Heterodinuclear Group 13 Element Complexes of N406-Type Dipyrrin with an Unsymmetrical Twisted Structure

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Heterodinuclear Group 13 Element Complexes of N_4O_6-Type Dipyrrin with an Unsymmetrical Twisted Structure

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Abstract: Heterodinuclear group 13 element complexes of an N_4O_6-type dipyrrin cyclic dimer were synthesized by the stepwise reaction with boron and the group 13 elements (Al, Ga, and In). The macrocycles have a new type of unsymmetrical twisted (pseudo-figure-of-eight) structure.

Introduction

Helical structures obtained by winding linear molecules often contribute to constructing elaborately organized architectures in biological and artificial molecular systems.[1]–[3] On the other hand, figure-of-eight helical motifs are produced by twisting macrocyclic compounds, and are found in natural circular DNA and oligopeptides. In some artificial figure-of-eight macrocycles,[4]–[8] the twisted configurations are maintained by metal-coordination[9]–[14] and intramolecular non-covalent interactions such as intramolecular hydrogen bonds.[15]–[17] The figure-of-eight structure is also formed without such constraints when the conformation is intrinsically the most stable.[18]–[29]

We have recently reported a figure-of-eight homodinuclear boron complex [**L**B_2] obtained from a macrocyclic N_4O_6-type dipyrrin ligand, H_6**L** (Figure 1).[30],[31] The figure-of-eight helicity of [**L**B_2] arises from a tetrahedral geometry around each boron center chelated by the tetradentate N_2O_2 dipyrrin unit.[32]–[34] The same macrocyclic ligand also coordinates to aluminum ions, but the resultant homodinuclear complex [**L**$Al_2(CH_3OH)_4$] has a planar structure (Figure 1).[31] Furthermore, a mononuclear boron complex [H_3**L**B] can be selectively synthesized from this ligand; this mononuclear complex has a twisted unsymmetrical (pseudo-figure of eight) conformation and leaves a N_2O_2 coordination site in its macrocyclic framework (Figure 1). Thus, the ligand H_6**L** would be useful to create variously-shaped macrocyclic main-group-element complexes.

In contrast to the symmetrical artificial figure-of-eight molecules, a limited number of unsymmetrical ones have been reported.[10],[35]–[39] The unsymmetrical framework would give more elaborate molecular structures and functions, such as tuning of the chiroptical properties and stimuli-induced inversion of a helical preference.[36] Although coordination bonds seem to be effective to prepare the unsymmetrical figure-of-eight structures, only three examples were reported in which two different transition metal ions were introduced step by step into a symmetrical macrocyclic ligand.[10],[37],[39] We envisaged that the mononuclear macrocyclic boron complex [H_3**L**B] would bind to the element other than boron to produce unsymmetrical dinuclear complexes with a twisted structure. We now report the first unsymmetrical pseudo-figure-of-eight helical heterodinuclear macrocycle [**L**BM$(MeOH)_2$] (M = Al, Ga, In) containing main group elements instead of transition metal ions (Figure 1). These compounds were synthesized by the stepwise reactions of H_6**L** with two different group 13 elements. In the unique helical macrocyclic scaffolds, the twisting angles of the complexes depend on the combination of the two central elements.

Results and Discussion

The complex [H_3**L**B] was synthesized from the bis N_2O_2 macrocyclic ligand H_6**L** by the condensation with 2.4 molar equivalent of boric acid in chloroform (Figure 1).[30] By introducing a trivalent group 13 element (Al, Ga, In) into the vacant N_2O_2 coordination site of [H_3**L**B], we have successfully obtained the heterodinuclear complexes [**L**BM$(CH_3OH)_2$] (M = Al,

