

Chiral Lanthanide Complexes

Homoleptic Chiral Benzamidinate Complexes of Rare-Earth Elements: Synthesis, Structure, Luminescence, and Magnetism

Meng He,^[a] Zhi Chen,^[b] Eufemio Moreno Pineda,^[b] Xue Liu,^[c] Elisabeth Bouwman,^[c] Mario Ruben,^[b,d] and Peter W. Roesky^{*[a]}

Abstract: The new enantiopure amidinate (*S,S*)-*N,N'*-bis[1-(2-naphthyl)ethyl]benzamidinate [(*S*)-NEBA] was introduced into the chemistry of the rare-earth elements. Firstly, the synthesis of the corresponding amidine [(*S*)-HNEBA] is described. Amine elimination reactions of (*S*)-HNEBA with [Ln{N(SiMe₃)₂}₃] [Ln = Y (1), Sm (2), Tb (3), Dy (4), Er (5), Yb (6), Lu (7)] gave a series of enantiomerically pure homoleptic rare-earth metal complexes

[Ln{(*S*)-NEBA}₃]. All complexes have a chiral metal center, but of the two possible diastereomers exclusively that having Δ configuration along the helical axis was formed. The solid-state structures of all complexes and proligands were established by single-crystal XRD. The luminescence properties of **2** and **3** and the magnetic properties of **3–6** were investigated.

Introduction

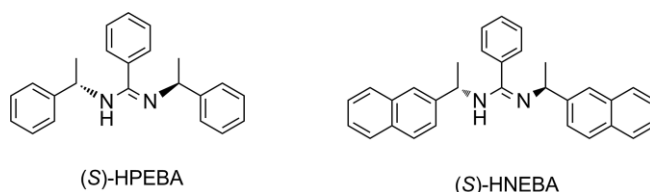
Amidines, [R¹NC(R₃)NR²][−], are bidentate N ligands that in most cases coordinate in a chelating fashion.^[1–8] By modifying the three substituents R¹, R², and R³, a large variety of sterically and electronically different amidines are accessible. This broad variety of the substituent pattern, the ease of accessibility, and the flexible coordination mode have made amidines and the closely related guanidines a popular and well-established class of ligands that have been used for almost all metals.^[4,9,10]

In rare-earth metal chemistry, amidinate and guanidinate ligands almost exclusively coordinate in an *N,N'*-chelating mode.^[4,5,7] Since the early 1990s amidinate ligands have been used as chelating agents in rare-earth metal chemistry.^[1–7,11–13] Although amidinates and guanidates are nowadays a common and well-established class of ligands in rare-earth metal chemistry,^[2,3,5,6,14,15] no amidinate complexes with chiral ligands have been published prior to our work. Achiral amidinate complexes of the rare-earth metals are known for their use in different applications, for example, homogeneous catalysis and precursors for atomic layer deposition and metal–organic chemical vapor deposition.^[5–8,16–26]

On the basis of early contributions by Brunner et al.,^[27,28] we recently published an improved synthesis of the chiral amidine *N,N'*-bis(1-phenylethyl)benzamidinate (HPEBA) and its corresponding lithium and potassium salts (LiPEBA and KPEBA).^[29]

Reaction of KPEBA with anhydrous lanthanide trichlorides (Ln = Sm, Er, Yb, Lu) afforded, regardless of the stoichiometric ratio and the ionic radius of the metal center, the tris-amidinate complex [Sm{(*S*)-PEBA}₃], the bis-amidinate complexes [Ln(PEBA)₂(μ-Cl)]₂ (Ln = Sm, Er, Yb, Lu), and the mono-amidinate complexes [Ln(PEBA)(Cl)₂(thf)_{*n*}] (Ln = Sm, Yb, Lu). In a comparable approach, the chiral mono-amidinato bis-borohydride rare-earth metal complexes [Ln{(*S*)-PEBA}(BH₄)₂(thf)₂] (Ln = Sc, La, Nd, Sm, Yb, Lu) were prepared from (*S*)-KPEBA and the homoleptic tris-borohydrides [Sc(BH₄)₃(thf)₂] and [Ln(BH₄)₃(thf)₃] (Ln = La, Nd, Sm, Yb, Lu).^[30] Furthermore, the chiral bis-amidinate amido complexes [Ln{(*S*)-PEBA}₂N(SiMe₃)₂] (Ln = Y, Lu) were synthesized by amine elimination reactions and salt metathesis. By using these enantiomeric pure amido complexes as precatalysts, good catalytic activities and high enantioselectivities in hydroamination/cyclization reactions were observed.^[31,32]

Herein, we describe the synthesis and characterization of a new chiral amidine ligand, namely, (*S,S*)-*N,N'*-bis[1-(2-naphthyl)ethyl]benzamidinate [(*S*)-HNEBA] (Scheme 1). By treating this proligand with [Ln{N(SiMe₃)₂}₃], a series of enantiomerically



Scheme 1. Chiral amidines (*S*)-HPEBA (previous work) and (*S*)-HNEBA (this contribution).

