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Magnesium(II) and Zinc(II) Complexes Containing a 14-Membered Hexaaza Macrocyclic Ligand

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Magnesium(II) and zinc(II) complexes of 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo$[13.3.1.1^{6,10}]$*eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decane ligand (L) have been prepared by the template condensation of 2,6-diacetylpyridine with hydrazine. They include* $[MgL(H_2O)_2](ClO_4)_2\cdot 2H_2O$, $[MgL(H_2O)_2](NO_3)_2\cdot 2H_2O$, *and* $[ZnL(H_2O)_2](NO_3)_2\cdot 2H_2O$. *Based on spectral data, thermal and elemental analysis, these complexes are proposed to have six-coordinate and octahedral geometry. The synthesis of the free macrocycle has been also achieved in two stages under high dilution conditions without the use of the coordination template effect, albeit with very low yield.*

Introduction

Although metal complexes of naturally occurring ligands have been known for more than fifty years, it is only during the past fifteen years that a large number of synthetic macrocyclic compounds have been prepared and investigated [1]. The significance of metal complexes containing synthetic macrocyclic ligands is most obvious as it relates to such naturally occurring macrocycles as the metalloporphyrins, vitamin B_{12}, and chlorophylls. The possibility of using synthetic macrocycles as models for more intricate biological macrocyclic systems has been recognized [2]. Of these, macrocyclic complexes with four nitrogen donor atoms have attracted considerable attention. In general, complexes of this nature have been synthesized by means of the so-called 'coordination template effect'. This effect consists of a metal ion being used in a reaction to direct the steric course of the condensation process which ultimately ends with ring closure. For a number of such complexes the macrocycles have not been isolated free of their metal ions and, for these, the template syntheses remain their only mode of preparation. The metal ions acting as a template have almost invariably been transition metal ions capable of forming coordinate bonds with nitrogen donors. In this paper the template action of magnesium(II) and zinc(II) ions in the synthesis of a planar hexaaza quadridentate macrocycle is reported.

Magnesium ion generally forms weak complexes with nitrogen ligands. An important exception to this rule is provided by the naturally occurring macrocyclic complexes of tetrapyrrole systems, the parent compound of which is porphine. The most important of such derivatives are chlorophylls and related compounds. Zinc also appears to be one of the biologically most important metals [3]. In view of the high abundance of magnesium and zinc ions in living systems, the possibility of the template action of these metals in the synthesis of quadridentate nitrogen-donor macrocycles seems to be of interest.

Experimental

Preparation of the Complexes

All reactions were performed under similar conditions. A mixture of the metal salt (2 mmol) in ethanol (25 ml) and 2,6-diacetylpyridine (1 mmol) in ethanol was heated at 80 °C under reflux with stirring. To this solution, hydrazine hydrate (1 mmol) in ethanol (15 ml) was added dropwise. The reaction was carried out for 24 hours. The resulting yellow precipitate was filtered off, washed with hot ethanol and dried under vacuum. *Anal.* Calc. for $[Mg(C_{18}H_{18}N_6)(H_2O)_2](ClO_4)_2\cdot 2H_2O$: C, 35.23, H, 4.27, N, 13.69. Found: C, 35.14, H, 4.27, N, 13.51%. Calc. for $[Mg(C_{18}H_{18}N_6)(H_2O)_2](NO_3)_2\cdot 2H_2O$: C, 40.13, H, 4.86, N, 20.80. Found: C, 39.71, H, 4.91, N, 20.52%. Calc. for $[Zn(C_{18}H_{18}N_6)(H_2O)_2](NO_3)_2\cdot 2H_2O$: C, 37.29, H, 4.52, N, 19.33. Found: C, 37.51, H, 4.48, N, 19.41%.

Preparation of the Free Macrocycle

The synthesis of the bis(diacetylpyridine)azine (I)

To the solution of 2,6-diacetylpyridine (0.01 mol) in benzene (1700 ml) hydrazine (0.05 mol) was added dropwise. The solution was heated under reflux with stirring for 28 hours. Solvent was then removed and the residue extracted with benzene. Bis-

(diacetylpyridine)azine ($C_{18}H_{18}N_4O_2$) was isolated from the benzene extract by column chromatography on silica gel with dichloromethane as eluent. Recrystallization from ethanol gave yellow crystals in 22% yield. *Anal.* Calc. for $C_{18}H_{18}N_4O_2$: C, 67.11, H, 5.63, N, 17.38. Found: C, 67.10, H, 5.66, N, 17.40%. *Mass spectrum*: Calc. for $C_{18}H_{18}N_4O_2$: 322.1428. Found: 322.1415; m/e: 322 (M^+) (3.9%), 307 (85.2%), 202 (43.8%), 146 (15.4%), 43 (100%). *N.m.r.* ($CDCl_3$): τ 7.6 (s, 6H, 2 CH_3CN), 7.28 (s, 6H, 2CH_3CO), 2.3–1.7 (m, 6H, aromatic protons).

