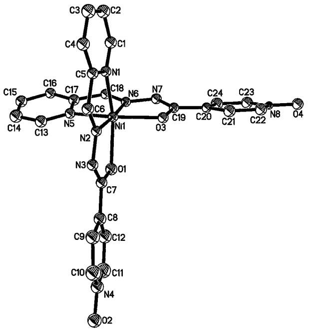


Figure 1. Perspective view of the coordination geometry of the Ni atom in the metalloligand **1**. The H atoms have been omitted for clarity. Thermal ellipsoids are shown at 30% probability level.

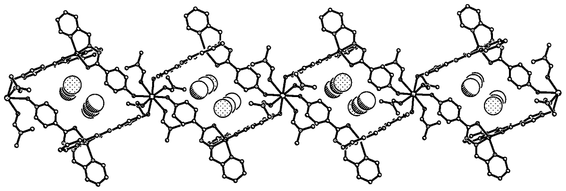


Figure 2. View along the crystallographic *b*-axis showing the 1D chain (the acetonitrile molecules in the square units are highlighted).

---

(8) Long, D. L.; Blake, A. J.; Champness, N. R.; Wilson, C.; Schröder, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 2443.

(9) For examples, see: (a) Chen, X.-M.; Aubin, S. M. J.; Wu, Y.-L.; Yang, Y.-S.; Mak, T. C. W.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 9600. (b) Costes, J.-P.; Dahan, F.; Dupuis, A.; Laurent, J.-P. *Inorg. Chem.* **1997**, *36*, 3429. (c) Chen, X.-M.; Wu, Y.-L.; Yang, Y.-Y.; Aubin, S. M. J.; Hendrickson, D. N. *Inorg. Chem.* **1998**, *37*, 6186.

(10) Crystal data for **1**: C$_{67}$H$_{63}$Cl$_2$N$_{19}$O$_{17}$Ni$_2$, M_r = 1594.68, monoclinic, space group $P2_1/c$, a = 14.8460(10) Å, b = 23.6352(2) Å, c = 20.8378(2) Å, β = 105.4531(4)°, V = 7047.41(10) Å^3, T = 180 K, Z = 4, μ(Mo Kα) = 0.663 mm^{-1}, 101437 reflections measured, 16049 unique (R_{int} = 0.053). Refinement of 801 parameters with 20 restraints gave R1 = 0.1034, wR2 (all data) = 0.3556.

(11) (a) Denti, G.; Serroni, S.; Campagna, S.; Juris, A.; Ciano, M.; Balzani, V. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; VCH: New York, 1992. (b) Ren, Y.-P.; Long, L.-S.; Mao, B.-W.; Yuan, Y.-Z.; Huang, R.-B.; Zheng, L.-S. *Angew. Chem., Int. Ed.* **2003**, *42*, 532.

(12) Crystal data for **2**: C$_{35}$H$_{40.5}$Cl$_2$N$_{12}$O$_{15}$Gd$_{0.5}$Ni, M_r = 1077.53, monoclinic, space group $P2/c$, a = 13.7063(4) Å, b = 12.4103(4) Å, c = 30.2541(8) Å, β = 92.781(2)°, V = 5140.1(3) Å^3, T = 180 K, Z = 4, μ(Mo Kα) = 0.663 mm^{-1}, 44981 reflections measured, 11631 unique (R_{int} = 0.050). Refinement of 613 parameters with 92 restraints gave R1 = 0.0814, wR2 (all data) = 0.2470. Crystal data for **3**: C$_{35}$H$_{41}$Cl$_2$N$_{12}$O$_{15}$Tb$_{0.5}$Ni, M_r = 1078.87, monoclinic, space group $P2/c$, a = 13.7842(3) Å, b = 12.4662(4) Å, c = 30.2055(11) Å, β = 92.7503(18)°, V = 5184.4(3) Å^3, T = 180 K, Z = 4, μ(Mo Kα) = 0.663 mm^{-1}, 40890 reflections measured, 9089 unique (R_{int} = 0.063). Refinement of 613 parameters with 92 restraints gave R1 = 0.0783, wR2 (all data) = 0.2376. Crystal data for **4**: C$_{80}$H$_{92}$Cl$_3$N$_{25}$O$_{25}$DyNi$_2$, M_r = 2190.06, triclinic, space group $P\bar{1}$, a = 12.6146(4) Å, b = 13.8847(5) Å, c = 30.3707(12) Å, α = 91.9936(18)°, β = 91.8370(20)°, γ = 91.4112(12)°, V = 5311.7(3) Å^3, T = 180 K, Z = 2, μ(Mo Kα) = 0.663 mm^{-1}, 49192 reflections measured, 17658 unique (R_{int} = 0.087). Refinement of 1109 parameters with 30 restraints gave R1 = 0.1160, wR2 (all data) = 0.3362.

