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SYNTHESIS AND SPECTRAL STUDIES OF NICKEL (II) COMPLEXES WITH 18-MEMBERED MACROCYCLIC LIGAND DERIVED FROM MALONODIHYDRAZIDE AND DIKETONES

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ABSTRACT

18-Membered macrocyclic complexes of Ni (II) of the type [Ni(H_2Cz)] have been synthesized and characterized on the basis of spectral, magnetic and conductivity studies. The macrocyclic ligands H_4Cz are tetrabasic having four imido hydrogen but behave in a dibasic manner. Out of eight nitrogens, four are imido and four are imino. Ligands utilize four imido nitrogens for square planar coordination forming four 7 : 6 : 7 : 6 chelate rings giving rise to a 18 membered macrocyclic framework. Nickel (II), complexes having red color are diamagnetic. Low molar conductivity values in the range 7-12 ohm^{-1} cm^2 mol^{-1} suggest complexes to be non-electrolytic in nature. High dilute conditions have been employed in the synthesis of macrocyclic complexes in order to dispense with polymerization reaction.

Key words: Conductivity, Malonodihydrazide complexes, Macrocyclization, Spectral study, Orientation effect.

INTRODUCTION

Worldwide attention has been given to studies on macrocyclic complexes with tetraaza system[1-5]. Consequently, in the present communication, in continuation of our earlier interest[6-9], nickel (II) macrocyclic complexes (obtained by macrocyclization) between bis-(malonodihydrazide) metal (II) precursors with diketones such as 1-phenyl propane-1,2, dione: butane-2, 3-dione: pentane-2, 3-dione: and octane 2, 3-dione have been reported. Stoichiometry of the complexes have been found to be of the type [Ni(H_2Cz$^{1-4}$)]; H_4Cz^1 = 8, 18-dimethyl-9, 17-diphenyl- 3, 5, 12, 14-tetraoxa, 1, 2, 6, 7, 10, 11, 15, 16-octaaza

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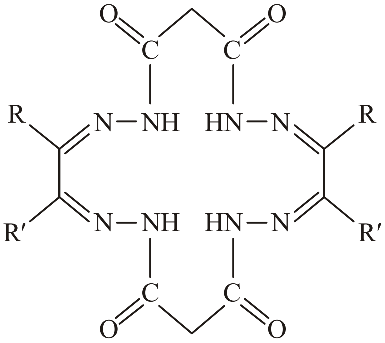
cyclooctadeca (18), 7, 9, 16-tetraene, H_4Cz^2 = 8, 9,17, 18,-tetramethyl- 3, 5, 12, 14-tetraoxa, 1, 2, 6, 7, 10, 11, 15, 16-octaaza cyclooctadeca (18), 7, 9, 16-tetraene; H_4Cz^3 = 8, 18-dimethyl-9, 17- diethyl-3, 5, 12, 14-tetraoxa, 1, 2, 6, 7, 10, 11, 15, 16-octaaza cyclooctadeca (18), 7,9, 16-tetraene and H_4Cz^4 = 8, 18-dimethyl-9, 17-dipentyl-3, 5, 12, 14-tetraoxa, 1, 2, 6, 7, 10, 11, 15, 16-octaaza cyclooctadeca[1] (18), 7, 9, 16-tetraene.



R = CH_3; R' = CH_3, C_2H_5, C_5H_{11} or C_6H_5

Fig. 1: Structure of ligand H_2Cz

EXPERIMENTAL

All solvents and chemicals were of reagent grade. Solvents were dried over 4Å molecular sieves and degassed with dry nitrogen before use. Synthesis and manipulation were carried out under nitrogen atmosphere.

Nickel (II) acetate tetrahydrate was prepared by dissolving the carbonate in acetic acid of BDH quality followed by crystallization. Malonodihydrazide was prepared according to literature procedure[10] and recrystallized several times before use.

Although the synthetic procedure of these compounds are reported in the literature, we developed a new method. Preparation of one of the complex is described here.

