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HEXAAZA 18-MEMBERED CU(II) MACROCYCLIC COMPLEXES DERIVED FROM DIFFERENT A-DIKETONES AND 1,5-DIAMINO-3-AZAPENTANE

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ABSTRACT: Cu (II) complexes of 18-membered hexaazamacro cycles are derived from 1,5-Diamino-3-azapentane 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, Hexaazamacrocycles of Cu (II), IR spectra, Magnetic moments

I.INTRODUCTION

During last few decades, the chemistry of macrocyclic compounds has been an interesting and fascinating area. Macrocyclic complexes lie at the centre of organic and inorganic chemistry and became the basis for development of bioinorganic chemistry. Mohammed et al[.1] 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 significance[2]. The importance of these complexes also is due to the role they play as models for protein metal binding sites in biological systems[3],electrocatalysts infuel cells[4],MRI contrast agents[5], luminescent sensors[6], and anticancer activity[7]. These extensive applications have been worth investigating for the design of new macrocyclic ligands[8] for biological and industrial applications.[2,9] Recently 18-membered Ni(II) hexaazamacrocyclic complexes derived from 1,5-Diamino-3-azapentane and different α-diketones such as 2,3-butanedione; 2,3-pentanedione and benzil have been reported[10]. In the present paper the template synthesis of Cu(II) complexes of 18-membered hexaazamacrocycles are derived from 1,5-diamino-3-azapentane and different α-diketones such as 2,3-butanedione; 2,3-pentanedione and benzil are reported, their corresponding formulas and names are [Me_4[18]tetraeneN_6] (2,3,11,12-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene);[Me_2Et_2[18]tetraeneN_6](2,11-dimethyl-3,12-diethyl-1,4,7, 10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene) and [Ph_4[18]tetraeneN_6] (2,3,11,12-tetra phenyl - 1,4,7,10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene).

II.EXPERIMENTAL

Materials

$CuCl_2.2H_2O$ (BDH) and $Cu(NO_3)_2.3H_2O$(BDH) was of GR/AR grade. 1,5-diamino-3-azapentane (Fluka); 2,3-butanedione (Aldrich) and 2,3-pentanedione (Aldrich) was 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. 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 and conductance was measured using a Systronics Direct Reading Conductivity meter 304.

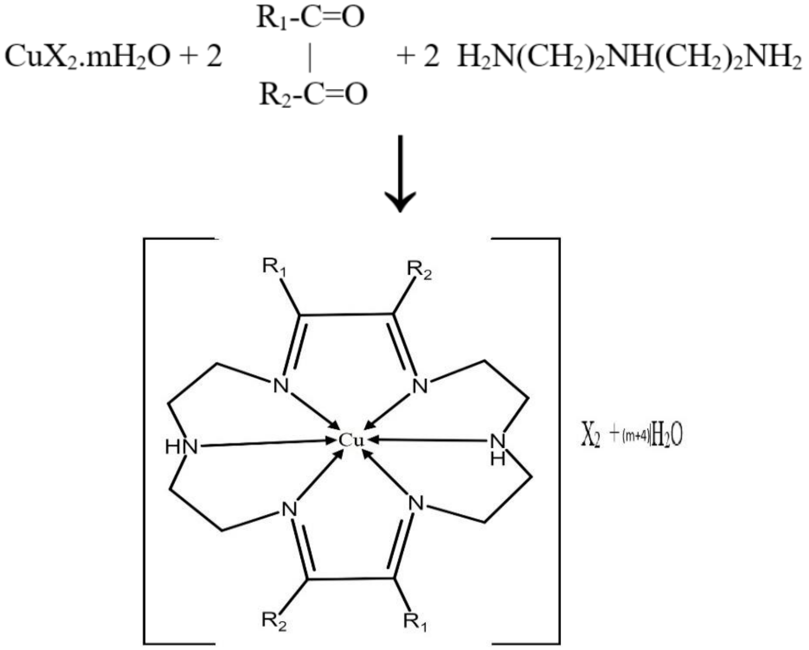
Synthesis

To the n-butanolic solution of $Cu(NO_3)_2.3H_2O$ (4.22 mmol in ~15 ml n-butanol) a solution of 2,3-butanedione (8.44 mmol in ~20 ml n-butanol) was added. To this, a solution of 1,5-diamino-3-azapentane (8.44 mmol in ~15 ml n-butanol) was added dropwise with constant stirring. After ~4 hrs, a solid appeared which is filtered, washed with n-butanol and dried in vacuo.

Other hexaazamacrocyclic complexes were prepared similarly by the reaction of 1,5-diamino-3-azapentane with 2,3-butanedione or 2,3-pentanedione in the presence $CuCl_2.2H_2O$. The hexaazamacrocyclic complexes derived from benzil were prepared using $Cu(NO_3)_2.3H_2O$ or $CuCl_2.2H_2O$ in hot n-butanol.

