$[Zn_2(\mu\text{-}OH)_2]^{2+}$ Cluster Assembly inside a New Macrobicyclic Ditopic Receptor

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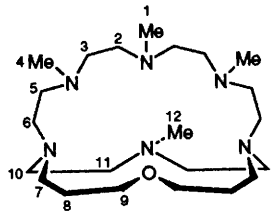
The novel macrobicyclic ligand 17-oxa-4,7,10,23-tetramethyl-1,4,7,10,13,23-hexaazabicyclo[11.7.5]pentacosane **L** reacts with Zn^{2+} to give the $\{[Zn_2(\mu\text{-}OH)_2]L\}^{2+}$ complex which selectively recognises substrate molecules in solution

Macrocyclic and macropolycyclic ligands are successful devices for the recognition and assembly of organized chemical species.[1] Transition metal ions fix the coordination geometry.[2–5] When the primary ligand does not complete the first coordination sphere of the included metal cations, the latter terminates its steric algorithm by propagating the assembly by the coordination of secondary ligands from the medium.[1,6,7]

Very recently it has been observed that metal complexes containing the $[Zn_2(\mu\text{-}OH)_2]^{2+}$ cluster are important model compounds for mimicking the active sites of a variety of enzymes.[8,9] The two Zn^{2+} ions are located 3.0 Å (2.992[9] and 3.024 Å[8]) from each other when bridged by OH^- ions. In order to avoid cleavage of the binuclear structure, appropriate receptor molecules including two Zn^{2+} ions inside a unique cavity should be selected. To this purpose we designed the macrobicyclic ligand **L** whose structure is ideally composed of a monooxatriaza-macrocycle overstructured by a triaza-bridge. Preliminary molecular modelling[10] showed this ligand contains two almost orthogonal potential coordinative moieties and the two Zn^{2+} ions coordinated within them could be bridged by one or two OH^- anions, lying about 3.5 and 3.0 Å apart, respectively. It is well known that both moieties of **L** are capable of binding transition metal ions that occupy only a few positions in their coordination spheres. **L** reacts in alcoholic media with 2 equiv. of Zn^{2+} assembling the $[Zn_2(\mu\text{-}OH)_2]^{2+}$ cluster inside its cavity.† ^{13}C NMR spectra of **L**,‡ in the presence of Zn^{2+} at different metal to ligand molar ratios, R ($0 \leq R \leq 3$), account for the formation of a unique, stable, dibridged dizinc(II) complex in solution with $R = 2$, while at lower R values a mononuclear species is also observed.



L

Crystals of $\{[Zn_2(\mu\text{-}OH)_2]L\}(ClO_4)_2 \cdot H_2O \cdot 0.5MeOH$§ contain the $\{[Zn_2(\mu\text{-}OH)_2]L\}^{2+}$ cluster (Fig. 1). The coordination environments of Zn^{2+} define two binding moieties within the ligand **L**. The geometry around Zn(1) is fairly distorted octahedral, while that around Zn(2) is intermediate between a trigonal bipyramid and a square pyramid. The dibridged cluster is planar with Zn–Zn distance of 2.982(2) Å.

As observed by ^1H NMR measurements in MeOD,‡ $\{[Zn_2(\mu\text{-}OH)_2]L\}^{2+}$ species can suitably bind molecular substrates such as cytosine and 2-hydroxo-pyridine in their deprotonated forms. A downfield shift (*ca.* 0.1–0.2 ppm) is observed in the ^1H spectra of both substrates in the presence of the receptor complex. On the other hand, the remaining isomers of 2-hydroxo-pyridine, 3- and 4-hydroxo-pyridine, do not give rise to any detectable interaction with $\{[Zn_2(\mu\text{-}OH)_2]L\}^{2+}$ either in pure methanol or in 0.1–1 mol dm^{-3}