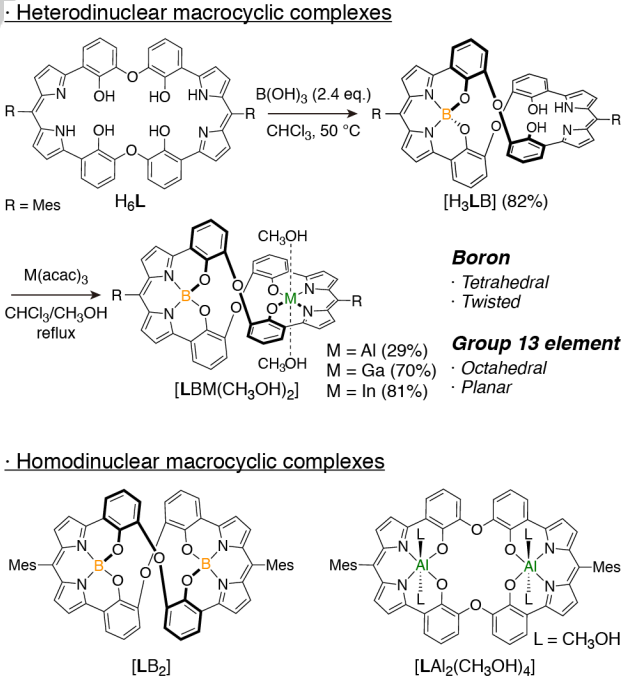

Figure 1. Heterodinuclear (top) and homodinuclear (bottom) macrocyclic complexes of bis-N_2O_2-dipyrrin macrocycle H_6**L** (Mes: 2,4,6-trimethylphenyl).

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Ga, In). They were synthesized by the reaction of an acetylacetonato complex of the group 13 element [M(acac)$_3$] with the mononuclear boron complex [H$_3$**L**B] (Figure 1). The complexes are neutral in charge and the coordination is strong due to tetradentate chelation, which allowed the purification by column chromatography.

Single crystal X-ray diffraction analyses revealed the uniquely twisted macrocyclic structures of the unsymmetrical complexes (Figure 2). The single crystal of [**L**BGa(CH$_3$OH)$_2$] was obtained by slow diffusion of a CH$_3$OH layer into a CH$_2$Cl$_2$/MeOH solution of the complex, and the single crystal of [**L**BIn(CH$_3$OH)$_2$] was obtained by the slow evaporation of its CHCl$_3$/CH$_3$OH solution. For both complexes, the boron center had a tetrahedral geometry, and the two phenoxy rings coordinating to the boron were pushed up and down, respectively, against the dipyrrin moiety. Meanwhile, the gallium and indium centers had an octahedral geometry, whose four equatorial sites were occupied by tetradentate chelation from the macrocycle and two axial sites were coordinated by CH$_3$OH. As a result, the tetradentate N$_2$O$_2$ dipyrrin unit with gallium or indium has a planar conformation. This difference in the positions of the phenoxy rings resulted in the unsymmetrical twist of the macrocyclic framework. The N$_2$ dipyrrin unit in the boron complex and the one in the gallium or indium complex are almost perpendicular. The dihedral angle between the least square plane comprised of the two pyrrole rings (A and B, see Figure 2) and its in-between methine carbon and the plane comprised of the rings (C and D) and the methine carbon is 86.1° for [**L**BGa(CH$_3$OH)$_2$] and 88.4° for [**L**BIn(CH$_3$OH)$_2$]. These dihedral angles are similar to that of the mononuclear boron complex, [H$_3$**L**B].[30] Because of the twist induced by the tetrahedral boron center, the molecule [**L**BM(CH$_3$OH)$_2$] had a chirality, and both the *P* and *M* isomers[30],[34] existed in the racemic crystal.

Although the macrocyclic aromatic frameworks were twisted, the six oxygen atoms of the N$_4$O$_6$ dipyrrin ligand lay almost in the same plane; the root mean square distances from their least-squares plane were 0.085 Å and 0.017 Å for [**L**BGa(CH$_3$OH)$_2$] and [**L**BIn(CH$_3$OH)$_2$], respectively. The distance between the two phenoxy oxygens was different for the two complexes (2.63 Å for [**L**BGa(CH$_3$OH)$_2$] and 3.09 Å for [**L**BIn(CH$_3$OH)$_2$]), which reflects the atomic radii of the gallium and indium.

