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A Chiral 2,6-Bis(Oxazolinyl)Pyridine Ligand with Amide Groups to Form Isomorphous Complexes through All the Lanthanoid Series

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We newly synthesized the chiral pybox ligand, 2,6-bis[(4S)-*tert*-butylcarbamoyl-2-oxazolin-2-yl]pyridine, whose lanthanoid(III) complexes have formed isomorphous crystals through all the lanthanoid series. The luminescence properties of the Eu(III) complex have been investigated.

Lanthanoid(III) (Ln(III)) complexes have attracted a lot of attention in various fields such as imaging probes,[1,2] emissive materials,[3] and catalysts[4] because of their inherent magnetical, photophysical, and chemical properties. In particular, chiral luminescent Ln(III) complexes have been recently focused upon due to their high circularly polarized luminescent (CPL) activity.[5] In many cases, however, the high coordination number, the high lability, and the different ionic radii of Ln(III) ions have made the chemistry of Ln(III) complexes complicated.[6] Furthermore, the coordination geometry of the Ln(III) complexes frequently varies with the lanthanoid ions used, even if the complexes contain the same ligand.[6b−d] Although some isostructural series of Ln(III) complexes have been reported,[7] there has been only one example of isomorphous complexes, which have the same structures and same space groups, through all the lanthanoid series.[7a] Therefore, in order to further obtain general principles for lanthanoid complexes, it is desirable to explore the ligands, the coordination chemistry of which does not change with the lanthanide ions.

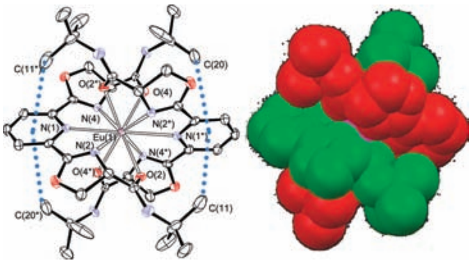
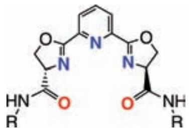


Figure 1. ORTEP view (left) and space-filling representation (right) of the [Eu((*S*,*S*)-^{t}Bu-pbxa)$_2$]$^{3+}$ cation. Blue dotted lines show CH−π interactions. Hydrogen atoms are omitted for clarity.

Chart 1. Chiral Pybox Ligands with Amide Groups



Some important classes of ligands using Ln(III) complexes are polypyridines and cyclic and acyclic polyalkylamines.[1−5] In addition, it has been recently reported that 2,6-bis(oxazolinyl)pyridine (pybox) is suitable to prepare the Ln(III) complexes which show highly catalytic activities[8] and superior emission properties.[6a] However, it should be noted that Ln(III) complexes with neutral ligands such as imines are prone to partial dissociation of the ligand.[6e] In order to overcome this issue, we newly synthesized a chiral pybox ligand having an amide group at the 4-position of each oxazoline ring (Chart 1).

This ligand has the following features: (i) Two amide oxygen atoms as well as three pybox nitrogen atoms function

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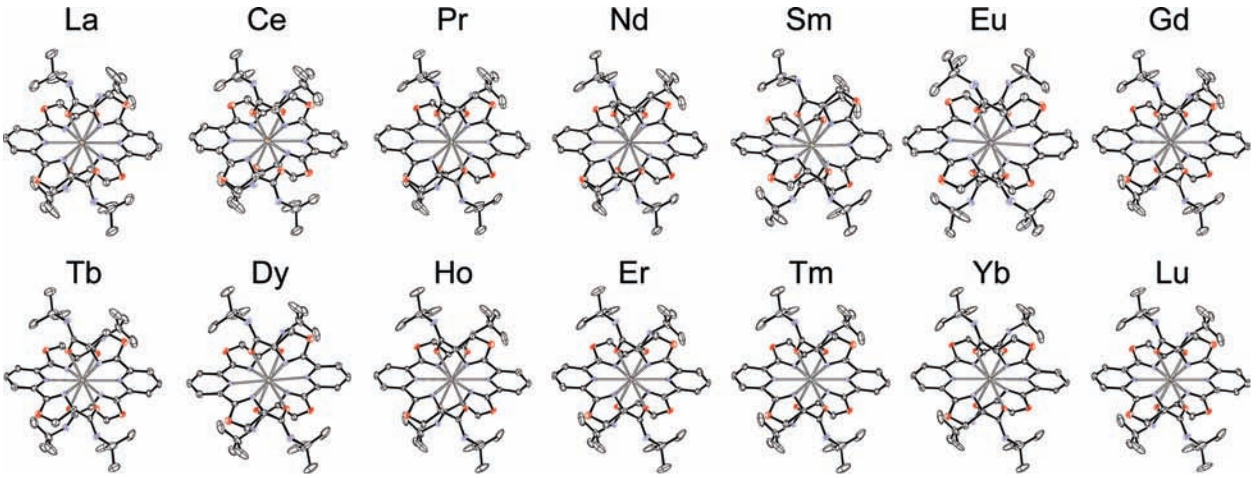