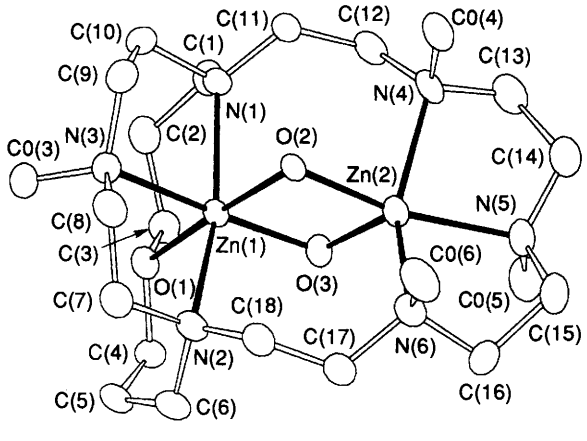


Fig. 1 Crystal structure of the $[Zn_2(\mathbf{L})(\mu\text{-}OH)_2]^{2+}$ cation. Selected distances (Å) and angles (°): Zn(1)–N(1) 2.277(7), Zn(1)–N(2) 2.293(7), Zn(1)–N(3) 2.162(6), Zn(1)–O(1) 2.203(6), Zn(1)–O(2) 2.092(5), Zn(1)–O(3) 1.983(5), Zn(2)–N(4) 2.128(8), Zn(2)–N(5) 2.148(7), Zn(2)–N(6) 2.125(7), Zn(2)–O(2) 2.052(4), N(2)–O(3) 1.941(6), Zn(1)–Zn(2) 2.982(2); N(2)–Zn(1)–N(3) 822.0(3), O(1)–Zn(1)–N(3) 93.0(2), O(1)–Zn(1)–N(2) 94.3(2), N(1)–Zn(1)–N(3) 82.0(3), N(1)–Zn(1)–N(2) 162.6(3), N(1)–Zn(1)–O(1) 93.3(2), O(3)–Zn(1)–N(3) 176.7(3), O(3)–Zn(1)–N(2) 98.1(2), O(3)–Zn(1)–O(1) 90.3(2), O(3)–Zn(1)–N(1) 97.5(2), O(2)–Zn(1)–N(3) 93.3(2), O(2)–Zn(1)–N(2) 87.6(2), O(2)–Zn(1)–O(1) 173.6(2), O(2)–Zn(1)–N(1) 86.6(2), O(2)–Zn(1)–O(3) 83.4(2), N(5)–Zn(2)–N(6) 84.0(3), N(4)–Zn(2)–N(6) 145.0(3), N(4)–Zn(2)–N(5) 83.7(3), O(3)–Zn(2)–N(6) 106.6(3), O(3)–Zn(2)–N(5) 112.1(3), O(3)–Zn(2)–N(4) 108.4(3), O(2)–Zn(2)–N(6) 92.3(3), O(2)–Zn(2)–N(5) 162.3(3), O(2)–Zn(2)–N(4) 89.8(3), O(2)–Zn(2)–O(3) 85.6(2), Zn(1)–O(2)–Zn(2) 92.1(2), Zn(1)–O(3)–Zn(2) 98.93(3).