[a] Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstr. 15, 76131 Karlsruhe, Germany
E-mail: roesky@kit.edu
<http://www.aoc.kit.edu/AK%20Roesky.php>

[b] Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Postfach 3640, 76021 Karlsruhe, Germany

[c] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands

[d] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS – Université de Strasbourg, 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2, France

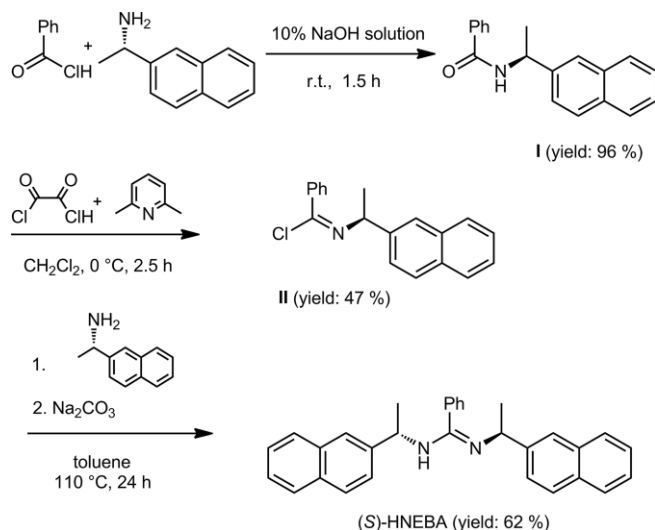
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pure homoleptic rare earth metal tris-amidinate complexes $[\text{Ln}\{(S)\text{-NEBA}\}_3]$ [$\text{Ln} = \text{Y}$ (**1**), Sm (**2**), Tb (**3**), Dy (**4**), Er (**5**), Yb (**6**), Lu (**7**)] were obtained. Besides full characterization, the luminescence and magnetic properties of some selected complexes were investigated.

Results and Discussion

Ligand Synthesis

On the basis of our previous work (Scheme 1),^[29] we designed the new enantiomerically pure amidine (*S,S*)-*N,N'*-bis[1-(2-naphthyl)ethyl]benzamidine [(*S*)-HNEBA] (Scheme 2). In the first step, benzoyl chloride was treated with enantiomerically pure (*S*)-[1-(2-naphthyl)ethyl]amine to give (*S*)-*N*-[1-(2-naphthyl)ethyl]benzamide (**I**) in good yield. In the second step, treatment of **I** with oxalyl chloride and 2,6-lutidine in CH_2Cl_2 resulted in (*S*)-*N*-[1-(2-naphthyl)ethyl]benzimidoyl chloride (**II**). This step is based on a method published by Cunico et al.^[33] In the third step, compound **II** and (*S*)-[1-(2-naphthyl)ethyl]amine were heated in toluene. The resulting oily residue was treated with Na_2CO_3 to give (*S*)-HNEBA as analytically pure white crystals (see Figures S9–S14 for NMR spectra).



Scheme 2. Synthesis of (*S*)-HNEBA.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of (*S*)-HNEBA in $[\text{D}_6]\text{DMSO}$ show two well-resolved sets of signals for the 1-(2-naphthyl)ethyl groups. Thus, in the ^1H NMR spectrum two doublets ($\delta = 1.26, 1.52$ ppm) for the methyl groups and two multiplets ($\delta = 4.20$ (dq), 5.39 (q) ppm) for the CH groups were identified.

The solid-state structure of (*S*)-HNEBA was also established by single-crystal XRD (Figure 1 and Figure S1). (*S*)-HNEBA crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules of (*S*)-HNEBA in the unit cell. (*S*)-HNEBA crystallizes in an (*E*)-*syn* configuration, which is typical for amidines in the solid state.^[33–35] The N–C and N=C bond lengths in the amidine group are 1.381(2) and 1.278(2) Å, which can be considered normal for these kinds of bonds in amidines.^[36] The N1–C1–C2–C3 torsion angle is $68.3(2)^\circ$, and there is no conjugation between the phenyl ring and the amidine group in the crystal.

Interestingly, although the ligand structure contains several aromatic groups, no π – π stacking interaction can be found in the solid-state structure.

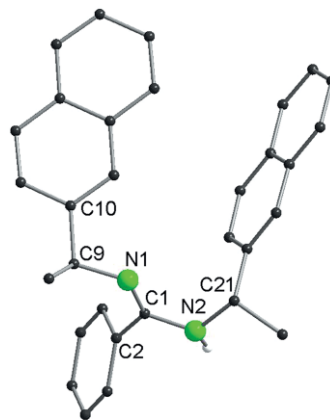
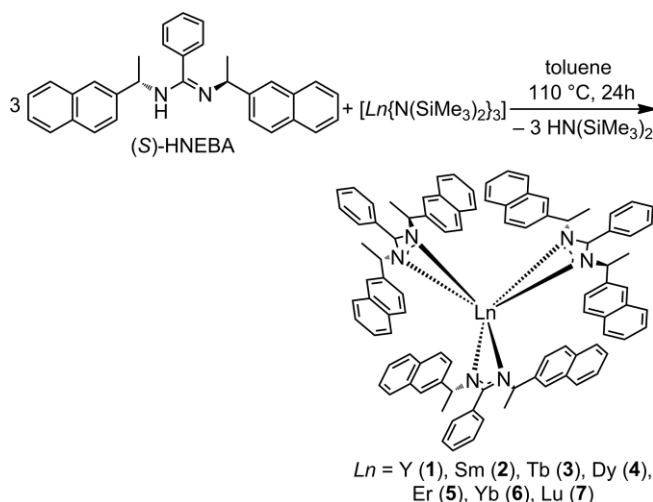


Figure 1. Solid-state structure of (*S*)-HNEBA. Carbon-bound hydrogen atoms are omitted for clarity (see Supporting Information for an ellipsoid plot). Selected bond lengths [Å] and angles $^\circ$: N1–C1 1.273(2), N2–C1 1.381(2), C1–C2 1.504(2), N1–C9 1.453(2), N2–C21 1.465(2); N1–C1–N2 119.59(15), C1–N1–C9 120.35(14), C1–N2–C21 120.84(14).

