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Cu (II) Complexes of 12-membered Tetraazamacrocycles Derived From 1,8- Diamino-3,6-diazaoctane and Different α - Diketones

Ajay Kumar Gupta

Associate Professor, Department of Chemistry, Government P. G. College, Jhalawar, Rajasthan, India

ABSTRACT: Cu (II) complexes of 12-membered tetraazamacrocycles are derived from 1,8-diamino-3,6-diazaoctane and different α -diketones such as 2,3-butanedione; 2,3-pentanedione and benzil. 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

Mohammed et al¹ described the biological implication and emphasis of macrocyclic complexes. The chemistry of metal macrocycles is extensive because of their close relationship to molecules of biological significance². The importance of these complexes also is due to the role they play as models for protein metal binding sites in biological systems³, electrocatalysts in fuel cells⁴,

MRI contrast agents⁵, luminescent sensors⁶, and anticancer activity⁷. These extensive applications have been worth investigating for the design of new macrocyclic ligands⁸ for biological and industrial applications.^{2,9} Rai and Prasad reported Cr(III), Fe(III) and Co(II) complexes of tetraazamacrocycles derived from 2,3-butanedione or benzil with 1,8-diamino-3,6-diazaoctane¹⁰. Recently Ni(II) Complexes are also reported¹¹. In the present paper the template synthesis of Cu (II) complexes of 12-membered tetraazamacrocycles are derived from 1,8-diamino-3,6-diazaoctane and different α -diketones such as 2,3-butanedione; 2,3-pentanedione and benzil are reported their corresponding formulas and names are [Me₂[12]dieneN₄](2,3-dimethyl-1,4,7,10-tetraazacyclododeca-1,3diene); [MeEt[12]dieneN₄](2-methyl-3-ethyl-1,4,7,10-tetraazacyclododeca-1,3diene) and [Ph₂[12]dieneN₄](2,3-diphenyl-1,4,7,10-tetraazacyclododeca-1,3diene).

II. EXPERIMENTAL

Materials

CuCl₂·2H₂O (BDH) and Cu(NO₃)₂·3H₂O (BDH) were of GR/AR grade. 1,8-diamino-3,6-diazaoctane (Fluka); 2,3-butanedione (Aldrich) and 2,3-pentanedione (Aldrich) were used as such. Benzil (Sisco, India) was recrystallized from n-butanol.

Analytical methods and physical measurements

Carbon and hydrogen were determined on a Coleman C, H Analyser-33, which was standardized by benzoic acid. Nickel was determined volumetrically by EDTA using Eriochrome Black T 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, and conductance was measured using a Systronics Direct Reading Conductivity meter 304.

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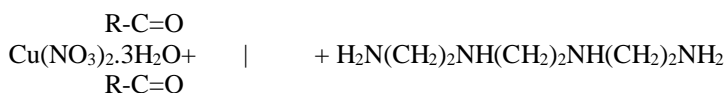
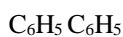
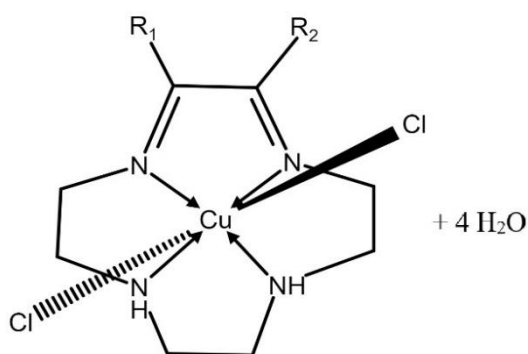
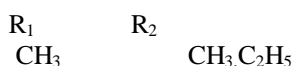
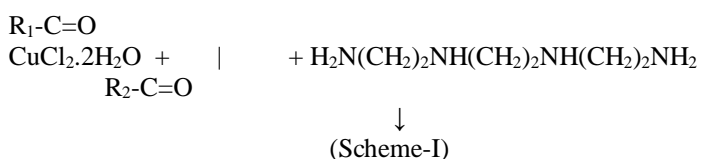
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Synthesis

