Synthesis and structure of a dinuclear zinc(II) triple helix of an *N*,*N*-bis-bidentate Schiff base: new building blocks for the construction of helical structures

Noboru Yoshida* and Kazuhiko Ichikawa

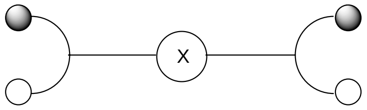
Laboratory of Molecular Functional Chemistry, Division of Material Science, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan

The formation of a novel helical zinc(II) complex of an *N*,*N*-bis-bidentate Schiff base is reported; the edge-to-face and face-to-face π···π interactions play an important role in the metal-assisted self-assembling process in solution.

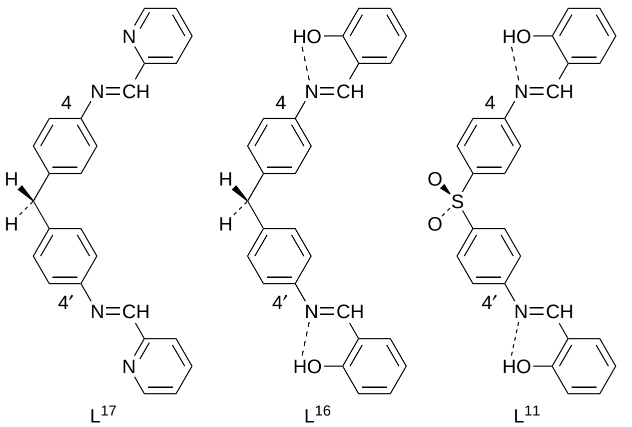
Weak non-covalent interactions play an important role in the kinetics of the molecular recognition by α-cyclodextrin in aqueous solution.[1] Contrary to our expectation, enthalpic rather than entropic factors are the principal driving force to form a regioselective host–guest complex[1*c–e*] in which weak interactions such as London dispersion forces, dipole–dipole and CH··π interactions[2] operate. Recently, great interest has been focused on metal-assisted self-assembly of helical[3] and box-like[4] supramolecular complexes in which the stereochemical preference of a labile metal centre is exploited.[3]

Another very important aspect of self-assembly investigations has been the development of the design at ligands which induces cooperative behaviour *via* the weak interactions. From this point of view, a new type of bis-bidentate ligand has been developed (Scheme 1).[5,6]

Recently, we have focused on some semi-*N*,*O*-bidentate and bis-*N*,*O*-bidentate Schiff-base ligands which can be electronically and configurationally controlled, leading to a systematic study of the self-assembly process in solution.[7] Thus, bis-*N*,*N*- and bis-*N*,*O*-bidentate Schiff-base ligands, L^{11}, L^{16} and L^{17}, have been designed (Scheme 2) to bind two separate metal ions owing to the fact that the bridging group (X = –$C_6H_4CH_2C_6H_4$– or –$C_6H_4SO_2C_6H_4$–) prevents the metal ions from forming 1 : 1 four coordinate complexes.



Scheme 1 X = –CONHC*H(R)CH_2C*H(R)NHCO– (ref. 5) or –$(CH_2)_n$– (ref. 6*a*); ▨ = strong donor atom, ○ = weak donor atom



Scheme 2

Here we report the facile synthesis of helical zinc(II) complexes utilizing weak interactions in which CH··π and π··π interactions of aromatic rings between two or three bridging groups (X = –$C_6H_4CH_2C_6H_4$– or –$C_6H_4SO_2C_6H_4$–) having high conformational freedom may be involved in the self-assembling process.

