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The first X-ray structurally characterized M_3L_2 cage-like complex with tetrahedral metal centres and its encapsulation of a neutral guest molecule

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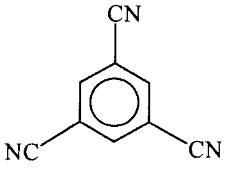
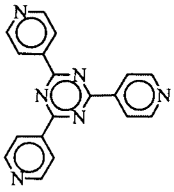
The first X-ray structurally characterized M_3L_2 cage-like complex with tetrahedral metal centres $[Zn_3(tib)_2(OAc)_6]\cdot xH_2O$ [tib = 1,3,5-tris(imidazol-1-ylmethyl)benzene, $x \approx 4$] obtained by reaction of zinc(II) acetate with the tripodal ligand tib exhibits guest inclusion properties of neutral molecule such as synthetic camphor in aqueous solution.

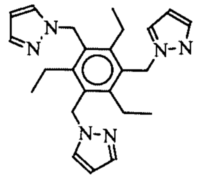
Metal-directed assembly has been proved to be a useful methodology in supramolecular chemistry.[1] Frameworks with specific topologies such as honeycomb grids and cages have been obtained by assembly of suitable metal ions with rationally designed tripodal ligands such as L^1, L^2 and L^3.[2–4] Among these, cage-like complexes have attracted much attention owing to their interesting properties and possible applications, *e.g.* molecular and chiral recognition.[5] The groups of Fujita, Steel, Robson, Stang and Raymond have performed outstanding work in the construction of cage-like complexes.[3–8] Most recently, an $M_{12}L_8$ type cage was obtained by assembly of a tri-bidentate ligand with Cu(II),[8] and larger cages with four organic moieties and eight-coordinate copper(III) centres have been reported by Beer's group.[9] However up to now, to our knowledge, no M_3L_2 cages have been isolated and characterized by X-ray structural analysis, although a guest-induced Pd_3L_2 cage-like complex [L = 1,3,5-tris(4-pyridylmethyl)benzene] and analogous cages have been reported.[6] Moreover, in reported M_6L_4 cage-like complexes, the metal ions are essentially square planar, *e.g.* Pd(II), Pt(II) or octahedral *e.g.* Ga(III), Fe(III),[3,4,6,7,10] with no case of the metal ion being tetrahedral being reported. Herein we report the assembly and X-ray crystal structure of an M_3L_2 cage-like complex formed between a novel tripodal ligand, 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib), and zinc ion, which has tetrahedral configuration. The complex shows the interesting property of guest inclusion in aqueous solution.



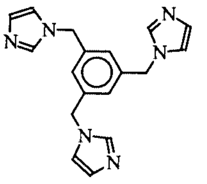
L^1



L^2



L^3



tib

The tib ligand was prepared from 1,3,5-tris(bromomethyl)benzene and imidazole in a molar ratio of 1 : 3 in dimethyl sulfoxide under strong alkali (KOH) conditions.† Its trinuclear zinc(II) complex $[Zn_3(tib)_2(OAc)_6]\cdot xH_2O$ ($x \approx 4$), was synthesized by self-assembly of the tib ligand with zinc acetate dihydrate in ethanol solution.‡ An X-ray crystal structural analysis provides direct evidence that the complex is an M_3L_2 cage.§ As shown in Fig. 1, two tib ligands that are both in *cis, cis, cis*-conformations adopt a face-to-face orientation and are joined together by three zinc atoms to generate an individual three-dimensional cage. Highly disordered water molecules may present in the cage as suggested by elemental analysis.‡ Each zinc atom is four-coordinate with two oxygen atoms from two acetate anions and two nitrogen atoms of imidazole from two different tib ligands. The coordination geometry of the zinc atoms is distorted tetrahedral with coordination angles ranging from 101.5(4) to 123.3(7)°. The distance between the zinc atoms are 9.10 Å and the two benzene ring planes are strictly parallel with each other with a separation of 9.49 Å.