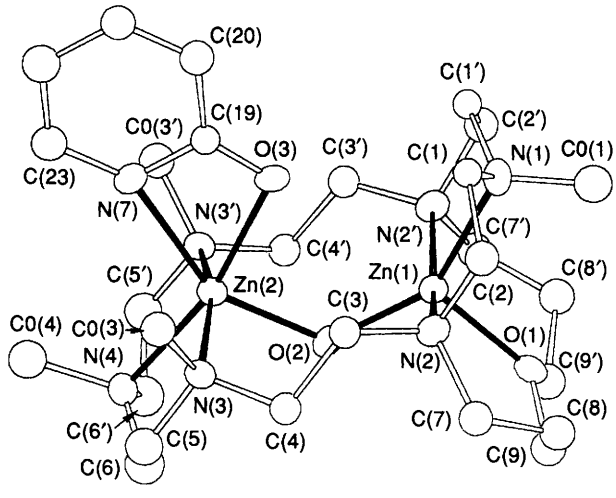


Fig. 2 Crystal structure of the $[Zn_2(\mathbf{L})(\mu\text{-}OH)$(2-hydroxypyridinate)$]^{2+}$ cation. The complex cation possesses a crystallographic symmetry plane containing Zn(1), Zn(2), the hydroxo-pyridinate group, O(1), O(2), N(1), N(4), CO(1) and CO(4). Selected distances (Å) and angles (°): Zn(1)–N(1) 2.13(2), Zn(1)–N(2) 2.27(1), Zn(1)–O(2) 1.87(1), Zn(1)–O(1) 2.04(1), Zn(2)–N(7) 2.29(1), Zn(2)–N(3) 2.34(1), Zn(2)–N(4) 2.14(2), Zn(2)–O(2) 1.99(1), Zn(2)–O(3) 2.12(1), Zn(2)–Zn(1) 3.460(3); N(2)–Zn(1)–N(2)′ 162.1(5), N(1)–Zn(1)–N(2) 82.2(3), O(1)–Zn(1)–N(2) 96.1(3), O(1)–Zn(1)–N(1) 103.9(6), O(2)–Zn(1)–N(2) 93.9(3), O(2)–Zn(1)–N(1) 145.6(6), O(2)–Zn(1)–O(1) 110.6(6), N(3)–Zn(2)–N(4) 81.1(3), N(3)–Zn(2)–N(3′) 162.0(4), N(7)–Zn(2)–N(4) 107.2(6), N(7)–Zn(2)–N(3) 93.9(3), O(3)–Zn(2)–N(4) 166.2(6), O(3)–Zn(2)–N(3) 98.9(3), O(3)–Zn(2)–N(7) 59.1(6), O(2)–Zn(2)–N(4) 104.6(6), O(2)–Zn(2)–N(3) 91.0(3), O(2)–Zn(2)–N(7) 148.3(6), O(2)–Zn(2)–O(3) 89.2(5), Zn(2)–O(2)–Zn(1) 127.2(7).

Me_4NOH methanolic solution, similarly to monodentate substrates like pyridine and phenol.

In order to get insight into the structural characteristics and the mechanism governing the observed molecular recognition, we have analyzed the crystal structure of the 2-hydroxo-pyridinate adduct $\{[Zn_2(\mu\text{-}OH)(2\text{-hydroxopyridinate})]\mathbf{L}\}(ClO_4)_2$§ containing discrete $\{[Zn_2(\mu\text{-}OH)(2\text{-hydroxopyridinate})]\mathbf{L}\}^{2+}$ cations (Fig. 2). The two zinc ions, 3.460(3) Å apart, have different coordination spheres. Zn(2) presents a distorted octahedral geometry while the coordination polyhedron around Zn(1) is intermediate between a trigonal bipyramid and a square pyramid.

The observed structures strongly suggest that the bridging hydroxy groups play an important role in determining the selectivity of the dizinc(II) complex towards substrate recognition. In fact, the binding of monodentate substrates to $\{[Zn_2(\mu\text{-}OH)_2]\mathbf{L}\}^{2+}$ should occur either *via* the involvement of a sixth coordinative position on Zn^{2+}, or by replacement of a bound donor. Both processes are generally not very favourable. Coordination of a bidentate ligand occurs only when the energy lost due to the loss of a bridging hydroxy ligand is regained by the formation of an appropriate chelated ring. Among the three isomers of hydroxo-pyridine only 2-hydroxo-pyridine has the suitable bite.

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Footnotes

† **L** was obtained by reacting 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane and 3,3′-oxydi(propionyl) chloride.[11] Crystals of $\{[Zn_2(\mu\text{-}OH)_2]\mathbf{L}\}(ClO_4)_2\cdot H_2O\cdot 0.5MeOH$ **1** were obtained in quantitative yield by slow evaporation of methanolic solutions containing **L** and $Zn(ClO_4)_2\cdot 6H_2O$ in 1:2 molar ratio. Addition of equimolar quantities of 2-hydroxo-pyridine to methanolic solution of **1** produced after evaporation crystals of $\{[Zn_2(\mu\text{-}OH)(2\text{-hydroxo-pyridinate})]\mathbf{L}\}(ClO_4)_2$ in almost quantitative yield.

‡ NMR titrations were performed by adding a 5×10^{-2} mol dm^{-3} methanolic solution of $Zn(ClO_4)_2\cdot 6H_2O$ to a 5×10^{-3} mol dm^{-3} solution of **L** in MeOD. 200.0 MHz ^1H and 50.32 MHz ^{13}C NMR spectra were recorded at 298 K in a Bruker AC-200 spectrometer. Peak positions are reported relative to TMS.

