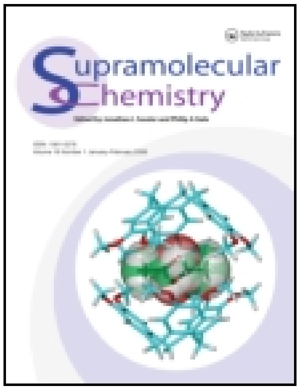

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Zinc(II)-included hemicryptophane: coordination of an acetonitrile guest within the cavity

Yoshimasa Makita[a]*, Kazuya Sugimoto[b], Kenta Furuyoshi[b], Keisuke Ikeda[b], Tomoyuki Fujita[b], Shin-Ichi Fujiwara[a] and Akiya Ogawa[b]

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A zinc(II)-included hemicryptophane, which has a zinc(II) centre embedded in the cavity, was synthesised in high yield and characterised by fast atom bombardment mass spectrometry, ^{1}H NMR spectroscopy and X-ray crystal structure analysis. The X-ray crystal structure shows that zinc(II)-included hemicryptophane has a preorganised cavity, formed by the cyclotriveratrylene and tris(aminoethyl)amine (tren) moieties. The zinc(II) centre is coordinated to the N_4 core of the tren cap and to the nitrogen atom in acetonitrile. The acetonitrile guest is stabilised through CH–π interactions. The absolute configuration of the nitrogen atom in the amino group was assigned by anomalous X-ray scattering; the results indicated that a chiral zinc(II)-included hemicryptophane was obtained by spontaneous asymmetric crystallisation.

Keywords: hemicryptophane; zinc; capsule; spontaneous asymmetric crystallisation

Introduction

Molecular capsules have been of much interest to chemists because they provide a precise space as a site for recognition and catalysis (*1*). Although a number of molecular capsules have been reported, there have been few examples of molecular capsules that contain a functional group within the internal space (*2*). Hemicryptophane, which is composed of a cyclotriveratrylene (CTV) host unit, is capable of constructing a catalytic site and a suitable binding pocket for specific substrates in the internal space (*3*). We recently synthesised a hemicryptophane composed of a racemic CTV host unit, a tris(aminoethyl)amine (tren) ligand and three rigid phenyl spacers encapsulating the acetonitrile guest molecule within the internal space. We also synthesised a zinc(II)-included hemicryptophane which had a catalytic site in the internal space (*4*). Here, we show that the novel chiral zinc(II)-included hemicryptophane, which is formed by spontaneous asymmetric crystallisation, has a binding pocket specifically suitable for an acetonitrile molecule.

Results and discussion

Synthesis and characterisation

The synthetic pathway for the preparation of **2** is outlined in Scheme 1. Addition of racemic hemicryptophane **1** (*4*) to an acetonitrile solution of zinc perchlorate hexahydrate resulted in the formation of **2** · MeCN in 92% yield. The zinc complex of **2** was observed by fast atom bombardment mass spectrometry (FAB-MS), but the host–guest complex of **2** · MeCN was not detected. The ^{1}H NMR spectrum of **2** is shown in Figure 1. The signal which can be assigned to the encapsulated acetonitrile molecule was not observed probably because H_2O included in DMSO-d_6 easily displaced the inner acetonitrile molecule.

Crystal structure of zinc(II)-included hemicryptophane 2

Slow diffusion of tetrahydrofuran into an acetonitrile solution of **2** resulted in single crystals suitable for X-ray crystal structure analysis. The X-ray crystal structure of **2** is shown in Figure 2. The X-ray crystallographic analysis shows that **2** crystallises in the orthorhombic space group $P2_12_12_1$ and has a C_3-symmetric conformational structure. The crystal structure of **2** shows that a good preorganised cavity is formed by the CTV and tren moieties; there are three 23-membered entrances to the cavity. The zinc(II) centre is coordinated to the N_4 core of the tren cap and to the nitrogen atom in acetonitrile. The acetonitrile guest is centred in the cavity and is stabilised through CH–π interactions [$d(\mathrm{C}\cdots\mathrm{C{=}C}) = 3.8$ Å]. The Zn—N average distances for the trigonal base of the pyramid are 2.098 Å and the capping tertiary nitrogen atom is more loosely bound to the metal ion [$d(\mathrm{Zn1{-}N1}) = 2.214$ Å] than is the nitrogen atom in acetonitrile [$d(\mathrm{Zn1{-}N5}) = 2.095$ Å]. Selected bond distances (Å) and angles (°) for **2** are listed in Table 1. The absolute (*R*) configuration of the nitrogen