The synthesis of the free macrocycle (II)

Hydrazine (5 mmol) was added dropwise to the solution of (I) (0.5 mmol) in n-butanol (180 ml). The ammonium chloride (0.35 mmol) was added to catalyze the cyclization reaction. The reaction mixture was heated under reflux with stirring for 18 hours and then evaporated to a small volume. The residue was diluted with benzene and the ammonium chloride was removed by washing with water. The benzene solution was dried with anhydrous sodium sulphate. The macrocycle was isolated by column chromatography on alumina using benzene–ethyl acetate (10:1) as eluent. The product was crystallized from ethanol. Yield 7%. *Anal.* Calc. for $C_{18}H_{18}N_6$: C, 67.95, H, 5.70, N, 26.42. Found: C, 67.74, H, 5.79, N, 26.30%. *Mass spectrum*: Calc. for $C_{18}H_{18}N_6$: 318.1592. Found: 318.1610; m/e 318 (M^+) (9.7%), 303 (2.5%), 275 (61.3%), 186 (30.8%), 145 (24%), 130 (62.2%), 104 (100%), 77 (87.1%).

Measurements

The infrared spectra were recorded on KBr pellets using a Perkin-Elmer 580 infrared spectrophotometer in the region 4000–400 cm^{-1}. The reflectance electronic spectra of the solid complexes were determined on a Unicam SP 700 ultraviolet and visible spectrophotometer fitted with the SP 735 reflectance attachment. Thermogravimetric measurements were performed using the Derivatograph OD-102, MOM. Mass spectra were obtained on a JEOL-JMS mass spectrometer. The n.m.r. spectra were run on Varian EM-360 60 MHz spectrometer for solutions in deuteriochloroform.

Results and Discussion

Hexaaza macrocyclic ligand complexes of stoichiometry $[MgL(H_2O)_2](ClO_4)_2\cdot 2H_2O$, $[MgL(H_2O)_2](NO_3)_2\cdot 2H_2O$ and $[ZnL(H_2O)_2](NO_3)_2\cdot 2H_2O$ were prepared by reacting 2,6-diacetylpyridine with hydrazine in the presence of $Mg(ClO_4)_2$, $Mg(NO_3)_2\cdot 6H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$ with yields of 61, 72, and 63% respectively. The formulations of these complexes follow from spectral and thermal analyses as discussed below, and elemental analyses.

In addition to the above major products small amounts of 2,6-pyridinediacetyldihydrazone were isolated from the reaction and identified by infrared spectra and elemental analysis. Reaction conditions were employed (reaction time, ratios and method of adding starting materials) such as to minimize the yield of hydrazone and increase the yield of complexes. The complexes are yellow, air stable solids, practically insoluble in common organic solvents.

The infrared spectra in the region 4000–400 cm^{-1} provide some information regarding the bonding in the complexes. These three complexes all give very similar infrared spectra except for anion vibrational modes. All the complexes show medium to strong bands at *ca.* 1610, 1570, and 1460 cm^{-1} as expected for C=N stretch and the two high energy pyridine vibrations [4, 5]. The low frequency pyridine modes at 604 and 406 cm^{-1} are shifted in the complexes to about 635 and 420 cm^{-1}, respectively. It is well known that the infrared spectrum of the coordinated pyridine can be readily distinguished from that of the free pyridine by an increase in frequency of *ca.* 20–30 cm^{-1} on coordination [6–8].

The infrared spectra of all the complexes are devoid of uncondensed functional group (–NH_2, C=O) stretching modes of the starting materials. It is concluded that cyclization has occurred to give the desired macrocycle complexes.

The infrared spectra of all three complexes show a broad diffuse band of strong intensity in the 3500–3200 cm^{-1} region which is usually assigned to O–H stretching modes for lattice water [9]. In addition, a weak absorption is found at *ca.* 1640 cm^{-1} and may indicate the H–O–H bending mode for lattice water. A weak absorption at 530 cm^{-1} may suggest that coordinated water is also present. Absorption in this region is assigned to wagging or rocking modes of coordinated water [10].

In the infrared spectrum of $[MgL(H_2O)_2](ClO_4)_2\cdot 2H_2O$ there is a single band at 625 cm^{-1} which along with a strong and broad band at about 1100 cm^{-1} with shoulder at 1035 cm^{-1} indicates the perchlorate ion. A very weak absorption at 940 cm^{-1} is also observed which is theoretically forbidden in the infrared but appears to be characteristic of noncoordinated perchlorate anions [11, 12]. Perchlorate anions are known to coordinate under special conditions, but such interactions normally manifest themselves by a splitting of the antisymmetric Cl–O stretching mode due to reduced symmetry of the coordinated species. No such splitting of the ClO_4^- absorption band at 1100 cm^{-1} was observed.

