



14-to 32-membered Large Ring Tetraazamacrocyclic Complexes of Cu (II) Derived From 2,3-Butanedione and Diaminoalkanes

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ABSTRACT: Cu (II) complexes of large ring (14 to 32-membered) tetraazamacrocycles are derived from 2,3-butanedione and aliphatic diamines such as 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; 1,8-diaminooctane, and 1,12-diaminododecane formed by template synthesis. The complexes have been characterized by elemental analysis, IR spectra, conductance measurements, and magnetic moments.

KEYWORDS: Macrocyclic complexes, Tetraazamacrocycles of Cu (II), IR spectra, Magnetic moments

I. INTRODUCTION

Fe(II), Co(II), Ni(II) and Cu(II) complexes of 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene (TIM), a 14-membered N₄ macrocycle, have been synthesized by 2+2 condensation of 2,3-butanedione and 1,3-diaminopropane using metal ion templates.¹⁻³ Cu(II) complexes of a 12-membered macrocycle derived from benzil and 1,2-diaminoethane also prepared by template procedure.⁴ Sulekh Chandra et al.⁵ studied the synthesis and characterization of tetraazamacrocyclic ligand and its complexes with Co(II), Ni(II) and Cu(II) in which the ligand acts in a tetradentate manner coordinating through four nitrogen atoms of azomethine groups. Ravinder et al.⁶ synthesized the Cu(II) tetraazamacrocyclic complexes and carried out spectral and antibacterial studies in which they found that some complexes are of square planar and some of them are distorted octahedral geometry. A series of mononuclear Fe(II), Co(II), Ni(II), Cu(II) and Pd(II) complexes correspond to tetradentate macrocyclic nitrogen ligand metal(II) complexes, have been synthesized by template condensation reaction.⁷ Prasad et al.⁸⁻¹³ reported Zn(II), Cd(II) and Co(II) complexes of such large ring tetraazamacrocycles and in the present paper the template synthesis of Cu(II) tetraazamacrocycles derived from 2,3-butanedione and diaminoalkanes such as 1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane; 1,8-diaminooctane and 1,12-diaminododecane are reported their corresponding formulas and names are [Me₄[14] tetraeneN₄ (2,3,9,10-tetraMethyl-1,4,8,11-tetra azacyclotetradeca-1,3,8,10-tetraene); [Me₄[16] tetraeneN₄](2,3,10,11-tetramethyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene); [Me₄[20]tetraeneN₄](2,3,12,13-tetramethyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene); [Me₄[24]tetraeneN₄](2,3,14,15-tetramethyl-1,4,13,16-tetraazacyclotetracos-1,3,13,15-tetraene); and [Me₄[32]tetraene N₄] (2,3,18,19-tetramethyl-1,4,17,20-tetraazacyclodotriaconta-1,3,17, 19-tetraene).

II. EXPERIMENTAL

Materials

CuCl₂·2H₂O (BDH) and Cu(NO₃)₂·3H₂O (BDH) were of GR/AR grade. 1,3-diaminopropane; 1,4-diaminobutane and 1,6-diaminohexane were obtained from Fluka and distilled before use. 1,8-diaminooctane (Fluka) and 1,12-diaminododecane (Fluka) and 2,3-butanedione (Aldrich) were used as such.

Analytical methods and physical measurements

Carbon and hydrogen were determined on a Coleman C, H Analyser-33 which was standardized by benzoic acid. Copper was determined volumetrically by sodium thiosulphate (Hypo) solution using starch indicator. Nitrogen by Kjeldahl's method and chlorine gravimetrically as AgCl. Infrared spectra were recorded as KBr pellets in the region