Figure 2. ORTEP views (50% probability) of all [Ln((*S*,*S*)-^{t}Bu-pbxa)$_2$]$^{3+}$ cations prepared in this study. Hydrogen atoms are omitted for clarity.

as binding sites to metal ions; thus this ligand acts as a pentadentate chelator. (ii) Various substituent groups can be easily introduced to the ligand through the amide groups. (iii) The chiral oxazoline moiety in the ligand provides their complexes with asymmetric properties such as CPL activity. We have found that the chiral pybox ligand with a tert-butyl carbamoyl group at the 4-position of oxazoline, 2,6-bis[(4*S*)-*tert*-butylcarbamoyl-2-oxazolin-2-yl]pyridine ((*S*,*S*)-^{t}Bu-pbxa; R = ^{t}Bu in Chart 1), is an effective ligand for all Ln(III) ions. In this report, the structural and luminescence properties of the Ln(III) complexes with (*S*,*S*)-^{t}Bu-pbxa have been described.

(*S*,*S*)-^{t}Bu-pbxa is easily synthesized by the reaction of L-serine *tert*-butyl amide hydrochloride salt and dimethyl pyridine-2,6-dicarboximidate in acetonitrile in the presence of triethylamine using a literature method[9] with some modifications. The reaction of the ligand with Ln(III) nitrate salts in the ratio L/Ln = 2:1 in methanol gives the corresponding Ln(III) complexes, [Ln((*S*,*S*)-^{t}Bu-pbxa)$_2$](NO$_3$)$_3$ (Ln = La–Lu without *Pm*), in good yields (ca. 70%). The formation of bis- or tris-(ligand) complexes bearing neutral imine ligands starting from nitrate salts of the lanthanoid is rare because of the high affinity of nitrates to Ln(III) ions.[10]

In all cases, single crystals of the complexes suitable for X-ray analysis were formed by the slow diffusion of diethyl ether in the methanol solution of the complex. The ORTEP view of the cation [Eu((*S*,*S*)-^{t}Bu-pbxa)$_2$]$^{3+}$ on behalf of all Ln(III) complexes is shown in Figure 1.[11] All crystal structures are depicted in Figure 2. All 14 crystals belong to the same orthorhombic space group $P2_12_12$ with similar cell parameters (Table S1, Supporting Information). All complexes have crystallographic C_2 axes passing through the Ln(III) ions and form left-handed double-helical structures. Their metal ions are coordinated by two ^{t}Bu-pbxa molecules using the one pyridine nitrogen atom (N$_{py}$: N(1)), two oxazoline nitrogen atoms (N$_{ox}$: N(2) and N(4)), and two amide oxygen atoms (O$_{am}$: O(2) and O(4)) of the ligand. The crystals of all lanthanoid complexes synthesized here are therefore isomorphous.

The bond lengths around the metal ion of [Ln((*S*,*S*)-^{t}Bu-pbxa)$_2$]$^{3+}$ are in the ranges 2.717(5)−2.600(5), 2.637(5)−2.427(5), and 2.570(4)−2.393(4) for Ln−N$_{py}$, Ln−N$_{ox}$, and Ln−O$_{am}$, respectively. The Ln−N$_{ox}$ bond lengths are shorter than the Ln−N$_{py}$ ones, suggesting more strong coordination of the oxazolinyl nitrogen atoms. Furthermore, the averaged distances between the carbon atoms (C(11) and C(20)) of the two *tert*-butyl groups of one ligand and the pyridyl plane of another ligand in the complex are in the range of 4.13−3.89 Å, which indicates the existence of CH−π interactions. Accordingly, two ^{t}Bu-pbxa molecules form the cryptand-like dimer locked by the CH−π interaction with each other. The bond lengths around the metal center and the CH−π interactions are sequentially reduced with an increase of the atomic number of the lanthanoid, reflecting the lanthanoid contraction (Figure 3A).