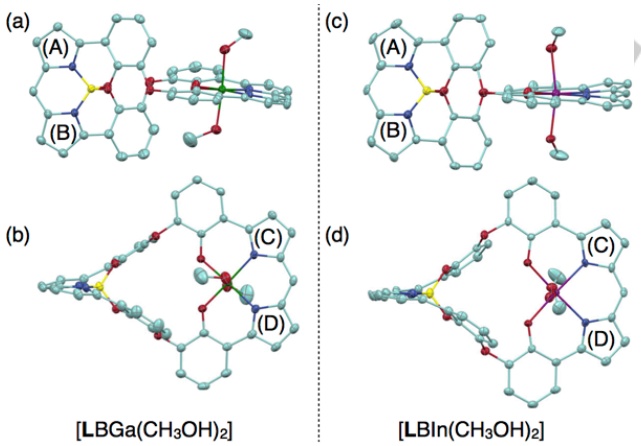

Figure 2. The molecular structures of [**L**BGa(CH$_3$OH)$_2$] and [**L**BIn(CH$_3$OH)$_2$] determined by X-ray crystallographic analyses. An ellipsoidal model (50% probability). Hydrogen atoms, solvents, and Mes groups are omitted for clarity. C, light blue; N, blue; O, red; B, yellow; Ga, green; In, purple. (a and b) [**L**BGa(CH$_3$OH)$_2$], top and side views. An *M*-[**L**BGa(CH$_3$OH)$_2$] isomer in the crystal of *rac*-[**L**BGa(CH$_3$OH)$_2$] is shown. (c and d) [**L**BIn(CH$_3$OH)$_2$], top and side views. An *M*-[**L**BIn(CH$_3$OH)$_2$] isomer in the crystal of *rac*-[**L**BIn(CH$_3$OH)$_2$] is shown.

Figure 3 shows the absorption and emission spectra of [**L**BGa(CH$_3$OH)$_2$] in toluene/CH$_3$OH = 95/5 (v/v). A strong absorption that peaked at 614 nm was observed, which was derived from both the N$_2$O$_2$ boron-dipyrrin[30] and gallium-dipyrrin units. The complex exhibited a sharp emission band at 653 nm, but its emission was weak and the emission quantum yield was below 1%. The absorption and emission properties of [**L**BM(CH$_3$OH)$_2$] (M = Al, Ga, In) have similar characteristics irrespective of the elements (Table 1). DFT calculations for [**L**BGa(MeOH)$_2$] suggest that the quenching of fluorescence is probably due to the photoinduced electron transfer (Figure S10). Detailed investigations of the photophysical properties of a family of the complexes are currently ongoing.

To the best of our knowledge, this is the first example of the 1:1 complexes of the gallium-dipyrrin (GADIPY) and indium-dipyrrin (INDIPY) derivatives, although the tris(dipyrrinato) complexes[40]–[42] or the porphyrin derivatives[43]–[45] of the late group 13 elements have been reported. The tetradentate chelation of the N$_2$O$_2$ dipyrrin unit employed in this study successfully yielded stable neutral complexes of these Lewis acidic elements in methanol. The study of these new chromophores contributes to the active fields of coordination and photophysical chemistry for a series of dipyrrin-metal complexes.[46]–[48]

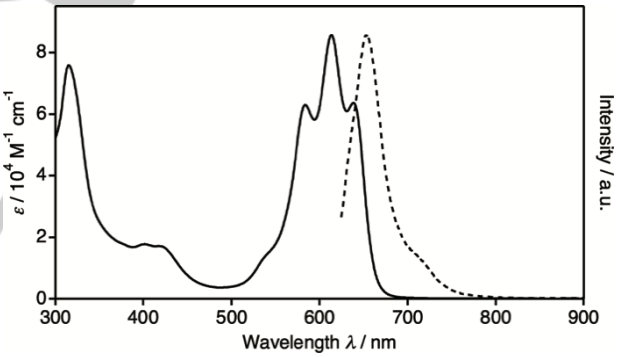

Figure 3. UV-vis absorption (solid line) and emission (dashed line) spectra of [LBGa(CH$_3$OH)$_2$] in toluene/CH$_3$OH = 95/5 (v/v) (λ_{ex} = 614 nm).

Table 1. Optical properties of [LBAl(CH$_3$OH)$_2$], [LBGa(CH$_3$OH)$_2$], and [LBIn(CH$_3$OH)$_2$] in toluene/CH$_3$OH = 95:5 (v/v). The excitation wavelength was 614 nm (Al, Ga) or 613 nm (In).

	λ_{abs} / nm	λ_{em} / nm	Φ_F
[LBAl(CH$_3$OH)$_2$]	614	644	< 0.01
[LBGa(CH$_3$OH)$_2$]	614	653	< 0.01
[LBIn(CH$_3$OH)$_2$]	613	653	< 0.01

Conclusions

In conclusion, we have successfully synthesized heterodinuclear macrocyclic dipyrrin complexes by the stepwise reaction with boron and the group 13 elements (Al, Ga, and In). The macrocycles have a new type of unsymmetrical twisted frameworks. The axial sites of the octahedral aluminum, gallium,

and indium centers were occupied by labile methanol molecules, indicating their possible use for the molecular recognition. The unique chiral complex with two perpendicular dipyrrin chromophores is a promising platform for enantioselective molecular sensing and functional chiroptical chemistry.