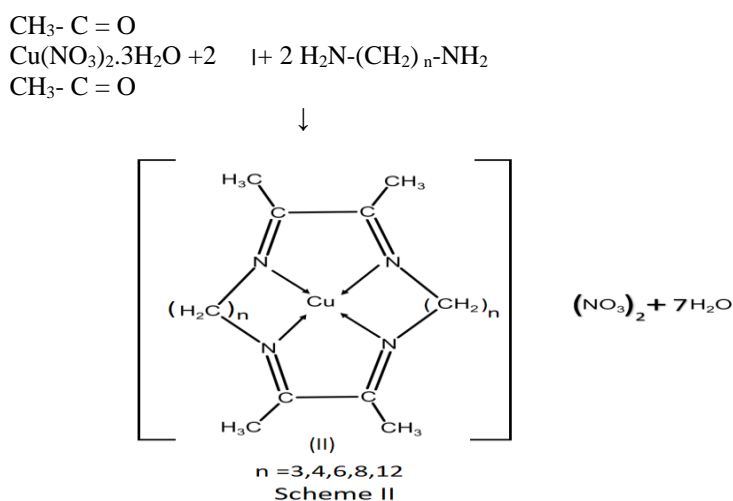
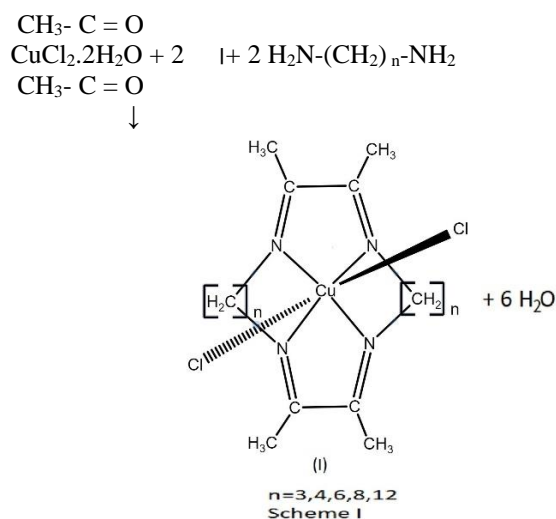
4000 to 200 cm^{-1} on a NICOLET DXIR spectrophotometer. Magnetic measurements were conducted using a CAHN-2000 magnetic balance. Conductance was measured using a Systronics Direct Reading Conductivity meter 304.

Synthesis of Cu (II) tetraazamacrocyclic complexes

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (~4 m mol) was dissolved in ~ 20 ml n-butanol and 2,3-butanedione (~8m mol) dissolved in 30 ml n-butanol was added. To this, a hot solution of 1,3-diaminopropane (~ 8 m mol in 20 ml n-butanol) was added dropwise with constant stirring. A solid appeared during the addition and stirring was continued for 3-4 hrs. maintaining the temperature at 60-70 $^\circ\text{C}$. The precipitate was filtered, washed with hot n-butanol and dried in vacuo. Similarly, the reaction of 1,4-diaminobutane, 1,6-diaminohexane, 1,8-diaminooctane and 1,12-diaminododecane with 2,3-butanedione have been conducted using $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

III. RESULTS AND DISCUSSION

Cu(II) complexes (I) have been synthesized by 2:2 cyclocondensation of 2,3-butanedione and different diaminoalkanes viz ,1,3-diaminopropane; 1,4-diaminobutane; 1,6-diaminohexane;1,8-diaminooctane or 1,12-diaminododecane in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Scheme I). Similarly, the reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with diamines and 2,3-butanedione have been carried out to give nitrate complexes (II) (Scheme II).



All the complexes are coloured solids and are stable at room temperature. They are soluble in Dimethylsulphoxide (DMSO) but insoluble in most common organic solvents such as chloroform, carbon tetrachloride, methanol, acetone, etc. The elemental analysis and characteristics of these complexes are given in Table-1.

Table –1 Analysis and physical characteristics of tetraazamacrocyclic complexes of Cu (II)

| S.N | Complex | Color & Decomposition Temperature (°C) | Yield % | Analysis (%) found (calculated) | | | | |
|-----|---|--|---------|---------------------------------|-------------|---------------|---------------|---------------|
| | | | | C | H | N | Cu | Cl |
| 1 | [Cu (Me ₄ [14] tetraene N ₄)](NO ₃) ₂ | Brown (124) | 46 | 37.81 (38.39) | 5.79 (5.52) | 13.38 (13.25) | 14.40 (14.50) | - |
| 2 | [Cu (Me ₄ [16] tetraene N ₄)](NO ₃) ₂ | Brown (128) | 47 | 41.21 (41.42) | 6.21 (6.07) | 12.04 (12.07) | 13.45 (13.63) | - |
| 3 | [Cu (Me ₄ [20] tetraene N ₄)](NO ₃) ₂ | Brown * | 95 | 45.51 (46.19) | 7.07 (6.97) | 10.74 (10.77) | 12.59 (12.21) | - |
| 4 | [Cu (Me ₄ [24] tetraene N ₄)](NO ₃) ₂ | Brown * | 82 | 48.99 (50.03) | 7.88 (7.69) | 9.38 (9.72) | 11.06 (11.02) | - |
| 5 | [Cu (Me ₄ [32] tetraene N ₄)](NO ₃) ₂ | Green * | 89 | 55.57 (55.83) | 8.95 (8.78) | 9.34 (9.23) | 9.44 (9.23) | - |
| 6 | [Cu (Me ₄ [14] tetraene N ₄)Cl ₂] | Blue (180) | 43 | 43.75 (43.92) | 6.18 (6.31) | 14.54 (14.63) | 16.46 (16.59) | 18.40 (18.52) |
| 7 | [Cu (Me ₄ [16] tetraene N ₄)Cl ₂] | Green (210) | 47 | 45.79 (46.77) | 6.93 (6.86) | 13.51 (13.63) | 15.39 (15.46) | 17.20 (17.25) |
| 8 | [Cu (Me ₄ [20] tetraene N ₄)Cl ₂] | Brown (240) | 45 | 51.99 (51.44) | 7.54 (7.76) | 11.90 (11.99) | 13.61 (13.60) | 14.97 (15.18) |
| 9 | [Cu (Me ₄ [24] tetraene N ₄)Cl ₂] | Brown (248) | 66 | 54.83 (55.11) | 8.61 (8.47) | 10.75 (10.71) | 11.98 (12.14) | 13.46 (13.55) |
| 10 | [Cu (Me ₄ [32] tetraene N ₄)Cl ₂] | Brown (255) | 62 | 60.81 (60.50) | 9.24 (9.51) | 8.91 (8.81) | 9.92 (10.00) | 11.04 (11.16) |