§ *Crystal data* for $\{(Zn_2(\mu\text{-}OH)_2]\mathbf{L}\}(ClO_4)_2\cdot H_2O\cdot 0.5CH_3OH$ **1**: $C_{22.5}H_{54}Cl_2N_6O_{12.5}Zn_2$, $M = 810.37$, colourless plate-shaped crystals ($0.5 \times 0.3 \times 0.2$ mm), monoclinic, space group $P2_1/c$, with $a = 8.552(2)$, $b = 39.23(1)$, $c = 11.419(3)$ Å, $\beta = 111.90(2)°$, $V = 3554(2)$ Å^3, $Z = 4$, $D_c = 1.514$ g cm^{-3}. $F(000) = 1700$, μ(Cu-Kα) = 36.4 cm^{-1}. For $\{[Zn_2)\mu\text{-}OH)(2\text{-hydroxo-pyridinate})]\mathbf{L}\}(ClO_4)_2$ **2**: $C_{27}H_{53}Cl_2N_7O_{11}Zn_2$, $M = 853.42$, colourless prismatic crystals ($0.4 \times 0.2 \times 0.1$ mm), monoclinic, space group $P2_1/m$, with $a = 11.796(3)$, $b = 13.035(6)$, $c = 14.842(3)$ Å, $\beta = 107.75(2)°$, $V = 2173(1)$ Å^3, $Z = 2$, $D_c = 1.304$ g cm^{-3}. $F(000) = 892$. μ(Mo-Kα) = 13.0 cm^{-1}, 6464 ($2.5 < \theta < 65$; $\theta - 2\theta$ scan; T 298 K) for **1** and 4159 independent reflections ($2.5 < \theta < 25$; $\theta - 2\theta$ scan; **T** 298 K) for **2** were measured on an Enraf-Nonius CAD4 diffractometer using graphite monochromatized Cu-Kα ($\lambda = 1.5418$ Å) for **1** and Mo-Kα ($\lambda = 0.71069$ Å) for **2**.

Atomic coordinates, bond lengths and angles, and thermal parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 J.-M. Lehn, *Pure Appl. Chem.*, 1980, **52**, 2441.
2 J.-M. Lehn and A. Rigault, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1095; P. Baxter, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem. Int. Ed. Engl.*, 1993, **32**, 69; T. M. Garrett, U. Koert, J.-M. Lehn, A. Rigault, D. Meyer and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1990, 557.
3 C. O. Dietrich-Buchecker, J. P. Sauvage and J. P. Kintzinger, *Tetrahedron Lett.*, 1983, **24**, 5095; C. O. Dietrich-Buchecker, J. P. Sauvage and J. M. Kern, *J. Am. Chem. Soc.*, 1984, **106**, 3043; C. O. Dietrich-Buchecker and J. P. Sauvage, *Chem. Rev.*, 1987, **87**, 795; C. O. Dietrich-Buchecker and J. P. Sauvage, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 189; J. C. Chambron, V. Heitz and J. P. Sauvage *J. Chem. Soc., Chem. Commun.*, 1992, 1131.
4 M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.
5 J. R. Bradbury, J. L. Hampton, D. P. Martone and A. W. Maverick, *Inorg. Chem.* 1989, **28**, 2392.
6 J. Comarmond, B. Dietrich, J.-M. Lehn and R. Louis, *J. Chem. Soc., Chem. Commun.*, 1995, 74.
7 A. Bencini, A. Bianchi, P. Paoletti and P. Paoli, *Coord. Chem. Rev.*, 1992, **120**, 51.
8 P. Chaudhuri, C. Atockheim, K. Wieghrdt, W. Deck, R. Gregorzic, H., Vahrenkamp, B. Nuber and J. Weiss, *Inorg. Chem.*, 1992, **31**, 1451.
9 N. N. Murthy and K. D. Karlin, *J. Chem. Soc., Chem. Commun.*, 1993, 1236.
10 HyperChem, AUTODESK.
11 A. Bianchi, M. Ciampolini, M. Micheloni, N. Nardi and B. Valtancoli, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1131.