It is clear from the X-ray structural analysis that the title complex has a large cavity inside the cage and therefore is

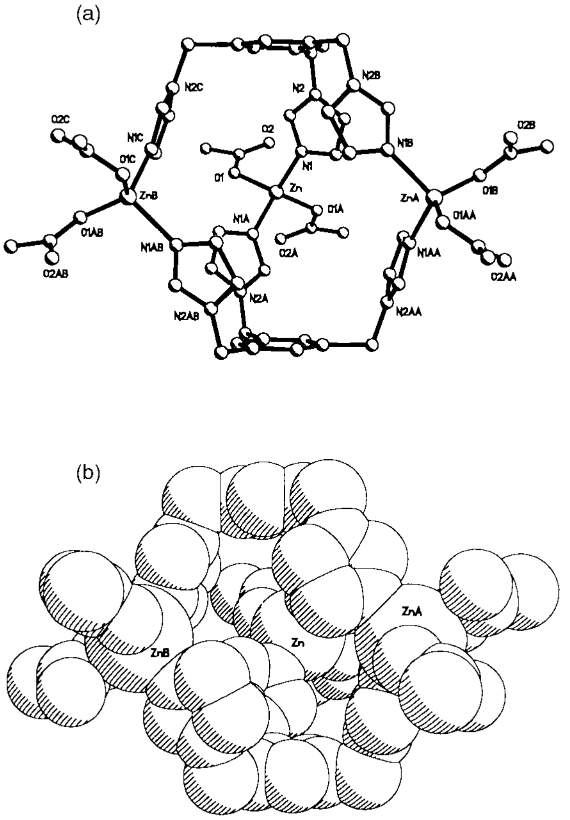


Fig. 1 Perspective view (a) and space-filling representation (b) of the X-ray crystal structure of $[Zn_3(tib)_2(OAc)_6]$. Selected bond lengths (Å) and angles (°): Zn–O1 1.84(2), Zn–N1 2.022(7); O1–Zn–O1A 123.3(7), O1A–Zn–N1A 110.3(4), O1–Zn–N1A 101.5(4), O1A–Zn–N1 101.5(4), O1–Zn–N1 110.3(4), N1A–Zn–N1 109.6(4).

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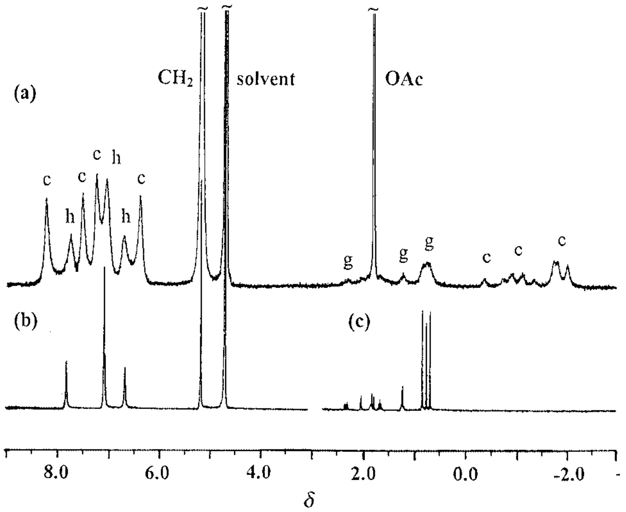

Fig. 2 ^1H NMR spectra in D_2O at 293 K: (a) camphor (3.0 mM) + $[Zn_3(tib)_2(OAc)_6]$ (3.0 mM); (b) downfield region for $[Zn_3(tib)_2(OAc)_6]$ (3.0 mM); (c) camphor (3.0 mM). c refers to complexed species; h to host species and g to guest species.

