

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 5, May 2018

Ni (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: Ni (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 Ni (II), IR spectra, Magnetic moments

I. INTRODUCTION

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} 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. In the present paper the template synthesis of Ni (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

NiCl₂.6H₂O (Fluka) and Ni(NO₃)₂.6H₂O (BDH) was 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.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

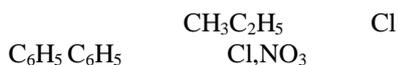
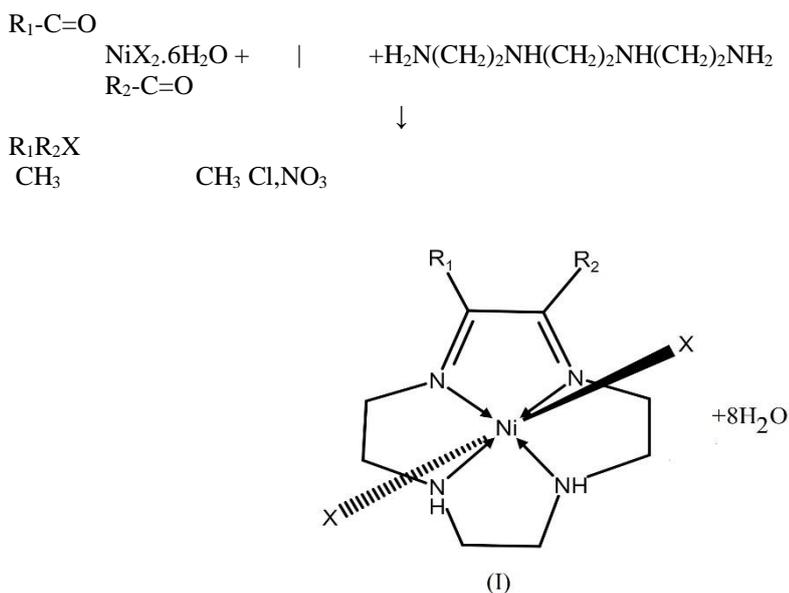
Vol. 7, Issue 5, May 2018

Synthesis

In ~20 ml of n-butanol, 4.10 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

III. RESULTS AND DISCUSSION

Ni(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 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. (Scheme I)



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.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 5, May 2018

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

S.N	Complex	Colour & Decomposition Temperature (°C)	Yield %	Analysis (%) found (calculated)				
				C	H	N	Ni	Cl
1	[Ni (Me ₂ [12] diene N ₄) (NO ₃) ₂]	Brown (153)	72	31.33 (31.69)	5.22 (5.31)	14.71 (14.78)	15.42 (15.49)	-
2	[Ni (Me ₂ [12] diene N ₄) Cl ₂]	Brown (174)	37	36.97 (36.85)	6.28 (6.18)	17.03 (17.18)	18.10 (18.01)	21.62 (21.75)
3	[Ni (MeEt[12] diene N ₄) Cl ₂]	Green (160)	33	38.80 (38.86)	6.75 (6.52)	16.37 (16.48)	17.39 (17.27)	20.72 (20.85)
4	[Ni (Ph ₂ [12] tetraene N ₄) (NO ₃) ₂]	Violet (172)	73	46.79 (47.74)	4.96 (4.80)	11.20 (11.13)	11.56 (11.66)	-
5	[Ni (Ph ₂ [12] diene N ₄) Cl ₂]	Violet (183)	55	53.18 (53.37)	5.54 (5.37)	12.22 (12.44)	13.20 (13.04)	15.59 (15.75)

The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions¹¹. The template condensation methods lie at the heart of macrocyclic chemistry¹². Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions¹³. The transition metal ions are used as the template reactions¹⁴. The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products¹⁵.

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 size¹⁶. 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 calculated¹⁷⁻¹⁹. 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 complexes²⁰.

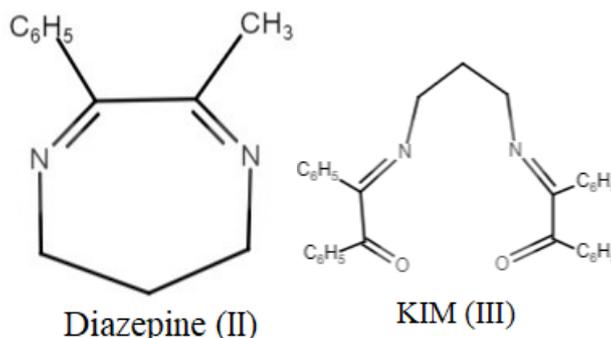
During the template synthesis of Fe (II), Co (II), and Ni (II) complexes of MePhTIM, Eggleston, and Jackels²¹ have ruled out the possibility of formation of diazepine (II), a heterocyclic product of 1+1 condensation based on ¹H NMR studies. Henery et al.²² have isolated and characterized a macrocyclic 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).

