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Structure of a Barium(II) Complex Sandwiched by a Schiff Base Macrocycle

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A barium complex sandwiched by an octaaza Schiff base macrocycle prepared by [2 + 2] condensation of diimine and phenanthroline dicarbaldehyde has been studied; the ten-coordinate structure of the complex and increase of absorption intensity on coordination has been revealed.

In the field of molecular recognition, macrocycles such as crown ethers and calixarenes have been extensively studied in the past few decades.[1] Applications of the compounds for catalysis and NMR imaging have also been reported.[2] It is well-known that a slight modification of the structures of macrocyclic ligands can alter the selectivity toward incorporated ions. For example, many macrocycles containing two aminomethyl groups have been reported, and adjustment of the length of the connectors between the groups can make the macrocycle incorporate a metal ion of very large ionic radius, e.g. Ba^{2+}.[3,4]

Meanwhile, a large number of metal complexes with 1,10-phenanthroline (phen) derivatives have been prepared and interesting photophysics for the complexes have been studied.[5,6] Several polyazamacrocycles containing phenanthroline moieties and their metal complexes have also been reported.[7] However, there are few reports studying macrocycles, which incorporate more than one phenanthroline moiety.[8] In this study, we successfully obtained a new macrocycle incorporating two phenanthroline moieties. The structure and properties of a Ba^{2+} complex of the ligand are also presented.

Treatment of 1,10-phenanthroline-2,9-dicarbaldehyde with an equimolar amount of 1,3-diaminopropane in methanol readily gave a macrocyclic Schiff base ligand, L^1, by [2 + 2] condensation (Chart 1). Surprisingly, the condensation occurs even in the absence of template cations and no other larger macrocycles were obtained. Elemental analysis and mass spectrum support the formation of the macrocycle. In the ^{1}H NMR spectrum, a lower-field singlet at δ 9.0 suggests the formation of CH=N bonds. The signals assigned to methylene protons are at δ 3.8 and δ 2.5 as a quintet and triplet, respectively. To be exact, all protons on the methylene groups are nonequivalent, however, each methylene signal appears as if the geminal protons are equivalent due to rapid dynamic exchange between different conformers in solution.

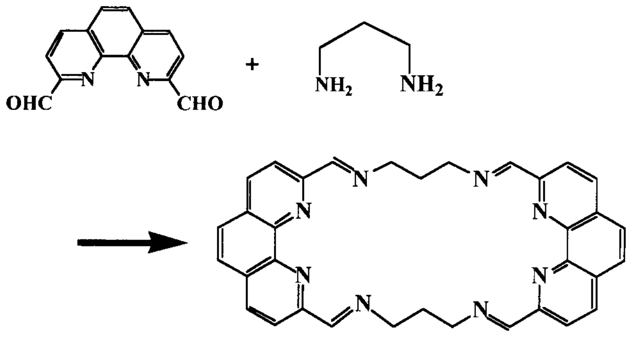

Chart 1.

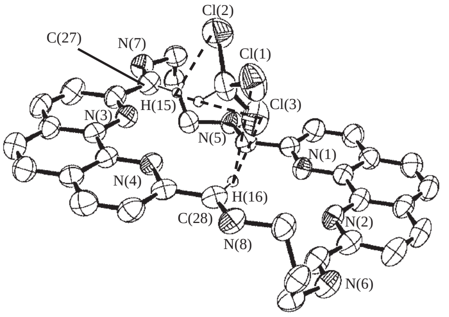

Fig. 1. An ORTEP structure of macrocycle L^1 (Second chloroform molecule is omitted).

The X-ray structure of L^1 is shown in Fig. 1. In solid state, a step-like structure, i.e. Z-shaped structure, is found. Two $CHCl_3$ molecules are contained in an asymmetric unit as solvent of crystallization. Four imino protons direct toward the inside the macrocyclic ring, therefore each lone pair of imino nitrogen is pointing outward. It is known for usual cryptands having oxygen donor atoms that free cryptands show a conformation in which the lone pairs of oxygen point outward in solution.[9] Furthermore, the conformation may be stabilized by weak interactions between the imino protons and the Cl atoms of an adjacent chloroform molecule, since the distances of H(16)···Cl(1), H(15)···Cl(2), and H(15)···Cl(3) are short, being 2.95(4), 3.14(6), and 3.13(5) Å, respectively. Bond lengths of C=N range from 1.248(6) to 1.258(6) Å, which suggests that the bond order of this unit is two.

