

Ca(II) complexes of tetraazamacrocycles derived from 3,4-hexanedione and diaminoalkanes

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(Received 8 January 2004)

Abstract: Ca(II) macrocyclic complexes $[(Et_4[n]tetraeneN_4)CaX_2]$ (where $n = 14, 16, 20, 24, 32$, $X = Cl^-, NCS^-$) have been synthesized *via* cyclocondensation of 3,4-hexanedione with aliphatic diamines, such as 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane or 1,12-diaminododecane. The synthesized complexes were characterized by elemental analyses, conductance measurements and IR and 1H -NMR spectroscopy.

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

INTRODUCTION

Interest in synthetic macrocyclic complexes has developed due to their relevance concerning naturally occurring biomolecules. Synthesis of several azamacrocycles using metal ions as templates has been reported. In addition to the wide use of transition metal ions as templates,^{1–12} alkaline earth metal ions have also been found useful as templates in the synthesis of a few macrocycles. Drew *et al.*¹³ synthesized Mg(II) complexes of an N_5 macrocycle derived from 2,6-diacetylpyridine and 1,8-diamino-3,6-diazaoctane using Mg^{2+} as the template. The 2 + 2 condensation of 2,5-diformulfuran and 1,3-diaminopropane using Ba^{2+} as the template has been reported to yield a Ba(II) macrocyclic complex.¹⁴ Ca(II), Sr(II) and Ba(II) complexes of macrocycles derived from 2,6-diacetylpyridine and ethylenediamine have been reported by Nelson and Drew.¹⁵ The synthesis of a conjugated 18-membered N_6 macrocycle derived from 2,6-diacetylpyridine and *o*-phenylenediamine in which Ca^{2+} , Sr^{2+} and Ba^{2+} act as effective templates has also been reported.¹⁶

Earlier Mg(II) complexes^{17,18} of large ring tetraazamacrocycles derived from α -diketones and diaminoalkanes were reported and in the present paper the Ca(II) complexes of such macrocycles derived from 3,4-hexanedione are described.

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EXPERIMENTAL

Materials

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and KCNS (Merck) were of AR grade. 3,4-Hexanedione (Merck), 1,3-diaminopropane (Fluka) and 1,4-diaminobutane (Fluka) were used after distillation. 1,8-Diaminooctane (Fluka) and 1,2-diaminododecane (Fluka) were used as received. Methanol and 1-butanol were distilled before use.

Analytical methods and measurements

Calcium was determined volumetrically by EDTA using Eriochrome Black T as indicator¹⁹ and nitrogen was determined by the Kjeldahl method. The IR spectra were recorded as KBr pellets in the region $4000\text{--}200\text{ cm}^{-1}$ on a Perkin Elmer 577 Grating Infrared Spectrophotometer. The ¹H-NMR spectra were recorded in DMSO-*d*₆ on a Jeol FX-90Q FT NMR spectrometer at 90 MHz using TMS as the reference. Conductances were determined on a Systronics Direct Reading conductivity meter-304 using 10^{-3} M solutions in dimethylsulfoxide.

Synthesis of thiocyanatocalcium(II) complexes of tetraazamacrocycles

To a 1-butanol solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (4.6 mmol) a 1-butanol solution of 3,4-hexanedione (9.2 mmol) was added and 1,3-diaminopropane (9.2 mmol) in 1-butanol was added dropwise under constant stirring. Stirring was continued for 5–6 h and the reaction mixture was then refluxed for 6–9 h. KCNS (9.2 mmol) dissolved in methanol was added and the contents were stirred for about an hour. The solid which separated was filtered, washed with 1-butanol and dried under reduced pressure.

Similarly, the reactions with 1,4-diaminobutane, 1,6-diaminohexane and 1,8-diaminooctane in 1 : 2 : 2 mole ratios were carried out. The solid products were separated and dried. However, no solid product could be obtained from 1,12-diaminododecane. The analyses and the characteristics of the complexes are given in Table I.

Synthesis of chlorocalcium(II) complexes of tetraazamacrocycles

To a 1-butanol solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (7.7 mmol), a butanol solution of 3,4-hexanedione (15.4 mmol) was added. 1,3-Diaminopropane (15.4 mmol) in 1-butanol was added dropwise under constant stirring. Stirring was continued for 5–6 h and solid which separated was filtered, washed with 1-butanol and dried under reduced pressure.

