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

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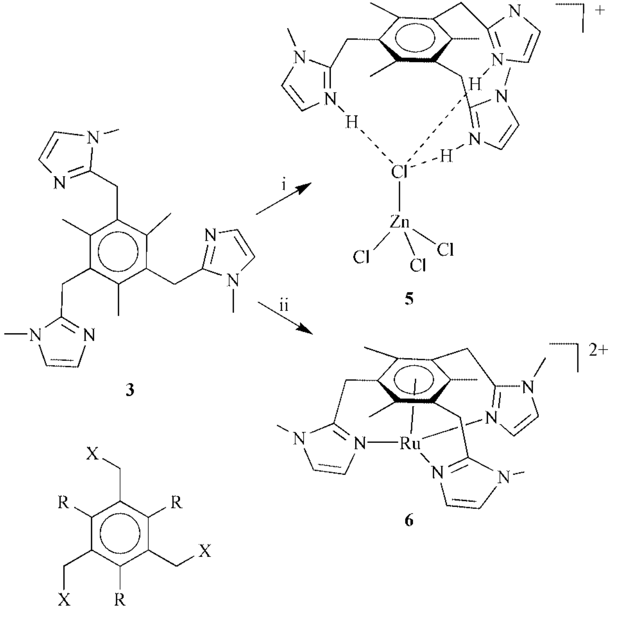
Tripodal ligand 1,3,5-tris(1-methylimidazol-2-ylmethyl)-2,4,6-trimethylbenzene (3) forms a parachute-like non-covalent complex with zinc tetrachloride, 5·[Zn_2Cl_6]$_{0.5}$, where the imidazoles of the ligand are protonated and bind to the metal ion through NH···Cl hydrogen bonds.

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 NH···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. [$ZnCl_4$]$^{2-}$ 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 NH···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**·[Zn_2Cl_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 N–H···Cl hydrogen bonds. Therefore, **5** looks like a parachute in which [$ZnCl_4$]$^{2-}$ 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 [$ZnCl_4$]$^{2-}$ unit excluding the triple N–H···Cl(12) bonds described above: C(14)–H···Cl(11) [$r_{C(14)–Cl(11)}$ = 3.517(8) Å], C(11A)–H···Cl(11) [$r_{C(11A)–Cl(11)}$ = 3.707(6) Å], C(54)–H···Cl(13) [$r_{C(54)–Cl(13)}$ = 3.602(7) Å] and C(101A)–H···Cl(14) [$r_{C(101A)–Cl(14)}$ = 3.768(8) Å]. The unit shown in Fig. 2(a) can be repeated and joined by



	R	X
1	CH_3	Imidazol-1-yl
2	H	Imidazol-1-yl
3	CH_3	1-Methylimidazol-2-yl
4	H	Benzimidazol-2-yl

Scheme 1 *Reagents*: i, $ZnCl_2$ + HCl; ii, Ru(DMSO)$_4$Cl$_2$. For details see notes of preparations.

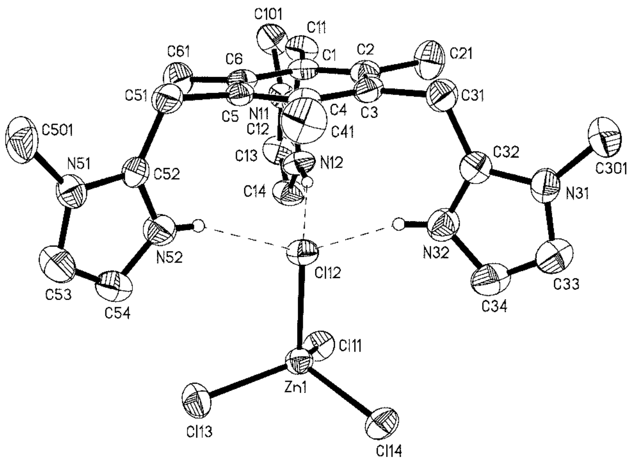


Fig. 1 Crystal structure of **5**, thermal ellipsoids are drawn at 50% probability and the N–H···Cl hydrogen bonds are indicated by dashed lines. Selected bond lengths (Å) and angles (°): Zn1–Cl11 = 2.269(1), Zn1–Cl12 = 2.360(1), Zn1–Cl13 = 2.242(2), Zn1–Cl14 = 2.249(2), N12–Cl12 = 3.199(4) [H1–Cl12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

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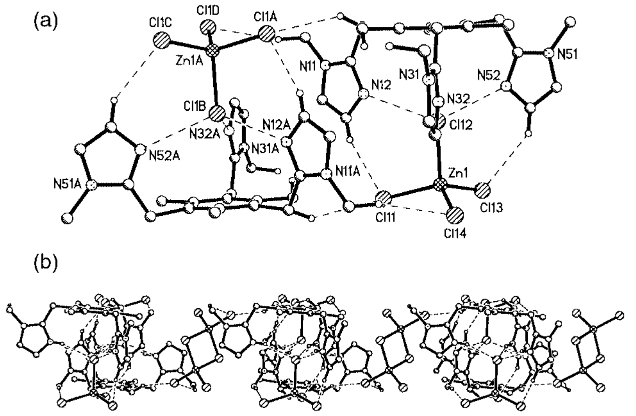

Fig. 2 Two adjacent parachute-like molecules with normal and upside down orientations (a) and one-dimensional chain (b) linked by hydrogen bonds.

$[Zn_2Cl_6]^{2-}$ through hydrogen bonds to generate an infinite one-dimensional chain [Fig. 2(b)]: C(301A)–H···Cl(22) [$r_{C(301A)-Cl(22)}$ = 3.620(8) Å] and C(21A)–H···Cl(22) [$r_{C(21A)-Cl(22)}$ = 3.530(8) Å].

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 $Ru(DMSO)_4Cl_2$ 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 $[\mathbf{3} + 2H]^{2+}$, $[Ru(\mathbf{3})]^{2+}$, $[\mathbf{3} + H]^+$ and $[\mathbf{3} + H_2O + H]^+$, 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 Ru(II) complex is formed by the reaction of **3** with $Ru(DMSO)_4Cl_2$. In the ^{13}C NMR spectrum of $\mathbf{6}\cdot Cl_2$, 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**.[6]¶ This means that **3** may encapsulate the Ru(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.

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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. $\delta_H(CDCl_3)$: 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. $C_{24}H_{33}N_6Cl_7Zn_2$ requires C, 36.75; H, 4.24; N, 10.71%. $\delta_H(D_2O$, 298 K): 7.32 (s, 3H), 7.12 (s, 3H), 4.42 (s, 6H), 3.83 (s, 9H), 2.05 (s, 9H).

§ *Crystal data* for $\mathbf{5}\cdot[Zn_2Cl_6]_{0.5}$ ($C_{24}H_{33}N_6Cl_7Zn_2$): M = 784.50, triclinic, space group $P\bar{1}$, a = 13.593(4), b = 13.788(4), c = 10.821(3) Å, α = 108.41(2), β = 112.25(2), γ = 104.09(2)°, U = 1621(1) Å^3, Z = 2, D_c = 1.606 g cm^{-3}, μ = 2.081 mm^{-1}, $F(000)$ = 796, T = 296(1) K. The data collection was carried out on a Rigaku AFC5R four-circle diffractometer by $\omega - 2\theta$ scan techniques using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Total 7720 reflections were collected of which 7408 are independent (R_{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 Å^{-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 $Ru(DMSO)_4Cl_2$ (48.9 mg, 0.1 mmol) in EtOH–H_2O (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. $\delta_H(D_2O$, 313 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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