Experimental Section

Materials and methods

Unless otherwise noted, solvents and reagents were purchased from TCI Co., Ltd., Wako Pure Chemical Industries, Ltd., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Co., and used without further purification. Alumina for column chromatography was purchased from Wako Pure Chemical Industries, Ltd. (alumina, activated (about 75 mm)).

NMR spectroscopy: ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-400 or 600 spectrometers. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ^{1}H and ^{13}C NMR measurements.

Single-crystal X-ray crystallography: Single-crystal X-ray crystallographic measurements were performed using a Bruker APEX II ULTRA with MoKα radiation (graphite-monochromated, λ = 0.71073 Å) at 120 K. The collected diffraction images were processed by Bruker APEX2. The initial structure was solved using SHELXS-2013[49] and refined using SHELXL-2016,[50] which were running on Yadokari-XG crystallographic software.[51] CCDC 1848533 (for [**L**BGa(CH$_3$OH)$_2$]) and 1848537 (for [**L**BIn(CH$_3$OH)$_2$]) contain the data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Mass spectroscopy: MALDI-TOF mass data were recorded on an AB SCIEX TOF/TOF 5800 system.

UV-vis and fluorescence spectroscopies: UV-Vis spectra were recorded on a JASCO V-660 or V-670 spectrophotometer. Emission spectra were recorded on a JASCO FP-8600 fluorescence spectrophotometer. Absolute fluorescence quantum yields were determined with a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02. Solvents used for measurements were air-saturated.

DFT calculations: DFT calculations were carried out using the Spartan '16 software (Wavefunction, Inc. Irvine, CA). The geometry optimization of [**L**BGa(MeOH)$_2$] were performed at the B3LYP/6-31G(d) level.[52]

Elemental analysis: Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar.

Synthesis and characterization

[LBAl(CH$_3$OH)$_2$]. A 10 mL round-bottom flask was charged with [H$_3$**L**B][30] (5.3 mg, 5.7 μmol) and tris(2,4-pentanedionato)aluminum(III) (18.0 mg, 55.5 μmol). Chloroform (2 mL) and methanol (0.5 mL) were added to the flask. The mixture was refluxed for 21 h. After cooling, the mixture was concentrated in vacuo. The crude was purified by column chromatography on alumina (eluent: chloroform/methanol = 100/0 ~ 100/2) to give [**L**BAl(CH$_3$OH)$_2$] (1.7 mg, 1.7 μmol, 29%). Red solid, m.p. > 300 °C. ^{1}H NMR (400 MHz, CDCl$_3$/CD$_3$OD = 2/1 (v/v)) δ 7.49 (dd, *J* = 4.8, 1.6 Hz, 2H), 7.42 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.02 (s, 2H), 6.96 (s, 2H), 6.91 (d, *J* = 4.4 Hz, 2H), 6.88 (d, *J* = 2.0 Hz, 2H), 6.86 (dd, *J* = 3.2, 1.6 Hz, 2H), 6.83 (d, *J* = 6.4 Hz, 2H), 6.81 (d, *J* = 2.8 Hz, 2H), 6.61 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.55 (t, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 4.4 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.17 (s, 6H), 2.16 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$/CD$_3$OD = 2:1 (v/v)) δ 158.0, 156.1, 151.04, 150.94, 144.2, 143.1, 140.31, 140.25, 139.0, 137.9, 137.45, 137.44, 137.0, 135.48, 135.28, 129.76, 129.65, 128.61, 128.42, 128.0, 125.0, 124.2, 122.3, 120.5, 120.2, 117.8, 116.4, 115.9, 115.32, 115.22, 21.25, 21.21, 20.3, 19.9. HRMS (MALDI-TOF) Calcd for C$_{60}$H$_{43}$BAlN$_4$O$_6$ [**L**BAl·H]$^+$: *m/z* 953.3091 Found: *m/z* 953.3111.