Similarly, the reactions with 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane in 1 : 2 : 2 mole ratios were carried out. The solid which separated was filtered, washed with 1-butanol and dried under reduced pressure. The analyses and the characteristics of the complexes are given in Table I.

RESULTS AND DISCUSSION

Reaction of 3,4-hexanedione, 1,3-diaminopropane and calcium nitrate in the presence of KCNS resulted in the formation of the Ca(II) complex (I) of a 14-membered tetraazamacrocycle according to the following scheme (Scheme 1).

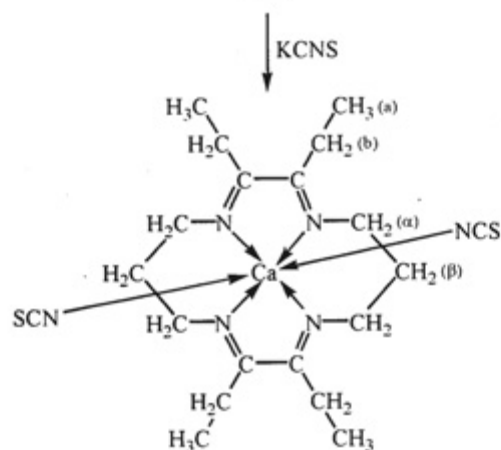
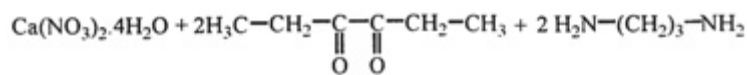
Similar reactions with 1,4-diaminobutane, 1,6-diaminohexane and 1,8-diaminooctane resulted in the formation of Ca(II) complexes of macrocycles having 16, 20 and 24-membered rings, respectively.

Reactions of calcium chloride with 3,4-hexanedione and diaminoalkanes, such as 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane, in 1 : 2 : 2 mole ratios yielded the Ca(II) complexes (II) of 14- to 32-membered tetraazamacrocycles.

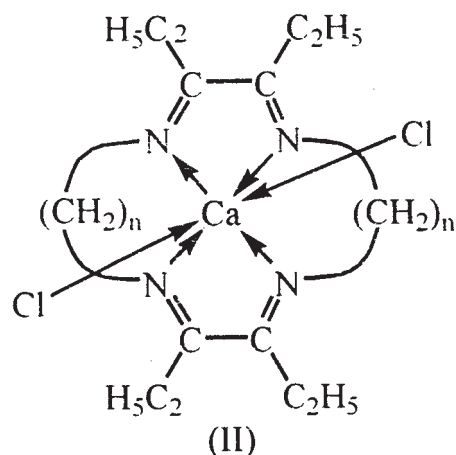
TABLE I. Analyses and characteristics of the studied Ca(II) complexes of tetrazamacrocycles

Sample No.	Complex	Colour and decomposition temp./°C	Analyses/%				Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
			C Found (Calcd.)	H Found (Calcd.)	N* Found (Calcd.)	Ca Found (Calcd.)	
1.	[(Et ₄ [14]tetraeneN ₄)CaCl ₂]	Yellow	51.96 (52.03)	7.65 (7.76)	13.33 (13.48)	9.58 (9.64)	8.0
2.	[(Et ₄ [16]tetraeneN ₄)CaCl ₂]	Yellow	53.87 (54.16)	8.27 (8.18)	12.55 (12.63)	9.02 (9.03)	8.7
3.	[(Et ₄ [20]tetraeneN ₄)CaCl ₂]	Yellow	56.76 (57.69)	8.79 (8.87)	11.19 (11.21)	7.98 (8.02)	10.4
4.	[(Et ₄ [24]tetraeneN ₄)CaCl ₂]	Yellow	60.95 (60.51)	9.39 (9.43)	10.03 (10.08)	7.18 (7.21)	15.2
5.	[(Et ₄ [32]tetraeneN ₄)CaCl ₂]	Yellow	64.87 (64.73)	10.15 (10.26)	8.31 (8.38)	5.98 (6.00)	18.0
6.	[(Et ₄ [14]tetraeneN ₄)Ca(NCS) ₂]	Yellow	46.89 (46.92)	6.91 (7.00)	12.03 (12.16)	8.65 (8.69)	9.5
7.	[(Et ₄ [16]tetraeneN ₄)Ca(NCS) ₂]	Yellow	48.96 (48.37)	7.29 (7.31)	11.34 (11.28)	8.02 (8.07)	11.3
8.	[(Et ₄ [20]tetraeneN ₄)Ca(NCS) ₂]	Yellow	52.67 (52.90)	8.19 (8.08)	10.15 (10.28)	7.30 (7.36)	14.2
9.	[(Et ₄ [24]tetraeneN ₄)Ca(NCS) ₂]	Yellow	55.23 (55.96)	8.69 (8.72)	9.30 (9.32)	6.62 (6.67)	17.5