Synthesis of Metal Complexes

To obtain a broad spectrum of rare-earth metal complexes for NMR, magnetic, and photophysical investigations, a series of homoleptic rare-earth tris-amidinate complexes $[\text{Ln}\{(S)\text{-NEBA}\}_3]$ [$\text{Ln} = \text{Y}$ (**1**), Sm (**2**), Tb (**3**), Dy (**4**), Er (**5**), Yb (**6**), Lu (**7**)] was synthesized by amine elimination from $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ ^[37] and (*S*)-HNEBA in refluxing toluene (Scheme 3). Interestingly, on changing the molar ratio of $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]/(\text{S})\text{-HNEBA}$ from 1:3 to 1:1, only **1–7** and unconverted $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3]$ were obtained. Compounds **1–7** were recrystallized from pentane/toluene to yield single crystals.



Scheme 3. Synthesis of $[\text{Ln}\{(S)\text{-NEBA}\}_3]$ (**1–7**).

All compounds were characterized by single-crystal XRD. Compounds **1–7**, which are isostructural, crystallize in the chiral trigonal space group $R\bar{3}$ (Figure 2 and Figures S2–S8). Each

asymmetric unit consists of one third of the molecule and one molecule of toluene. Each Ln ion is sixfold-coordinated by six N atoms from three (S)-NEBA ligands. Since the hexacoordinate metal ion lies on a crystallographic C_3 axis, only one crystallographically independent (S)-NEBA ligand is observed in each molecule. The four-membered metallacycles formed by the (S)-NEBA ligand and metal ion (N–C–N–Ln) are slightly rotated against each other with formation of a propeller-type structure. The helical chirality is typical for octahedral tris-chelate complexes. In the solid state, the enantiomerically pure ligands all have (S) configuration, and of the two possible diastereomers they form exclusively that having Δ configuration along the helical axis. As a result, all molecules are chiral at the metal center, and all complexes are enantiomerically pure.^[32] Similar behavior was observed earlier for the chiral amidinate complex $[\text{Sm}\{(S)\text{-PEBA}\}_3]$.^[32] As seen in $[\text{Sm}\{(S)\text{-PEBA}\}_3]$, but in contrast to $\text{tris}[N,N'\text{-bis}(\text{trimethylsilyl})\text{benzamido}] \text{ samarium(III)}$,^[38] there are no vacant coordination sites at the metal center. The central metal ion thus is completely shielded by the ligands.

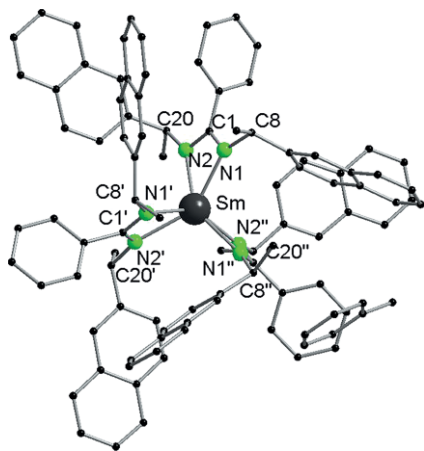


Figure 2. Solid-state structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] (data for the isostructural compounds **1** and **3–7** are also given): **2**: Sm–N1 2.445(3), Sm–N2 2.426(4), Sm–C1 2.858(4), N1–C1 1.345(6) Å, N2–C1 1.321(6); N1–Sm–N2 55.43(12), N1–C1–N2 116.3(4). **1**: Y–N1 2.376(4), Y–N2 2.362(4), Y–C1 2.793(5), N1–C1 1.346(6), N2–C1 1.317(7); N1–Y–N2 56.78(15), N1–C1–N2 115.6(5). **3**: Tb–N1 2.410(3), Tb–N2 2.393(3), Tb–C1 2.820(4), N1–C1 1.344(5), N2–C1 1.325(5); N1–Tb–N2 56.37(11), N1–C1–N2 116.3(3). **4**: Dy–N1 2.400(5), Dy–N2 2.378(5), Dy–C1 2.805(5), N1–C1 1.343(7), N2–C1 1.326(7); N1–Dy–N2 56.8(2), N1–C1–N2 116.5(5). **5**: Er–N1 2.359(4), Er–N2 2.377(4), Er–C1 2.788(5), N1–C1 1.335(7), N2–C1 1.342(7); N1–Er–N2 57.26(5), N1–C1–N2 116.0(4). **6**: Yb–N1 2.357(3), Yb–N2 2.338(3), Yb–C1 2.765(4), N1–C1 1.338(5), N2–C1 1.329(5); N1–Yb–N2 57.59(11), N1–C1–N2 115.9(3). **7**: Lu–N1 2.351(3), Lu–N2 2.329(3), Lu–C1 2.759(3), N1–C1 1.342(5), N2–C1 1.330(5); N1–Lu–N2 57.81(10), N1–C1–N2 115.7(3).

Since all compounds crystallize in an isostructural manner, only the bonding parameters of compound **2** are discussed, because of the good comparison to that of the chiral tris-amidinate complex $[\text{Sm}\{\text{(S)-PEBA}\}_3]$. The Sm–N distances [Sm–N1 2.445(3) and Sm–N2 2.426(4) Å] are in the range of those of $[\text{Sm}\{\text{(S)-PEBA}\}_3]$ [Sm–N1 2.440(4) Å, Sm–N2 2.437(4) Å]. Also, the N–C1 distances are in the expected range: N1–C1 1.345(6) Å, N2–C1 1.321(6) Å vs. N1–C1 1.325(6) Å, N2–C1 1.333(6) Å in $[\text{Sm}\{\text{(S)-PEBA}\}_3]$.^[32] The N1–C1–N2 bite angle of the (S)-NEBA ligand is 116.3(4)°.