III.RESULTS AND DISCUSSION

The 1:2:2 molar reaction of $Cu(NO_3)_2.3H_2O$ or $CuCl_2.2H_2O$ with 1,5-diamino-3-azapentane and α-Diketones such as 2,3-butanedione; 2,3-pentanedione or benzil to give Cu(II) macrocyclic complexes (I) may be represented by the Scheme I.



$$CuX_2.mH_2O + 2 \begin{array}{c} R_1\text{-}C{=}O \\ | \\ R_2\text{-}C{=}O \end{array} + 2\ H_2N(CH_2)_2NH(CH_2)_2NH_2$$

R_1	R_2	X	m
CH_3	CH_3	Cl	2
CH_3	CH_3	NO_3	3
CH_3	C_2H_5	Cl	2
C_6H_5	C_6H_5	Cl	2
C_6H_5	C_6H_5	NO_3	3

The resulting macrocyclic complexes are blue coloured solid, complexes are quite stable and some of them are sensitive to exposure to atmosphere. On heating these complexes decompose at 110-184 ^{0}C. All the complexes are insoluble in chloroform, carbon tetrachloride, acetonitrile, acetone, and nitromethane and soluble in dimethylsulphoxide(DMSO).The elemental analysis and characteristics of these complexes are given in Table-1.

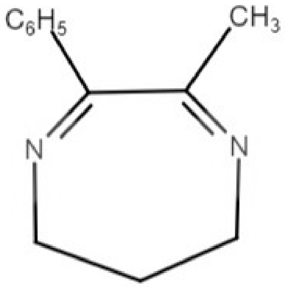
Table –1 Analysis and physical characteristics of hexaazamacrocyclic complexes of Cu (II)

S.N.	**Complex**	**Colour & Decomposition Temperature (^{0}C)**	**Yield %**	**Analysis (%) found (calculated)**				
				C	**H**	**N**	**Cu**	**Cl**
1	[Cu (Me$_4$ [18] diene N$_6$)] (NO$_3$)$_2$	Blue (184)	95	37.77 (38.90)	6.25 (6.11)	17.27 (17.01)	12.83 (12.86)	-
2	[Cu (Me$_4$ [18] diene N$_6$)] Cl$_2$	Blue (110)	82	44.01 (43.58)	6.65 (6.85)	18.96 (19.06)	14.31 (14.41)	15.96 (16.08)
3	[Cu (Me$_2$ Et$_2$ [18] diene N$_4$)] Cl$_2$	Blue (165)	75	46.11 (46.10)	7.19 (7.30)	17.78 (17.92)	13.40 (13.55)	14.98 (15.11)
4	[Cu (Ph$_4$ [18] diene N$_6$)] (NO$_3$)$_2$	Blue (157)	65	58.80 (58.25)	5.21 (5.19)	11.28 (11.32)	8.50 (8.56)	-
5	[Cu (Ph$_4$ [18] diene N$_6$)] Cl$_2$	Blue (196)	62	62.69 (62.74)	5.33 (5.55)	12.00 (12.19)	9.18 (9.21)	10.18 (10.28)

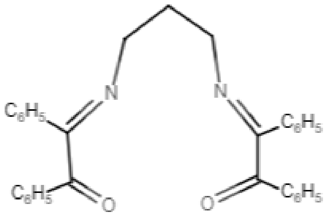
The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions[11]. The template condensation methods lie at the heart of macrocyclic chemistry[12]. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions[13]. The transition metal ions are used as the template reactions[14].The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products[15].

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 size[16]. 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 calculated [17-19]. 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 complexes[20].

During the template synthesis of Fe (II), Co (II), and Ni (II) complexes of MePhTIM, Eggleston, and Jackels[21] 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.[22] 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).



Diazepine (II)



KIM (III)

Infrared Spectra

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

Table –2 IR, magnetic moment, and molar conductance of Cu (II) hexaazamacrocyclic complexes

S.N.	Complex	IR Absorption Bands(cm^{-1})				μ_{eff} B.M.	Molar Conductance ($\Omega^{-1}cm^2mol^{-1}$) of 10^{-3} M sol.
		υ C=N	ionic NO_3	Cu-N	υ NH		
1	[Cu (Me_4 [18] diene N_6)] $(NO_3)_2$	1620	730,830,1360	506	3180	1.73	65.1
2	[Cu (Me_4 [18] diene N_6)] Cl_2	1580		511	3240	1.75	50.8
3	[Cu (Me_2 Et_2 [18] diene N_4)] Cl_2	1580		513	3220	1.74	63.2
4	[Cu (Ph_4[18] diene N_6)] $(NO_3)_2$	1570	730,830,1370	514	3220	1.77	58.3
5	[Cu (Ph_4 [18] diene N_6)] Cl_2	1580		516	3230	1.76	52.6

