Ni (II) Complexes of Large Ring Tetraazamacrocycles Derived From 2,3-Pentanedione and Diaminoalkanes

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Abstract: Ni (II) complexes of large ring (14 to 32-membered) tetraazamacrocycles are derived from 2,3-pentanedione 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 Ni (II), IR spectra, Magnetic moments

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1.INTRODUCTION

Transition metal complexes of tetraazamacrocycles are very similar to naturally occurring biological systems and help in understanding their functions. The synthesis of siroheme model compound 5,10,15,20-tetramethylisobavteriochorinato nickel (II) have been reported[1]. Co (II), Ni(II) and Cu (II) tetraazamacrocyclic complexes derived from benzoyalacetone and O-phenylenediamine have been screened for fungicidal activity[2]. Complexes of Co (II), Ni (II) and Cu(II) containing macrocyclic tetradentate nitrogen donor (N_4) ligand have been screened in vitro against pathogenic fungi and bacteria to access their growth inhibiting potential[3]. For anticancer activity novel N_4macrocyclic metal complexes have been reported[4]. Earlier Cd(II), Zn(II), Cr(II) and Co(II) large ring tetraazamacrocycles derived from 2,3-butanedione, 3,4-hexanedione or benzil with such aliphatic diamines have been reported by Prasad et al.[5-10] Recently Ni(II) and Cu(II) complexes of tetraazamacrocycles containing two α-diamine groups were reported by 2+2 condensation of benzil and diaminoalkanes,[11,12] and in the present paper the template synthesis of Ni(II) tetraazamacrocycles derived from 2,3-pentanedione 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 [Me_2Et_2[14]tetraeneN_4](2,9-dimethyl-3,10-diethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene);[Me_2Et_2[16]tetraeneN_4](2,10-dimethyl-3,11-diethyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene);[Me_2Et_2[20]tetraeneN_4](2,12-dimethyl-3,13-diethyl-1,4,11,14-tetraazacycloeicosa-1,3,11,13-tetraene);[Me_2Et_2[24]tetraeneN_4](2,14-dimethyl-3,15-diethyl-1,4,13,16-tetraazacyclotetracosa-1,3,13,15-tetraene) and [Me_2Et_2[32]tetraeneN_4](2,18-dimethyl-3,19-diethyl-1,4,17,20-tetraazacyclodotriaconta1,3,17, 19-tetraene).

EXPERIMENTAL

Materials

$NiCl_2.6H_2O$(Fluka) was 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); 1,12-diaminododecane (Fluka) and 2,3-pentanedione (Aldrich)were used as such.

Analytical methods and physical measurements

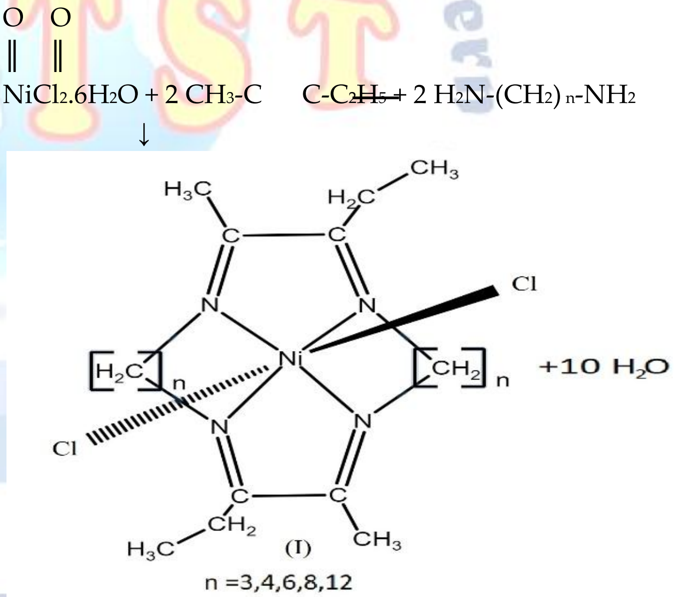
Carbon and hydrogen were determined on a Coleman C, H Analyser-33, which was standardized by benzoic acid. Nickel was determined volumetrically by EDTA using Eriochrome Black T indicator. Nitrogen by Kjeldahl's method and chlorine gravimetrically as AgCl. Infrared spectra were recorded as KBr pellets 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 of Ni (II) tetraazamacrocyclic complexes

