

Synthesis and characterization of 2,3,13,14-tetramethyl (ethyl or *p*-tolyl)-1,4,12,15-tetraazacyclodocosa-1,3,12,14-tetraene complexes of Mg(II), Ca(II), Sr(II) and Ba(II)

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(Received 28 January 2002)

2+2 Cyclocondensation of 1,7-diaminoheptane with α -diketones, viz. 2,3-butanedione, 3,4-hexanedione or 4,4'-dimethylbenzil, in the presence of Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} ions as templates yields a series of complexes of the type $[ML(X)_2]$ (where L = N_4 macrocycle having a 22-membered ring and X = Cl or NCS). The resulting complexes were characterized by elemental analysis, conductance measurements and IR and 1H -NMR spectral studies.

Keywords: macrocyclic complexes, alkaline earth metal complexes, conductances, IR spectra, NMR spectra.

INTRODUCTION

The rapidly developing field of bioinorganic chemistry is centered on the presence of macrocyclic compounds in living systems. A variety of macrocycles such as crown ethers, mixed donor macrocycles and azamacrocycles have been synthesized. Crown ethers have strong tendency to form stable complexes with alkali and alkaline earth metal ions.^{1,2} Drew *et al.*³ synthesized barium complexes of mixed donor macrocycle derived from 2,5-diformylfuran and 1,3-diaminopropane. Nelson and coworkers⁴ synthesized Ba(II) complex of a 30-membered N_6O_4 macrocycle by 2+2 condensation of 2,6-diacetylpyridine or 2,6-diformylpyridine with 3,6-dioxaoctane-1,8-diamine. Nitrogen containing macrocycles have strong tendency to form stable complexes with transition metals^{5,6} and have little tendency to form complexes with non-transition metals. Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of azamacrocycles derived from α and β -diketones and diaminoalkanes have been reported from our laboratories.^{7–12} Besides the d-block metals, complexes of alkaline earth metals with azamacrocycles have also been synthesized successfully in our laboratories and such complexes of Mg(II) have been reported earlier.^{13,14} In the present paper the synthesis and characterization of Mg(II), Ca(II), Sr(II) and Ba(II) complexes of 22-membered macrocycles

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2,3,13,14-tetramethyl (ethyl or *p*-tolyl)-1,4,12,15-tetraazacyclodocosa-1,3,12,14-tetraene are described.

EXPERIMENTAL

Materials

MgCl₂·6H₂O (BDH), Ca(NO₃)₂·4H₂O (CDH), SrCl₂·6H₂O (E. Merck) and BaCl₂·2H₂O (Glaxo) used were of AR grade. 1,7-Diaminoheptane (Aldrich), 2,3-butanedione (Fluka), 3,4-hexanedione (Aldrich) and 4,4'-dimethylbenzil (Aldrich) were used as supplied.

Analytical methods and physical measurements

Magnesium, calcium and strontium were determined volumetrically with EDTA using Eriochrome black T as indicator.¹⁵ Barium was determined gravimetrically as BaSO₄ and chlorine as AgCl. Nitrogen was determined by the Kjeldahl's method. IR spectra were recorded on a Nicolet Magna-550 FT Infrared Spectrophotometer as KBr pellets in the region 400–4000 cm⁻¹. ¹H-NMR spectra were recorded in DMSO-d₆ on a Zeol FX 90 Q FT NMR Spectrometer using TMS as reference. Conductances were measured in DMSO using a Systronics Direct Reading Conductivity Meter-304.

Synthesis of complexes

(a) *Synthesis of Mg(II) complexes of tetraazamacrocycles.* To a butanolic solution of MgCl₂·6H₂O (2.6 mmol in ≈25 ml), a butanolic solution of 2,3-butanedione (5.2 mmol) was added. Then a butanolic solution of 1,7-diaminoheptane (5.2 mmol) was added to this under continuous stirring. The contents were stirred for ≈6 h and the solid obtained was filtered, washed with butanol and dried *in vacuo*. Similarly, the reactions of MgCl₂·6H₂O with 1,7-diaminoheptane and 3,4-hexanedione or 4,4'-dimethylbenzil were carried out and the Mg(II) complexes of 22-membered tetraazamacrocycles were isolated.