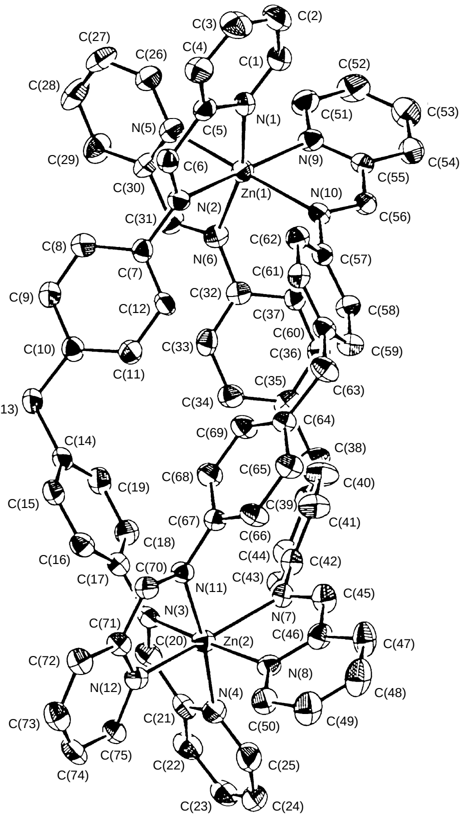


Fig. 1 Molecular structure of the complex cation of **1**. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–N(1) 2.158(6), Zn(1)–N(2) 2.195(5), Zn(1)–N(5) 2.186(7), Zn(1)–N(6) 2.193(6), Zn(1)–N(9) 2.154(6), Zn(1)–N(10) 2.176(6), Zn(2)–N(3) 2.174(6), Zn(2)–N(4) 2.132(7), Zn(2)–N(7) 2.247(6), Zn(2)–N(8) 2.167(6), Zn(2)–N(11) 2.200(6), Zn(2)–N(12) 2.187(6); N(1)–Zn(1)–N(2) 76.7(2), N(1)–Zn(1)–N(5) 91.3(3), N(1)–Zn(1)–N(6) 164.7(2), N(1)–Zn(1)–N(9) 98.4(2), N(1)–Zn(1)–N(10) 94.5(2), N(2)–Zn(1)–N(5) 87.6(2), N(2)–Zn(1)–N(6) 93.5(2), N(2)–Zn(1)–N(9) 173.6(2), N(2)–Zn(1)–N(10) 99.9(2), N(5)–Zn(1)–N(6) 76.5(2), N(5)–Zn(1)–N(9) 96.7(2), N(5)–Zn(1)–N(10) 171.4(2), N(6)–Zn(1)–N(9) 92.1(2), N(6)–Zn(1)–N(10) 98.7(2), N(9)–Zn(1)–N(10) 76.2(2), N(3)–Zn(2)–N(4) 77.3(3), N(3)–Zn(2)–N(7) 96.0(2), N(3)–Zn(2)–N(8) 170.1(2), N(3)–Zn(2)–N(11) 100.6(2), N(3)–Zn(2)–N(12) 97.9(2), N(4)–Zn(2)–N(7) 93.2(2), N(4)–Zn(2)–N(8) 97.1(3), N(4)–Zn(2)–N(11) 173.3(2), N(4)–Zn(2)–N(12) 98.4(2), N(7)–Zn(2)–N(8) 76.1(2), N(7)–Zn(2)–N(11) 93.4(2), N(7)–Zn(2)–N(12) 163.6(2), N(8)–Zn(2)–N(11) 85.8(2), N(8)–Zn(2)–N(12) 90.9(2), N(11)–Zn(2)–N(12) 75.4(2).

Reactions of L^{16} and L^{11} with $Zn(MeCO_2)_2 \cdot 2H_2O$ in 1 : 1 molar ratio in hot ethanol afforded a strongly fluorescent yellow powder with many long fibres at the wall of the reaction vessel. The melting point of the formed zinc(II) complexes were > 300 °C. They were insoluble in all organic solvents. Elemental analysis indicated formation of 1 : 1 polymeric complexes. Ligand L^{17} was synthesized by Schiff-base condensation[8] of bis(4-aminophenyl)methane and pyridine-2-aldehyde and reaction with $Zn(ClO_4)_2 \cdot 6H_2O$ in methanol at room temp. gave a pale yellow crystalline powder (yield *ca*. 60%).† This was recrystallized from dmf–MeCN (1 : 2)–diethyl ether to give crystals of **1**·2MeCN·dmf; MeCN was indispensable for crystallization. Elemental analysis and FAB mass spectroscopy were consistent with the empirical formula of a 2 : 3 complex $[Zn_2L^{17}{}_3][ClO_4]_4 \cdot dmf \cdot 2MeCN$.

The structure of **1** shown in Fig. 1‡ confirms the existence of a dinuclear triple helix. The complex contains two Zn^{II} ions and three L^{17} ligands. The building units, particularly the bridging groups ($–C_6H_4CH_2C_6H_4–$), are stacked face-to-face ($\pi \cdot\cdot \pi$) and edge-to-face ($CH \cdot\cdot \pi$) to each other. Formation of a helix arises from a twisting of these bridging groups. Each Zn^{II} ion is six-coordinate with Zn–N(pyridyl) distances in the range 2.132(7)–2.187(6) Å and Zn–N(–CH=N) 2.174(6)–2.247(6) Å. There are three sets of bond angles N–Zn–N in the range 75.4(2)–77.3(3)°, 85.8(2)–100.6(2), and 163.6(2)–173.6(2)°, respectively. A pseudo-octahedral array of nitrogen atoms provided by three pyridylazomethine ($C_5H_4NCH{=}N–$) moieties are in *fac* configuration. The pyridyl nitrogen atom as a stronger donor of one ligand is situated *trans* to the weaker azomethine (–CH=N–) nitrogen atom of another ligand (Fig. 1 and Scheme 1).[8]

The new ligand system in this study is notable with regard to the synthetic advantage that the use of the C=N bond[9] allows a wide range of different supramolecular structures. This provides a basis for modelling many structural aspects and the utilization of the weak interactions in metallosupramolecular chemistry.

Footnotes

* E-mail: nyoshida@high.hokudai.ac.jp

† **CAUTION**. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and handled with care.

‡ Since the crystals were sensitive to moisture in the air, all measurements were conducted with the sample sealed in a glass capilliary using a Rigaku RAXIS IV imaging plate area detector with graphite monochromated Mo-Kα radiation.

Crystal data: **1**·dmf·2MeCN: $C_{82}H_{73}Cl_4N_{15}O_{17}Zn_2$; approximate dimensions 0.30 × 0.10 × 0.05 mm, M = 1813.14, pale yellow crystal, monoclinic, space group $C2/c$ (no. 15), a = 54.89(2), b = 13.822(2), c = 22.01(1) Å, β = 95.40(3)°, U = 16639.9004 Å^3, Z = 8, D_c = 1.447 g cm^{-3}, μ(Cu-Kα) = 7.82 cm^{-1}, $F(000)$ = 7472.00. Data were collected on a Rigaku RAXISII diffractometer, 10268 reflections, 6756 observed [$I > 3\sigma(I)$]. The structure was solved by direct methods, and expanded using Fourier techniques. The final cycle of full-matrix least-squares refinements was based on 65756 observed reflections [$I > 3\sigma(I)$] and 1081 variable parameters and converged at R = 0.061, R_w = 0.084, Maximum, minimum residual electron density: +0.80, −0.61 e Å^{-3}. All calculations were performed using the teXsan crystallographic software package of the Molecular Structure coorporation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/452.

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