(13) (a) Gawryszewska, P.; Jerzykiewicz, L.; Pietraszkiewicz, M.; Legendziewicz, L.; Riehl, J. P. *Inorg. Chem.* **2000**, *39*, 5365. (b) Amoroso, A. J.; Burrows, M. W.; Gelbrich, T.; Haigh, R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2415.

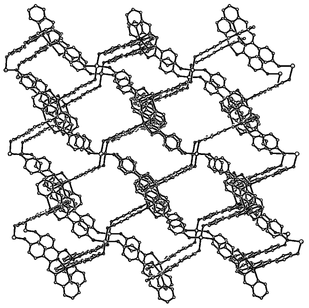


Figure 3. Packing diagram of compounds **2**, **3**, and **4** showing the channel structure down the *b*-axis. The solvent molecules, coordinated DMF, and counterions are omitted for clarity.

As shown in Figure 2, each Gd(III) center acts as a four-connected node bridged by two orthogonal metalloligands to the adjacent Gd(III) center, resulting in an infinite 1D chain of squares. The metalloligand retains its orthogonal skeleton when coordinated to Gd(III) ions. The two adjacent Gd(III) ions and two bridging metalloligands form a square unit with four metal centers in the same plane, and these units are linked together by sharing the common Gd(III) nodes, giving rise to a 1D chain extending along the *c* direction. The adjacent square units within the chain are essentially perpendicular with a dihedral angle of 88.7°. For a square unit, the edge Gd−Ni distances are 9.90 and 10.02 Å, and the transannular Gd−Gd distance is 12.41 Å (for **3**, the related distances are 9.87, 10.03, and 12.46 Å, respectively). Two parallel acetonitrile molecules thread through the square unit.

The 1D chains of squares stack in register along the *a* and *b* directions such that 1D interchain channels are formed along both directions (Figure 3). The channels are occupied by coordinated DMF molecules, solvent DMF molecules, and ClO_4^- ions. There exist interchain $\pi-\pi$ stacking interactions between adjacent pyridine rings related by the $(2 - x, 1 - y, -z)$ operation (the ring···ring distance, center···center distance, and the nearest atom···atom distance are 3.45, 3.60, and 3.49 Å, respectively).

Compound **4** is isostructural with **2** and **3**, although the space groups are different.[12] Within the square unit, the edge Dy−Ni separations are 10.00 and 10.04 Å, and the transannular Dy−Dy separation is 12.62 Å.

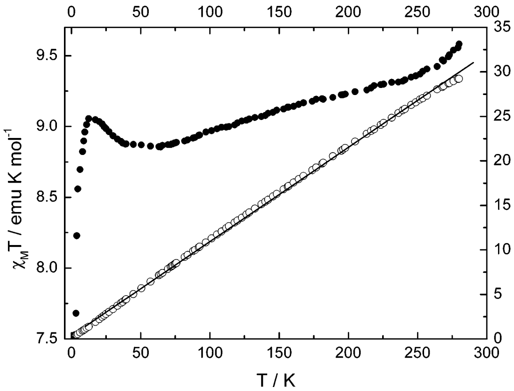


Figure 4. Experimental $\chi_M T$ (●) and χ_M^{-1} (○) versus *T* plot for compound **2** in an applied field of 5000 G.

The temperature dependence of the magnetic susceptibility for compound **2** was measured in the temperature range 2−280 K, with an applied field of 5000 G. The plot of $\chi_M T$ and χ_M^{-1} versus *T* is shown in Figure 4. As the temperature is lowered, $\chi_M T$ first decreases slowly, reaches a minimum at ca. 64 K, and then increases, indicating that the complex behaves as a ferrimagnetic chain with antiferromagnetic interactions between the neighboring paramagnetic centers with uncompensated spins. In addition, upon further cooling, the $\chi_M T$ reaches a maximum at ca. 12 K and then decreases dramatically, which may be due to secondary effects such as the zero-field splitting of the Ni(II) ions and/or interchain antiferromagnetic interactions. The fit of the experimental data to the Curie−Weiss law leads to $C = 9.46$ emu K mol^{-1}, $\theta = -3.4$ K. The negative value of θ suggests an overall antiferromagnetic interaction.

In summary, we have demonstrated a facile synthesis of a TM−Ln heterometallic framework. We took advantage of the predictable nature of the coordination geometry of transition metal ions to get the predesigned orthogonal bridging unit, which was in turn employed to propagate in one dimension the coordination geometry of the lanthanide ions. The modular nature of the structures implies that there is a wide range of permutations that could be readily available from a synthetic perspective. Besides, the properties deriving from the presence of the heterometallic arrays are also attractive, as exemplified by the magnetic behaviors of Ni−Gd species. Further investigations are underway to expand this approach.

Acknowledgment. This work is supported by NSFC (90201014, 20023005, 29831010, 20201009), MOST (G19980613), and MOE of China and the Founder Foundation of PKU.

Supporting Information Available: X-ray crystallographic file in CIF format and the synthesis of the ligand and the complexes are available. These materials are available free of charge via the Internet at http://pubs.acs.org.

IC026271N