A New Imidazole-containing Octadentate Ligand, Capable of binding Two Metal Ions; the *X*-Ray Structure of the Dinuclear $ZnCl_2$ Adduct of 1,1,4,7,7-penta(benzimidazol-2-ylmethyl)-1,4,7-triazaheptane

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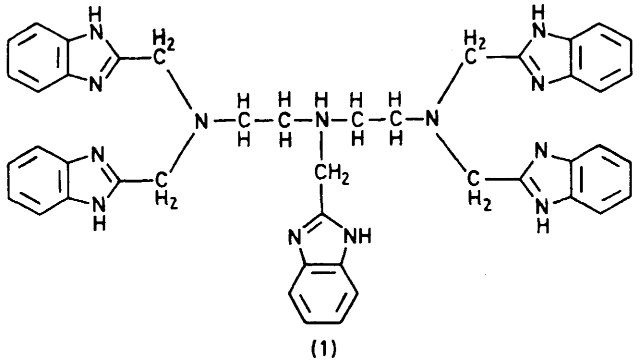
Summary Dinuclear Cu^{II} and Zn^{II} compounds of the new ligand 1,1,4,7,7-penta(benzimidazol-2-ylmethyl)-1,4,7-triazaheptane were synthesized; the *X*-ray structure of the Zn compound shows that one Zn atom is six-co-ordinated by one Cl and five N atoms, whereas the second Zn atom is five-co-ordinated by three N and two Cl atoms.

MONO- and DI-NUCLEAR Cu and Zn co-ordination compounds can be prepared with chelating multidentate ligands containing imidazole groups. These compounds serve as interesting models for the active sites of a number of metalloproteins such as hemocyanin, superoxide dismutase, plastocyanin, and carbonic anhydrase.[1–5] Condensation of carboxylic acids with 1,2-diaminobenzene leads to the formation of benzimidazole derivatives.[2,3,5] We recently prepared Cu complexes of a new hexadentate ligand[3] derived in this way from ethylenediaminetetra-acetic acid (EDTA), containing four co-ordinating benzimidazole groups. This ligand can bind one or two metal ions depending on the conditions of the reaction.[3,4,6] As an extension of this work we synthesized the title compound.



(1)

This new related ligand (**1**) (DTPB) with five benzimidazole groups is derived from diethylenetriaminepenta-acetic acid. DTPB.$3H_2O$ was prepared by melting diethylenetriaminepenta-acetic acid and 1,2-diaminobenzene in a 1 : 5 molar ratio for 3 h at 190 °C. After cooling to