$NiCl_2.6H_2O$ (~ 4 m mol) was dissolved in 20 ml n-butanol and 2,3-pentanedione (~ 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 ^{0}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-pentanedione have been conducted.

RESULTS AND DISCUSSION

The 1:2:2 molar reaction of $NiCl_2.6H_2O$ with 2,3-pentanedione and different diaminoalkanes viz 1,3-diaminopropane;1,4-diaminobutane;1,6-diaminohexane;1,8-diaminooctaneand 1,12-diaminododecane have yielded the macrocyclic complex (I) according to the following general Scheme-I.



$$NiCl_2.6H_2O + 2\,CH_3\text{-}\overset{\overset{O}{\|}}{C}\quad\overset{\overset{O}{\|}}{C}\text{-}C_2H_5 + 2\,H_2N\text{-}(CH_2)_n\text{-}NH_2 \downarrow$$

(I)

n =3,4,6,8,12

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.

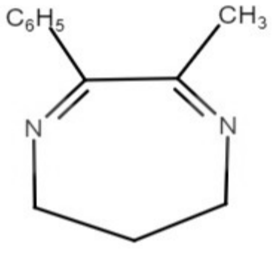
Table –1 Analysis and physical characteristics of tetraazamacrocyclic complexes of Ni (II)

S.N.	Complex	Colour & Decomposition Temperature (⁰C)	Yield %	Analysis (%) found (calculated)				
				C	H	N	Ni	Cl
1	[Ni (Me_2 Et_2 [14] tetraene N_4) Cl_2]	Brown (155)	27	47.42 (47.33)	7.02 (6.95)	13.66 (13.79)	14.51 (14.45)	17.34 (17.46)
2	[Ni (Me_2 Et_2 [16] tetraene N_4) Cl_2]	Green (255)	21	49.69 (49.80)	7.25 (7.42)	12.76 (12.90)	13.26 (13.52)	16.29 (16.33)
3	[Ni (Me_2 Et_2 [20] tetraene N_4) Cl_2]	Green (210)	23	53.88 (53.90)	8.40 (8.22)	11.51 (11.42)	12.02 (11.97)	14.35 (14.46)
4	[Ni (Me_2 Et_2 [24] tetraene N_4) Cl_2]	Green (200)	25	57.00 (57.16)	8.97 (8.85)	10.22 (10.25)	10.62 (10.74)	12.90 (12.97)
5	[Ni (Me_2 Et_2 [32] tetraene N_4) Cl_2]	Green (160)	24	61.92 (62.04)	9.88 (9.74)	8.33 (8.51)	8.86 (8.92)	10.63 (10.77)

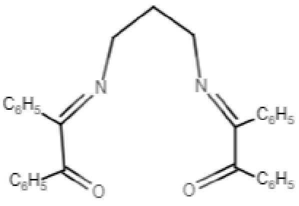
Boraey and Gammal[4] pointed out the importance of template synthesis. The template condensation for the preparation of macrocyclic ligands often offers selective routes towards products that are not formed without metal ions[13]. The template condensation methods lie at the heart of macrocyclic chemistry[14]. Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated during the template reactions[15]. The transition metal ions are used as the template reactions[16].The transition metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products[17].

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[18]. 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 [19-21]. 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[22].