expected to have the ability to encapsulate guest molecules.[6] Thus we observed remarkable ability of the complex to encapsulate neutral molecules in its aqueous solution. It has been reported that ^1H NMR spectroscopy is a powerful method for investigation of host–guest complexation.[6,11] Fig. 2(a) shows the ^1H NMR spectrum of the complexation of the $[Zn_3(tib)_2(OAc)_6]$ with camphor in deuterated aqueous solution. Two kinds of signal were observed for both the host and guest species when the guest camphor was added to a D_2O solution of $[Zn_3(tib)_2(OAc)_6]$. One set remains unshifted compared with the corresponding signals of the host [Fig. 2(b)] and of the guest [Fig. 2(c)], *i.e.* the unshifted signals originate from uncomplexed species. The other set of upfield shifted signals are from the guest camphor molecules, while for the signals of the host molecule, both up- and down-field shifts were observed. These up- and down-field shifted signals for the host and guest species arise from complexed species.[11] The integration ratio of the host and guest signals in the ^1H NMR spectrum confirmed the 1 : 1 stoichiometry for the complexation between the cage complex and camphor and indicated that *ca.* 60% of the camphor was complexed [Fig. 2(a)]. The results indicate that the camphor molecule, which has a diameter of *ca.* 6 Å, is large enough so that species inside and outside of the cavity of the complex can be distinguished on the NMR time scale. The broadening of the signals as observed in Fig. 2(a) is due to slow exchange between the free and complexed species, since the signals become much broader when the temperature is raised. The kinetic process of the complexation of the cage with camphor was investigated by two-dimensional exchange spectroscopy (2D EXSY).¶ The rate constants for the forward (complexation) and reverse (decomplexation) process are 3.9×10^3 M^{-1} s^{-1} and 32.9 s^{-1}, respectively, giving an equilibrium constant of 117.6 M^{-1}. For chain-like molecules such as ethanol, ethyl acetate, diethyl ether or *n*-butyl alcohol, no complexation was observed.

In conclusion, the present study shows that an M_3L_2 cage is assembled from five small component molecules by the rational design of a suitable tripodal ligand and metal ions, and provides example of supramolecules with interesting properties such as guest inclusion.

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Notes and references

† The tib ligand was prepared from 1,3,5-tris(bromomethyl)benzene and imidazole in a molar ratio of 1 : 3 in dimethyl sulfoxide under strong alkali conditions and was isolated in 30% yield. ^1H NMR (D_2O): δ 5.08 (6H, s, CH_2), 6.93 (3H, s, $^4H_{im}$), 6.95 (3H, s, $^5H_{im}$), 6.96 (3H, s, H_{bz}), 7.63 (3H, s, $^2H_{im}$). H_{im} refers to imidazole protons and H_{bz} refers to benzene-ring protons.

‡ *Experimental*: a solution of tib (32 mg, 0.1 mmol) in ethanol (10 ml) was added to a ethanol (10 ml) solution of $Zn(OAc)_2{\cdot}2H_2O$ (33 mg, 0.15 mmol) at room temperature. The mixture was filtered after stirring for *ca.* 10 min and the filtrate was allowed to stand at ambient temperature for several days. Colorless crystals were collected in 56% yield. Single prismatic crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the filtrate. (Found: C, 45.94; H, 4.82; N, 13.24. $C_{48}H_{62}N_{12}O_{16}Zn_3$ $\{[Zn_3(tib)_2](OAc)_6{\cdot}(H_2O)_4\}$ requires C, 45.78; H, 4.96; N, 13.34%. ^1H NMR (D_2O, 298 K): δ 1.80 (18H, s, CH_3), 5.18 (12H, s, CH_2), 6.67 (6H, s, $^4H_{im}$), 7.07 (6H, s, $^5H_{im}$), 7.09 (6H, s, H_{bz}), 7.81 (6H, s, $^2H_{im}$).

§ *Crystal data* for $[Zn_3(tib)_2](OAc)_6$: M_w = 1187.14, rhombohedral, space group $R32$, a = 17.661(2), b = 17.661(2), c = 20.722(4) Å, γ = 120°, U = 5597.5(14) Å^3, Z = 3, D_c = 1.057 g cm^{-3}, μ = 1.007 mm^{-1}, $F(000)$ = 1836, T = 294(2) K. A single crystal with dimensions of 0.56 × 0.54 × 0.24 mm was mounted and data collection were performed on a Siemens-P4 four-circle diffractometer by the ω-scan technique using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). 2385 reflections were collected of which 2081 are independent (R_{int} = 0.0231). The structure was solved by direct method with SHELXS-86 and refined by full-matrix least-squares calculations on F^2 with SHELXL-93. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.1209P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$; $R1$ = 0.0684 and $wR2$ = 0.1641 [$I > 2\sigma(I)$], max. min. residual density: +0.434, −0.282 e Å^{-3}. CCDC 182/1563. See http://www.rsc.org.suppdata/cc/b0/b000259n for crystallographic files in .cif format.

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