

Novel tripodal chelating ligand for appending and encapsulating metal ions. Crystal structure of a parachute-like hydrogen bonded complex

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Received (in Cambridge, UK) 9th May 2000, Accepted 19th June 2000

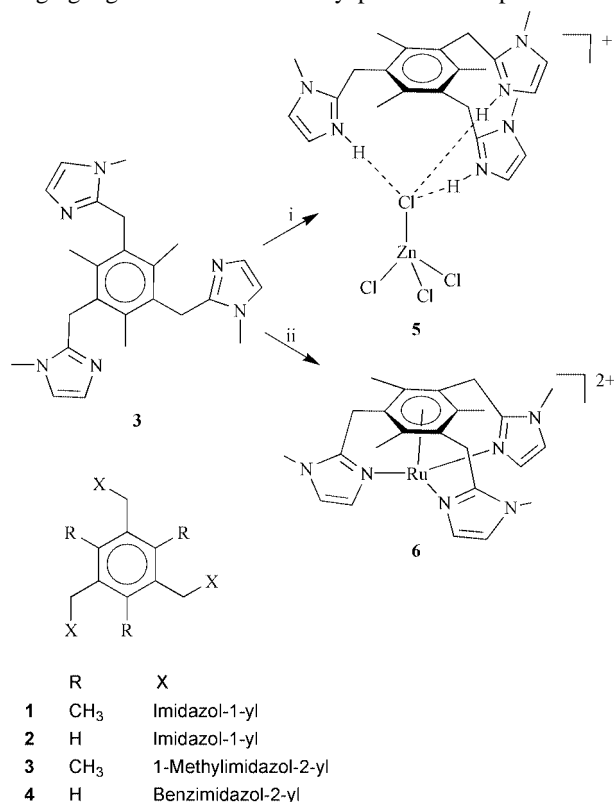
Tripodal ligand 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene (**3**) forms a parachute-like non-covalent complex with zinc tetrachloride, $5\cdot[\text{Zn}_2\text{Cl}_6]_{0.5}$, where the imidazoles of the ligand are protonated and bind to the metal ion through $\text{NH}\cdots\text{Cl}$ hydrogen bonds.

Although biological systems efficiently organize simple units into aggregates with intricate and wonderful functions by non-covalent interactions, self-assembly of frameworks with specific topology, interesting properties and functions is still a challenge for chemists.¹ A number of hydrogen-bonded aggregates have been obtained by self-organization of organic or organic-inorganic components.^{1–3} We herein report a parachute-like complex obtained by assembly of organic tripodal ligand 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene (**3**) and inorganic zinc tetrachloride. In this complex, protonation of the imidazoles of the ligand and its binding to the metal ion through $\text{NH}\cdots\text{Cl}$ hydrogen bonds provides a good example of a dual role for a single ligand.

We are currently engaged in the systematic study of self-assembly of tripodal ligands **1–4** (Scheme 1) with various metal ions and are investigating the influence of linkage mode of bridging ligands on the assembly process of supramolecular

complexes.⁴ Up to now, tripodal ligands **1** and **2**, and others also having benzene or other arene as the ring core such as 2,4,6-tris(4-pyridyl)-1,3,5-triazine, 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene have been reported to form polymeric networks or multinuclear metallocages with metal ions.^{4,5} The ligand **3** was demonstrated for the first time to form a parachute-like non-covalently bonded complex with zinc tetrachloride. $[\text{ZnCl}_4]^{2-}$ has been used as a counterion for crystallization of Ru(II) and Co(II) complexes.^{6,7} In the present complex, this anion binds to **3** through $\text{NH}\cdots\text{Cl}$ interactions in which the Cl atom acts as an acceptor of hydrogen bonds.

Assembly of 3^+ with ZnCl_2 in hydrochloric acid solution gave the hydrogen bonded complex, $5\cdot[\text{Zn}_2\text{Cl}_6]_{0.5}$ (Scheme 1).[‡] As shown in Fig. 1,[§] all three imidazole groups of **3** are protonated which was confirmed by IR spectral measurements. The distances between each imidazole proton and Cl(12) ranges from 2.32 to 2.45 Å which indicates the presence of triple $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bonds. Therefore, **5** looks like a parachute in which $[\text{ZnCl}_4]^{2-}$ acts as an appending group. The atom Cl(12) is located under **3** with a distance of 3.43 Å between Cl(12) and the center of the benzene ring plane. Two adjacent molecules of **5** with normal and upside down orientations linked by hydrogen bonds are illustrated in Fig. 2(a). There are four additional hydrogen bonds in each $[\text{ZnCl}_4]^{2-}$ unit excluding the triple $\text{N}\cdots\text{H}\cdots\text{Cl}(12)$ bonds described above: C(14)–H \cdots Cl(11) [$r_{\text{C}(14)\text{--Cl}(11)} = 3.517(8)$ Å], C(11A)–H \cdots Cl(11) [$r_{\text{C}(11\text{A})\text{--Cl}(11)} = 3.707(6)$ Å], C(54)–H \cdots Cl(13) [$r_{\text{C}(54)\text{--Cl}(13)} = 3.602(7)$ Å] and C(101A)–H \cdots Cl(14) [$r_{\text{C}(101\text{A})\text{--Cl}(14)} = 3.768(8)$ Å]. The unit shown in Fig. 2(a) can be repeated and joined by



Scheme 1 Reagents: i, $\text{ZnCl}_2 + \text{HCl}$; ii, $\text{Ru}(\text{DMSO})_4\text{Cl}_2$. For details see notes of preparations.

