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Synthesis of a Macrocyclic Schiff Base Ligand H_4 mac^{1-3} and Their Nickel (II) Complexes

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Abstract

Macrocyclic complexes of the type [Ni H_2 mac^{1-3}] containing a pair of alpha diimine groups were synthesized by metal ion catalysed template condensation of bis- oxalo dihydrazide Ni(II) complexes with biacetyl, benzil or furil. Cyclisation has taken place due to organizational role of metal ions.Characterization of the complexes has been done on the basis of elemental analysis for molecular formula, IR spectra for node of bonding, magnetic moment and electronic spectra for stereochemistry & molar conductivity for electrolytic nature of the complexes. Amidic nitrogens have taken part in coordination.Structure of the complexes has been found to be square planar.Complexes are non- electrolytic in nature.

H_4mac^1=1,2,5,6,9,10,13,14-octaaza-7,8,15,16-tetraoxo-3,4,11,12-tetramethyl-1,6,9,14-tetrahydro-cyclohexadeca-2,4,10,12-tetraene

H_4mac^2=1,2,5,6,9,10,13,14-octaaza-7,8,15,16-tetraoxo-3,4,11,12-tetrafuryl-1,6,9,14-tetrahydro-cyclohexadeca-2,4,10,12-tetraene

H_4mac^3=1,2,5,6,9,10,13,14-octaaza-7,8,15,16-tetraoxo-3,4,11,12-tetraphenyl-1,6,9,14-tetrahydro-cyclohexadeca-2,4,10,12-tetraene

Key Words: Macrocyclic complexes, Oxalodihydrazide, Nickel (II)

1.0 INTRODUCTION

Extensive studies have been done in recent years on 12-, 14-, 16 - & 18 membered mononuclear metal(II) complexes with Schiff base macrocyclic ligands derived by condensation of dicarbonyls & diamines [1-21].Consequently a series of 16- membered Ni(II) macrocyclic complexes by using bis-oxalodihydrazide Ni (II) complexes as precursors to react with active carbonyl function such as diacetyl, benzil or furil.

2.0 EXPERIMENTAL

2.1 Materials & Methods

Hydrazine hydrate & Ni (II) acetate tetrahydrate was of BDH quality. The oxalodihydrazide was prepared according to literature method[22]. Diketone were Aldrich reagents and were used as obtained.

2.2 PREPARATION OF THE COMPLEXES

[Ni (H_2 mac^1)]

About 2.4g (0 .02 mol) of oxalodihydrazide was dissolved in 200ml of hot water. A solution of nickel (II) chloride 6-hydratye (2.4 g , 0 .01 mol) in 100 ml of water was added to the above mentioned solution. The result in greenish-blue solution was refluxed. About 1.8 ml of diacetyl (0.02 mol) diluted with 25 ml of rectified sprit was added drop by drop to the refluxing solution. The color of the reaction mixture changed

almost immediately to blood-red and a red compound separated out. The reflux was allowed to continue for 3h. The resulting product was filtered, washed with warm water and methanol and dried in vacuo. The yield was ~ 90%. It was analyzed as Ni ($C_{12}H_{14}N_8O_4$).

[Ni (H_2 mac^2)]

A solution of 1.9g (0.016 mol) of oxalodihydrazide in 150 ml of hot water was treated with 100 ml of aqueous solution of nickel (II) chloride 6-hydrate (1.9g,0.008mol). The resulting greenish blue solution was refluxed while 3.04 g (0.016 mol) of small quantities over a period of 10h. The reflux was continued for10h. The color of reaction mixture gradually deepend and a chocolate red compound separated out. It was filtered, washed with methanol and dried in air. It was analyzed as Ni ($C_{24}H_{14}N_8O_4$).

[Ni (H_2 mac^3)]

About 1.9 g (0.016 mol) of mzidealondihydra was dissolved in 200 ml of hot water . An aqueous solution of nickel (II) chloride 6-hydrate (1.6 g , 0.008 mol)in 100ml of water was added to the malonodihydrazide solution . The resulting greenish-blue solution was refluxed while 3.36 g (0.016 mol) of benzyl dissolved in minimum volume of hot ethanol was added to it in small portions. The color of the reaction mixture gradually changed to red and a red solid separated . The reflux was allowed to continue for 24h for optimum condensation and cyclization. The resulting red colored solid was filtered ,washed with warm water and methanol, and dried in air. It was analyzed as Ni ($C_{32}H_{22}N_8O_4$).

