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Hexaaza 18-membered Ni(II) Macrocyclic Complexes Derived from Different α - Diketones and 1,5-Diamino-3-azapentane

Ajay Kumar Gupta

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

ABSTRACT: Ni (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. The complexes have been characterized by elemental analysis, IR spectra, conductance measurements, and magnetic moments.

KEYWORDS-Macrocyclic complexes, Hexaazamacrocycles of Ni (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 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} In the present paper the template synthesis of Ni (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 [Me₄[18]tetraeneN₆](2,3,11,12-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene); [Me₂Et₂[18]tetraeneN₆](2,11-dimethyl-3,12-diethyl-1,4,7,10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene); and [Ph₄[18]tetraeneN₆](2,3,11,12-tetraphenyl-1,4,7,10,13,16-hexaazacyclooctadeca-1,3,10,12-tetraene).

II. EXPERIMENTAL

Materials

NiCl₂·6H₂O (Fluka) and Ni(NO₃)₂·6H₂O (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. 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.

Synthesis

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To the n-butanolic solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The hexaazamacrocyclic complexes derived from benzil were prepared using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in hot n-butanol.

III. RESULTS AND DISCUSSION

The 1:2:2 molar reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ with 1,5-diamino-3-azapentane and α -Diketones such as 2,3-butanedione; 2,3-pentanedione or benzil to give Ni(II) macrocyclic complexes (I) may be represented by the Scheme I.

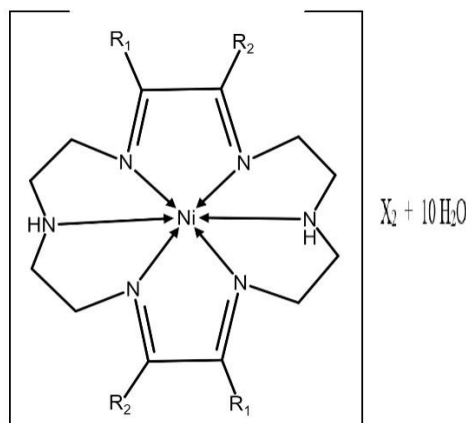
$\text{R}_1\text{-C=O}$

$\text{NiX}_2 \cdot 6\text{H}_2\text{O} + 2$

$\text{R}_2\text{-C=O}$

$+ 2 \text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$

↓



(I)

Scheme-I

$\text{R}_1\text{R}_2\text{X}$

CH_3

$\text{CH}_3 \text{ Cl, NO}_3$

$\text{CH}_3\text{C}_2\text{H}_5$

Cl

$\text{C}_6\text{H}_5 \text{ C}_6\text{H}_5$

Cl, NO_3

The resulting macrocyclic complexes are coloured solid, complexes are quite stable and some of them are sensitive to exposure to atmosphere. On heating these complexes decompose at 164-196 °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.

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

| S.N | Complex | Colour & Decomposition Temperature (°C) | Yield % | Analysis (%) found (calculated) | | | | |
|-----|--|---|---------|---------------------------------|----------------|------------------|------------------|------------------|
| | | | | C | H | N | Ni | Cl |
| 1 | [Ni (Me ₄ [18] tetraene N ₆)] (NO ₃) ₂ | Brown (173) | 57 | 38.88 (39.28) | 6.04 (6.18) | 16.96 (17.17) | 12.04 (12.00) | - |
| 2 | [Ni (Me ₄ [18] tetraene N ₆)] Cl ₂ | Green (196) | 33 | 43.48 (44.07) | 6.62 (6.93) | 19.20 (19.27) | 13.43 (13.46) | 16.18 (16.26) |
| 3 | [Ni (Me ₂ Et ₂ [12] tetraene N ₄)] Cl ₂ | Green (168) | 28 | 46.02 (46.58) | 7.14 (7.38) | 18.19 (18.10) | 12.68 (12.65) | 15.23 (15.27) |
| 4 | [Ni (Ph ₄ [18] tetraene N ₆)] (NO ₃) ₂ | Violet (164) | 47 | 58.11 (58.63) | 5.23 (5.19) | 11.32 (11.39) | 8.00 (7.96) | - |
| 5 | [Ni (Ph ₄ [18] tetraene N ₆)] Cl ₂ | Violet (192) | 24 | 63.02 (63.18) | 5.61 (5.59) | 12.25 (12.28) | 8.36 (8.57) | 10.34 (10.36) |

The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions¹⁰. The template condensation methods lie at the heart of macrocyclic chemistry¹¹. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions¹². The transition metal ions are used as the template reactions¹³. The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products¹⁴.

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 size¹⁵. 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 calculated¹⁶⁻¹⁸. 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 complexes¹⁹.

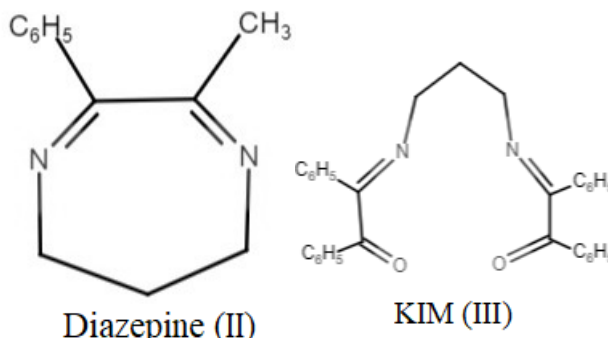
During the template synthesis of Fe (II), Co (II), and Ni (II) complexes of MePhTIM, Eggleston, and Jackels²⁰ have ruled out the possibility of formation of diazepine (II), a heterocyclic product of 1+1 condensation based on ¹H NMR studies. Henery et al.²¹ have isolated and characterized a macrocyclic 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).