(b) *Synthesis of Ca(II) complexes of tetraazamacrocycles.* To a butanolic solution of Ca(NO₃)₂·4H₂O (1.1 mmol in ≈20 ml), a butanolic solution of 2,3-butanedione (2.2 mmol) was added. To this reaction mixture a butanolic solution of 1,7-diaminoheptane (2.2 mmol) was added under continuous stirring. As no solid appeared, a butanolic solution of potassium thiocyanate (2.2 mmol) was added. The contents were stirred for ≈8 h and the temperature was maintained at 70 °C throughout the course of the reaction. The solid obtained was filtered, washed with butanol and dried under *vacuo*. Similarly, the reaction of Ca(NO₃)₂·4H₂O with 1,7-diaminoheptane and 3,4-hexanedione was carried out to obtain the Ca(II) complex of 22-membered tetraazamacrocycle.

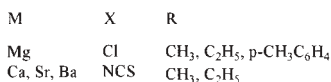
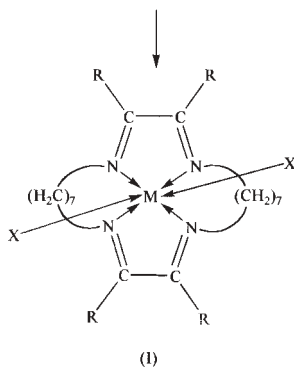
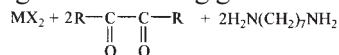
(c) *Synthesis of Sr(II) complexes of tetraazamacrocycles.* To a methanolic solution of SrCl₂·6H₂O (1.9 mmol in ≈20 ml), a methanolic solution of 2,3-butanedione (3.8 mmol) was added. Then a methanolic solution of 1,7-diaminoheptane (3.8 mmol) was added dropwise under continuous stirring. As no solid appeared, a methanolic solution of potassium thiocyanate (3.8 mmol) was added under continuous stirring. The stirring was continued for ≈10 h. The solid obtained was filtered, washed with methanol and dried *in vacuo*. Similarly, the reaction of SrCl₂·6H₂O with 1,7-diaminoheptane and 3,4-hexanedione was carried out and the Sr(II) complex of 22-membered tetraazamacrocycle was isolated.

(d) *Synthesis of Ba(II) complexes of tetraazamacrocycles.* BaCl₂·2H₂O (2.0 mmol) was dissolved in ethanol-water (1:1) and an ethanolic solution of 2,3-butanedione (4.0 mmol) was added. Then an ethanolic solution of 1,7-diaminoheptane (4.0 mmol) was added dropwise under continuous stirring. As no solid appeared, an ethanolic solution of potassium thiocyanate (4.0 mmol) was added. After 15 minutes a precipitate appeared. Stirring was continued for ≈10 h. The solid obtained was filtered, washed with ethanol and dried *in vacuo*. Similarly, the reaction of BaCl₂·2H₂O with 1,7-diaminoheptane and 3,4-hexanedione was carried out and the Ba(II) complex of 22-membered tetraazamacrocycle was obtained.

RESULTS AND DISCUSSION

The reactions of metal chlorides/nitrates with 1,7-diaminoheptane and α -diketones, *viz.* 2,3-butanedione, 3,4-hexanedione or 4,4'-dimethylbenzil, in a 1:2:2 mole ratio resulted

in the formation of the M(II) complexes (I) of 22-membered tetraazamacrocycles 2,3,13,14-tetramethyl (ethyl or *p*-tolyl)-1,4,12,15-tetraazacyclodocosa-1,3,12,14-tetraene according to the following general scheme (Scheme 1):



Scheme 1.

The resulting complexes were obtained as brown, yellow or white solids. These complexes decompose on heating and are insoluble in chloroform and nitromethane but soluble in DMSO. The analyses and characteristics of the complexes are given in Table I.

TABLE I. Analyses and characteristics of the M(II) complexes of tetraazamacrocycles

Sample No.	Complex	Colour and temp. of decomposition	(%) Analyses			Molar conductance ohm ⁻¹ cm ² mol ⁻¹
			M Found (Calcd.)	N Found (Calcd.)	Cl Found (Calcd.)	
1.	[Mg(Me ₄ [22] tetraene N ₄) Cl ₂]	Brown	5.21	12.23	15.43	36
		185	(5.33)	(12.29)	(15.55)	
2.	[Mg(Et ₄ [22] tetraene N ₄) Cl ₂]	White	4.62	10.92	13.91	79
		160	(4.74)	(10.94)	(13.85)	
3.	[Mg{(4-MePh) ₄ [22] tetraene N ₄ } Cl ₂]	White	3.09	7.19	9.15	97
		200	(3.18)	(7.33)	(9.27)	
4.	[Ca(Me ₄ [22] tetraene N ₄) (NCS) ₂]	Brown	7.68	10.83		99
		225	(7.75)	(10.84)		
5.	[Ca(Et ₄ [22] tetraene N ₄) (NCS) ₂]	White	6.95	9.72		192
		240	(6.99)	(9.77)		
6.	[Sr (Me ₄ [22] tetraene N ₄) (NCS) ₂]	Brown	15.47	9.88		16
		205	(15.52)	(9.92)		