Treatment of L^1 with $Ba(CF_3SO_3)_2$ in THF gave a complex incorporating barium ion, $[Ba(CF_3SO_3)_2(L^1)]$ (Chart 2). Attempts to isolate the complexes with other alkali earth or lanthanide ions have not yet been successful.

The X-ray structure of $[Ba(CF_3SO_3)_2(L^1)]$ is shown in Fig. 2. The macrocyclic ligand has a folded structure rather than a step-like one observed in the free ligand. The barium ion was incorporated within the U-shaped macrocyclic ligand. The structure is similar to the reported barium complex sandwiched by a macrocycle with pyridine moieties. The barium ion shows ten-coordination; all eight nitrogen atoms in L^1 coordinate to the barium ion, and an additional two oxygen atoms of triflate ions coordinate to the barium center. The complex has approximate C_{2v} symmetry, and the geometry around the barium ion is a pentagonal prism. Selected bond lengths and angles are shown in Table 1. The Ba–N bond lengths range from 2.971(5) to 3.052(5) Å. They are longer than those of pre-

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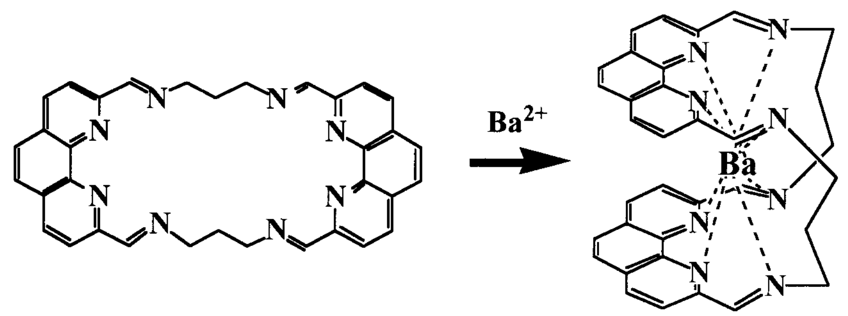

Chart 2.

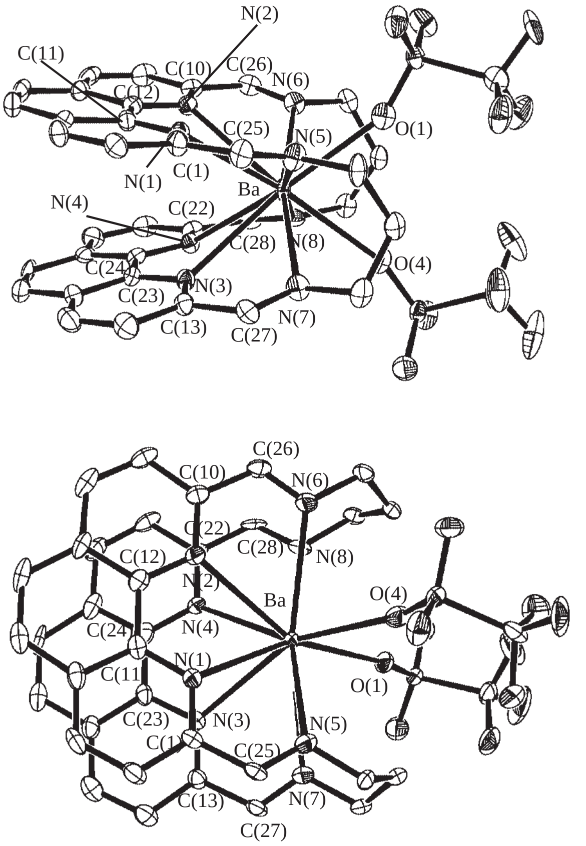

Fig. 2. An ORTEP drawing of [Ba(CF_3SO_3)$_2$(L^1)]: a side view (above) and a view from the direction where phenanthroline is stacked (below).