In ~20 ml of n-butanol, 4.10 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was dissolved with stirring. To this, a solution of 2,3-butanedione (4.10 mmol in ~15 ml n-butanol) was added dropwise followed by 4.10 mmol of 1,8-diamino-3,6-diazaoctane in ~15 ml n-butanol. After ~4 hrs of stirring a coloured solid appeared which was filtered, washed with n-butanol and dried in vacuo. In case of reaction with benzil hot n-butanol was used. Other tetraazamacrocyclic complexes were synthesised in a similar way by the reaction of 2,3-butanedione; 2,3-pentanedione or benzil with 1,8-diamino-3,6-diazaoctane in the presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

III. RESULTS AND DISCUSSION

Cu (II) complexes of tetraazamacrocycles (I) have been synthesised by 1:1 cyclocondensation of α -diketones such as 2,3-butanedione; 2,3-pentanedione or benzil with 1,8-diamino-3,6-diazaoctane in presence of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Scheme I) or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Scheme II).



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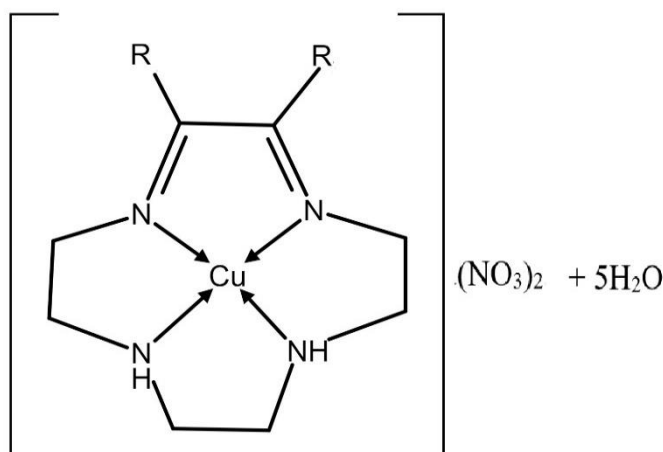
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(Scheme-II)

R = CH₃, C₆H₅

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	Colour & Decomposition Temperature (°C)	Yield %	Analysis (%) found (calculated)				
				C	H	N	Cu	Cl
1	[Cu (Me ₂ [12] diene N ₄) (NO ₃) ₂]	Blue (195)	77	30.66 (31.30)	5.17 (5.21)	14.53 (14.60)	16.27 (16.56)	-
2	[Cu (Me ₂ [12] diene N ₄) Cl ₂]	Violet (186)	81	35.10 (36.33)	6.17 (6.05)	16.78 (16.94)	19.18 (19.22)	21.35 (21.44)
3	[Cu (MeEt[12] diene N ₄) Cl ₂]	Violet (180)	75	37.79 (38.32)	6.22 (6.43)	16.23 (16.24)	18.32 (18.43)	20.48 (20.56)
4	[Cu (Ph ₂ [12] tetraene N ₄) (NO ₃) ₂]	Blue (173)	77	46.48 (47.29)	4.52 (4.76)	11.00 (11.02)	12.41 (12.52)	-
5	[Cu (Ph ₂ [12] diene N ₄) Cl ₂]	Blue (169)	69	52.89 (52.81)	5.23 (5.31)	12.21 (12.31)	13.83 (13.96)	15.47 (15.58)

The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions¹². The template condensation methods lie at the heart of macrocyclic chemistry¹³. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions¹⁴. The transition metal ions are used as the template reactions¹⁵. The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products¹⁶.

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

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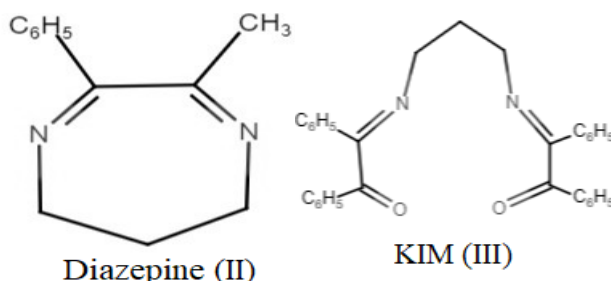
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function of their ring size¹⁷. For tetraazamacrocycles, ideal ring sizes of metal ions have been investigated, and the M-N distance for which the strain energy in the macrocycle is minimum has been calculated¹⁸⁻²⁰. A larger or smaller metal ion would 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 complexes²¹.