NMR spectra were recorded for the diamagnetic compounds **1** and **7**. Due to the similar structure of all compounds, NMR spectra of the paramagnetic compounds were not measured. Due to the deprotonation of (S)-HNEBA the ligands are symmetrical. Furthermore, all NMR spectra indicate symmetrical coordination of the ligand in solution. Thus, only one set of signals is observed for each 1-(2-naphthyl)ethyl moiety of the ligand. The most characteristic signals result from the methyl and the NCH groups. These were observed for the methyl groups at $\delta = 1.72$ (**1**) and 1.69 ppm (**7**) and for the NCH groups at $\delta = 4.39$ (**1**) and 4.46 ppm (**7**) (Figures S15–S19). In general, in comparison to the amidine (S)-HNEBA, a downfield shift of ca. 0.1 ppm is observed in both cases for the signal of the methyl groups. Whereas for the Y compound **1** broad signals were observed at room temperature in the ^1H NMR spectrum, well-resolved signals are seen for Lu complex **7**. The difference in resolution may be a result of the different ionic radii of the metal centers, which cause slightly different coordinations of the ligand. A 2D ^1H , ^{89}Y gHMBC NMR spectrum (gHMBC = gradient-selected heteronuclear multiple-bond coherence) shows an ^{89}Y peak at $\delta = 447$ ppm, which couples to the NCH proton of the ligand.

The IR spectra of all seven compounds show a very strong band at 1590–1610 cm^{-1} , which was assigned to the C=N stretching mode.

Luminescence

Under the irradiation of a high-pressure Hg UV lamp ($\lambda_{\text{ex}} = 366 \text{ nm}$), ligand HNEBA shows weak blue emission. Only compounds **2** and **3** show visible luminescence emission. The solid-state photoluminescence spectra of **2**, **3**, and HNEBA are shown in Figures 3 and 4, and Figure S20. On the basis of the emission spectra of **2** and **3**, the CIE chromaticity coordinates were calculated. The CIE diagram including these data is depicted in Figure S21.

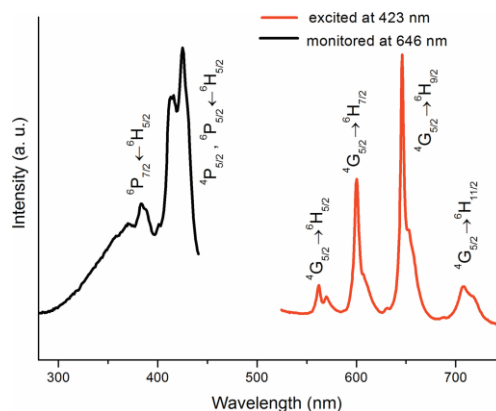


Figure 3. Excitation (black) and emission (red) spectra of **2**.

Under excitation of 423 nm UV light, compound **2** exhibits typical Sm^{III} sharp emission peaks at 562, 600, 646, and 710 nm, which were assigned to the $^4G_{5/2} \rightarrow ^6H_J$ ($J = 5/2, 7/2, 9/2$, and $11/2$) transitions (Figure 3).^[39–41] The emission spectrum is dom-

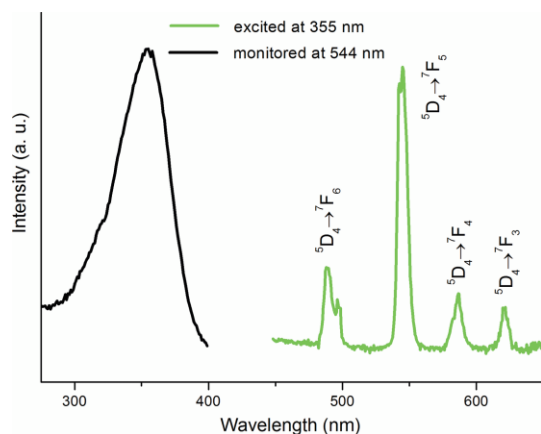


Figure 4. Excitation (black) and emission (green) spectra of **3**.

inated by the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition, which is of electric-dipole nature.^[42] The $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition is of magnetic-dipole nature and its intensity is less sensitive to the coordination environment of the Sm^{III} ion.^[43] The $^4G_{5/2} \rightarrow ^6H_{5/2}$ transition is less intense than the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition (Figure 3). This indicates that the emitting Sm^{III} center adopts a noncentrosymmetric coordination environment, which is in agreement with the single-crystal structure.^[44,45] The excitation spectrum of **2** comprises narrow lines at 385 ($^6P_{7/2} \leftarrow ^6H_{5/2}$) and 423 nm [$(^6P_{5/2}, ^4P_{5/2}) \leftarrow ^6H_{5/2}$], which are due to direct excitation of Sm^{III} .^[46–49]

When excited at 355 nm, compound **3** exhibits four characteristic Tb^{III} emission peaks at 489, 544, 584, and 620 nm, which were assigned to the $^5D_4 \rightarrow ^7F_J$ ($J = 6-3$) transitions of the Tb^{III} ion (Figure 4).^[50–57] The strongest $^5D_4 \rightarrow ^7F_5$ transition is responsible for the green color emission. A broad band is observed in the excitation spectrum of **3**, which indicates the occurrence of ligand-centered excitation.

Magnetism

Anisotropic lanthanide-containing molecules have attracted extensive attention due to their single-molecule magnet (SMM) behavior.^[58–61] To probe whether the series of compounds described herein could exhibit such behavior, we investigated their static and dynamic magnetic properties by performing dc and ac magnetic susceptibility measurements, respectively.

