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A spontaneously resolved chiral molecular box: a cyclic tetranuclear Zn^{II} complex with DPTZ (DPTZ = 3,6-di-2-pyridyl-1,2,4,5-tetrazine)

Xian-He Bu,*[abc] Hiromasa Morishita,[d] Kentaro Tanaka,[a] Kumar Biradha,[b] Sanae Furusho[e] and Mitsuhiko Shionoya*[a]

[a] *Department of Chemistry, School of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: shionoya@chem.s.u-tokyo.ac.jp*
[b] *Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan*
[c] *Department of Chemistry, Nankai University, Tianjin 300071, P.R. China*
[d] *The Graduate University for Advanced Studies, Myodaiji, Okazaki 444-8585, Japan*
[e] *Jasco International Co Ltd., Myojin, Hachioji, Tokyo 192-0046, Japan*

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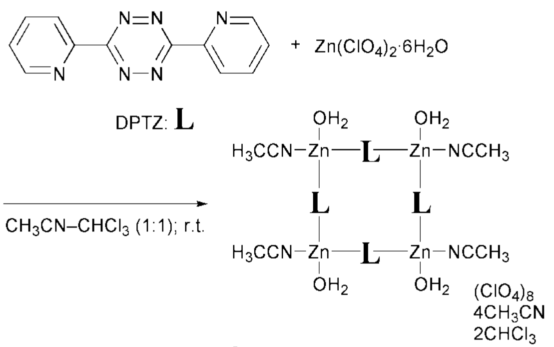
A quantitative synthesis of a novel cyclic tetranuclear Zn^{II} complex with 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ), which was spontaneously resolved as chiral crystals, has been developed.

The rational design of discrete self-assembling systems is one of the most challenging tasks in the exploitation of supramolecular synthons. In particular, the metal-assisted assembly of cyclic molecular arrays plays an integral part in the development of inclusion chemistry as well as 'engineering up' molecular architectures. To date, the groups of Fujita,[1] Stang,[2] and others[3] have been exploiting the coordination-based syntheses of molecular squares or rectangles with right angles at their corners, which are one of the simplest members of the polygon family. The creation of a new class of artificial *chiral* supramolecular species *via* spontaneous self-assembly has been one key to further development of this rapidly expanding field. Stang and coworkers have explored the syntheses of chiral Pt^{II}_4 or Pd^{II}_4 molecular squares by using either chiral chelating ligands or C_{2h}-symmetrical bridging ligands.[4] As described previously, there are several ways of creating chiral supramolecular architectures, of which use of an inherently chiral octahedral metal complex has been recognized as a promising strategy. Unlike the square-planar Pt^{II} or Pd^{II} complexes, octahedral metal complexes are inherently chiral[5] and therefore no chiral auxiliary ligands are required. Recently, Wang and coworkers have reported a Co^{II} molecular square complex that exhibits a chiral molecular structure in the solid state,[6] where no chiral auxiliary ligands were employed, and the individual single crystal was found to consist of one enantiomer only. However, the reaction yield was low and the solution behavior of the molecular square remains unsolved.

We report herein a *quantitative* preparation of a novel cyclic tetranuclear Zn^{II} complex that was *spontaneously resolved* as *chiral* crystals. The bridging ligand used in this study is 3,6-di-2-pyridyl-1,2,4,5-tetrazine (DPTZ). Although the two pyridyl groups of DPTZ can rotate around the C–C bonds between the pyridine rings and tetrazine ring, upon coordinating to metal ions the three aromatic rings can become almost coplanar to bridge two metal centers. We therefore anticipated that DPTZ would serve as a rigid multitopic spacer ligand and that a thermodynamically stable yet kinetically labile chiral assembly could be formed by the use of the Zn^{II} ion which is inherently chiral in an octahedral coordination geometry.[7]



Scheme 1

The reaction of Zn^{II}(ClO$_4$)$_2$·6H$_2$O with an equimolar amount of DPTZ in chloroform–acetonitrile at ambient temperature produced orange prisms of $[Zn^{II}_4(DPTZ)_4(H_2O)_4(CH_3CN)_4](ClO_4)_8 \cdot 2CHCl_3 \cdot 4CH_3CN$ **1**, in 90% yield (Scheme 1). The structure of **1** was determined by a single-crystal X-ray diffraction analysis with a Siemens CCD X-ray diffractometer. Complex **1** crystallizes in the chiral space group $C222_1$.[8] As shown in Fig. 1, complex **1** has a crystallographically imposed D_2 symmetry with half of the molecule being in the asymmetric unit. As a consequence of the D_2symmetry, the four Zn^{II} centers have identical chirality, *i.e.* either all Δ or all Λ optical geometry. The Flack parameter was nearly zero, indicating *each* individual crystal of **1** consists of *a single* enantiomer.[9] Indeed, all four Zn^{II} centers of the single crystal used in this analysis have Λ geometry and therefore complex **1** is a chiral molecular box in the solid state.

