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

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Abstract: Ca(II) macrocyclic complexes \( [(\text{Et}_n\text{tetraeneN}_4)\text{CaX}_2] \) (where \( n = 14, 16, 20, 24, 32 \), \( X = \text{Cl}^-, \text{NCS}^- \)) have been synthesized via cyclocondensation of 3,4-hexanediol 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 \(^1\)H-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, alkaline earth metal ions have also been found useful as templates in the synthesis of a few macrocycles. Drew et al. 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-diformylfuran and 1,3-diaminopropane using Ba\(^{2+}\) as the template has been reported to yield a Ba(II) macrocyclic complex. Earlier Mg(II) complexes of large ring tetraazamacrocycles derived from \( \alpha \)-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

Ca(NO₃)₂·4H₂O, CaCl₂·2H₂O 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 indicator and nitrogen was determined by the Kjeldahl method. The IR spectra were recorded as KBr pellets in the region 4000–200 cm⁻¹ on a Perkin Elmer 577 Grating Infrared Spectrophotometer. The ¹H-NMR spectra were recorded in DMSO-d₆ 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 Ca(NO₃)₂·4H₂O (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 CaCl₂·2H₂O (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-hexanediene, 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

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Complex</th>
<th>Colour and decomposition temp. °C</th>
<th>Analyses% C Found (Calcd.)</th>
<th>H Found (Calcd.)</th>
<th>N* Found (Calcd.)</th>
<th>Ca Found (Calcd.)</th>
<th>Molar conductance (ohm⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>((Et₄[16]tetraene₄)CaCl₂)</td>
<td>Yellow 295</td>
<td>53.87</td>
<td>8.27</td>
<td>12.55</td>
<td>9.02</td>
<td>8.7</td>
</tr>
<tr>
<td>3.</td>
<td>((Et₄[20]tetraene₄)CaCl₂)</td>
<td>Yellow 180</td>
<td>56.76</td>
<td>8.79</td>
<td>11.19</td>
<td>7.98</td>
<td>10.4</td>
</tr>
<tr>
<td>4.</td>
<td>((Et₄[24]tetraene₄)CaCl₂)</td>
<td>Yellow 280</td>
<td>60.95</td>
<td>9.39</td>
<td>10.03</td>
<td>7.18</td>
<td>15.2</td>
</tr>
<tr>
<td>5.</td>
<td>((Et₄[32]tetraene₄)CaCl₂)</td>
<td>Yellow 310</td>
<td>64.87</td>
<td>10.15</td>
<td>8.31</td>
<td>5.98</td>
<td>18.0</td>
</tr>
<tr>
<td>6.</td>
<td>((Et₄[14]tetraene₄)Ca(NCS)₂)</td>
<td>Yellow 320</td>
<td>46.89</td>
<td>6.91</td>
<td>12.03</td>
<td>8.65</td>
<td>9.5</td>
</tr>
<tr>
<td>7.</td>
<td>((Et₄[16]tetraene₄)Ca(NCS)₂)</td>
<td>Yellow 325</td>
<td>48.96</td>
<td>7.29</td>
<td>11.34</td>
<td>8.02</td>
<td>11.3</td>
</tr>
</tbody>
</table>

*The N values do not include thiocyanate nitrogen which is removed on treatment with H₂SO₄ in the Kjeldahl method.
The molar conductances of these complexes lay in the range 8.0–18.0 ohm$^{-1}$ cm$^2$ mol$^{-1}$ (Table I) in dimethylsulfoxide. This shows the non-electrolytic behaviour$^{20}$ 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)calcium$^{21}$ 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 >C=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 NH₂ or C=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[26.8.8]octacos-1(21),2,15,17,19-pentaene.

Nuclear magnetic resonance spectra

The ¹H-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 α-CH₂ protons appear as a triplet at δ 2.14 ppm and the β-CH₂ protons as a quintet at δ 0.89 ppm. In KIM (III), the α-CH₂ protons were reported to appear at δ 2.11 ppm. This downfield shift is due to the deshielding by the π-electrons of the C=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 α-CH₂ protons of the amine residue appear as a triplet at δ 2.77–2.78 ppm and the β-CH₂ protons appear as a broad multiplet at δ 1.33–1.35 ppm. The upfield shifting of the signals of the α- and β-CH₂ protons in these complexes as compared to KIM supports the coordination of the nitrogen of the macrocycle to the metal atom. In the other macrocyclic complexes, the α-CH₂ 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 macrocycle.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Complex</th>
<th>Amine residue</th>
<th>Ketone residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>α-CH₂</td>
<td>β and other CH₃</td>
</tr>
<tr>
<td>1.</td>
<td>[Et₄[14]tetraeneN₄]CaCl₂</td>
<td>2.77&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.33&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.</td>
<td>[Et₄[16]tetraeneN₄]CaCl₂</td>
<td>2.78&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.39&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.</td>
<td>[Et₄[20]tetraeneN₄]CaCl₂</td>
<td>2.75&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.42&lt;sup&gt;m&lt;/sup&gt;</td>
</tr>
<tr>
<td>4.</td>
<td>[Et₄[24]tetraeneN₄]CaCl₂</td>
<td>2.82&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.47&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5.</td>
<td>[Et₄[32]tetraeneN₄]CaCl₂</td>
<td>2.76&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.45&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6.</td>
<td>[Et₄[14]tetraeneN₄]Ca(NCS)₂</td>
<td>2.78&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.35&lt;sup&gt;bm&lt;/sup&gt;</td>
</tr>
<tr>
<td>7.</td>
<td>[Et₄[16]tetraeneN₄]Ca(NCS)₂</td>
<td>2.79&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.55&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>8.</td>
<td>[Et₄[20]tetraeneN₄]Ca(NCS)₂</td>
<td>2.82&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.56&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>9.</td>
<td>[Et₄[24]tetraeneN₄]Ca(NCS)₂</td>
<td>2.83&lt;sup&gt;t&lt;/sup&gt;</td>
<td>1.59&lt;sup&gt;p&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>t</sup> = Triplet, <sup>q</sup> = quartet, <sup>p</sup> = pentet, <sup>m</sup> = multiplet, <sup>b</sup> = 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 CH$_2$(b) protons appear as a quartet at δ 2.03–2.30 ppm and the CH$_3$(a) protons as a triplet at δ 0.96–0.99 ppm. In free 3,4-hexanedione, the CH$_2$ protons appear at δ 2.77 ppm as a quartet and the CH$_3$ protons at δ 0.99 ppm as a triplet. The high field shift of the CH$_2$ protons in the macrocyclic complexes confirms the coordination of the nitrogen of the macrocycle to the calcium atom.

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REFERENCES