

A family of nickel–lanthanide heterometallic dinuclear complexes derived from a chiral Schiff-base ligand exhibiting single-molecule magnet behaviors



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ABSTRACT

A new family of nickel–lanthanide heterometallic dinuclear complexes derived from a chiral Schiff-base ligand, (*R,R*)-*N,N'*-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine (H_2L), namely $[Ni(L)Ln(NO_3)_3 \cdot (H_2O)]$ ($Ln = Ce$ (**1**), Nd (**2**)) and $[Ni(L)Ln(NO_3)_3]$ ($Ln = Sm$ (**3**), Eu (**4**), Gd (**5**), Tb (**6**), Dy (**7**) and Yb (**8**)) have been synthesized and structurally characterized. X-ray single-crystal structure determination revealed that these complexes are diphenoxo-bridged Ni^{II} – Ln^{III} dinuclear clusters, which crystallize in the chiral space group *P1*. The solid circular dichroism (CD) spectra confirmed the optical activity and enantiomorphous properties of all these complexes. Magnetic investigations suggested that crystal-field effects and/or the possible antiferromagnetic dipole–dipole interaction between the molecules exist in the complexes and single-ion properties of Ln^{III} ions lead to their magnetic behaviors. The alternating current (ac) magnetic susceptibilities showed that complexes **6** and **7** exhibit field-induced single-molecule magnet behaviors due to the strong anisotropy and important crystal-field effect of the Tb^{III} or Dy^{III} ions. It is noteworthy that the quantum tunneling effect at low temperatures can be effectively suppressed by employing a 2 kOe direct current field.

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1. Introduction

The construction of molecule-based magnetic materials has been an active field in chemistry and materials science [1], especially after the discovery of single-molecule magnets (SMMs) in 1993 [2]. The SMMs have attracted much attention over the two decades mainly due to their potential applications in the high-density information storage at the molecular level or nanoscale [3]. However, there are two main issues for the realization of the SMM-based storage technology: (1) the slow magnetic relaxation of the SMMs is currently only accessible below liquid N_2 temperature, thus the magnetic blocking temperature needs to rise significantly; (2) the manufacturing of storage devices encounters great difficulties due to the individual molecules of the SMMs are hard to deposit and address on surfaces [4]. One of the grand challenges in researching for the molecule-based magnets is still, therefore, to design and synthesize the efficient SMMs.

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Recently, the lanthanide ions with unique electronic structures have attracted considerable attention because of their unrivaled single-ion anisotropies. The most notable heavy lanthanide ions, such as Dy^{III} [5], Tb^{III} [6], Ho^{III} [7] and Er^{III} [8], have been widely used as the magnetic centers to construct the SMMs [9]. Two strict prerequisites for a molecule as the SMM are that the electronic ground state must be bistable, and the magnetic anisotropy must be present. For the lanthanide ions, other than the ground electronic states of 1S_0 and $^8S_{7/2}$, the orbital contribution to the magnetic moment is large and unquenched, and the ligand-field effects in the lanthanide complexes can be regarded as a small-but-significant perturbation [10]. Therefore, the Ln -containing complexes can be considered as the SMMs more likely because of their large angular momentum in the ground electronic states and a large magnetic anisotropies [4]. And more significantly, the lanthanide-based SMMs have already shown considerable potentials to deposit on the surface for device manufacturing [11,4c]. The mononuclear lanthanide compound exhibiting slow relaxation of the magnetization could be called “single-ion magnets” (SIMs) due to the single-ion features [12], while the lanthanide-based SMMs usually include two or more lanthanide ions [4,13].

Since the first ferromagnetic Cu^{II}–Gd^{III} compound was reported by Gatteschi group [14], the 3d–4f heterometallic complexes have attracted a great deal of interests because they are efficient model compounds in understanding the magnetic exchange between the 3d and 4f metal ions, and especially, some of 3d–4f clusters behave as the SMMs [15]. The strong magnetic interaction between the 3d and 4f ions make it more easier to show the SMM behaviors. The 3d metal ions mainly include the Cu^{II} [16], Ni^{II} [17], Co^{II} [18], and Mn^{III} ion [19], and the polydentate Schiff-base ligands are often chose to construct the 3d–4f heterometallic SMMs [20]. Previous studies revealed that the symmetry of the ligand field around the lanthanide ion strongly affects the magnetic anisotropy [21]. When the chiral ligands are introduced into the magnetic complex, not only the chiral magnets may be obtained, but also the chiral asymmetric coordination environment around the metallic ions can affect the magnetic properties [22,23,4b]. In order to further study the effect of different ligands on the magnetic properties, the chiral hexadentate Schiff-base ligand (Scheme 1) was applied for the synthesis of target SMMs. Herein, we describe the syntheses, crystal structures, and magnetic properties of a new family of 3d–4f heterometallic dinuclear complexes, namely [Ni(L)Ln(NO₃)₃(H₂O)] (Ln = Ce (1), Nd (2)) and [Ni(L)Ln(NO₃)₃] (Ln = Sm (3), Eu (4), Gd (5), Tb (6), Dy (7) and Yb (8)) (H₂L = (R,R)-N,N'-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine (H₂L)). Remarkably, the Ni^{II}–Tb^{III} (6) and Ni^{II}–Dy^{III} (7) complexes display field-induced slow magnetic relaxation.