TABLE I. Continued

Sample No.	Complex	Colour and temp. of decomposition	(%) Analyses			Molar conductance $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
			M Found (Calcd.)	N Found (Calcd.)	Cl Found (Calcd.)	
7.	[Sr(Et ₄ [22] tetraene N ₄) (NCS) ₂]	Yellow	14.08	8.98		23
		195	(14.12)	(9.02)		
8.	[Ba(Me ₄ [22] tetraene N ₄) (NCS) ₂]	Brown	22.31	9.12		10
		215	(22.36)	(9.12)		
9.	[Ba(Et ₄ [22] tetraene N ₄) (NCS) ₂]	Light yellow	20.40	8.32		21
		190	(20.49)	(8.35)		

The molar conductances of 10^{-3} M solutions of the M(II) complexes of tetraaza-macrocycles are given in Table I. All the complexes are non-electrolytic in nature which indicates that both the chloro and thiocyanato groups are coordinated to the metal atom. Thus, the metal atoms are hexacoordinated in these complexes. By 2+2 condensation of 2,6-diacetylpyridine with hydrazine in the presence of Mg^{2+} as a template, Paryzek¹⁶ prepared macrocyclic complexes in which the magnesium is hexacoordinated. For some Mg(II) and Ca(II) complexes the conductance values are higher. However, the IR spectra of the complexes show that both the thiocyanate groups are coordinated to the metal atom. It is, therefore, inferred that the higher values of the conductances may be due to the displacement of coordinated chloro or thiocyanato groups by the solvent molecules because such type of complexes are generally hexacoordinated as reported earlier.^{13,14}

Infrared spectra

The important IR absorption bands of the M(II) complexes of the macrocycles are given in Table II. All the complexes exhibit a strong band at $1580\text{--}1630 \text{ cm}^{-1}$ due to $\nu(\text{C}=\text{N})$. Drew *et al.*¹⁷ reported bands at $1620\text{--}1640 \text{ cm}^{-1}$ due to the coordinated imine groups in Ca(II), Sr(II) and Ba(II) complexes of macrocycles derived from 2,6-diacetylpyridine and *o*-phenylenediamine. For TIM complexes of Co(II),¹⁸ $\nu(\text{C}=\text{N})$ bands have been reported at $1550\text{--}1600 \text{ cm}^{-1}$. No absorption band at 1700 cm^{-1} characteristic of $\nu(\text{C}=\text{O})$ is observed in any of the spectra of these complexes and the absence of absorption bands at $3200\text{--}3300 \text{ cm}^{-1}$ shows the absence of unreacted primary amine groups. Thus the C=O and the NH₂ groups must have reacted, to give C=N linkages. In the case of Fe(II), Co(III) and Ni(II) complexes of macrocycles derived from 2,6-diacetylpyridine and 3,6-dioxo-1,8-diamine, Drew *et al.*¹⁹ reported the absence of absorption bands at 1700 cm^{-1} and $3200\text{--}3400 \text{ cm}^{-1}$ which could occur only if residual carbonyl or primary amino groups were present. N-Bonded thiocyanate stretching frequencies are observed at $2050\text{--}2070 \text{ cm}^{-1}$. The lowering of this frequency in Ca(II), Sr(II) and Ba(II) complexes as compared to that reported for free thiocyanate (2100 cm^{-1}) supports the coordination of the thiocyanate group to the metal atom through nitrogen. Fenton and Cook²⁰ reported N-bonded thiocyanate stretching frequencies at 2063 , 2073 and 2081 cm^{-1} in Ca(II), Sr(II) and Ba(II) complexes, respectively, of the macrocycle 3,15,21-triaza-6,9,12-trioxabicyclo(15.3.1)-he-

neicosa-1(21),2,5,17,19-pentaene. The Mg(II) complex of 2,3,13,14-*p*-tolyl-1,4,12,15-tetraaza-cyclodocosa-1,3,12,14-tetraene shows an absorption band at 1560 cm⁻¹ which may be attributed to the $\nu(\text{C}=\text{C})$ of phenyl groups and a band at 760 cm⁻¹ assignable to C–H out of plane bending of the phenyl groups. In Co(II) complexes of PhTIM, Welsh and coworkers²¹ assigned the bands at 1580–1600 cm⁻¹ to $\nu(\text{C}=\text{C})$ of the phenyl ring. In the Fe(II) complexes of PhTIM, bands in the region 700–760 cm⁻¹ were assigned to C–H out of plane bending of phenyl group.²² All the macrocyclic complexes synthesized during the present investigations exhibit bands at 2910–2940 cm⁻¹ which may be assigned to $\nu(\text{C}-\text{H})$ vibrations. Jackels *et al.*²³ reported similar bands in the region 2900–3000 cm⁻¹ in Co(MePhTIM). The chloro complexes exhibit bands at 430–440 cm⁻¹ which may be assigned to coordinated chloro groups.²⁴