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Infrared Spectra

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

Table –2 IR, magnetic moment, and molar conductance of Ni (II) hexaazamacrocyclic 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 | ionic NO_3 | Ni-N | ν NH | | |
| 1 | [Ni (Me ₄ [18] tetraene N ₆) (NO ₃) ₂] | 1620 | 730,820,1370 | 435 | 3240 | 3.28 | 58.6 |
| 2 | [Ni (Me ₄ [18] tetraene N ₆) Cl ₂] | 1570 | | 430 | 3240 | 3.28 | 59.7 |
| 3 | [Ni (Me ₂ Et ₂ [12] tetraene N ₄) Cl ₂] | 1580 | | 440 | 3180 | 3.29 | 58.8 |
| 4 | [Ni (Ph ₄ [18] tetraene N ₆) (NO ₃) ₂] | 1620 | 730,830,1380 | 435 | 3240 | 3.30 | 61.8 |
| 5 | [Ni (Ph ₄ [18] tetraene N ₆) Cl ₂] | 1580 | | 430 | 3230 | 3.30 | 62.1 |

Ni(II) Complexes do not exhibit absorption band at 1700 cm^{-1} which assigned to residual $>\text{C}=\text{O}$ group. Strong bands are observed in the region $3180\text{--}3240\text{ cm}^{-1}$ due to ν N-H. Nelson and co-worker's²² have not observed any absorption band at 1700 cm^{-1} in Fe(III) complexes of N₅ 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 ν N-H vibrations have been reported in the region $3100\text{--}3300\text{ cm}^{-1}$ by Fenton and co-worker's²³. In Ni(II) complexes²⁴ of macrocycles derived from α -diketones or β -diketones and 1,11-diamino-3,6,9-triazaundecane a pair of ν N-H absorption were observed near 3160 and 3205 cm^{-1} . For Ni(II), Co(II) and Cu(II) complexes of tetraazamacrocyclic²⁵ derived from 2,4-pentanedione and m-phenylenediamine, the ν N-H band has been reported at 3200 cm^{-1} .

All complexes exhibit a strong absorption band in the region $1570\text{--}1620\text{ cm}^{-1}$ assigned to coordinated ν 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's²⁶ have reported the ν C=N band at $1620\text{--}1630\text{ cm}^{-1}$. In Ni(II) pentaazamacrocyclic complexes a band at $\sim 1575\text{ cm}^{-1}$ has been assigned to ν C=N²⁴. The Sharp band found in the region $430\text{--}440\text{ cm}^{-1}$ for all the complexes which is attributed to ν Ni-N^{27,28}.

Nitrate complexes show absorption at $730, \sim 820$ and $\sim 1380\text{ cm}^{-1}$ which can be assigned to ionic nitrate. For Cd(II) and Hg(II) complexes²⁹ of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetra decane free nitrate absorption bands

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have been reported at 720,829 and 1380 cm^{-1} Maguire et al.³⁰ have reported a band at 1380 cm^{-1} for $\nu \text{N}=\text{O}$ of ionic nitrate in cis and trans-[Cr(cyclam) (NO_3)₂] $\text{NO}_3 \cdot \text{XH}_2\text{O}$ (X= 2 or ½).

In case of Ni(II) complexes of macrocycles derived from benzil a band at 1550 cm^{-1} is observed which is attributed to $\nu \text{C}=\text{C}$ of phenyl groups. For Co(III) complexes of macrocycles derived from benzil and 1,3-diaminopropane or 1,3-diamino-2-hydroxypropane absorption bands at 1560 cm^{-1} and 1600 cm^{-1} were assigned to phenyl groups³¹. In Cu(II) complexes of MePhTIM, Coltrain and Jackels³² have reported $\nu \text{C}=\text{C}$ in the region 1569-1590 cm^{-1} .

Conductance

Molar conductance of 10⁻³ M solutions of these complexes in DMSO range from 58.6 to 62.1 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ (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-phenanthroline and hydrazinehydrate or methylhydrazine have been reported to be 2:1 electrolyte exhibiting conductance in the range 50-80 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in DMSO³³. Thus, both nitrate and chloride groups are not coordinated, and nickel possesses six-coordination in these complexes. The crystal structure of cis- and trans-isomers of [NiL(NCS)₂](where L= 3,4:9,10:17,18:23,24-tetrabenzo-1,12,15,26-tetraaza-5,8,19,22-tetraoxacyclooctacosane) have been reported in which nickel has pseudo-octahedral environment^{34,35}. Crystal structure of [Ni L(OCIO₃)]ClO₄(where L= pyridine containing pentaazamacrocyclic, 7-[2'-(1''-pyrrolidinyl)ethyl]ethyl]-3,7,11,17-tetraazabicyclo[11.3.1]-heptadeca-1(17),13,15-triene has been reported and the complex has been found to octahedral³⁶. X-Ray structure of Ni(II) complex [chloro{9-(methoxymethyl)}-1,4,6,9,11,14-hexaazabicyclo[12.2.2]heptadecane) nickel(II)perchlorate reveals its octahedral geometry³⁷.

Magnetic moments

The μ_{eff} values for Ni(II) hexaazamacrocyclic complexes at room temperature (~298 °C) range from 3.28 to 3.30 B.M. (Table-2) and are in accord with high spin octahedral Ni(II) complexes Rana et al.²⁵ reported μ_{eff} in the range 3.05-3.25 B.M. for Ni(II) complexes of a macrocycle derived from 2,4-pentanedione and m-phenylenediamine and have assigned pseudooctahedral geometry. For Ni(II) complexes of a 14-membered N₆ tetradentate macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine μ_{eff} has been observed in the range 3.24-3.35 B.M. and distorted octahedral geometry has been inferred³⁸.

V. CONCLUSIONS

In the present communication, five 18-membered Ni (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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