Firstly, we studied the static magnetic behavior for compounds **3–6** using neat polycrystalline powders under an applied dc field of 1 kOe in the temperature range of 2–300 K (Figure 5). The room-temperature χ_M profile (where χ_M is the molar magnetic susceptibility) in all cases is in good agreement with the expected values for isolated lanthanide ions: 11.78, 14.27, 11.47, and 2.47 $\text{cm}^3 \text{K mol}^{-1}$ respectively; the values for isolated lanthanide ions are 11.82 $\text{cm}^3 \text{K mol}^{-1}$ [for Tb^{III} (7F_6), $g_J = 3/2$, $J = 6$], 14.17 $\text{cm}^3 \text{K mol}^{-1}$ [for Dy^{III} ($^6H_{15/2}$), $g_J = 4/3$, $J = 15/2$], 11.48 $\text{cm}^3 \text{K mol}^{-1}$ [for Er^{III} ($^4I_{15/2}$), $g_J = 6/5$, $J = 15/2$] and 2.57 $\text{cm}^3 \text{K mol}^{-1}$ [for Yb^{III} ($^2F_{3/2}$), $g_J = 8/7$, $J = 7/2$], respectively. For compounds **3–5** the $\chi_M T$ value slowly decreases to 9.72, 12.69, and 9.19 $\text{cm}^3 \text{K mol}^{-1}$ on cooling from

300 to 30 K; on further cooling, their $\chi_M T$ values decrease quickly to 4.76, 7.33, and 4.84 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K, respectively. For compound **6**, on cooling, the $\chi_M T$ value decreases slantwise to 1.07 $\text{cm}^3 \text{K mol}^{-1}$ at 7 K, and then sharply decreases to 0.86 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K. The continuous decrease in the $\chi_M T$ value on lowering the temperature for all these systems may be due to progressive depopulation of m_J sublevels and magnetic anisotropy of the lanthanide ions.^[62]

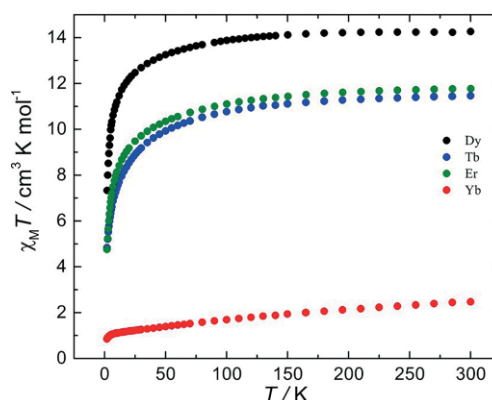


Figure 5. Plots of $\chi_M T(T)$ for compound **3–6** under an applied dc field of 1 kOe.

Secondly, the dynamic behavior of all anisotropic compounds was tested at 2 K in the frequency range of 1–1500 Hz without and with applied dc field (0–1.5 kOe) and an oscillating magnetic field of 3.5 Oe. However, no out-of-phase component in the frequency range [$\chi''_M(\nu)$] was observed for compounds **3**, **5**, and **6**, and thus they are not SMMs. Conversely, compound **4** showed some frequency-dependent behavior at 2 K, but the fact that no maximum was reached in the frequency range indicated fast quantum tunneling (QT) (Figure S22). To test whether intermolecular interactions were responsible for the fast QT, a diluted sample of **4** was prepared in a diamagnetic matrix of compound **1**.^[63] A diluted sample consisting of 5 % $\text{Dy}@\{\text{Y}[(\text{S})\text{-NEBA}]_3\}$ was synthesized by adding 5 % of $[\text{Dy}(\text{N}(\text{SiMe}_3)_2)_3]$ during the synthesis of compound **1**. The ac test performed on this sample did not show any improvement from the profile first observed (Figure S23); therefore, intermolecular interactions are not responsible for the absence of maxima in $\chi''_M(\nu)$, and higher frequencies or lower temperatures would be needed to reveal the SMM characteristics of compound **4**.

Conclusion

The new enantiopure amidinate (S)-NEBA was introduced into the chemistry of the rare-earth elements. Besides the synthesis of [(S)-HNEBA], enantiomerically pure homoleptic rare earth metal complexes $[\text{Ln}\{(\text{S})\text{-NEBA}\}_3]$ were prepared. All complexes are chiral at the metal center, but of the two possible diastereomers exclusively those having Δ configuration along the helical axis were formed. The luminescence properties of compounds **2** and **3** were investigated; they show the expected orange and green luminescence. Moreover, the magnetic properties of

compounds **3–6** and the diluted compound $\text{Dy}@\text{Y}(\text{S})\text{-NEBA}_3$ were studied. Under an applied dc field, the expected paramagnetic behavior was observed for **3–6**. In an oscillating magnetic field compound **4** showed some frequency-dependent behavior at 2 K, but the fact that no maximum was reached in the frequency range indicated fast QT.

Experimental Section

General Methods: All air- and water-sensitive materials were prepared under nitrogen by using a Schlenk line or glove box. Toluene and *n*-pentane were obtained from an MBRAUN solvent purification system (SPS-800). Deuterated solvents were purchased from Aldrich (99 atom-% D), dried, and stored in vacuo with CaH_2 . The other chemicals were purchased and used without further purification. NMR spectra were recorded with a Bruker Avance II 300 MHz or Avance III 400 MHz NMR spectrometer. Elemental analyses were carried out with an Elementar Vario micro cube. IR spectra were recorded with a Bruker TENSOR 37 spectrometer by using the attenuated total reflection (ATR) method.