Analytical data are represented in Table I

Compounds	Color	% of elements Found (Calculated)			
		Ni	% C	% H	% N
[Ni (H_2 mac^1)] [Ni ($C_{12}H_{14}N_8O_4$)]	Yellow	13.91 (13.94)	39.58 (29.94)	4.02 (4.31)	26.41 (26.61)
[Ni (H_2 mac^2)] [Ni ($C_{24}H_{14}N_8O_8$)]	Orange brown	9.03 (9.33)	49.33 (49.63)	2.59 (2.88)	17.74 (17.81)
[Ni (H_2 mac^3)] [Ni ($C_{32}H_{22}N_8O_4$)]	Pink red	8.69 (8.77)	60.95 (61.01)	4.12 (3.91)	16.36 (16.74)

3.0 RESULT AND DISCUSSION

3.1 Synthesis

The synthetic reactions taking place for the preparation of the complexes can be shown asin scheme I. Characterization of the complexes has been done on the basis of IR spectra electronic spectra & magnetic moment and conductivity.

3.2 IR SPECTRA

The infrared spectra of the complexes are well resolved and the structurally dominant bands are recorded in the tables II. The

spectra are clearly marked by a strong band in the region 3350 to 3200 cm^{-1} indicating the presence of NH groups of one kind belonging to the amide functions. The lack of multiplicity of N-H stretching vibrations in this region further illustrates that the terminal $–NH_2$ groups of the diketons to yield the macrocyclic complexes.

In the fingerprint regions, the macrocyclic complexes show differences in their spectral features from one another and from parent precursors. The profiles of the spectra are strikingly dependent on the subsequent on the α- diimine moieties, nevertheless the Vibrational bands corresponding to amide I , amide II, amide III and C-N stretching bands are clearly displayed in the regions 1680 – 1630 cm^{-1}, 1570- 1515 cm^{-1}, -1270 cm^{-1} and 1220 -1020 cm^{-1} respectively.

The Vibrational spectra of [Ni (H_2 mac^1)]complexes shows a well defined band near 1600 cm^{-1} which possesses the attributed of C….N stretching vibrations. For [Ni (H_2 mac^2)] and [Co(H_2 mac^3)], a large number of band are observed in the range 1600 -1400 cm^{-1}. The band appear in a close proximity and this is the region where we expect ring brathing vibrations of furyl and phenyl groups.

Although from intensity consideration, we have been able to identify C…N stretching vibration near 1600 cm^{-1}, for the [Ni (H_2 mac^3)]. However, the band is not distinct in case of [Ni (H_2 mac^2)]. Additional bands have been observed in the region 900-600 cm^{-1} due to out of plane deformation vibration for phenyl and furyl group of the macrocyclic complexes besides some of the bands observed for the dihydrazide moieties.

TABLE II

Principal infrared spectra bands (in cm^{-1}) for [Ni (H_2 mac^{1-3})]

[Ni (H_2 mac^1)]	[Ni (H_2 mac^2)]	[Ni (H_2 mac^3)]	Band Assigned
3315	3310	3320	ν(N-H)
2930	2920	3040	ν(C-H)
1685	1670	1070	ν(C… H) amide I
1600	1570	1610	ν(C… N)
1515	1550	1570	amide II
1435	1470	1500	ν_{as} (C-CH_3)
1370	1400	1490	ν_s (C-CH_3)
1310	1390	1460	δ(CH_3)

1265	1330	1260	amide III
1085	1270	1180	v(C-N)
1130	1160	1000	
1045	1030	950	
1010	930	845	
970	890	805	Skeletal vibration
890	875	775	
835	865	715	
790	835	700	
680	800	615	
610	760	-	

The spectra clearly demonstrate template condensation of the bis – oxalodihydrazide complexes with the α diketons. The structural features of these complexes involve bonding of amide group with the metal centers and the macrocyclic ligand exits in a dianionic form. The di-anionic form of the ligand for the group of macrocycles appear to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands. this interaction results in the enclosing of the metal ion in the macrocyclic cavity forming 5- membered chelate ring with the amide moieties and 7- membered ring involving αdiimine groups.