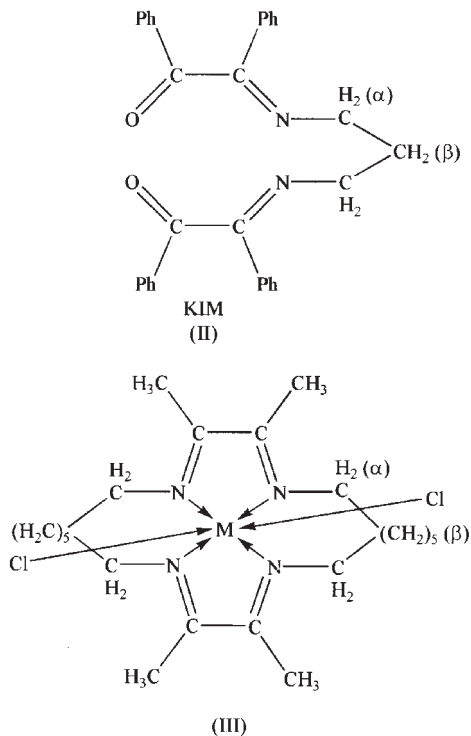
TABLE II. Important IR bands of the tetraazamacrocyclic complexes

Sample No.	Complex	IR bands/cm ⁻¹			
		$\nu(\text{C}=\text{N})$	$\nu(\text{NCS})$	$\nu(\text{C}=\text{C})$ Phenyl	C-H Phenyl bending
1.	[Mg(Me ₄ [22] tetraene N ₄) Cl ₂]	1620			
2.	[Mg(Et ₄ [22] tetraene N ₄)Cl ₂]	1590			
3.	[Mg{(4-MePh) ₄ [22] tetraene N ₄ }Cl ₂]	1600		1560	760
4.	[Ca(Me ₄ [22] tetraene N ₄) (NCS) ₂]	1630	2070		
5.	[Ca(Et ₄ [22] tetraene N ₄) (NCS) ₂]	1600	2060		
6.	[Sr (Me ₄ [22] tetraene N ₄) (NCS) ₂]	1600	2050		
7.	[Sr(Et ₄ [22] tetraene N ₄) (NCS) ₂]	1600	2070		
8.	[Ba(Me ₄ [22] tetraene N ₄) (NCS) ₂]	1580	2050		
9.	[Ba(Et ₄ [22] tetraene N ₄) (NCS) ₂]	1600	2070		

Nuclear magnetic resonance spectra

The structures of the complexes of tetraazamacrocycles were confirmed by ¹H-NMR spectra. In Table III are given the δ values (ppm) for different protons. A peak in the region δ 2.44–2.65 ppm is observed in the spectra of all the complexes due to the residual protons of the solvent DMSO-*d*₆.

In free diamines, the α -CH₂ protons appear as a triplet at δ 2.69–2.79 ppm, while β and other CH₂ protons appear as a quintet at δ 1.33–1.60 ppm.²⁵ In KIM (II) (Scheme 2), the α -CH₂ protons were reported to appear as a triplet at δ 3.64 ppm and the β -CH₂ protons as a quintet at δ 2.11 ppm.²⁶ This downfield shift as compared to the protons of free diamines is due to deshielding by the π electrons of the C=N bond. The free macrocycles, though not isolated, would have exhibited these resonances at almost identical positions as in KIM. In the macrocyclic complexes of Mg(II), the α -CH₂ protons exhibit a triplet at δ 2.71–2.74 ppm ($J = 6-7$ Hz) and the other methylene protons of the amine residues are ob-



Scheme 2.