*The N values do not include thiocyanate nitrogen which is removed on treatment with H₂SO₄ in the Kjeldahl method



Scheme 1.



$$n = 3, 4, 6, 8, 12$$

Scheme 2.

The molar conductances of these complexes lay in the range $8.0\text{--}18.0\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ (Table I) in dimethylsulfoxide. This shows the non-electrolytic behaviour²⁰ of the complexes and supports the coordination of both the thiocyanate and chloro groups to the metal. Thus calcium is hexacoordinated in these complexes. Octahedral coordination of calcium has been reported in bis(urea)bis(dihydrogenphosphato)calcium²¹ and tetramethylammonium calcium triazide.²²

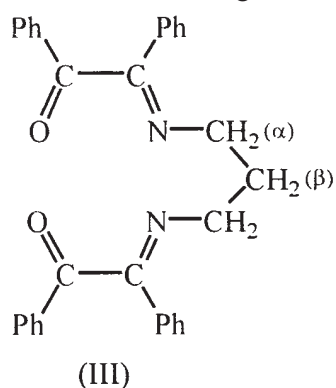
Infrared spectra

The infrared spectra of the Ca(II) complexes of tetraazamacrocycles show bands

at 1580–1640 cm^{-1} , characteristic of coordinated $>\text{C}=\text{N}$ groups. Cabral and coworkers²³ reported such bands at 1630–1650 cm^{-1} in the Ca(II), Sr(II) and Ba(II) complexes of a macrocycle derived from 2,6-diacetylpyridine and ethylenediamine. None of the spectra exhibited absorption bands at 3100–3400 cm^{-1} or at 1700 cm^{-1} attributable to unreacted NH_2 or $\text{C}=\text{O}$ groups, respectively. N-Bonded thiocyanate CN stretching frequencies were observed at 2040–2080 cm^{-1} . The lowering of this frequency in the calcium complexes compared to that observed for free thiocyanate (2100 cm^{-1})²³ supports the coordination of thiocyanate to the metal atom. Fenton and Cook²⁴ reported N-bonded thiocyanate CN stretching frequencies at 2065, 2081 and 2073 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] heneicosa-1(21),2,15,17,19-pentaene.

Nuclear magnetic resonance spectra

The $^1\text{H-NMR}$ spectra of the Ca(II) complexes were recorded and the δ values (ppm) are given in Table II. The spectra confirm the structures of the complexes. In free 1,3-diaminopropane, the $\alpha\text{-CH}_2$ protons appear as a triplet at δ 2.14 ppm and the $\beta\text{-CH}_2$ protons as a quintet at δ 0.89 ppm. In KIM (III), the $\alpha\text{-CH}_2$ protons were reported to appear at δ 2.11 ppm.⁷ This downfield shift is due to the deshielding by the π -electrons of the $\text{C}=\text{N}$ bond. The free macrocycles would have exhibited these resonances at almost the same positions as in KIM. In the NMR spectra of Ca(II) complexes of macrocycle derived from 3,4-hexanedione and 1,3-diaminopropane, the $\alpha\text{-CH}_2$ protons of the amine residue appear as a triplet at δ 2.77–2.78 ppm and the $\beta\text{-CH}_2$ protons appear as a broad multiplet at δ 1.33–1.35 ppm. The upfield shifting of the signals of the α - and $\beta\text{-CH}_2$ protons in these complexes as compared to KIM supports the coordination of the nitrogen of the macrocycle to the metal



Scheme 3.

atom. In the other macrocyclic complexes, the $\alpha\text{-CH}_2$ protons exhibit a triplet at almost the same position as in the complexes of the macrocycle derived from 3,4-hexanedione and 1,3-diaminopropane and the other methylene protons of the