Space-filling diagrams of the molecular box **1** are shown in Fig. 2. Each Zn^{II} ion of complex **1** has a typical octahedral coordination geometry with two DPTZ ligands bridging the other two Zn^{II} centers. The other two coordination sites of the Zn^{II} ion are occupied by one acetonitrile and one water molecule. It is noteworthy that there should be many possible structures in the four Zn^{II} centers if the acetonitrile and water molecules occupy their positions randomly. However, all the

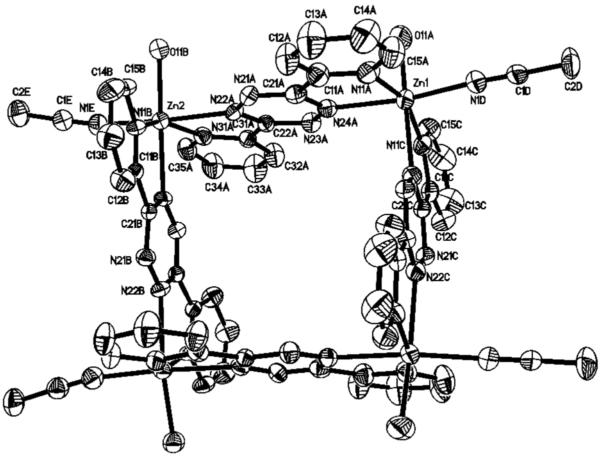


Fig. 1 ORTEP view of the molecular structure of **1** with 50% thermal ellipsoids and labeling scheme. Perchlorate anions and solvent molecules are omitted for clarity.

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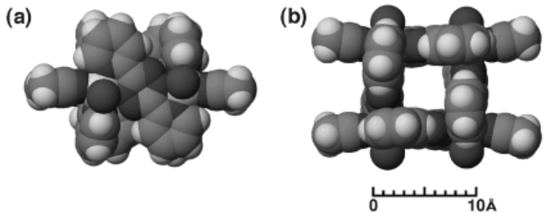

Fig. 2 Space-filling diagrams showing (a) a side-view and (b) a top-view of the box cavity of complex **1**.

four acetonitrile and four water molecules coordinate to Zn^{II} in a highly symmetrical manner, and the formation of a single diastereomer was observed. The $Zn^{II}\cdots Zn^{II}$ distances along the corners of the box are *ca.* 7.2 Å. The dimensions of the box cavity are estimated to be *ca.* 4 Å × 4 Å [Fig. 2(b)]. It is of interest that one perchlorate ion and two chloroform molecules are encapsulated within the box cavity of **1**, where the two chloroform molecules interpose the perchlorate ion like two caps to close the box. Such guest molecules may facilitate the cyclization and therefore stabilize the resulting cyclic box structure.

The ^1H NMR spectrum of **1** in CD_3CN showed one set of proton signals for the pyridine parts of DPTZ,[10] suggesting that the DPTZs are bridging ligands and are coordinated symmetrically between two Zn^{II} centers. The discrete tetrameric structure of **1** in acetonitrile was confirmed by ESI-TOF mass spectroscopy. The isotopically resolved ESI-TOF mass spectrum of this assembly is shown in Fig. 3. The signals of Zn^{II} tetrameric species for **1** are centered at *m/z* 2166.6, 1954.6, 1900.6 and 1664.6, which correspond to the +1 charged cationic species [Fig. 3(a)].[11] For example, the enlarged plot of the signal for *m/z* 1954.6 $[Zn^{II}_4(DPTZ)_4(H_2O)_3(CH_3CN)_2(OH)(ClO_4)_6]^+$ gave excellent agreement between the experimental and theoretical isotopic distributions, indicating the tetrameric character of **1** [Fig. 3(b) and 3(c)]. These results establish that the cyclic Zn^{II} tetramer is stable in solution.

A solution of complex **1** in acetonitrile exhibited an essentially zero optical rotation, indicating that the bulk of the crystals is a racemate. Although the single-crystal X-ray diffraction analysis demonstrated that each individual crystal of **1** consists of one enantiomer only, the question of whether the single enantiomer of **1** undergoes racemization in solution still remains unsolved because the individual chiral crystals of **1** are too small to allow any meaningful kinetic study and circular dichroism measurement. Attempts for preferential crystallization of either enantiomer Δ or Λ through seeding of the racemic supersaturated solution with a seed of one crystal were unsuccessful.

The present molecular box **1** is the first example of spontaneous resolution of a quantitatively self-assembled Zn^{II} molecular box.