[LBGa(CH$_3$OH)$_2$]. A 10 mL round-bottom flask was charged with [H$_3$**L**B][30] (14.4 mg, 15.5 μmol) and tris(2,4-pentanedionato)gallium(III) (11.8 mg, 32.1 μmol). Chloroform (6 mL) and methanol (2 mL) were added to the flask. The mixture was refluxed for 9 h. After cooling, the mixture was concentrated in vacuo. The crude was purified by column chromatography on alumina (eluent: chloroform/methanol = 100/0 – 0/100) and was concentrated in vacuo. The obtained solid was dissolved in CHCl$_3$/MeOH and recrystallized by slow evaporation of the solvent to give [**L**BGa(CH$_3$OH)$_2$] (11.4 mg, 10.8 μmol, 70%). Purple crystal, m.p. > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$/CD$_3$OD = 2/1 (v/v)) δ 7.52 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.43 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.02 (s, 2H), 6.97 (s, 2H), 6.91 (d, *J* = 4.2 Hz, 2H), 6.91 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.89 (d, *J* = 4.8 Hz, 2H), 6.88 (d, *J* = 4.2 Hz, 2H), 6.84 (t, *J* = 8.1 Hz, 2H), 6.60 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.57 (t, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 4.2 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.17 (s, 6H), 2.15 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$/CD$_3$OD = 2:1 (v/v)) δ 158.5, 158.1, 150.9, 150.9, 144.5, 143.2, 140.0, 139.1, 139.0, 137.8, 137.7, 137.5, 137.1, 135.5, 135.0, 129.8, 128.6, 128.4, 128.1, 125.6, 124.2, 120.6, 120.4, 120.3, 117.9, 116.4, 115.7, 115.5, 115.4, 21.25, 21.22, 20.3, 19.9. Elemental analysis: Calcd for C$_{61.5}$H$_{45}$BCl$_3$GaN$_4$O$_{6.5}$ (**L**BGa·(CH$_3$OH)$_{2.5}$·(CHCl$_3$)): C, 63.82; H, 4.47; N, 4.69. Found: C, 63.60; H, 4.29; N, 4.85. HRMS (MALDI-TOF) Calcd for C$_{60}$H$_{43}$BGaN$_4$O$_6$ [**L**BGa·H]$^+$: *m/z* 995.2531 Found: *m/z* 995.2502.

[LBIn(CH$_3$OH)$_2$]. A 5 mL round-bottom flask was charged with [H$_3$**L**B][30] (6.0 mg, 6.5 μmol) and tris(2,4-pentanedionato)indium(III) (5.8 mg, 14 μmol). Chloroform (2.4 mL) and methanol (0.8 mL) were added to the flask. The mixture was refluxed for 13 h. After cooling, the mixture was concentrated in vacuo. The crude was purified by column chromatography on alumina (eluent: chloroform/methanol = 100/0 – 0/100) to give [**L**BIn(CH$_3$OH)$_2$] (5.8 mg, 5.3 μmol, 81%). Purple crystal, m.p. > 300 °C. ^{1}H NMR (600 MHz, CDCl$_3$/CD$_3$OD = 2:1 (v/v)) δ 7.59 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.45 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.01 (s, 2H), 7.00 (dd, *J* = 6.6, 1.2 Hz, 2H), 6.96 (d, *J* = 4.8 Hz, 2H), 6.96 (s, 2H), 6.91 (d, *J* = 4.2 Hz, 2H), 6.89 (d, *J* = 4.2 Hz, 2H), 6.82 (t, *J* = 8.1, Hz, 2H), 6.65 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.61 (t, *J* = 7.8, Hz, 2H), 6.54 (d, *J* = 4.2 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 2.14 (s, 6H), 2.12 (s, 6H). ^{13}C NMR (151 MHz, CDCl$_3$/CD$_3$OD = 2:1 (v/v)) δ 159.6, 158.9, 151.0, 150.4, 145.7, 143.5, 140.6, 139.8, 138.9, 137.54, 137.51, 137.13, 137.08, 136.0, 135.4, 131.0, 129.8, 128.6, 128.1, 128.0, 126.7, 123.4, 121.5, 120.6, 119.9, 118.0, 116.6, 116.4, 115.7, 115.0, 21.24, 21.22, 20.4, 19.8. MALDI-TOF MS. Calcd for C$_{60}$H$_{42}$BInN$_4$O$_6$Na [**L**BIn·Na]$^+$: *m/z* 1063.2 Found: *m/z* 1063.4. HRMS (MALDI-TOF) Calcd for C$_{60}$H$_{43}$BInN$_4$O$_6$ [**L**BIn·H]$^+$: *m/z* 1041.2314 Found: *m/z* 1041.2308.

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Keywords: Dipyrrin • Group 13 elements • Twisted structure • Macrocycle • Heteronuclear complex

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