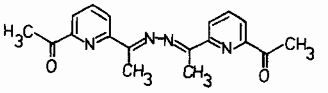
In the infrared spectra of magnesium and zinc nitrate complexes a broad absorption band centered at *ca.* 1390 cm^{-1} and a sharp medium band at 830 cm^{-1} occur which are typical for noncoordinated nitrate ions [13–16].

The diffuse reflectance spectra of the complexes contain a broad band at *ca.* 36700 cm^{-1} and at *ca.* 30000 cm^{-1} (shoulder). Absorption in this region is attributable to the coordinated macrocycle [17] and may be assigned to the $\pi \rightarrow \pi^*$ transition [18].

Thermogravimetric analysis indicates for magnesium perchlorate complex loss of $2H_2O$ at 40–75 °C, $2H_2O$ at 140–180 °C, and decomposition above 300 °C; for magnesium nitrate complex loss of $2H_2O$ at 35–70 °C, $2H_2O$ at 140–170 °C, and decomposition above 280 °C, and for zinc nitrate complex loss of $2H_2O$ at 40–100 °C, $2H_2O$ at 130–200 °C, and decomposition above 260 °C.

Elemental analysis figures (see Experimental) are consistent with the proposed formulations of the complexes.

The possibility of direct synthesis of the free macrocycle has been investigated. Condensation reactions between carbonyl compounds and amines are known to be acid-catalyzed [1]. In experiments in which the 2,6-diacetylpyridine and 2,6-pyridinediacetyldihydrazone in various solvents with a variety of acids as catalysts were allowed to react in the absence of metal, only resinous insoluble material was obtained. This material appears to be an acyclic compound of formula $C_{36}H_{36}N_{10}O_2$ terminated with carbonyl function. The formulation follows from the infrared spectrum (strong band at 1700 cm^{-1} and at *ca.* 1610 cm^{-1} characteristic of the carbonyl groups and C=N stretching vibration, no bands at 3300 cm^{-1} and 3150 cm^{-1} typical of N–H vibration), mass spectrum (the highest mass peak at m/e 625 corresponding to the parent ion less methyl group) and elemental analysis. Attempts to obtain a free macrocycle in the reaction of the 2,6-diacetylpyridine with hydrazine using acid as catalyst were also unsuccessful and resulted in the formation of similar yellow product of polymeric character. In view of the above unsuccessful experiments other attempts were undertaken to prepare a free macrocycle. The reaction of 2,6-diacetylpyridine with hydrazine in benzene without using acid as catalyst resulted in the formation of a mixture of products from which the bis(diacetylpyridine)azine (I) of formula $C_{18}H_{18}N_4O_2$ was isolated as yellow crystals. This compound was identified by the i.r., n.m.r., and mass spectra as well as elemental analysis. All the data are in accord with the above formula. The ring closure has been achieved in the reaction of bis(diacetylpyridine)azine with hydrazine in n-butanol using ammonium chloride as catalyst. The evidence for the formation of the desired macrocycle (II) of formula $C_{18}H_{18}N_6$ comes from the infrared spectrum, mass spectrum and elemental analysis. The most diagnostic absorption band is the C=N stretching mode at 1610 cm^{-1}. There is no absorption at 1700 cm^{-1} nor at 3300–3100 cm^{-1} which would occur if residual carbonyl or amine groups were present. The parent ion (m/e 318.1610) of the free macrocycle in the mass spectrum corresponds to the formula $C_{18}H_{18}N_6$ (calculated 318.1592). These data along with analysis of the molecular models support the proposed structure (II) of the hexaaza macrocycle.



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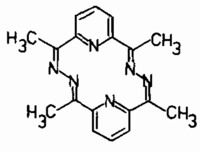
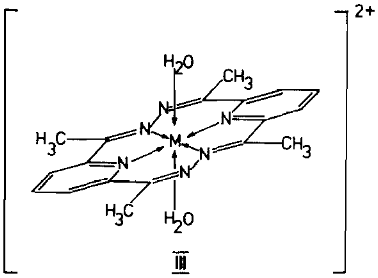


II

The inner 14-membered ring of the macrocycle is fully conjugated and incorporates $(4n + 2)\pi$ electrons satisfying the Hückel criterion, and is therefore expected to be planar [2].