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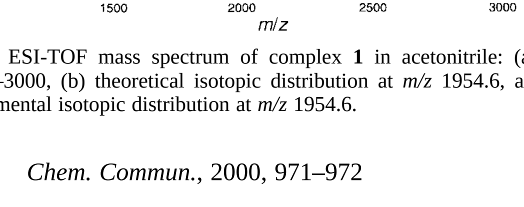

Fig. 3 ESI-TOF mass spectrum of complex **1** in acetonitrile: (a) *m/z* 1300 –3000, (b) theoretical isotopic distribution at *m/z* 1954.6, and (c) experimental isotopic distribution at *m/z* 1954.6.

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7 Very recently, a synthesis and structure of a cyclic tetranuclear Ni(II) complex with DPTZ and its magnetic properties have been developed independently. See: C. S. Campos-Fernandez, R. Clerac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477.

8 *Crystal data* for complex **1**: $C_{66}H_{66}Cl_{14}Zn_4N_{32}O_{36}$, $M_w = 2641.28$, orthorhombic, space group $C222_1$, $a = 13.6982(17)$, $b = 30.091(4)$, $c = 25.195(3)$ Å, $V = 10\,385\ (2)$ Å^3, $Z = 4$, $\mu = 13.68\ \mathrm{cm}^{-1}$, $D_c = 1.689\ \mathrm{g\ cm}^{-3}$, $F(000) = 5304$. Data were collected over the 2θ range 3.18–57.56° at 193(2) K on a Siemens CCD X-ray diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å). A total of 15576 reflection data were collected, of which 10552 ($R_{\mathrm{int}} = 0.0327$) were independent. Convergence to the final R values of $R_1 = 0.0505$, $wR_2 = 0.1129$ [$I > 2\sigma(I)$] and $R_1 = 0.0886$, $wR_2 = 0.1239$ (all data) for **1** was achieved by using 10 552 unique reflections and 687 parameters (on F^2), with $S = 0.941$ and maximum residual peak of 0.563 e Å^{-3}.

CCDC 182/1596. See http://www.rsc.org/suppdata/cc/a9/a909742b/ for crystallographic files in .cif format.

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10 ^1H NMR [500 MHz, CD_3CN, external TMS–CD_3CN]: for **1**; δ 8.14 (d, *J* 7.5 Hz, 8H, 3,3′-H), 8.33 (ddd, *J* 1.0, 5.0, 8.0 Hz, 8H, 5,5′-H), 8.54 (ddd, *J* 1.5, 7.8, 7.8 Hz, 8H, 4,4′-H), 9.26 (d, *J* 4.5 Hz, 8H, 6,6′-H); for DPTZ: δ 7.66 (ddd, *J* 1.3, 4.8, 7.7 Hz, 2H, 5,5′-H), 8.09 (ddd, *J* 1.7, 7.8, 7.8 Hz, 2H, 4,4′-H), 8.65 (ddd, *J* 1.1, 1.1, 7.9 Hz, 2H, 3,3′-H), 8.94 (ddd, *J* 0.9, 1.6, 4.6 Hz, 2H, 6,6′-H).

11 *MS* (*ESI-TOF*) *data* for **1** (CH_3CN): *m/z* 2166.6 $[M - (H_2O)_6 + H^+]^+$, 1954.6 $[M - (CH_3CN)_2 - (ClO_4)_2 - H^+]^+$, 1900.6 $[M - (CH_3CN)_2 - (H_2O)_3 - (ClO_4)_2 - H^+]^+$, 1690.8 $[M - Zn^{II} - (CH_3CN)_2 - (ClO_4)_4 - H^+]^+$, 1664.6 $[M - L - (CH_3CN)_2 - (H_2O)_3 - (ClO_4)_2 - H^+]^+$, 1554.6 $[M - L - Zn^{II} - (CH_3CN)_2 - (ClO_4)_3]^+$, 1454.7 $[M - L - Zn^{II} - (CH_3CN)_2 - (ClO_4)_4 - H^+]^+$, 1400.7 $[M - L - Zn^{II} - (CH_3CN)_2 - (H_2O)_3 - (ClO_4)_4 - H^+]^+$, 1136.9 $[M - L - Zn^{II}_2 - (CH_3CN)_2 - (H_2O)_3 - (ClO_4)_6 - H^+]^+$, 900.8 $[M - L_2 - Zn^{II}_2 - (CH_3CN)_2 - (H_2O)_3 - (ClO_4)_6 - H^+]^+$, 635.0 $[M - L_2 - Zn^{II}_3 - (CH_3CN)_4 - (H_2O)_4 - (ClO_4)_7]^+$, 439.9 $[M - L_3 - Zn^{II}_3 - (CH_3CN)_3 - (H_2O)_4 - (ClO_4)_7]^+$, where $M = [L_4Zn^{II}_4(H_2O)_4(CH_3CN)_4](ClO_4)_8$ and L = DPTZ.