The averaged bite angles for $\angle$N$_{py}$−M−N$_{ox}$ are similar among the different metals (the averaged bite angles are 60.8° and 61.9° for La(III) and Lu(III) complexes, respectively). On the other hand, the averaged bite angles for $\angle$N$_{ox}$−M−O$_{am}$ and the averaged torsion angles between two N(2)−O(2*)−N(4)−O(4*) planes slightly increase in the order from La to Lu (Figure 3B). Furthermore, the dihedral angles between two pyridyl rings are in the range of 77.6−69.8° and sequentially decrease with an increase of the atomic number of the lanthanoid. These results indicate that, in [Ln((*S*,*S*)-^{t}Bu-pbxa)$_2$]$^{3+}$, the flexible change of these angles allows the complexes of the ligand to accept various ionic radii of Ln(III) ions. The selected geometric parameters for all complexes are summarized in Table S2 (Supporting Information).

The ^{1}H NMR studies of the diamagnetic species, La(III) and Lu(III) complexes, in methanol-d_4 were carried out. In each case, their NMR signals are sharp and show high symmetry of the complexes as well as the crystal structure (Figure S1, Supporting Information). On decreasing the temperature to 213 K, no additional peaks were found, although broadening and very slight shifts of the signals have been observed for the La(III) complex (Figure S2, Supporting Information). This result suggests that a fast equilibrium between diastereomers has not occurred at room temperature within the NMR time scale.[12] All pyridyl and oxazolinyl protons in the complexes indicate downfield shifts on

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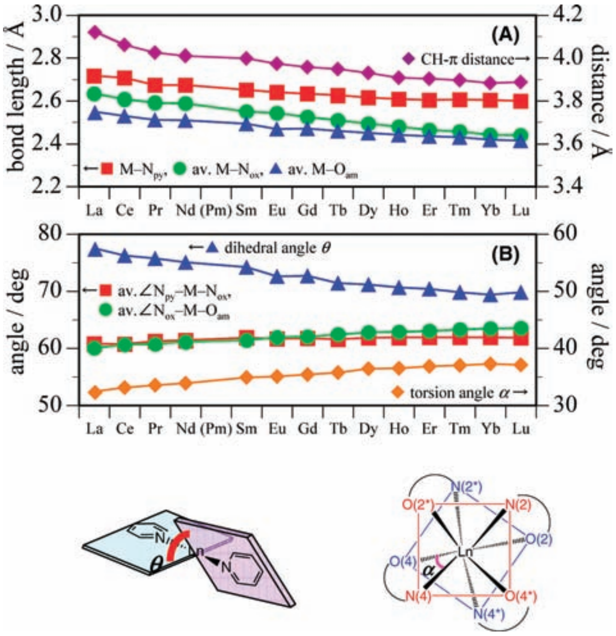

Figure 3. Geometric parameters in $[Ln((S,S)\text{-}^{t}Bu\text{-}pbxa)_2]^{3+}$. (A) Bond lengths around the metal ions and averaged distances between *tert*-butyl groups and a pyridine ring. (B) Bond angles around metal ions, dihedral angles, θ, between two pyridyl planes, and averaged torsion angles, α, between two N(2)−O(2*)−N(4)−O(4*) planes.

complexation due to the coordination of those groups to the metal ion. On the other hand, the *tert*-butyl protons shift to the high-field in comparison with the ligand, which suggests that the CH−π interactions observed in their crystal structures also operate in the solution. Similar noncovalent interaction such as π−π interaction was observed in other LnL_2 (L = neutral ligand) complexes.[10b] Such interactions may contribute to maintaining the LnL_2 form in the solution state.