2. Experimental

2.1. General methods

All the reagents and solvents were purchased from the commercial sources and used as received. (R,R)-1,2-diaminocyclohexane and 3-methoxysalicylaldehyde were purchased from the Aldrich Chemical Co., Inc. The rare earth metal salts Ln(NO₃)₃·6H₂O were prepared from the high purity Ln₂O₃ (99.99%, Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy and Yb). Elemental analyses for C, H, and N were carried out on a Perkin-Elmer 240C analyzer for complexes. Infrared spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the region 400–4000 cm⁻¹. The circular dichroism

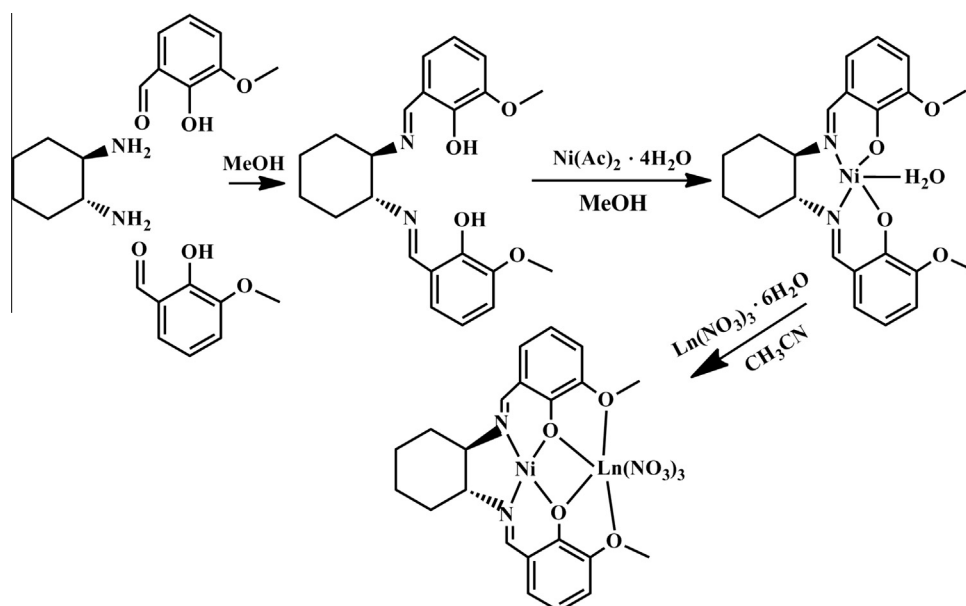
spectra were recorded on a JASCO J-1500 spectropolarimeter with KBr pellets. Single crystal data were collected on Bruker Apex-II Smart CCD diffractometer using monochromated Mo K α radiation. The PXRD spectra were recorded on an Empyrean (PANalytical B.V.) diffractometer for a Cu-target tube and a graphite monochromator. Simulation of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at <http://www.iucr.org>. Variable-temperature magnetic susceptibility, zero-field alternating current (AC) magnetic susceptibility, and field dependence of magnetization were measured on a Quantum Design MPMS XL-5 (SQUID) magnetometer. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms. The AC susceptibility measurements were carried out in a 2.5 Oe AC field oscillating at 10–1000 Hz, under a 0.1 T static field. To avoid torqueing of the crystallites in the presence of the magnetic field, the samples were crushed before measurements.

2.2. Syntheses of [Ni(L)]·H₂O

The chiral Schiff-base ligand (R,R)-H₂L or (S,S)-H₂L (H₂L = N,N'-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine) was synthesized by the condensation of (R,R)-1,2-diaminocyclohexane or (S,S)-1,2-diaminocyclohexane with 3-methoxysalicylaldehyde in methanol and directly used without further separation. A methanolic solution (10 mL) of Ni(CH₃COO)₂·4H₂O (2 mmol) was added to a methanolic solution (50 mL) containing the Schiff-base (R,R)-H₂L or (S,S)-H₂L (2 mmol), and the reaction mixture was stirred for 2 h at room temperature. The solvents were removed under vacuo and the resulting orange-yellow solid was washed two times with acetone. The orange-yellow needle-shaped crystals were obtained by recrystallization in acetonitrile. Single crystal measurements showed that the [Ni(L)]·H₂O is a mononuclear Ni^{II} complex crystallized in the chiral space group P2₁2₁2₁ (Fig. S1, SI).

2.3. Syntheses of [Ni(L)Ln(NO₃)₃(H₂O)_x] (1–8, Ln = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb)

A acetonitrile solution (10 mL) of Ln(NO₃)₃·6H₂O (0.1 mmol) was added to [Ni(L)]·H₂O (0.1 mmol) in acetonitrile (10 mL), after



Scheme 1. The synthetic route of the complexes.

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