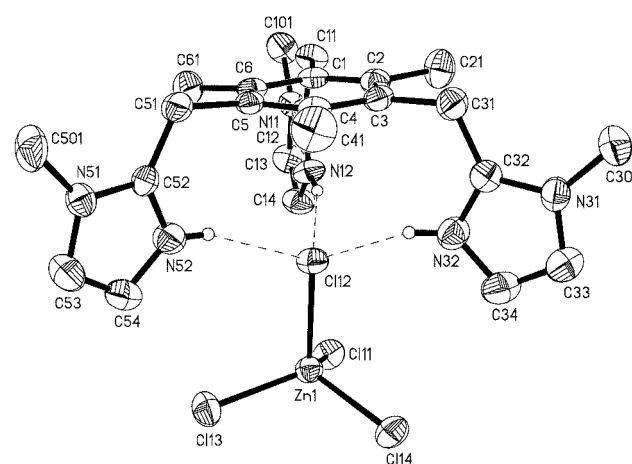


Fig. 1 Crystal structure of **5**, thermal ellipsoids are drawn at 50% probability and the $\text{N}\cdots\text{H}\cdots\text{Cl}$ hydrogen bonds are indicated by dashed lines. Selected bond lengths (Å) and angles ($^\circ$): $\text{Zn1}\text{--Cl11} = 2.269(1)$, $\text{Zn1}\text{--Cl12} = 2.360(1)$, $\text{Zn1}\text{--Cl13} = 2.242(2)$, $\text{Zn1}\text{--Cl14} = 2.249(2)$, $\text{N12}\text{--Cl12} = 3.199(4)$ [$\text{H1}\text{--Cl12} = 2.32$], $\text{N32}\text{--Cl12} = 3.194(5)$ [$\text{H2}\text{--Cl12} = 2.40$], $\text{N52}\text{--Cl12} = 3.254(5)$ [$\text{H3}\text{--Cl12} = 2.45$]; $\text{N12}\text{--H1}\text{--Cl12} = 163$, $\text{N32}\text{--H2}\text{--Cl12} = 154$, $\text{N52}\text{--H3}\text{--Cl12} = 162$, $\text{Cl12}\text{--Zn1}\text{--Cl11} = 104.64(5)$, $\text{Cl12}\text{--Zn1}\text{--Cl13} = 105.86(6)$, $\text{Cl12}\text{--Zn1}\text{--Cl14} = 108.23(6)$, $\text{Cl11}\text{--Zn1}\text{--Cl13} = 113.71(6)$, $\text{Cl11}\text{--Zn1}\text{--Cl14} = 110.28(6)$, $\text{Cl13}\text{--Zn1}\text{--Cl14} = 113.49(6)$.

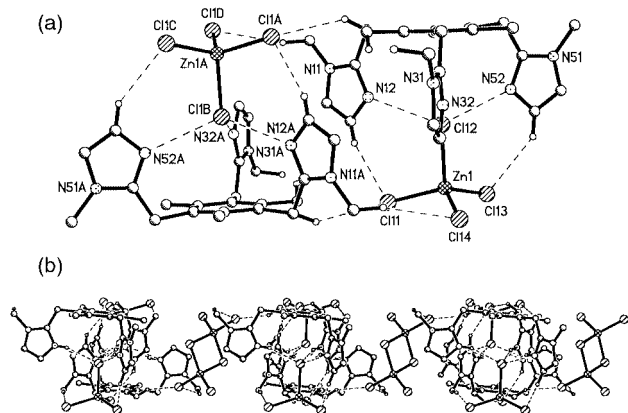


Fig. 2 Two adjacent parachute-like molecules with normal and upside down orientations (a) and one-dimensional chain (b) linked by hydrogen bonds.

$[\text{Zn}_2\text{Cl}_6]^{2-}$ through hydrogen bonds to generate an infinite one-dimensional chain [Fig. 2(b)]: $\text{C}(301\text{A})\text{--H}\cdots\text{Cl}(22)$ [$r_{\text{C}(301\text{A})\text{--Cl}(22)} = 3.620(8) \text{ \AA}$] and $\text{C}(21\text{A})\text{--H}\cdots\text{Cl}(22)$ [$r_{\text{C}(21\text{A})\text{--Cl}(22)} = 3.530(8) \text{ \AA}$].