Luminescence Measurements: Solid-state excitation spectra were measured with a Shimadzu RF-5301PC spectrofluorophotometer. Solid-state emission spectra were recorded with an irradiance-calibrated CCD spectrometer (Avantes AvaSpec-2048UA). A 1000 W xenon lamp (LOT) and a Spex monochromator were used as excitation source.

Magnetic Measurements: Due to the air-sensitive nature of the samples, sample preparation for all compounds was carried out in a glove box under argon. The samples were ground and placed on a gelatin capsule with a small amount of eicosane to avoid movement during the measurement. Magnetic susceptibility data were collected in the temperature range of 2–300 K on powdered samples under an applied dc field of 1000 Oe by employing a Quantum Design model MPMS-XL SQUID magnetometer. Data were corrected for diamagnetism by means of Pascal constants and sample-holder correction. The dynamic magnetic behavior of anisotropic systems was probed at 2 K in the frequency range of 1–1500 Hz with 0–5 kOe applied dc fields and a 3.5 Oe oscillating field.

Synthesis of (S,S)-N,N'-Bis[1-(2-naphthyl)ethyl]benzamidinium [(S)-HNEBA]: The ligand (S)-HNEBA was synthesized by applying a modified procedure from the literature.^[29]

(S)-N-[1-(2-Naphthyl)ethyl]benzamide (I): (S)-1-(2-Naphthyl)ethylamine (4 g, 23.35 mmol) was dissolved in aqueous sodium hydroxide solution (10 %, 24 mL). Benzoyl chloride (3.53 g, 25 mmol) was added dropwise to this solution, which was stirred at room temperature for 1.5 h. A white precipitate formed, which was collected by filtration, washed with water, and dried under reduced pressure. Yield 6.17 g (96 %). ^1H NMR (300.13 MHz, CDCl_3 , 298 K): δ = 7.86–7.78 (m, 5 H, Ar), 7.53–7.40 (m, 6 H, Ar), 6.42 (d, J = 7.2 Hz, 1 H, Ar), 5.52 (m, J = 6.8 Hz, 1 H, CH), 1.71 (d, J = 6.8 Hz, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CDCl_3 , 298 K): δ = 166.7 (O=C–N), 140.5 (Ar), 134.6 (Ar), 133.4 (Ar), 132.8 (Ar), 131.5 (Ar), 128.6 (Ar), 128.6 (Ar), 127.9 (Ar), 127.7 (Ar), 127.0 (Ar), 126.3 (Ar), 126.0 (Ar), 124.8 (Ar), 124.7 (Ar), 49.3 (CH), 21.7 (CH_3) ppm.

(S)-N-[1-(2-Naphthyl)ethyl]benzimidoyl Chloride (II): Compound **I** (6.17 g, 22.44 mmol) and 2,6-lutidine (2.56 g, 2.78 mmol) were dissolved in dry CH_2Cl_2 (70 mL) and the solution was cooled to 0 °C. A solution of oxalyl chloride (2.10 g, 16.47 mL) in dry CH_2Cl_2 (40 mL) was added slowly to the mixture over 0.5 h. The reaction mixture was stirred at 0 °C for 0.5 h and at room temperature for a further

0.5 h. The solvent was removed in vacuo, and *n*-pentane (100 mL) was added to the residue. The mixture was stirred at room temperature for 1 h. The precipitate was removed by filtration, and the filtrate was reduced to dryness in vacuo. Yield: 3.08 g (47 %). ^1H NMR (300.13 MHz, CDCl_3 , 298 K): δ = 8.10 (d, 2 H, Ar), 7.92 (s, 1 H, Ar), 7.85 (dt, J = 7.8, 7.3, 2.7 Hz, 3 H, Ar), 7.66 (dd, J = 8.5, 1.8 Hz, 1 H, Ar), 7.51–7.42 (m, 5 H, CH, Ar), 5.36 (q, J = 6.6 Hz, 1 H, CH), 1.67 (d, J = 6.6 Hz, 3 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CDCl_3 , 298 K): δ = 166.6 (NCCl), 142.2 (*i*-Ar), 141.1 (Ar), 135.6 (Ar), 133.4 (Ar), 132.7 (Ar), 131.5 (Ar), 129.2 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.6 (Ar), 126.0 (Ar), 125.6 (Ar), 125.1 (Ar), 125.0 (Ar), 63.2 (CH), 23.5 (CH_3) ppm.