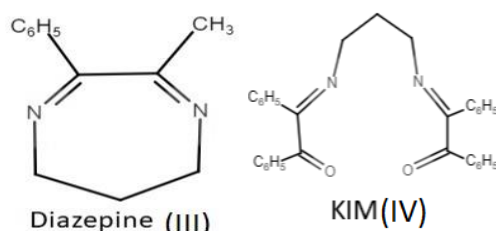
* Does not decompose up to 300° C

Boraey and Gammal¹⁴ pointed out the importance of template synthesis. The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions¹⁵. The template condensation methods lie at the heart of macrocyclic chemistry¹⁶. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions¹⁷. The Transition metal ions are used as the template reactions¹⁸. The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products¹⁹.

In general, the metal ion radius and size of the macrocyclic cavity are essential in forming macrocyclic complexes. Stable complexes are formed when the metal ion is of such a size that it can adequately fit in the macrocycle cavity. The selectivity of polyether's towards alkali, and alkaline earth metal ions have been studied as a function of their ring size²⁰. For tetraazamacrocycles, ideal ring sizes of metal ions have been investigated, and the M-N distance for which the strain energy in the macrocycle is minimum has been calculated²¹⁻²³. A larger or smaller metal ion would require a change in M-N distance with an accompanying increase in the strain energy of the ligand, causing distortion. The M-N bond length for transition metal complexes of 12- to 16- membered saturated tetraazamacrocycles ranges from 1.8 – 2.4 Å, many macrocycles of varying ring sizes coordinate readily to transition metal ions to give stable complexes²⁴.

The complexes synthesized during the present investigation involve macrocycles with larger rings, i.e., containing up to 32-atoms. There will be greater flexibility in such larger rings due to which metal ions smaller than the macrocyclic ring size can be conveniently accommodated, resulting in the formation of stable complexes. A comparison of open chain polyamines and tetraazamacrocycles has been made. It has been suggested that metal ion selectivity is controlled by chelate ring size rather than the macrocyclic ring size²⁵. Formation constants of macrocyclic and nonmacrocyclic ligands have been compared. It has been confirmed that chelate ring size is vital in controlling metal ion size-based selectivity and usually overweighs the macrocyclic ring size in this regard²⁶⁻²⁹. Molecular mechanics calculations have also shown that due to the flexibility of the large macrocyclic ring, there is an exceedingly

small effect of macrocyclic ring size on the stability of the complexes³⁰. During the template synthesis of Fe(II), Co(II), and Ni(II) complexes of MePhTIM, Eggleston, and Jackels³¹ have ruled out the possibility of formation of diazepine (III), a heterocyclic product of 1+1 condensation based on ¹H NMR studies. Henery et al.³² have isolated and characterized a macrocyclic precursor 1,2,8,9-tetraphenyl-diazaduohepta-2,7-diene-1,9-dione (KIM, IV) during 2+2 cyclocondensation of benzil and 1,3-diaminopropane in the presence of Co (II).



Infrared Spectra

Important infrared absorption bands of complexes are given in Table-2.

Table -2 IR, magnetic moment and molar conductance of Cu (II) tetraazamacrocyclic complexes