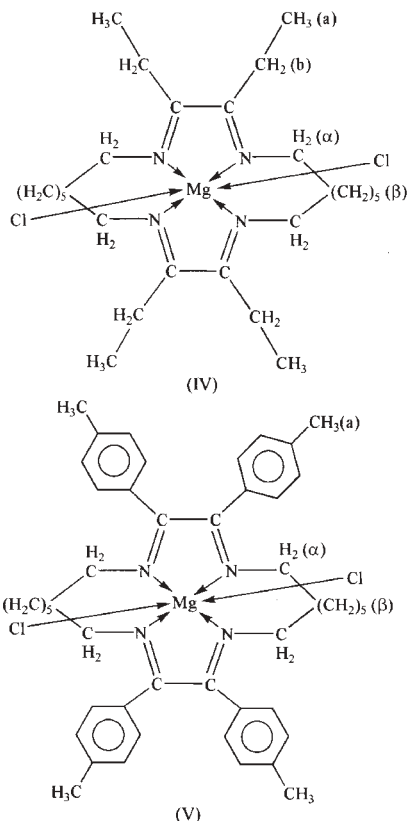
served as a broad peak at δ 1.27–1.33 ppm. The upfield shift of the α and β -CH₂ protons in these complexes as compared to KIM supports the coordination of nitrogen to the metal atom.

TABLE III. ¹H-NMR chemical shifts (δ , ppm) of the tetraazamacrocyclic complexes

Sample No.	Complex	Amine residue		Ketone residue		Aromatic protons
		α -CH ₂	β -CH ₂	CH ₃ ^a	CH ₂ ^b	
1.	[Mg(Me ₄ [22] tetraene N ₄)Cl ₂]	1.71 t	1.27 b	0.86 t		
2.	[Mg(Et ₄ [22] tetraene N ₄)Cl ₂]	2.74 t	1.27 b	0.96 t	2.13 q	
3.	[Mg{(4-MePh) ₄ [22] tetraene N ₄ }Cl ₂]	2.74 t	1.33 b	2.41 d		7.23 d ; 7.38 d ; 7.47 d ; 7.70 d

d = Doublet, t = triplet, q = quartet, b = broad

In complex (III) (Scheme 2) of the macrocycle derived from 2,3-butanedione (CH₃COCOCH₃) and 1,7-diaminoheptane, the methyl protons of the ketone residue appear as a triplet at δ 0.86 ppm due to a long range coupling with the α -CH₂ protons of the amine residues, similar to the homoallylic type coupling observed in compounds having unsaturated linkage of the type H₃C-CH=NCH₂.²⁷ In free 2,3-butanedione, the methyl protons ap-



Scheme 3.

pear at δ 1.46 ppm. The upfield shift of the methyl protons in the macrocyclic complex confirms the coordination of the nitrogen of the macrocycle to a magnesium atom.

In free 3,4-hexanedione ($\text{CH}_3^a\text{CH}_2^b\text{COCOCH}_3$), the methyl protons appear as a triplet at δ 1.10 ppm and the methylene protons as a quartet at δ 2.77 ppm. In complex (IV) (Scheme 3), the methylene protons (CH_2^b) of the ketone residue appear as a quartet at δ 2.13 ppm. The upfield shift of these CH_2 peaks supports the coordination of the $\text{C}=\text{N}$ group to the metal atom. However, the methyl protons (CH_3^a) of the ketone residue are shifted very slightly upfield (0.96 ppm). This may be due to the fact that these protons are far removed from the $\text{C}=\text{N}$ group and, hence, are not affected much by coordination of this group.

In complex (V) (Scheme 3) of the macrocycle derived from 4,4'-dimethylbenzil, the CH_3^a protons give a doublet at δ 2.41 ppm. This may be due to the long range coupling of the CH_3 protons with the $\text{C}-\text{H}$ protons of the ring. In the aromatic region, four doublets at δ 7.23, 7.38, 7.47 and 7.70 ppm are observed and this may be due to the non-equivalence of the aromatic protons (b) as a result of restricted rotation.

Acknowledgements: The authors are thankful to the Head of the Chemistry Department of the University of Rajasthan, Jaipur for providing laboratory facilities.

ИЗВОД

СИНТЕЗА И КАРАКТЕРИСАЊЕ КОМПЛЕКСА Mg(II), Ca(II), Sr(II), И Ba(II) СА
2,3,13,14-ТЕТРАМЕТИЛ (ЕТИЛ)
p-ТОЛИЛ-1,4,12,15-ТЕТРААЗАЦИКЛОДОКОСА-1,3,12,14-ТЕТРАЕНОМ

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2 + 2 кондензацијом 1,7-диаминохептана са α -дикетонима, као што су 2,3-бутандион, 3,4-хександион или 4,4'-диметилбензил у присуству Mg^{2+} , Ca^{2+} , Sr^{2+} и Ba^{2+} јона као темплата дају низове комплекса типа $ML(X_2)$ (где је $L = N_4$ макроцикл са прстеном од 22 члана, а X је Cl или NCS). Настали комплекси су карактерисани елементалном анализом, мерењем проводљивости, као и IR и 1H -NMR спектроскопијом.

(Примљено 28. јануара 2002)

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