(S,S)-N,N'-Bis[1-(2-naphthyl)ethyl]benzamidinium [(S)-HNEBA]: (S)-N-[1-(2-Naphthyl)ethyl]benzimidoyl chloride (3.18 g, 10.49 mmol) and (S)-[1-(2-naphthyl)ethyl]amine (1.8 g, 10.51 mmol) were dissolved in toluene (25 mL). The mixture was heated at reflux for 24 h. The solvent was decanted at –30 °C. The oily residue was dissolved in CH_2Cl_2 (50 mL) and washed with saturated sodium carbonate solution (2 × 25 mL). The organic phase was concentrated in vacuo. For purification, the product was crystallized from hot ethanol. Yield: 2.78 g (62 %). Overall yield: 27.8 %. $\text{C}_{31}\text{H}_{28}\text{N}_2$ (428.58): calcd. C 86.88, H 6.59, N 6.54; found C 86.94, H 6.90, N 6.34. ^1H NMR (300.13 MHz, DMSO, 298 K): δ = 7.99–7.89 (m, 4 H, Ar), 7.70–6.86 (m, 15 H, Ar), 6.50 (d, J = 8.2 Hz, 1 H, Ar), 5.39 [m, J = 7.0 Hz, 1 H, $\text{CH}_{(\text{near C=N})}$], 4.20 [q, J = 6.3 Hz, 1 H, $\text{CH}_{(\text{near C=N})}$], 1.52 [d, J = 7.1 Hz, 3 H, $\text{CH}_{3(\text{near C=N})}$], 1.26 [d, J = 6.4 Hz, 3 H, $\text{CH}_{3(\text{near C=N})}$] ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, DMSO, 298 K): δ = 156.5 (N=C–N), 146.2 (Ar), 145.3 (Ar), 136.1 (Ar), 133.6 (Ar), 133.1 (Ar), 132.6 (Ar), 131.8 (Ar), 128.9 (Ar), 128.7 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 127.6 (Ar), 127.4 (Ar), 127.0 (Ar), 126.3 (Ar), 125.6 (Ar), 125.5 (Ar), 125.1 (Ar), 124.6 (Ar), 123.9 (Ar), 57.4 [$\text{CH}_{(\text{near C=N})}$], 50.4 [$\text{CH}_{(\text{near C=N})}$], 27.2 [$\text{CH}_{3(\text{near C=N})}$], 23.6 [$\text{CH}_{3(\text{near C=N})}$] ppm. IR (ATR): $\tilde{\nu}$ = 3426 (w), 2960 (m), 1653 (s), 1598 (m), 1507 (m), 1478 (s), 1369 (m), 1309 (m), 1291 (m), 1266 (m), 1180 (m), 1124 (m), 1069 (m), 948 (m), 912 (m), 893 (m), 856 (m), 815 (s), 744 (s), 703 (vs), 488 (s), 480 (s), 475 (vs) cm^{-1} .

General Synthetic Process for Lanthanide Amidinate Complexes $\{\text{Ln}[(\text{S})\text{-NEBA}]_3$ [Ln = Y (1), Sm (2), Tb (3), Dy (4), Er (5), Yb (6), Lu (7)]: Toluene (10 mL) was condensed at –78 °C onto a mixture of $[\text{Ln}(\text{N}(\text{SiMe}_3)_2)_3]$ (0.33 mmol) and (S)-HNEBA (428 mg, 1 mmol). The mixture was heated to reflux for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was washed with *n*-pentane (10 mL), and the product was recrystallized from toluene/*n*-pentane. All products were isolated as single crystals, which contain three molecules of toluene in the lattice.

1: Colorless solid (292 mg, 0.177 mmol, yield: 53 %). ^1H NMR (400.13 MHz, CDCl_3 , 333 K): δ = 7.93–7.83 (m, 3 H, Ar), 7.58 (t, J = 7.5 Hz, 12 H, Ar), 7.44 (d, J = 7.9 Hz, 6 H, Ar), 7.37–7.20 (m, 24 H, Ar), 7.11 (t, J = 7.3 Hz, 6 H, Ar), 6.73 (d, J = 7.1 Hz, 6 H, Ar), 4.39 (q, J = 6.4 Hz, 6 H, CH), 1.72 (d, J = 6.4 Hz, 18 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3 , 298 K): δ = 145.6 (N–C–N), 135.4 (Ar), 133.2 (Ar), 132.2 (Ar), 129.0 (Ar), 128.3 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.0 (Ar), 126.2 (Ar), 125.5 (Ar), 125.3 (Ar), 125.0 (Ar), 124.7 (Ar), 57.6 (CH), 26.6 (CH_3) ppm. $^{89}\text{Y}\{^1\text{H}\}$ NMR (19.61 MHz, CDCl_3 , 298 K): δ = 447 ppm. IR (ATR): $\tilde{\nu}$ = 3426 (m), 3051 (m), 2961 (m), 2921 (m), 2845 (m), 1653 (vs), 1598 (s), 1478 (vs), 1443 (m), 1369 (m), 1297 (m), 1266 (m), 1180 (w), 1124 (w), 1070 (w), 1023 (w), 952 (w), 893 (m), 856 (s), 816 (s), 772 (s), 745 (m), 702 (s), 477 (m) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{N}_6\text{Y}$ (1647.94): calcd. C 83.08, H 6.42, N 5.12; found C 83.15, H 6.15, N 5.73.

2: Colorless solid (178 mg, 0.104 mmol, yield: 31 %). IR (ATR): $\tilde{\nu}$ = 3052 (w), 2965 (w), 2924 (w), 1630 (m), 1599 (m), 1495 (w), 1446 (s), 1368 (m), 1319 (m), 1297 (m), 1269 (m), 1190 (m), 1126 (m), 1073 (m), 950 (w), 892 (m), 856 (s), 818 (s), 784 (m), 746 (vs), 701 (s), 669 (vs), 477 (s), 430 (w) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{N}_6\text{Sm}$ (1709.38): calcd. C 80.10, H 6.19, N 4.92; found C 80.68, H 6.30, N 5.63.

3: White solid (206 mg, 0.120 mmol, yield: 36 %). IR (ATR): $\tilde{\nu}$ = 3425 (m), 3053 (m), 2964 (m), 2922 (m), 1631 (s), 1599 (m), 1440 (vs), 1403 (s), 1369 (m), 1322 (m), 1298 (m), 1269 (m), 1178 (m), 1125 (m), 1073 (w), 1020 (w), 950 (w), 892 (m), 856 (m), 819 (s), 785 (m), 747 (s), 730 (m), 701 (s), 477 (m), 417 (w), 362 (m) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{N}_6\text{Tb}$ (1717.95): calcd. C 79.70, H 6.16, N 4.89; found C 79.95, H 6.10, N 5.42.