In both solid and methanol solution, $[Eu((S,S)\text{-}^{t}Bu\text{-}pbxa)_2](NO_3)_3$ shows a characteristic emission based on f−f transitions of the Eu(III) ion upon irradiation of UV light (Figure S3, Supporting Information). The absorption spectra of (*S*,*S*)-^{t}Bu-pbxa and its Eu(III) complex in methanol are similar to each other and to the excitation spectrum of the Eu(III) complex (Figure S4 and inset, Supporting Information). Therefore, the ligand should function as a good light-capturing antenna. Considering that the La(III) and Lu(III) complexes in the solution state maintain similar structures to their crystal structures (*vide supra*), the similarity of the emission spectra in both the solid and solution states suggests that no noticeable structural change occurs on the Eu(III) complex in the solution state. Furthermore, each emission band originating from the magnetic dipole allowing transition ($^5D_0 \rightarrow {}^7F_1$) and the electric dipole allowing transition ($^5D_0 \rightarrow {}^7F_2$) shows CPL activity (Figure S5, Supporting Information). The magnitudes of the luminescence dissymmetry factor, g_{lum}, for these emission bands are −0.18 and +0.03 at 592.2 and 616.2 nm, respectively.[13] The former is comparable to those of other chiral Eu(III) complexes.[14] The relatively large g_{lum} may be attributed to the left-handed double-helical structure kept in solution.

Table 1. Photophysical Properties of $[Eu((S,S)\text{-}^{t}Bu\text{-}pbxa)_2](NO_3)_3$ in MeOH

λ_{max}^{abs}/nm (ε/M^{-1} cm^{-1})	λ_{max}^{em}/nm	τ/ms	Φ/%	g_{lum}
245 (1.9 × 10^4)	593.8, 616.6, 685.2	1.66	17(1)	−0.18^a
285 (7.8 × 10^3)	(593.8, 616.6, 685.2)^b	1.47,^{b} 1.38,^{c} 2.54^d		+0.03^e

^{a} At 592.2 nm. ^{b} In solid. ^{c} In H_2O. ^{d} In D_2O. ^{e} At 616.2 nm.

The emission corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition decays single-exponentially in both the solid and solution states, and the emission lifetimes are 1.47 and 1.66 ms in a solid and methanol, respectively.[15] The *q* value,[16] which is the number of coordinated water molecules calculated from the lifetimes[15] in H_2O and D_2O, is almost zero ($q = 0.03$), which means that the Eu(III) ion is effectively shielded by two (*S*,*S*)-^{t}Bu-pbxa molecules, as shown in the crystal structure even in an aqueous solution.[17] For this reason, the luminescent quantum yield (17(1)%) in methanol is significantly high in comparison with that of other Eu(III) complexes.[14] The photophysical properties of $[Eu((S,S)\text{-}tBu\text{-}pbxa)_2](NO_3)_3$ are summarized in Table 1.

In summary, the chiral pybox ligand, (*S*,*S*)-^{t}Bu-pbxa, is able to form the isomorphous crystals of the Ln(III) complexes through all the lanthanoid series. These Ln(III) complexes are essentially inert for solvation since their metal ions are fully shielded by two ^{t}Bu-pbxa molecules which form a cryptand-like dimer locked by CH−π interactions with each other. Furthermore, $[Eu((S,S)\text{-}^{t}Bu\text{-}pbxa)_2](NO_3)_3$ has remarkable luminescence properties including CPL activity. These observations suggest that chiral pybox ligands having amide groups act as effective chelators for all Ln(III) ions. A detailed study for such ligands is now in progress.

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Supporting Information Available: Syntheses of a ligand and complexes, experimental details, crystallographic data, selected geometric parameters, ^{1}H NMR spectra, emission spectra, absorption spectra, CPL spectra, emission decay plot, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) The g_{lum} value of $[Eu((S,S)\text{-}^{t}Bu\text{-}pbxa)_2](NO_3)_3$ was estimated from that of tris(3-trifluoroacetyl-(+)-camphorato)europium(III) in dry DMSO (Figure S6, Supporting Information). The g_{lum} value of $[Eu((S,S)\text{-}^{t}Bu\text{-}pbxa)_2](NO_3)_3$ at 593.4 nm being the CPL peak wavelength is −0.15. Details of the measurement are described in the Supporting Information.

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(17) Unfortunately, the NMR spectra of the La(III) and Lu(III) complexes were not obtained in D_2O, due to low solubility of these complexes for water. However, given the *q* value and the NMR results in methanol-d_4, Ln(III)-(*S*,*S*)-^{t}Bu-pbxa complexes probably maintain a LnL_2 form in water.