Cu(II) Complexes do not exhibit absorption band at 1700 cm^{-1} which assigned to residual >C=O group. Strong bands are observed in the region 3180-3240 cm^{-1} due to υ N-H. Nelson and co-worker's [23] have not observed any absorption band at 1700 cm^{-1} in Fe(III) complexes of N_5 macrocycles derived from 2,6-diacetylpyridine and 1,9-diamino-3,7-diazanonane indicating the

absence of unreacted keto group while the band at 3240 cm^{-1} was assigned to secondary amino group. For Co(II), Ni(II) and Cu(II) complexes of 15- to 19- membered oxygen-nitrogen donor macrocycles υ N-H vibrations have been reported in the region 3100-3300 cm^{-1} by Fenton and co-worker's [24]. In Ni(II) complexes [25] of macrocycles derived from α-diketones or β -diketones and 1,11-diamino-3,6,9-triazaundecane a pair of υ N-H absorption were observed near 3160 and 3205 cm^{-1}. For Ni(II), Co(II) and Cu(II) complexes of tetraazamacrocycle[26] derived from 2,4-pentanedione and m-phenylene diamine, the υ N-H band has been reported at 3200 cm^{-1}.

All complexes exhibit a strong absorption band in the region 1570-1620 cm^{-1} assigned to coordinated υ C=N. For Co(II) and Ni(II) complexes of macrocycle derived from 2,6-diacetylpyridine and 3,3'-diamino-N-methyldipropylamine, Nelson and co-worker's [27] have reported the υ C=N band at 1620-1630 cm^{-1} . In Ni(II) pentaazamacrocyclic complexes a band at ~ 1575 cm^{-1} has been assigned to υ C=N[25]. The Sharp band found in the region 506-516 cm^{-1} for all the complexes which is attributed to υ Cu-N[28].

Nitrate complexes show absorption at 730, 830 and ~1370 cm^{-1} which can be assigned to ionic nitrate. For Cd(II) and Hg(II) complexes[29] of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetra decane free nitrate absorption bands have been reported at 720,829 and 1380 cm^{-1} Maguire et al.[30] have reported a band at 1380 cm^{-1} for υ N=O of ionic nitrate in cis and trans-[Cr(cyclam) $(NO_3)_2$] $NO_3.XH_2O$(X= 2 or ½).

In case of Cu(II) complexes of macrocycles derived from benzil a band at 1570 cm^{-1} is observed which is attributed to υ C=C of phenyl groups. For Co(III) complexes of macrocycles derived from benzil and 1,3-diaminopropane or 1,3-diamino-2-hydroypropane absorption bands at 1560 cm^{-1} and 1600 cm^{-1} were assigned to phenyl groups[31]. In Cu(II) complexes of MePhTIM, Coltrain and Jackels[32] have reported υ C=C in the region 1569-1590 cm^{-1} .

Conductance

Molar conductance of 10^{-3} M solutions of these complexes in DMSO range from 50.8 to 65.1 $ohm^{-1}cm^2mol^{-1}$ (Table-2) indicating 2:1 electrolytic behaviour. Mn(II),Fe(II),Ni(II),Zn(II),Cd(II), Hg(II) and Ag(I) complexes with quadridentate ligands derived from 2,9-dichloro-1,10-phenanthrolene and hydrazinehydrate or methylhydrazine have been reported to be 2:1 electrolyte exhibiting conductance in the range 50-80 $ohm^{-1}cm^2mol^{-1}$ in DMSO[33]. Thus, both nitrate and chloride groups are not coordinated, and copper possesses six-coordination in these complexes. Rana et al.[26]

have reported hexacoordinated Cu(II) complexes of the macrocycle dibenzo(f,n)-2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca[16]1,3,9,11-tetraene. Cu(II) complexes of a 16-membered N_6 tetradentate macrocycle have been reported to be hexacoordinated in which two anions are coordinated[34]. Fenton and co-worker's [24] have reported X-ray structure of hexacoordinated Cu(II) complex [Cu L(NO_3)](NO_3) (L=6,7-dihydro-15,19-nitrodibenzo (j,p)-1,9,12,15-dioxadiazacyclo heptadecine) in which all five donor atoms are coordinated to the copper and the six position is occupied by nitrate ion.

Magnetic moments

The μ_{eff} values for Cu(II) hexaazamacrocyclic complexes at room temperature (~298 ^0C) range from 1.73 to 1.77 B.M. (Table-2) and are in accord with one unpaired electron. Malik and co-worker's [35] have observed μ_{eff} values in the range 1.76-1.84 B.M. For Cu(II) complexes of a macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine. For Cu(II) complexes of the macrocycle dibenzo(f,n)-2,4,10,12-tetramethyl-1,5,9,13-tetraazacyclohexadeca[16]1,3,9,11-tetraene, μ_{eff} values in the range 1.75-1.82 B.M. have been reported[26]. In Cu(II) complexes of a 16-membered N_6 tetradentate macrocycle derived from 2,6-diaminopyridine and dibenzoylmethane, Singh and Rana[34] have observed magnetic moments in the range 1.75-1.82 B.M. For [Cu(pyane-N_5)]$(PF_4)_2$ the μ_{eff} has been reported to be 1.90 B.M.

IV.CONCLUSIONS

In the present communication, five 18-membered Cu (II) hexaazamacrocyclic complexes have been synthesized by template synthesis. Based on analytical and spectral data, these complexes are assumed to distorted octahedral geometry.

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