Table 1. Selected Bond Lengths (Å), Angles (°), and Torsion Angles (°) for [Ba(CF_3SO_3)$_2$(L^1)]

Ba–N(1)	3.008(6)	Ba–N(2)	3.003(6)
Ba–N(3)	2.999(5)	Ba–N(4)	2.971(5)
Ba–N(5)	3.032(5)	Ba–N(6)	3.040(5)
Ba–N(7)	3.052(5)	Ba–N(8)	3.019(5)
Ba–O(1)	2.750(5)	Ba–O(4)	2.757(5)
N(1)–Ba–N(3)	65.5(1)	N(2)–Ba–N(4)	65.7(1)
N(5)–Ba–N(7)	54.8(1)	N(6)–Ba–N(8)	54.4(1)
O(1)–Ba–O(4)	74.2(1)		
Ba–N(1)–C(11)–C(12)		31.0(7)	
Ba–N(2)–C(12)–C(11)		30.8(7)	
Ba–N(3)–C(23)–C(24)		31.8(7)	
Ba–N(4)–C(24)–C(23)		32.6(7)	
Ba–N(5)–C(25)–C(1)		21.4(8)	
Ba–N(6)–C(26)–C(10)		18.2(8)	
Ba–N(7)–C(27)–C(13)		18.6(8)	
Ba–N(8)–C(28)–C(22)		21.1(8)	

viously reported barium complex, [Ba(hfac)$_2$(phen)$_2$] (average distance is 2.91 Å),[10] whereas slightly shorter than those of the Schiff base complex reported by Drew et al. (3.016(7)–3.109(9) Å).[11] Bond angles of Ba–N–C range from 116.9(4) to 120.4(4)°. As described in Table 1, the torsion angles of Ba–N–C–C showing deviation of barium atom from the coordination plane, e.g. Ba–N(1)–C(11)–C(12), are relatively large, which suggests the character of the coordination bonds is ionic rather that covalent. The deviation from planarity of the π-conjugated –N=CH–(phen)–CH=N– moieties is small (maximum deviation of non-hydrogen atoms involved in the conjugated system from the best plane is 0.128 Å of C(28)). The dihedral angle between two planes containing phenanthroline is 12.32(7)°, which shows that the π-conjugated planes are nearly parallel with each other. The closest interatomic distance between phenanthroline rings is 3.238(7) Å (N(2)···N(4)). It suggests that there is a weak π-stacking interaction between the π-conjugated rings, which possibly stabilizes the folded structure.

In the ^{1}H NMR spectrum, the signal assigned to CH=N is shifted to higher field (δ 8.4) compared to that of the free ligand, suggesting that the imino nitrogen atoms are coordinated to barium ion. Furthermore, broadening and splitting of the signals assigned to methylene groups compared to those of free ligand were observed. This fact shows that each signal of essentially nonequivalent geminal protons on the methylene groups in the barium complex can exist as endo- and exo-proton separately due to the formation of a rigid structure on complexation even in solution. It has been reported that similar splitting is observed especially in U-shaped conformers of dinuclear organopalladium complexes.[12]

Absorption spectra of L^1 and [Ba(CF_3SO_3)$_2$(L^1)] are shown in Fig. 3. Both compounds have several absorption bands in a wavelength region shorter than 400 nm. Absorption maximum of [Ba(CF_3SO_3)$_2$(L^1)] is observed at ca. 300 nm (ε: ca. 3.0×10^4 mol^{-1} dm^3 cm^{-1}), whereas that of free L^1 is ca. 280 nm ($\varepsilon = 5.3 \times 10^4$ mol^{-1} dm^3 cm^{-1}). Taking the ionic character of the coordination bonds into consideration, the variation of the spectra on complexation results from structural change rather than the coordination of the barium atom.

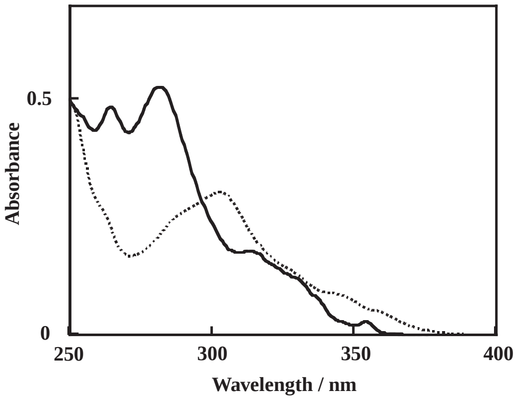

Fig. 3. Absorption spectra of L^1 and $[Ba(CF_3SO_3)_2(L^1)]$.