| S.N. | Complex | IR Absorption Bands (cm ⁻¹) | | | μ_{eff} (B.M.) | Molar Conductance (ohm ⁻¹ cm ² mol ⁻¹) of 10 ⁻³ M sol. |
|------|--|---|-----------------------------|-------|------------------------------|--|
| | | ν C=N | -NO ₃ unidentate | Cu-Cl | | |
| 1 | [Cu (Me ₄ [14] tetraene N ₄)] (NO ₃) ₂ | 1610 | 720,820,1380 | - | 1.90 | 69.0 |
| 2 | [Cu (Me ₄ [16] tetraene N ₄)] (NO ₃) ₂ | 1610 | 710,820,1380 | - | 1.89 | 68.4 |
| 3 | [Cu (Me ₄ [20] tetraene N ₄)] (NO ₃) ₂ | 1610 | 720,810,1380 | - | 1.73 | 67.8 |
| 4 | [Cu (Me ₄ [24] tetraene N ₄)] (NO ₃) ₂ | 1620 | 710,810,1390 | - | 1.84 | 66.2 |
| 5 | [Cu (Me ₄ [32] tetraene N ₄)] (NO ₃) ₂ | 1590 | 720,820,1380 | - | 1.75 | - |
| 6 | [Cu (Me ₄ [14] tetraene N ₄) Cl ₂] | 1580 | - | 270 | 1.81 | 9.7 |
| 7 | [Cu (Me ₄ [16] tetraene N ₄) Cl ₂] | 1580 | - | 270 | 1.80 | 13.5 |
| 8 | [Cu (Me ₄ [20] tetraene N ₄) Cl ₂] | 1580 | - | 270 | 1.82 | 12.5 |
| 9 | [Cu (Me ₄ [24] tetraene N ₄) Cl ₂] | 1580 | - | 270 | 1.78 | 14.2 |
| 10 | [Cu (Me ₄ [32] tetraene N ₄) Cl ₂] | 1580 | - | 270 | 1.79 | - |

The Infrared Spectra of the complexes do not exhibit any absorption band at 3200 or 1700 cm⁻¹ indicating the absence of >C=O or -NH₂ group³³⁻³⁵. All the complexes show a medium intensity absorption band in the region 1580-1620 cm⁻¹ which can be assigned to ν C=N, indicating the condensation of 2,3-butanedione and diaminoalkanes. For TIM complexes³⁶ of Cu(II) ν C=N has been reported at 1600-1620 cm⁻¹. For Zn (II) complexes of MePhTIM absorption at 1609-1615 cm⁻¹ and 1640-1660 cm⁻¹ were attributed to ν C=N (symmetric and asymmetric vibrations)³⁷. Nitrate complexes show absorption bands at ~1380, 810-820 and 720 cm⁻¹ attributed to ionic nitrate. In Cd (II) and Hg (II) complexes of tetra-N-methylcyclam the absorption at 1380, 829 and 720 cm⁻¹ have been reported for ionic nitrate.³⁸ Chloro complexes show bands at 270 cm⁻¹ due to coordinated chloro group. Rana et al.³⁹ have reported ν Cu-Cl at 270 cm⁻¹ in Cu (II) complexes of a 16 -membered tetraazamacrocycle derived from 2,4-pentanedione and m-phenylenediamine. For Cu (II) complexes⁴⁰ of an N₆ macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine ν Cu-Cl has been reported at 275 cm⁻¹.

Conductance

Molar conductance of 10⁻³M solutions of the complexes is given in Table -2. Chloro complexes behave as nonelectrolytes in dimethylsulphoxide (Λ_m ranging from 9.7 to 14.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) supporting hexacoordination of copper in these complexes.⁴¹ Nitrate complexes behave as 2:1 electrolytes in DMSO ($\Lambda_m = 66.2-69.0 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$)



indicating that copper is tetraordinated in these complexes.⁴² Several azamacrocyclic complexes of Cu(II) have been reported in which copper was found to be hexa and tetraordinated. Hexa and tetraordinated Cu (II) complexes of TIM and hexacoordinated complexes of MePhTIM have been reported.⁴³ Bhoon and Singh⁴ have synthesized six coordinated Cu (II) complexes of a macrocycle derived from benzil and ethylenediamine. Pajunen⁴⁴ has reported X-ray structure of six coordinated Cu(II) complex, Diaqo(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) Copper(II) nitrate. Hay and coworkers⁴⁵ have reported tetra coordination for Cu (II) complex of macrocycle 5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,10-diene.

Magnetic moments

The effective magnetic moments of Cu (II) macrocyclic complexes are given in the Table -2. The observed μ_{eff} values at room temperature ($\sim 298^{\circ}\text{K}$) range from 1.73 to 1.90 B.M. as expected for monomeric and noninteracting copper ions with one unpaired electron. For Cu (II) complexes of 28- membered N_4O_4 macrocycles μ_{eff} values in the range 1.84-1.94 B.M. have been reported.⁴⁶ For Cu(II) complexes of macrocycle derived from benzil and ethylenediamine μ_{eff} values in the range 1.84-1.94 B.M. have been reported.⁴ Coltrain and Jackels⁴³ have been reported magnetic moments in the range 1.80-1.89 B.M.

III. CONCLUSIONS

In the present communication, we have synthesized and characterized ten large ring (14- to 32 – membered) Cu(II) tetraazamacrocyclic complexes using template synthesis. Based on analytical and spectral data, synthesized chloro complexes are hexa-coordinated while nitro complexes are tetra-coordinated as copper has the general tendency to form hexa as well as tetra coordinated complexes.

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