The direct method is unsatisfactory for synthesis of macrocycle (II) because of the very low yield of the reaction. This fact appears to be in accord with the general observation that for the majority of macrocyclic compounds the template synthesis with the aid of a metal ion remains the best way of their preparation [1b]. The template synthesis of the macrocycle (II) on iron(II) has recently been described [19]. There are very few examples of macrocycles of related nature prepared in the uncomplexed state [1c, 1d]. The synthesis of a macrocycle in the absence of a metal ion is very often a very low-yield reaction as a result of the competing linear polymerization reaction, which may dominate the cyclization process. Even for those macrocycles which can be prepared directly, the addition of a metal ion in the synthesis is often accompanied by an increase in the yield of the macrocycle in the form of its metal complex. The importance of the metal ion in promoting the cyclic condensation of the reactants is thus apparent.

All three complexes described in this paper were prepared in good yield. On the basis of spectral and analytical data along with the molecular model analysis it seems reasonable to assume that these complexes of general formula $[ML(H_2O)_2]^{2+}$ have a six-coordinate octahedral structure (III) with the macrocycle occupying the equatorial plane and the axial positions being filled with water. This structure is highly stabilized by the formation of two five- and two six-membered chelate rings upon coordination, which allows the high resonance of the system [1b]. The complexes satisfy the Hückel criterion having 14 π-electron in the inner ring and therefore are chemically stable and comparable in



III

this regard with the derivatives of the phthalocyanines or porphyrins [1b]. The octahedral geometry is quite common for the other related zinc complexes [20–22].

The template action of magnesium ion in the synthesis of quinquedentate 15- and 16-membered macrocycles containing nitrogen and oxygen donor atoms was recently reported. However, attempts to synthesize 14-membered four nitrogen donor macrocycles with the aid of magnesium ion were so far unsuccessful [23, 24].

It has been found now that the magnesium ion, a strongly electropositive s-block metal with a low tendency to form classical complexes with nitrogen ligands [25], may act as a template for the synthesis of planar quadridentate nitrogen macrocycles. The synthetic macrocycle magnesium complexes of this type seem to be of interest because of the structural similarity to naturally occurring macrocycles, in which the equatorial macrocycle is quadridentate. In the natural porphine compounds the magnesium atom is formally four-coordinated but further interaction with either water or other solvent molecules is a common occurrence [3].

References

1 a) D. H. Busch, *Helv. Chim. Acta,* Fasciculus extraordinarius Alfred Werner, 174 (1967). b) L. F. Lindoy and D. H. Busch, in "Preparative Inorganic Reactions", ed. Jolly, vol. 6, p. 1, Interscience, New York, 1971. c) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev., 74,* 351 (1974). d) G. Newkome, J. D. Sauer, J. M. Roper, and D. C. Hager, *Chem. Rev., 77,* 513 (1977).
2 L. F. Lindoy, *Chem. Soc. Rev., 14,* 421 (1975).
3 G. L. Eichhorn, "Inorganic Biochemistry", Elsevier, London, 1973.
4 S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc., 92,* 1924 (1970).
5 J. D. Curry, M. A. Robinson, and D. H. Busch, *Inorg. Chem., 6,* 1570 (1967).
6 N. S. Gill, R. H. Nuttall, and D. E. Scaife, *J. Inorg. Nucl. Chem., 18,* 79 (1961).
7 D. P. Madden, M. M. Da Mota, and S. M. Nelson, *J. Chem. Soc. A,* 790 (1970).
8 C. Postums, *Inorg. Chem., 6,* 2030 (1976).
9 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley–Interscience, New York, 1970, pp. 175–176.
10 M. G. B. Drew, J. Grimshaw, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc. Dalton,* 1389 (1976).
11 B. J. Hathaway and E. Underhill, *J. Chem. Soc.,* 3091 (1961).
12 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 4,* 404 (1965).
13 C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.,* 613 (1960).
14 N. F. Curtis and Y. M. Curtis, *Inorg. Chem., 4,* 806 (1965).
15 B. K. Bayhs and J. C. Bailer, *Inorg. Chem., 9,* 641 (1970).
16 C. C. Addison and D. W. Amos, *J. Chem. Soc. A,* 808 (1967).
17 M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc. Dalton,* 1173 (1977).
18 J. F. Geldard, *Inorg. Chem., 4,* 417 (1965).
19 V. L. Goedken, Y. Park, S. M. Peng, and J. M. Morris, *J. Am. Chem. Soc., 96,* 7693 (1974).
20 P. A. Tasker and E. B. Fleischer, *J. Am. Chem. Soc., 92,* 7092 (1970).
21 N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc., 88,* 5468 (1970).
22 L. F. Lindoy, H. C. Lip, L. F. Power, and J. H. Rea, *Inorg. Chem., 15,* 1724 (1976).
23 M. G. B. Drew, A. H. Othman, S. G. McFall, and S. M. Nelson, *Chem. Commun.,* 819 (1975).
24 D. H. Cook, D. E. Fenton, M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J. Chem. Soc. Dalton,* 446 (1977).
25 F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd Edn., Interscience, London, 1972.