In this work, a new hexaaza Schiff base macrocycle containing two phenanthroline moieties has been prepared, and the novel barium complex, in which the macrocyclic ligand is fixed in a two-fold fashion, has been identified. Other metal complexes involving this specific structure, which would be potential stereoselective catalysts, may be obtained by transmetalation.

Experimental

Preparation of L^1. A solution of 1,3-diaminopropane (0.148 g, 2.00 mmol) in methanol (60 mL) was added dropwise to a solution of 1,10-phenanthroline-2,9-dicarbaldehyde (0.472 g, 2.0 mmol) in methanol (100 mL) at 50 °C over 3 h by addition funnel. The resulting suspension was filtered, and L^1 was obtained as a white powder. Yield 0.206 g (39%). Anal. Found: C, 67.25; H, 5.61; N, 18.23%. Calcd for $C_{34}H_{28}N_8 \cdot 3H_2O$: C, 67.76; H, 5.69; N, 18.59%. ^{1}H NMR ($CDCl_3$) δ 9.0 (CH=N, s, 4H), 8.5 (H^2, d, 4H), 8.4 (H^3, d, 4H), 7.8 (H^5, s, 4H), 3.8 (N–CH_2–, m, 8H), 2.5 (–CH_2–, m, 4H).

Preparation of $[Ba(CF_3SO_3)_2(L^1)]$. Barium trifluoromethanesulfonate (0.087 g, 0.20 mmol) dissolved in THF (400 mL) was added dropwise by addition funnel to a solution of L^1 ligand (0.110 g, 0.20 mmol) in THF (100 mL) over 2 h, followed by stirring for 3 h. The solution was evaporated to a small amount and the resulting precipitate was filtered. The complex was obtained as white powder. Yield 0.118 g (60%). Anal. Found: C, 39.67; H, 3.20; N, 10.28%. Calcd for $C_{36}H_{28}N_8F_6S_2O_6Ba \cdot 6H_2O$: C, 39.59; H, 3.69; N, 10.26%. ^{1}H NMR (CD_3CN, 400 MHz) δ 8.4 (CH=N, s, 4H), 8.2 (H^2, d, 4H), 7.5 (H^3, d, 4H), 7.5 (H^5, s, 4H), 4.5, 3.8 (N–CH_2, m, 8H), 3.4, 2.3 (–CH_2–, m, 4H).

X-ray Structure Determination. Single crystals suitable for analysis were obtained by slow diffusion of diethyl ether in chloroform solution of L^1, or in acetonitrile solution of $[Ba(CF_3SO_3)_2(L^1)]$. X-ray measurements were made on a Rigaku AFC5S diffractometer for L^1 at 296 K and a Rigaku Saturn 70 system for $[Ba(CF_3SO_3)_2(L^1)]$ at 123 K, respectively. The structures were solved reasonably by using a direct method and refined by full-matrix least-square procedures (SHELXL97).[13] Crystallographic data for L^1 and $[Ba(CF_3SO_3)_2(L^1)]$ are shown as follows; $C_{36}H_{30}N_8Cl_6$ ($L^1 \cdot 2CHCl_3$), triclinic, $P\bar{1}$ (#2), $a = 12.010(1)$ Å, $b = 16.760(3)$ Å, $c = 9.5447(7)$ Å, $\alpha = 102.183(9)°$, $\beta = 99.541(7)°$, $\gamma = 83.98(1)°$, $V = 1847.1(4)$ Å^3, $Z = 2$, $R_1 = 0.067$ ($I > 2.00\sigma(I)$), $wR_2 = 0.202$ for all 5502 reflections; $C_{38}H_{31}N_9F_6S_2O_6Ba$ ($[Ba(CF_3SO_3)_2(L^1)] \cdot CH_3CN$), triclinic, $P\bar{1}$ (#2), $a = 12.071(9)$ Å, $b = 12.478(9)$ Å, $c = 13.805(12)$ Å, $\alpha = 88.78(2)°$, $\beta = 88.40(2)°$, $\gamma = 73.14(2)°$, $V = 1989.0(27)$ Å^3, $Z = 2$, $R_1 = 0.063$ ($I > 2.00\sigma(I)$), $wR_2 = 0.202$ for all 8048 reflections. All calculations were carried out by using Crystal Structure software.[14] Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-662608 for L^1 and CCDC-662609 for $[Ba(CF_3SO_3)_2(L^1)]$. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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