# The $Mg^{2+}$ Ion as a Template for the Synthesis of Planar Nitrogen-donor Macrocyclic Ligands: Pentagonal Bipyramidal $Mg^{II}$ Complexes

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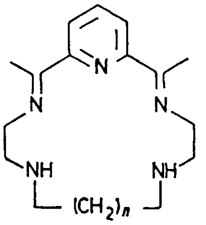
*Summary* Pentagonal bipyramidal complexes, $[Mg(macrocycle)(H_2O)_2]^{2+}$, containing planar pentadentate nitrogen-donor macrocyclic ligands, are formed in good yield in hydroxylic solvents by the template condensation of 2,6-diacetylpyridine with a linear tetramine in the presence of $Mg^{2+}$.

RECENTLY there has been much interest in the co-ordinating properties of macrocyclic ligands.[1] Usually, the macrocycles, including many of biological interest,[2] are synthesised with the aid of a metal ion which, acting as a template, brings the reactive centres of bifunctional reactants into the *cis*-relationship necessary for ring closure. The effective metal ions have almost invariably been transition-metal ions having $d^5$ to $d^{10}$ configurations capable of forming moderately strong, usually directed, semi-covalent bonds with nitrogen donors. We now report the first template synthesis of a nitrogen-donor macrocycle which uses a strongly electropositive, *s*-block, metal. In view of the relatively high abundance (compared with transition-metal ions) of $Mg^{2+}$ in living systems, particularly within cells, and of its occurrence in the chlorophylls, the effectiveness of $Mg^{2+}$ as a template for the synthesis of planar nitrogen-donor macrocycles is of interest in relation to the biosynthesis of porphyrins, and the activation of enzymes. Organo-magnesium compounds have previously been



(B); $n$ = 2
(C); $n$ = 3

employed in synthetic routes to tetra-azaporphins[3] and chlorins[4] but a template action was not demonstrated in these cases.

2,6-Diacetylpyridine, 1,8-diamino-3,6-diazaoctane (or 1,9-diaza-3,7-nonane), and $MgCl_2{\cdot}6H_2O$ in 1 : 1 : 1 molar ratio were digested at 65 °C in aqueous methanol for 12 h. Evaporation of the solvent and extraction of the residue with n-butanol, followed by recrystallization, yielded crystals of $Mg(B)Cl_2.6H_2O$ (I), or $Mg(C)Cl_2 2H_2O$ (II), in 40—60% yield, (B) and (C) being the 15- and 16-membered macrocycles respectively. The template action of $Mg^{2+}$ was demonstrated by control experiments in which the diketone and tetramine were reacted together in the absence of $Mg^{2+}$, or prior to the addition of metal ions, or in the presence of the Lewis acid $AlCl_3$. In all these cases the products were either resinous gums or amorphous powders having i.r. spectra and other properties consistent with an oligomeric or polymeric constitution. Attempts to isolate macrocyclic complexes from these materials were unsuccessful.

Derivatives of the co-ordinated macrocycles containing other anions may be obtained by simple metathetical reactions or by anion exchange methods. Apart from loss of water the complexes have high thermal stability. Thermogravimetric analysis indicated, for (I), loss of $4H_2O$ at 40—75 °C, $2H_2O$ at 130—190 °C, and decomposition above 280 °C; and for (II), loss of $2H_2O$ at 150—230 °C and decomposition above 280 °C. The i.r. and u.v. spectra are closely similar to those of corresponding $Fe^{III}$ and $Fe^{II}$ complexes[5] and support their formulation as salts of the seven-co-ordinate cations $[Mg(macrocycle)(H_2O)_2]^{2+}$. An *X*-ray structure determination of (I) further defines the co-ordination geometry as pentagonal bipyramidal and similar to that found for the analogous $Fe^{II}$ and $Fe^{III}$ compounds.[5] The Mg–N distances range from 2·24 (1) to 2·31 (1) Å; the maximum deviation of a ring nitrogen from the least squares plane of $MgN_5$ being 0·18 Å. The axially co-ordinated oxygen atoms are 2·10 (1), 2·10 (1) Å from the metal. *Crystal data:* $C_{15}H_{35}MgN_5O_6Cl_2$, monoclinic, space-group $P2_1/a$, $M = 475{\cdot}5$, $D_m = 1{\cdot}34$ (1), $D_c = 1{\cdot}34$, $a = 26{\cdot}391$ (15), $b = 8{\cdot}562$ (8), $c = 11{\cdot}091$ (9) Å, $\beta = 110{\cdot}0$ (1) $Z = 4$. 1782 independent reflections significantly above background were measured by the stationary crystal, stationary counter method on a GeXRD6 diffractometer and have been refined to $R$ 0·082.

Powder patterns show that (I) is isomorphous with the previously reported[6] complex $Mn(B)Cl_2.6H_2O$. This is a further reflection of the similarity in the structural chemistry of $Mg^{2+}$ and $Mn^{2+}$ which, despite the difference in ionic size, seems to justify the use of $Mn^{II}$ as a (paramagnetic) probe in the study[7] of the biological functions of $Mg^{2+}$.

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