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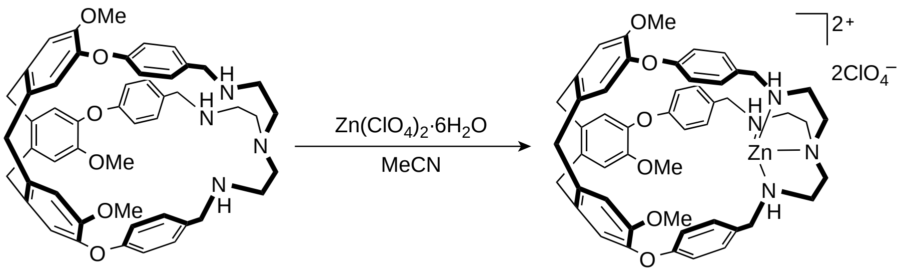

Scheme 1. Synthesis of zinc(II)-included hemicryptophane.

atom in the amino group in the crystal was determined by anomalous X-ray scattering, although the hemicryptophane **1** starting material was a racemic compound of *P* or *M* configuration. This indicates that spontaneous asymmetric crystallisation occurred in the recrystallisation of racemic **2** without any external chiral source (*5*).

Conclusions

We have demonstrated the synthesis and characterisation of a zinc(II)-included hemicryptophane **2**. The X-ray crystal structure of **2** reveals a well-defined cavity encapsulating an acetonitrile guest molecule, formed by solid and spontaneous asymmetric crystallisation of zinc(II)-included hemicryptophane. Further research on molecular recognition and chemical reactions, using a variety of metal-included hemicryptophanes as platforms, is currently under way.

Experimental procedure

Materials and methods

NMR spectra of **2** in DMSO-d_6 were obtained using a JEOL-400 spectrophotometer (JEOL, Tokyo, Japan). Single-crystal X-ray diffraction experiments were carried out with a Rigaku RAXIS-RAPID diffractometer (Rigaku, Tokyo, Japan). Acetonitrile was distilled over calcium hydride. Other chemicals were of reagent grade and used without further purification.

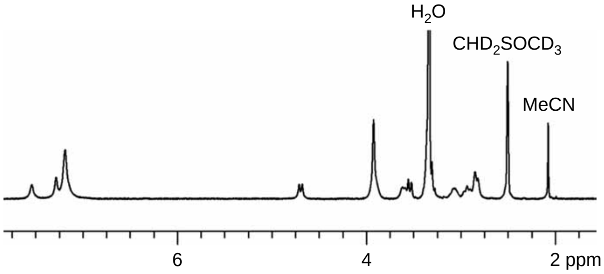

Figure 1. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **2**.

Synthesis of zinc(II)-included hemicryptophane 2

A solution of hemicryptophane **1** (120 mg, 148 μmol) and zinc perchlorate hexahydrate (54.8 mg, 148 μmol) in acetonitrile (20 ml) was stirred at ambient temperature for 1 h. The reaction mixture was recrystallised from acetonitrile and tetrahydrofuran to give 171 mg (92%) of **2** as colourless prisms.

Mp 230–231°C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 2.08 (s, 3H), 2.85–3.07 (m, 12H), 3.48 (d, 3H, $J = 6.0$ Hz), 3.56 (br s, 3H), 3.92 (br s, 6H), 4.69 (d, 3H, $J = 6.0$ Hz), 7.19 (br s, 12H), 7.28 (br s, 3H), 7.54 (br s, 3H); FAB-MS: calcd for $C_{51}H_{54}Cl_1N_4O_{10}Zn_1$: 985.2934 ([M − ClO$_4$]$^+$); found: 985.2933 [M − ClO$_4$]$^+$.