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 5, May 2018



Infrared Spectra

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

Table –2 IR, magnetic moment and molar conductance of Ni (II) tetraazamacrocyclic complexes

S.N.	Complex	IR Absorption Bands(cm^{-1})				μ_{eff} B.M.	Molar Conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) of 10^{-3} M sol.
		ν C=N	-NO ₃ unidentate	Ni-Cl	ν NH		
1	[Ni (Me ₂ [12] diene N ₄) (NO ₃) ₂]	1580	860,1020,1280	-	3220	3.36	18.2
2	[Ni (Me ₂ [12] diene N ₄) Cl ₂]	1590		290	3240	3.28	15.7
3	[Ni (MeEt[12] diene N ₄) Cl ₂]	1580		290	3200	3.29	11.8
4	[Ni (Ph ₂ [12] tetraene N ₄) (NO ₃) ₂]	1560	860,1020,1280	-	3200	3.29	8.5
5	[Ni (Ph ₂ [12] diene N ₄) Cl ₂]	1560		290	3200	3.27	8.7

The Infrared Spectra of the complexes do not exhibit any absorption band at 3200 or 1700 cm^{-1} indicating the absence of $>\text{C}=\text{O}$ or $-\text{NH}_2$ group²³⁻²⁵. All the complexes show a medium intensity absorption band in the region 1560-1590 cm^{-1} which can be assigned to ν C=N, indicating the condensation of 2,3-butanedione and diaminoalkanes. For TIM complexes²⁶ of Cu(II) ν C=N has been reported at 1600-1620 cm^{-1} . In the IR spectra of Cr(III), Fe(III), and Co(III) complexes of macrocycles²⁷ derived from dihydrazides and aromatic diketones, absorption bands at 1580-1640 cm^{-1} have been assigned to ν C=N.

Nitrate complexes exhibit absorption bands at ~ 1280 , ~ 1020 , and ~ 860 cm^{-1} which are consistent with the monodentate nature of nitrate group²⁸. Chloro complexes show bands at ~ 290 cm^{-1} due to the coordinated chloro group. Rana and co-workers²⁹ have shown the appearance of unidentate nitrate absorption at $\sim 1290, 1015$ and $865-870$ cm^{-1} and Ni-Cl band at ~ 290 cm^{-1} in Ni(II) complexes of tetraazamacrocycles derived from 2,4-pentanedione and *m*-phenylenediamine. Malik et al.³⁰ have reported bands at 1265, 1010, and 860 cm^{-1} for unidentate nitrate and a band at 280 cm^{-1} for ν Ni-Cl in Ni(II) complexes of the macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine.

All the macrocyclic complexes exhibit strong absorption bands in the region 3180-3360 cm^{-1} which can be attributed to ν NH. Mayer and Rose³¹ have been reported ν NH bands in the region 3220-3450 cm^{-1} in Ni(II) complexes of a macrocycle derived from 1,3-diaminopropane and methyl vinyl ketone.

The macrocyclic complexes derived from benzil exhibit strong band at ~ 1560 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. Coltraine and Jackels³² 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.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 5, May 2018

Conductance

Molar conductance of 10^{-3} M solutions of the complexes in dimethylsulphoxide (DMSO) is observed in the range 8.5– 18.2 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ [Table-2], supporting their nonelectrolyte behaviour³³. Thus, the chloro and nitrate groups are coordinated to the Nickel atom giving trans-octahedral geometry. Ito et al.³⁴ have reported the X-ray crystal structure of trans-dichloro (1,4,7,10-tetraazacyclotetradecane) nickel (II) hydrate and trans-dichloro (1,4,7,10-tetraazacyclohexadecane) nickel (II) in which Ni(II) is high spin and hexacoordinated. Trans octahedral structure has also been reported for [Ni L (NCS)₂] (where L=3,4:9,10:17,18:23,24-tetrabenzo-1,12,15,26-5,8,19,20-tetraazacyclooctacosane)³⁵.

Magnetic moments

The effective magnetic moments of Ni (II) macrocyclic complexes are given in Table-2. The observed μ_{eff} values at room temperature ($\sim 298^{\circ}\text{K}$) range from 3.27 – 3.36 BM. These values are in accordance with two unpaired electrons indicating a high spin (distorted) octahedral d^8 configuration. For Ni(II), complexes of macrocycles derived from 2,3-butanedione and 2,6-diaminopyridine Malik and coworkers³⁰ have reported μ_{eff} in the range 3.24 -3.35 BM and have assigned pseudo-octahedral geometry. For [Ni(TIM)(NCS)₂] the μ_{eff} has been reported to be 3.08 B.M.³⁶

V. CONCLUSIONS

In the present communication, five 12-membered Ni (II) tetraazamacrocyclic complexes have been synthesized by template synthesis. Based on analytical and spectral data, these complexes are assumed to distorted octahedral geometry.