TABLE II. $^1\text{H-NMR}$ chemical shifts (δ , ppm) of the studied Ca(II) complexes of tetraazamacrocycles

Sample No.	Complex	Amine residue		Ketone residue	
		$\alpha\text{-CH}_2$	β and other CH_2	$\text{CH}_3^{(a)}$	$\text{CH}_2^{(b)}$
1.	$[(\text{Et}_4[14]\text{tetraeneN}_4)\text{CaCl}_2]$	2.77 <i>t</i>	1.33 <i>b</i>	0.97 <i>t</i>	2.03 <i>q</i>
2.	$[(\text{Et}_4[16]\text{tetraeneN}_4)\text{CaCl}_2]$	2.78 <i>t</i>	1.39 <i>b</i>	0.97 <i>t</i>	2.05 <i>q</i>
3.	$[(\text{Et}_4[20]\text{tetraeneN}_4)\text{CaCl}_2]$	2.75 <i>t</i>	1.42 <i>m</i>	0.98 <i>t</i>	2.09 <i>q</i>
4.	$[(\text{Et}_4[24]\text{tetraeneN}_4)\text{CaCl}_2]$	2.82 <i>t</i>	1.47 <i>b</i>	0.99 <i>t</i>	2.10 <i>q</i>
5.	$[(\text{Et}_4[32]\text{tetraeneN}_4)\text{CaCl}_2]$	2.76 <i>t</i>	1.45 <i>b</i>	0.96 <i>t</i>	2.15 <i>q</i>
6.	$[(\text{Et}_4[14]\text{tetraeneN}_4)\text{Ca}(\text{NCS})_2]$	2.78 <i>t</i>	1.35 <i>bm</i>	0.98 <i>t</i>	2.30 <i>q</i>
7.	$[(\text{Et}_4[16]\text{tetraeneN}_4)\text{Ca}(\text{NCS})_2]$	2.79 <i>t</i>	1.55 <i>b</i>	0.97 <i>t</i>	2.10 <i>q</i>
8.	$[(\text{Et}_4[20]\text{tetraeneN}_4)\text{Ca}(\text{NCS})_2]$	2.82 <i>t</i>	1.56 <i>b</i>	0.96 <i>t</i>	2.13 <i>b</i>
9.	$[(\text{Et}_4[24]\text{tetraeneN}_4)\text{Ca}(\text{NCS})_2]$	2.83 <i>t</i>	1.59 <i>p</i>	0.97 <i>t</i>	2.14 <i>b</i>

t = Triplet, *q* = quartet, *p* = pentet, *m* = multiplet, *b* = broad

amine residue are observed at higher field (δ 1.39–1.59 ppm). The methyl and methylene protons of the ketone residue of these macrocyclic complexes exhibit weak signals. The CH₂^(b) protons appear as a quartet at δ 2.03–2.30 ppm and the CH₃^(a) protons as a triplet at δ 0.96–0.99 ppm. In free 3,4-hexanedione, the CH₂ protons appear at δ 2.77 ppm as a quartet and the CH₃ protons at δ 0.99 ppm as a triplet. The high field shift of the CH₂ protons in the macrocyclic complexes confirms the coordination of the nitrogen of the macrocycle to the calcium atom.

Acknowledgments: The authors thank the Head of the Department of Chemistry, University of Rajasthan, Jaipur, for providing laboratory facilities and the U.G.C., New Delhi, for grants and a fellowship through the career award project.

ИЗВОД

КОМПЛЕКСИ Ca(II) СА ТЕТРААЗАМАКРОЦИКЛИМА ИЗВЕДЕНИМ ОД
3,4-ХЕКСАНДИОНА И ДИАМИНОАЛКАНА

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Синтетизовани су макроциклични комплекси Ca(II) [(Et₄[*n*]tetraenN₄)CaX₂] (где је *n* = 14, 16, 20, 24, 32, X = Cl⁻, NCS⁻) циклокондензациом 3,4-хександиона са алифатским диаминима, као што су 1,3-диаминопропан, 1,4-диаминобутан, 1,8-диаминооктан или 1,12-диаминододекан. Синтетисани комплекси су карактерисани елементалном анализом, мерењем проводљивости, као и помоћу IR и ¹H-NMR спектроскопије.

(Примљено 8. јануара 2004)

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