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 size[23]. 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 regard[24-27]. 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 complexes[28]. During the template synthesis of Fe (II), Co(II), and Ni(II) complexes of MePhTIM, Eggleston, and Jackels[29] have ruled out the possibility of formation of diazepine (II), a heterocyclic product of 1+1 condensation based on ^{1}H NMR studies. Henery et al.[30] 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 Ni (II) tetraazamacrocyclic complexes

S. N.	**Complex**	**IR Absorption Bands(cm^{-1})**		**μ_{eff} (B.M.)**	**Molar Conductance ($Ohm^{-1}cm^2mol^{-1}$) of 10^{-3} M sol.**
		υ C=N	**Ni-Cl**		
1	[Ni (Me_2Et_2 [14] tetraene N_4) Cl_2]	1590	290	3.13	9.3
2	[Ni (Me_2Et_2 [16] tetraene N_4) Cl_2]	1580	290	3.30	11.8
3	[Ni (Me_2Et_2 [20] tetraene N_4) Cl_2]	1580	290	3.21	12.7
4	[Ni (Me_2Et_2 [24] tetraene N_4) Cl_2]	1580	290	3.15	14.8
5	[Ni (Me_2Et_2 [32] tetraene N_4) Cl_2]	1580	290	3.24	-

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 -NH_2 group[31-33]. All the complexes show a medium intensity absorption band in the region 1580-1590 cm^{-1} which can be assigned to υ C=N, indicating the condensation of 2,3-pentanedione and diaminoalkanes. For TIM complexes[34] of Cu (II) υ C=N has been reported at 1600-1620 cm^{-1}. In the IR spectra of Cr (III), Fe (III), and Co(III) complexes of macrocycles[35] derived from dihydrazides and aromatic diketones, absorption bands at 1580-1640 cm^{-1} have been assigned to υ C=N complexes show bands at ~ 290 cm^{-1} due to the coordinated chloro group. Rana and co-workers [36] Ni-Cl band at ~ 290 cm^{-1}in Ni (II) complexes of tetraazamacrocycles derived from 2,4-pentanedione and m-phenylenediamine. Malik et al.[37] have reported a band at 280 cm^{-1} for υ Ni-Cl in Ni (II) complexes of the macrocycle derived from 2,3-butanedione and 2,6-diaminopyridine.

Conductance

Molar conductance of 10^{-3} M solutions of the complexes in dimethylsulphoxide (DMSO) is observed in the range 9.2 – 17.5 $ohm^{-1}cm^2mol^{-1}$ [Table-2], supporting their nonelectrolyte behaviour[38]. Thus, the chloro groups are coordinated to the Nickel atom giving trans-octahedral geometry. Ito et al.[39] 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-tetra azacyclooctacosane)[40].

Magnetic moments

The effective magnetic moments of Ni (II) macrocyclic complexes are given in Table-2. The observed μ_{eff}values at room temperature (~ 298^0K) range from 3.22 – 3.29 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 coworkers[37] 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.[41]

CONCLUSIONS

In the present communication, five large rings (14,to 32–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, and their stability is due to the flexibility of large chelate rings.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

REFERENCES

[1] M.Fujiwara, T. Matsushita, and T. Shono, Polyhedron 3,1357(1984).

[2] Sulesh Chandra, Monika Tyagi, and Swati Agarwal, J.Serb.Chem.Soc.75(7),935(2010).

[3] S.R.Ghanti,J.B. Badiger, S. Kulkarni, S.V. Halse and S.D. Angadi, Int.J.Pharma,Bio.Sci.Vol.4(3)1002(2013).

[4] Hanna A. EL-Boraey and Ohyla A. EL-Gammel, Open Chemistry Journal,5,51(2018).

[5] R.N. Prasad, A.K. Gupta, P.K. Rai, Ann. Chim(Rome)81,85 (1991).

[6] P.K. Rai, A.K. Gupta, R.N. Prasad, Z. Naturforsch.47b,1701 (1992).

[7] R.N. Prasad, A.K. Gupta, P.K. Rai, Egyptian J. Chem. 36,341 (1993).