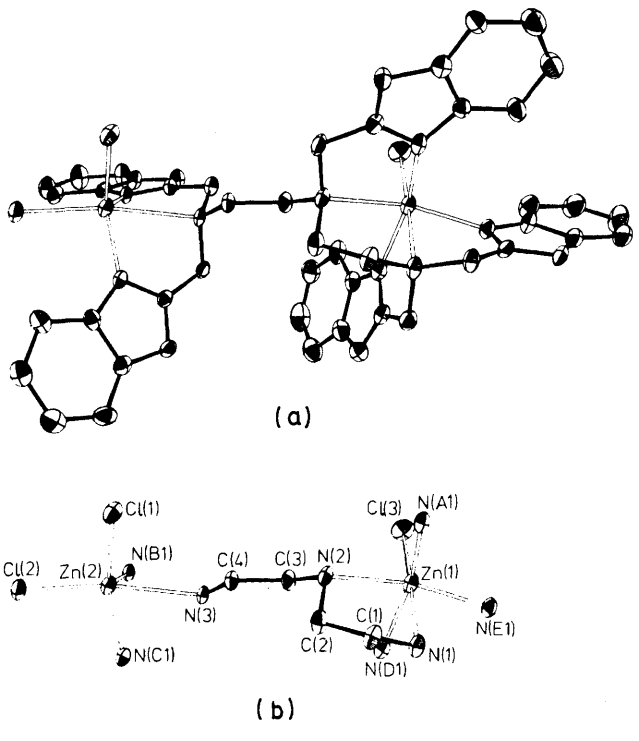


FIGURE. ORTEP drawing of the $Zn_2(DTPB)Cl_3^+$ ion showing the anisotropic vibration ellipsoids of the atoms (probability 20%) (a), and the two different metal binding sites in the complex ion with the atomic labelling (b). Nitrogen atoms of different benzimidazole groups are labelled with one-letter codes A to E. Bond distances to Zn(1) are (in Å): N(1) 2·41(1); N(2) 2·45(1); N(A1) 2·13(1); N(D1) 2·12(1); N(E1) 2·13(1); Cl(3) 2·282(5). To Zn(2): N(3) 2·53(1); N(B1) 2·02(1); N(C1) 2·04(1); Cl(1) 2·283(5); Cl(2) 2·351(4). Bond angles around Zn(1) are (in degrees): N(1), N(2), 75·2(4); N(1),N(A1) 85·6(5); N(1),N(D1) 76·8(5); N(1), N(E1) 73·9(4); N(2),N(A1) 74·5(5); N(2),N(D1) 85·2(5); N(2),Cl(3) 102·5(3); N(A1),N(E1) 94·0(5); N(A1),Cl(3) 95·2(4); N(D1),N(E1) 96·6(5); N(D1),Cl(3) 101·7(4); and N(E1),Cl(3) 108·7(4). Around Zn(2): N(3),N(B1) 74·1(4); N(3),N(C1) 74·3(5); N(3),Cl(1) 92·6(3); N(B1),N(C1) 116·6(5); N(B1),Cl(1) 113·2(4); N(B1),Cl(2) 102·9(3); N(C1),Cl(1) 121·6(4); N(C1),Cl(2) 99·6(4); and Cl(1),Cl(2) 96·9(2).

room temperature the dark reaction product was dissolved in ethanol, decolourised with carbon, and precipitated with diethyl ether. The product was characterised by satisfactory elemental analyses (C,H,N) and n.m.r. spectroscopy.†

Reaction of DTPB with $CuCl_2.2H_2O$ or $ZnCl_2$ in a molar ratio of 1 : 2 in hot ethanol yields solid precipitates analysing as $Cu_2(DTPB)Cl_4(H_2O)_{7\cdot5}$ and $Zn_2(DTPB)Cl_4(H_2O)_3$. The latter compound may be crystallised by vapour diffusion of acetonitrile into an aqueous solution of the compound.‡

The asymmetric $Zn(DTPB)Cl_3^+$ ion is shown in the Figure. The two Zn^{II} atoms in the structure have different co-ordination geometries. Zn(1) is six-co-ordinated by a chloride ligand and five N atoms from three benzimidazole and two aliphatic amine groups. The geometry can best be described as distorted octahedral. The long Zn(1)–N(2) distance is probably a result of the steric requirements of the ligand. The other Zn^{II} atom [Zn(2)] can be described as five-co-ordinated with one weakly bound ligand [N(3)] at a distance of 2·53(1) Å. If N(3) is considered as non-bonding the geometry is best described as tetrahedral. The Zn to ligand distances are given in the Figure caption together with some bond angles.

In this complex ion the two metal binding sites behave as different independent co-ordination compounds linked only by an ethylene bridge. The structure of the Cu compound is not likely to be similar and has a completely different i.r. spectrum.

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† ^1H N.m.r. data: $[(CD_3)_2SO, SiMe_4]$ δ 13·1 (5H, br.), 7·63 and 7·32 (20H, sym.), 4·01 (10H, s), and 2·76 (8H, s).

‡ *Crystal data:* triclinic, space group $P\bar{1}$, $a = 15{\cdot}380(2)$, $b = 14{\cdot}181(5)$, $c = 17{\cdot}325(2)$ Å, $\alpha = 93{\cdot}13(2)$, $\beta = 116{\cdot}515(9)$, $\gamma = 95{\cdot}61(2)$°, D_m could not be determined owing to crystal deterioration; D_c could not be calculated because of the unknown number of disorded solvent molecules in the cell. The intensities of 4341 independent reflections with $I > 2\sigma(I)$ were measured (Mo-K_α radiation) on a crystal which was sealed in a capillary with some mother liquor. The structure was solved by direct methods and was refined by block-diagonal least-squares (2 blocks) to a final R value of 0·074. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23193 (13pp.) from the British Library Lending Division. For details of how to obtain this material, see Notice to Authors No. 7, *J. Chem. Soc., Dalton* or *Perkin Trans.*, Index Issues.

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