4: Yellow solid (150 mg, 0.087 mmol, yield: 26 %). IR (ATR): $\tilde{\nu}$ = 3055 (w), 2967 (w), 2929 (w), 1631 (m), 1599 (m), 1495 (m), 1439 (vs), 1403 (s), 1370 (s), 1352 (s), 1322 (s), 1299 (s), 1176 (m), 1127 (s), 1074 (s), 951 (s), 892 (s), 857 (s), 820 (s), 785 (s), 747 (s), 670 (vs), 477 (s), 465 (s) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{DyN}_6$ (1721.53): calcd. C 79.53, H 6.15, N 4.88; found C 79.81, H 6.38, N 5.63.

5: Pink solid (366 mg, 0.212 mmol, yield: 64 %). IR (ATR): $\tilde{\nu}$ = 3054 (w), 2962 (w), 2923 (m), 1630 (m), 1599 (m), 1494 (m), 1440 (s), 1404 (m), 1370 (m), 1323 (m), 1299 (m), 1177 (m), 1126 (m), 1073 (m), 951 (m), 891 (m), 856 (s), 819 (vs), 785 (m), 746 (vs), 702 (s), 670 (vs), 477 (s), 465 (m) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{ErN}_6$ (1726.29): calcd. C 79.31, H 6.13, N 4.87; found C 79.81, H 6.36, N 5.47.

6: Yellow solid (270 mg, 0.156 mmol, yield: 47 %). IR (ATR): $\tilde{\nu}$ = 3053 (w), 2967 (w), 2929 (w), 1631 (w), 1599 (w), 1495 (w), 1449 (s), 1370 (m), 1323 (m), 1299 (m), 1270 (m), 1193 (m), 1127 (m), 1074 (m), 951 (w), 892 (m), 857 (s), 820 (s), 785 (m), 747 (s), 730 (vs), 702 (vs), 670 (s), 477 (vs), 430 (w) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{N}_6\text{Yb}$ (1732.07): calcd. C 79.05, H 6.11, N 4.85; found C 79.65, H 6.23, N 5.52.

7: Colorless solid (292 mg, 0.168 mmol, yield: 51 %). ^1H NMR (300.13 MHz, CDCl_3 , 298 K): δ = 7.91–7.82 (m, 3 H, Ar), 7.71–7.03 (m, 48 H, Ar), 6.71 (d, J = 6.5 Hz, 3 H, Ar), 6.63 (d, J = 6.5 Hz, 3 H, Ar), 4.46 (q, J = 6.7 Hz, 6 H, CH), 2.00 (d, J = 6.4 Hz, 18 H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.48 MHz, CDCl_3 , 298 K): δ = 145.4 (N–C–N), 137.9 (Ar), 135.7 (Ar), 133.3 (Ar), 132.2 (Ar), 129.1 (Ar), 128.3 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.0 (Ar), 126.0 (Ar), 125.5 (Ar), 125.3 (Ar), 124.9 (Ar), 57.5 (CH), 26.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3407 (m), 2955 (m), 2920 (w), 1637 (s), 1599 (w), 1483 (m), 1451 (m), 1414 (w), 1268 (w), 1248 (w), 1214 (w), 1072 (m), 968 (m), 928 (m), 863 (m), 765 (s), 759 (s), 607 (vs), 601 (m), 542 (s), 474 (w), 443 (w) cm^{-1} . $\text{C}_{114}\text{H}_{105}\text{LuN}_6$ (1734.01): calcd. C 78.96, H 6.1, N 5.1; found C 79.81, H 6.37, N 5.63.

X-ray Crystallographic Studies on (5)–HNEBA and 1–7: A suitable crystal was covered with mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or STOE StadiVari diffractometer. All structures were solved by using SHELXS-2014.^[64] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out with SHELXL-2014 by using full-matrix least-squares techniques against F^2 (all data).^[64] Hydrogen-atom positions were calculated. The locations of the largest peaks in the final difference Fourier map and the magnitude of the residual electron densities in each case were of no chemical significance. Data collection parameters are given in Table S1. CCDC 1489233 (for HNEBA), 1489234 (for **1**), 1489235 (for **2**), 1489236 (for **3**), 1489237 (for **4**), 1489238 (for **5**), 1489239 (for **6**), and 1489240 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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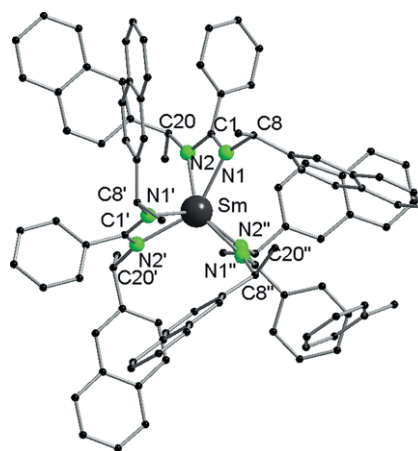
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Chiral Lanthanide Complexes

M. He, Z. Chen, E. M. Pineda,
X. Liu, E. Bouwman, M. Ruben,
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Homoleptic Chiral Benzamidinate Complexes of Rare-Earth Elements: Synthesis, Structure, Luminescence, and Magnetism



A series of enantiomerically pure homoleptic rare-earth metal amidinate complexes $[Ln\{(S)\text{-NEBA}\}_3]$ [(*S*)-NEBA = (*S,S*)-*N,N'*-bis[1-(2-naphthyl)ethyl]benzamidinate; Ln = Y, Sm, Tb, Dy, Er, Yb, Lu] is reported. The luminescence and magnetic properties of some selected compounds were investigated.

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