Another coordination mode of such a tripodal ligand is the encapsulation of the metal ion with additional coordination to the benzene ring as demonstrated by Hartshorn and Steel.⁶ We are also studying the reactions of **3** with other metal salts. The reaction between **3** and $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was investigated by electrospray mass (ES-MS) spectrometry and NMR spectroscopy.[¶] Four main peaks at m/z 202.3, 252.3, 403.4 and 420.8 were observed which correspond to $[\mathbf{3} + 2\text{H}]^{2+}$, $[\text{Ru}(\mathbf{3})]^{2+}$, $[\mathbf{3} + \text{H}]^+$ and $[\mathbf{3} + \text{H}_2\text{O} + \text{H}]^+$, respectively. All these assignments were confirmed by good agreements between the observed and calculated isotopic distributions. The results of ES-MS imply that only the mononuclear $\text{Ru}(\text{II})$ complex is formed by the reaction of **3** with $\text{Ru}(\text{DMSO})_4\text{Cl}_2$. In the ^{13}C NMR spectrum of $\mathbf{6}\cdot\text{Cl}_2$, the benzene ring carbons were shifted upfield by *ca.* 32 ppm compared with the corresponding signals of **3**. The NMR study suggests the coordination of Ru to the benzene ring of **3**.^{¶¶} This means that **3** may encapsulate the $\text{Ru}(\text{II})$ ion (**6**) as shown in Scheme 1.

In conclusion, the present study shows that the novel tripodal ligand **3** can append to the metal ion through non-covalent interactions and encapsulate the metal ion through chelation and η^6 -arene coordination.

The authors are grateful for funding from the National Nature Science Foundation of China for financial support of this work.

Notes and references

† The ligand **3** was prepared from 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, 1-methylimidazole and *n*-BuLi using standard Schlenk techniques in 45% isolated yield. $\delta_{\text{H}}(\text{CDCl}_3)$: 7.05 (s, 3H), 6.91 (s, 3H), 4.24 (s, 6H), 3.90 (s, 9H), 2.07 (s, 9H).

‡ *Experimental*: a solution of **3** (40.2 mg, 0.1 mmol) in MeOH (5 ml) was added to a 1 M HCl (10 ml) solution of ZnCl_2 (40.8 mg, 0.3 mmol) at room temperature. The mixture was filtered after stirring for about 10 min and the filtrate was stood at *ca.* 40 °C for several days. Light yellow crystals were collected in *ca.* 60% yield. Macroanal. Found: C, 36.64; H, 4.22; N, 10.66. $\text{C}_{24}\text{H}_{33}\text{N}_6\text{Cl}_7\text{Zn}_2$ requires C, 36.75; H, 4.24; N, 10.71%. $\delta_{\text{H}}(\text{D}_2\text{O}, 298 \text{ K})$: 7.32 (s, 3H), 7.12 (s, 3H), 4.42 (s, 6H), 3.83 (s, 9H), 2.05 (s, 9H).

§ *Crystal data* for $\mathbf{5}\cdot[\text{Zn}_2\text{Cl}_6]_{0.5}$ ($\text{C}_{24}\text{H}_{33}\text{N}_6\text{Cl}_7\text{Zn}_2$): $M = 784.50$, triclinic, space group $\text{P}\bar{1}$, $a = 13.593(4)$, $b = 13.788(4)$, $c = 10.821(3) \text{ \AA}$, $\alpha = 108.41(2)$, $\beta = 112.25(2)$, $\gamma = 104.09(2)^\circ$, $U = 1621(1) \text{ \AA}^3$, $Z = 2$, $D_c = 1.606 \text{ g cm}^{-3}$, $\mu = 2.081 \text{ mm}^{-1}$, $F(000) = 796$, $T = 296(1) \text{ K}$. The data collection was carried out on a Rigaku AFC5R four-circle diffractometer by $\omega - 2\theta$ scan techniques using graphite-monochromated Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$). Total 7720 reflections were collected of which 7408 are independent ($R_{\text{int}} = 0.017$). The structure was solved by direct methods with SIR92 and refined by full-matrix least-squares calculations. The final $R1 = 0.0431$ [$I > 2\sigma(I)$], max., min. residual density: +0.80, -0.96 e \AA^{-3} . CCDC 182/1693. See <http://www.rsc.org/suppdata/cc/b0/b003694n/> for crystallographic files in .cif format.

¶ A solution of **3** (40.2 mg, 0.1 mmol) and $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ (48.9 mg, 0.1 mmol) in EtOH-H₂O (1 : 3, 15 ml) was refluxed for 10 h. After filtration, the filtrate was stood at room temperature for several days and a brown powder was obtained. $\delta_{\text{H}}(\text{D}_2\text{O}, 313 \text{ K})$: 7.36 (s, 3H), 7.03 (s, 3H), 4.47 (s, 6H), 3.96 (s, 9H), 2.25 (s, 9H).

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