[8] P.K. Rai, A.K. Gupta, R.N. Prasad, Bull. Korean Chem. Soc. 14,179 (1993).

[9] P.K. Rai, R.N. Prasad, Synth. React. Inorg. Met.-org. Chem. 24,749 (1994).

[10] Raghu N. Prasad and Mala Mathur, J. Sarb. Chem. Soc. 67,(12)1825 (2002).

[11] Ajay Kumar Gupta, Global Thought,20,53April(2021).

[12] Ajay Kumar Gupta, Global Thought,21,1, July(2021).

[13] S.G. Kang, J. Song, J.H. Jeong, Inorg.Chim.Acta,357,605(2004).

[14] N.F. Curtis, Coord.Chem.Rev.3,3(1968).

[15] M.F. Niasari, F. Daver, Inorg.Chem.Commun.9,175(2006).

[16] R.N. Prasad, S. Gupta, S. Jangir, Indian Chem. Soc.84,1191(2007).

[17] T.A. Khan, S.S. Hasan, A.K. Mohamed, M. Shakir, IndianJ.Chem.,37,1123(1998).

[18] C.J. Pederson, J. Am. Chem. Soc. 89,7017 (1967).

[19] J.P. Collman and P.W. Schneider, Inorg. Chem. 5,1380 (1966).

[20] V.L. Goedken, J. Molin-Case and G.G. Christoph, Inorg. Chem. 12,2894 (1973).

[21] J.L. Hoard, M.J. Hamor, T.A. Hamor, and W.S. Gaughey, J. Am. Chem. Soc. 87,2313 (1965).

[22] L.Y. Martin, L.J. DeHayes, L.J. Zompa, and D.H. Busch, J. Am. Chem. Soc. 96,4046 (1974).

[23] R.D. Hancock, M.P. Ngwenya, A. Evers, P.W. Wade, J.C.A. Boeyens and S.M. Dobson, Inorg. Chem. 29,264 (1990).

[24] V.J. Thom and R.D. Hancock, J. Chem. Soc. Dalton Trans.,1877(1985).

[25] R.D. Hancock, Pure Appl. Chem. 58,1445 (1986).

[26] R.D. Hancock and A.E. Martell, Comments Inorg. Chem. 6,237 (1988).

[27] R.D. Hancock and M.P. Ngwenya, J. Chem. Soc. Dalton Trans.,2911 (1987).

[28] V.J. Thom, C.C. Fox, J.C.A. Boeyens and R.D. Hancock, J. Am. Chem. Soc. 106,5947 (1984).

[29] D.S. Eggleston and S.C. Jackels, Inorg. Chem. 19,1593 (1980).

[30] W.A. Welsh, G.J. Reynolds, and P.M. Henry, Inorg. Chem. 16,2558 (1977).

[31] R. Saraswat, S. Singh, V.B. Rana,J.Indian Chem.Soc.73,478(1996).

[32] 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).

[33] S.M. Nelson, M. McCann, C. Stevenson, M.G.B. Drew, J.Chem.Soc.Dalton Trans.1477(1979).

[34] M.J. Marony, N.J. Rose, Inorg.Chem.23,2252(1984).

[35] R. Sarswat, V.B. Rana, J.Indian Chem.Soc.74,493(1998).

[36] V.B. Rana, P Singh, and M.P. Teotia, Polyhedron 1,377 (1982).

[37] W.U. Malik, R. Bembi, and R. Singh, Polyhedron 2,369 (1983).

[38] W.J. Geary, Coord. Chem. Rev. 7,81 (1971).

[39] M. Sugimoto, J. Fujita, H. Ito, K. Toriumi and T. Ito,Inorg.Chem.22,955(1983).

[40] D.W. Reichgott and N.J. Rose, J. Am. Chem. Soc. 99,1813 (1977).

[41] L.Y. Martin, C.R. Sperati and D.H. Busch, J. Am. Chem. Soc. 99,2968 (1977).