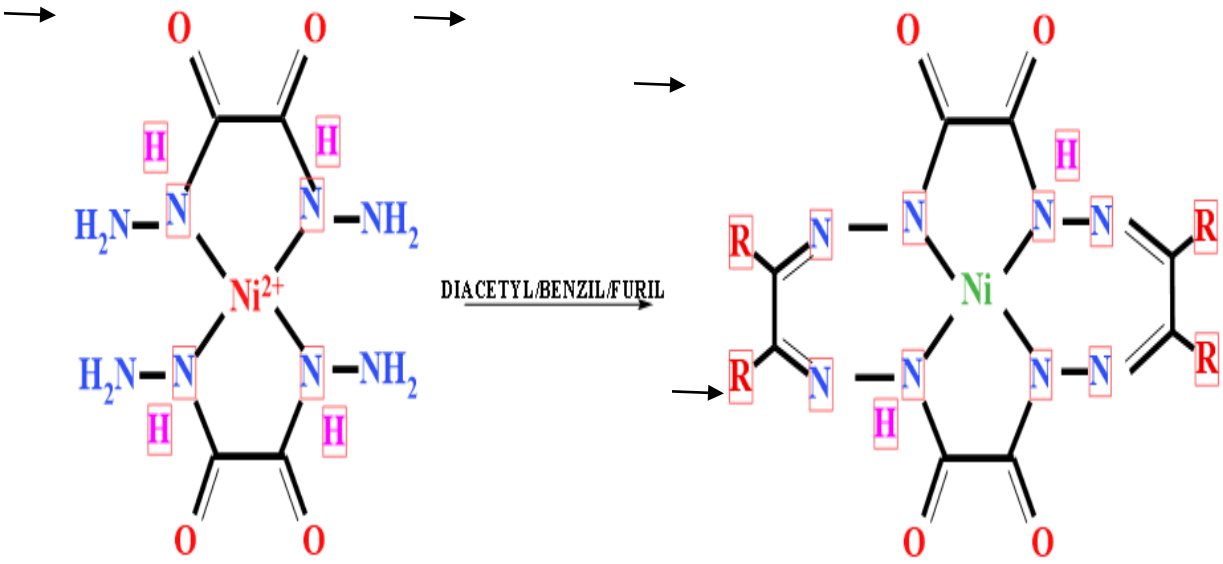
TABLE III

Electronic spectral bands (in cm^{-1}) of the macrocyclic Nickel (II) complexes

Sl.no	Complexes	L.F.Bands		C.T.Band
01	Ni ($C_{12}H_{14}N_8O_4$)	20000	23000	28500
02	Ni ($C_{24}H_{14}N_8O_8$)	19300	22700	27700
03	Ni ($C_{32}H_{22}N_8O_4$)	20800	22800	27300

3.3 ELECTRONIC SPECTRA & MAGNETIC MOMENT

The nickel (II) macrocyclic complexes are diamagnetic. The electronic spectra of the complexes have been measured in the visible and the ultraviolet regions in solid state. The absorption bands are recorded in table 4.15. Most of the diamagnetic nickel (II) complexes are known to possess square planar geometry. The electronic ground state for such complexes is the spin singlet $^1A_{1g}$. The singlet state ground term arises between dx^2- y^2 (b_{1g}) and d_{xy} (b_{2g}) is large. Majority of square planar diamagnetic nickel (II) complexes exhibit two transitions. The first one is usually observed in the region 15000 – 25000 cm^{-1} and is strong in intensity. This band is assigned to the transition $^1A_{1g}$ $^1A_{2g}$. The second band also normally having high intensity is found to occur in the region 28000 -30000 cm^{-1} and can be assigned to the transition $^1A_{1g}$ $^1B_{1g}$. The electronic spectra of the present diamagnetic macrocyclic complexes are dominated by two intense bands in the visible as well as in ultraviolet region. The first band for this group of complexes is observed in the region 19000 – 21000 cm^{-1} and second band is observed in the region 28000 – 29000 cm^{-1}. The transition are assigned to $^1A_{1g}$ $^1A_{2g}$ and $^1A_{1g}$ $^1B_{1g}$ under a square planar environment having NiN_4 chromophore. The higher energy band is however, found to be more intense and the intensity is believed to arise due to metal_ ligand (π^*) charge – transfer transition.



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