REFERENCES

1. A.A.Mohammed, A.M.Al-Daher, H.A. Mohamed and R.G.Harrison, Res.J.Chem.Sci. Vol-5(7),12-19, July(2015).
2. O.A.El-Gammel, M.M. Bekheit and S.A.El-Brashy, Spectrochim. Acta A, 137,207-219(2015).
3. M.K.Moi, C.F.Meares, M.J.McCall, W.C. Cole and S.J. Denard., Anal. Biochem., 148,249-253(1985).
4. L. Zhang, J.Zhang , D.P. Wilkinson and H.J. Wang, Power Sources, 156,171-182(2006).
5. N. Cakic, S. Gunduz, R.Rengarasu and G. Angelovski, Tetrahed. Lett. 56,759-765(2015).
6. V. Guerchais and J. Fillaut, Coord. Chem. Rev., 255,2448-2457(2011).
7. H.A. El-Boraey and O.A. El-Gammal, Spectrochim. Acta A, 138,553-562(2015).
8. A. Bieko, K.Suracka, J. Morzinski, R. Kruszynski and D.C. Bienko, J. Mole. Stru. 1019,135-142(2012).
9. E.R. Krishna, P.M. Reddy, M. Sarangapani, G. Hamanthu, B. Geeta and K.S. Rani, Spectrochim. Acta A, 97,189-196(2012).
10. P.K. Rai, R.N. Prasad, Monatshefte fur chemie,125(4),385-394(1994).
11. S.G. Kang, J. Song, J.H. Jeong, Inorg.Chim.Acta,357,605(2004).
12. N.F. Curtis, Coord.Chem.Rev.3,3(1968).
13. M.F. Niasari, F. Daver, Inorg.Chem.Commun.9,175(2006).
14. R.N. Prasad, S. Gupta, S. Jangir, Indian Chem. Soc.84,1191(2007).
15. T.A. Khan, S.S. Hasan, A.K. Mohamed, M. Shakir, Indian J.Chem.,37,1123 (1998).
16. C.J. Pederson, J. Am. Chem. Soc. 89,7017 (1967).
17. J.P. Collman and P.W. Schneider, Inorg. Chem. 5,1380 (1966).
18. V.L. Goedken, J. Molin-Case and G.G. Christoph, Inorg. Chem. 12,2894 (1973).
19. J.L. Hoard, M.J. Hamor, T.A. Hamor, and W.S. Gaughey, J. Am. Chem. Soc. 87,2313 (1965).
20. L.Y. Martin, L.J. DeHayes, L.J. Zompa, and D.H. Busch, J. Am. Chem. Soc. 96,4046 (1974).
21. D.S. Eggleston and S.C. Jackels, Inorg. Chem. 19,1593 (1980).
22. W.A. Welsh, G.J. Reynolds, and P.M. Henry, Inorg. Chem. 16,2558 (1977).
23. R. Saraswat, S. Singh, V.B. Rana, J.Indian Chem.Soc.73,478(1996).

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 5, May 2018

24. J.De O Cabral, M.F. Cabral, W.J. Cummins, M.G.B. Drew, A. Rodgers and S.M. Nelson, *Inorg. Chim. Acta.* 30,L313 (1978).
25. S.M. Nelson, M. McCann, C. Stevenson, M.G.B. Drew, *J.Chem.Soc.Dalton Trans.*1477(1979).
26. M.J. Marony, N.J. Rose, *Inorg.Chem.*23,2252(1984).
27. R. Sarswat, V.B. Rana, *J.Indian Chem.Soc.*74,493(1998).
28. M. Shakir, K.S. Islam, A.K. Mohamed, M/ Shagufta, S.S. Hussain, *Transition Met.* 24,577(1999)
29. V.B. Rana, P Singh, and M.P. Teotia, *Polyhedron* 1,377 (1982).
30. W.U. Malik, R. Bembi, and R. Singh, *Polyhedron* 2,369 (1983).
31. J.F. Mayer and N.J. Rose, *Inorg. Chem.* 12,1238(1973).
32. B.K. Coltrain and S.C. Jackels, *Inorg. Chem.* 20,2032(1981).
33. W.J. Geary, *Coord. Chem. Rev.* 7,81 (1971).
34. M. Sugimoto, J. Fujita, H. Ito, K. Toriumi and T. Ito, *Inorg.Chem.*22,955(1983).
35. D.W. Reichgott and N.J. Rose, *J. Am. Chem. Soc.* 99,1813 (1977).
36. L.Y. Martin, C.R. Sperati and D.H. Busch, *J. Am. Chem. Soc.* 99,2968 (1977).