X-ray crystallography

Suitable X-ray quality crystals of **2** were grown by slow evaporation of an acetonitrile/tetrahydrofuran solution of **2** at ambient temperature. A single crystal of **2** of appropriate dimensions was mounted on a glass fibre and used for data collection. Data were collected on a Rigaku RAXIS-RAPID diffractometer equipped with a graphite-monochromated Mo Kα radiation source ($k = 0.71075$ Å). Absorption

Table 1. Selected bond distances (Å) and angles (°) for **2**.

Bond lengths (Å)	
Zn1—N1	2.214(3)
Zn1—N2	2.107(3)
Zn1—N3	2.085(3)
Zn1—N4	2.102(3)
Zn1—N5	2.095(3)
Angles (°)	
N1—Zn1—N2	82.52(14)
N1—Zn1—N3	83.26(14)
N1—Zn1—N4	83.31(14)
N1—Zn1—N5	179.46(13)
N2—Zn1—N3	118.17(14)
N2—Zn1—N4	119.77(14)
N2—Zn1—N5	97.09(14)
N3—Zn1—N4	117.70(14)
N3—Zn1—N5	97.26(14)
N4—Zn1—N5	96.59(14)

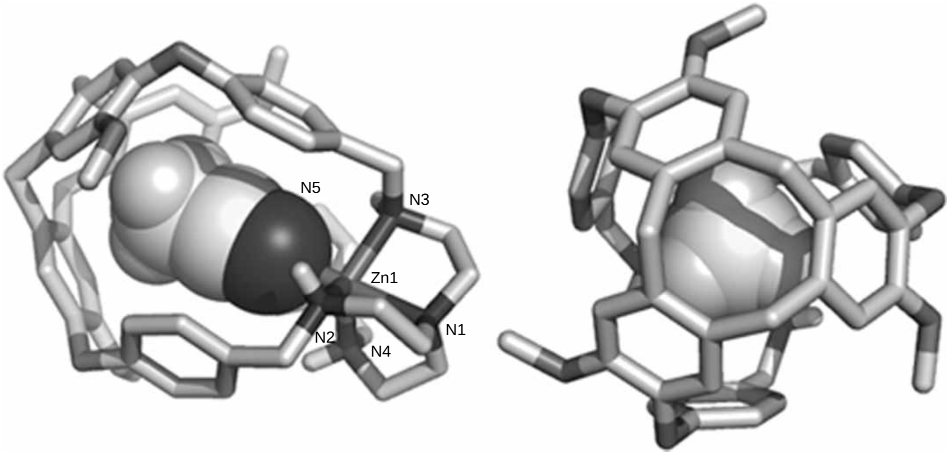

Figure 2. Crystal structure of **2** · MeCN (left: side view; right: top view). The locations of the hydrogen atoms of the amino groups and the acetonitrile molecule were calculated. Other hydrogen atoms and solvents of crystallisation were omitted for clarity.

Table 2. Crystal data and refinement details.

	2
Empirical formula	$C_{120}H_{136}Cl_4N_{13}O_{30}Zn_2$
Formula weight	2513.04
Crystal colour	Colourless
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	14.8931(4)
b (Å)	17.4628(4)
c (Å)	23.1703(6)
Volume (Å^3)	6026.0(3)
Z	2
D_{calcd} (mg/m^3)	1.385
μ (Mo Kα) (mm^{-1})	0.71075
R_1	0.0569
wR_2	0.1421
Goodness of fit (GOF) on F^2	1.135
Flack parameter	0.005(12)

correction was performed with the CrystalStructure (version 3.8) program. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques using SHELXL-97 (Table 2).

Supplementary Material available

Crystallographic data for the structure **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 783757.

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