During the template synthesis of Fe (II), Co (II), and Ni (II) complexes of MePhTIM, Eggleston, and Jackels²² have ruled out the possibility of formation of diazepine (II), a heterocyclic product of 1+1 condensation based on ¹H NMR studies. Henery et al.²³ have isolated and characterized a macrocyclic precursor 1,2,8,9-tetraphenyl-diazaduohepta-2,7-diene-1,9-dione(KIM,III) 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 ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) of 10 ⁻³ M sol.
		ν C=N	-NO ₃ unidentate	Cu-Cl	ν NH		
1	[Cu (Me ₂ [12] diene N ₄)] (NO ₃) ₂	1560	720,820,1370	-	3250	1.73	59.8
2	[Cu (Me ₂ [12] diene N ₄) Cl ₂]	1580		270	3200	1.75	11.9
3	[Cu (MeEt[12] diene N ₄) Cl ₂]	1580		270	3220	1.70	14.8
4	[Cu (Ph ₂ [12] tetraene N ₄)] (NO ₃) ₂	1550	720,800,1380	-	3240	1.78	16.5
5	[Cu (Ph ₂ [12] diene N ₄) Cl ₂]	1560		270	3220	1.72	13.5

All the macrocyclic complexes do not exhibit band at 1700cm⁻¹ which can be assigned to the residual >C=O group. Medium to strong absorption bands are observed in the region 3180-3360 cm⁻¹ due to ν NH. Nelson and co-worker's²⁴ have not observed any band at 1700 cm⁻¹ which could be attributed to unreacted keto group and a band at 3240 cm⁻¹ has been assigned to the secondary amino group. A medium intensity band in the region 1550-1580 cm⁻¹ is assigned to coordinated ν C=N. For Ni(II), Cu(II), Zn(II) and Hg(II) complexes of the macrocycle 5,6,12,13-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Hay and co-worker's²⁵ have reported ν C=N in the region 1638-1669 cm⁻¹. Nitrate complexes exhibit absorption bands at 1370-1380, 800-820 and 740 cm⁻¹ due to free nitrate. For Cd(II) and Hg(II) tetraazamacrocyclic complexes, Alcock et al.²⁶ have reported free nitrate absorptions at 1380, 829 and 720 cm⁻¹. In chloro complexes of Cu(II) band at 270 cm⁻¹ can be assigned to the coordinated chloro group. For

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Cu(II) complexes of an N₆ macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine Malik and co-worker's²⁷ have reported Cu-Cl at 275 cm⁻¹. Singh and Rana²⁸ have observed Cu-Cl at 270 cm⁻¹ in Cu(II) complexes of macrocycle derived from 2,6-diaminopyridine and dibenzylmethane. The macrocyclic complexes derived from benzil exhibit strong band at ~ 1550 cm⁻¹ due to ν C=C of phenyl groups and at ~ 750 cm⁻¹ due to C-H out of plane bending vibrations of phenyl groups. Coltrain and Jackels²⁹ have reported ν C=C in the region 1569-1590 cm⁻¹ and C-H out of plane bending vibrations of phenyl at ~710 cm⁻¹ and ~745 cm⁻¹ in Cu(II) complexes of 2,9-dimethyl-3,10-diphenyl[14]-1,4,8,11-tetraene.

Conductance

Molar conductance of 10⁻³ M solutions of the complexes is given in Table-2. Chloro complexes behave as nonelectrolytes in dimethylsulphoxide (Λ_m ranging from 9.7 to 18.0 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) supporting hexacoordination of copper in these complexes.³⁰ Nitrate complexes behave as 2:1 electrolyte in DMSO ($\Lambda_m = 62.7-69.8 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$) indicating that copper is tetracoordinated in these complexes.³¹ Hexa and tetracoordinated Cu(II) complexes of TIM and hexacoordinated complexes of MePhTIM have been reported.²⁹ Bhoon and Singh³² have synthesized six coordinated Cu(II) complexes of a macrocycle derived from benzil and ethylenediamine. Pajunen³³ 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 co-worker's²⁵ 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 (~ 298⁰K) range from 1.79 to 1.84 B.M. as expected for monomeric and noninteracting copper ions with one unpaired electron. For Cu(II) complexes of 28- membered N₄O₄ macrocycles μ_{eff} values in the range 1.84-1.94 B.M. have been reported.³⁴ 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.³² Coltrain and Jackels²⁹ have been reported magnetic moments in the range 1.80-1.89 B.M.

IV. CONCLUSIONS

In the present communication, five 12-membered Cu (II) tetraazamacrocyclic complexes have been synthesized by 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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