[Ni(H_4Cz^4)] 8, 18-Dimethyl-9, 17-dipentyl- 3, 5, 12, 14-tetraoxa- 1, 2, 6, 7, 10, 11, 15, 16-octaaza cyclooctadeca[1] (18), 7, 9, 16-tetraene

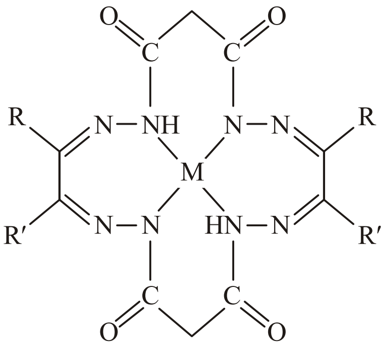
About 2.4 g (0.02 mol) of malonodihydrazide was dissolved in 200 mL of hot water. A solution of Ni (II) chloride hexahydrate (2.4 g, 0.01 mol) in 100 mL of water was added to malonodihydrazide solution. A greenish blue solution was formed and it was refluxed for an hour. Octane-2, 3-dione (2.84 g, 0.02 mol) dissolved in a minimum amount of hot ethanol was added to the refluxing solution in small portions. The reflux was continued for a day. A mauve coloured solid was obtained. It was cooled, filtered and washed with warm water and hot ethanol and dried in vacuo. The dry solid was analysed. Analytical data, colour, magnetic moment and conductivity data have been shown in Table 1.

Table 1: Analytical, colour, magnetic moment and molar conductivity data for nickel (II) macrocyclic complexes of the type [Ni(H_2Cz)]

Compound (Colour)	% Analysis found (Calculated)				μ_{eff}	Conductivity (Ω^{-1}cm^2 mol^{-1})
	M	C	N	H		
Ni(H_2Cz^1) (Pink)	14.71 (14.75)	41.72 (41.89)	27.86 (27.90)	4.95 (4.99)	Diamagnetic	8
Ni(H_2Cz^2) (Violet)	10.82 (10.89)	52.54 (52.46)	20.63 (20.58)	4.39 (4.44)	Diamagnetic	9
Ni(H_2Cz^3) (Mauve)	12.99 (13.19)	42.64 (42.68)	24.88 (24.98)	5.33 (5.34)	Diamagnetic	10
Ni(H_2Cz^4) (Yellow)	10.32 (10.37)	45.63 (45.99)	19.46 (19.38)	6.22 (6.29)	Diamagnetic	12

RESULTS AND DICUSSION

Macrocyclic complexes (Fig. 2) containing a pair of α-diimine groups were synthesized by metal ion assisted template condensation of bis-(malonodihydrazide) (II) complexes with vicinal diketones like 1-phenyl propane-1,2,dione; butane-2,3-dione; pentane-2,3-dione; and octane-2, 3-dione;



M = Ni (II); R = CH_3; R’ = CH_3, C_2H_5, C_5H_{11}, C_6H_5

Fig. 2: Structure of complex

The cyclisation reactions with diketones take place readily and was marked by rapid change of colour. Besides, these reagents being comparatively less soluble in alcohol, dropwise addition of the ketones was carried out at longer intervals to avoid their precipitation and the reaction was likewise followed by observing gradual change of intensity of colour as the reaction progressed.

Infrared spectra

Spectra have been recorded in the range 4000-400 cm^{-1} and important bands have been reported in Table 2. The spectra are clearly marked by a strong band in the region 3350 to 3200 cm^{-1} testifying 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 parent dihydrazide complexes have entered into condensation with α-diketones to yield the macrocyclic complexes.

Table 2: Important IR spectral bands (cm^{-1}) of malonodithydrazide, precursors [Ni(dihydrazide)$_2$Cl$_2$] and macrocycles [Ni(H$_2$Cz)]

Compound	V_{N-H}	$^{V}S(NH_2)$	$^{V}S(NH_2)$	Amide I	Amide II	Amide III	V_{C-N}	V_{M-X}
Malonodihydrazide	3290	3150	3015	1690	1620	1285	1120	
[Ni(dihyd)$_2$Cl$_2$]	3350	3155	3010	1630	1615	1260	1100	460
[Ni(H$_2$Cz^1)]	3380	3200		1650	1540	1200	1120	465
[Ni(H$_2$Cz^2)]	3385	3205		1645	1545	1220	1110	470
[Ni(H$_2$Cz^3)]	3375	3210		1640	1540	1215	1115	465
[Ni(H$_2$Cz^4)]	3360	3205		1655	1550	1210	1110	460

In the fingerprint region, 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 substituents 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} and 1270-1220 cm^{-1}, respectively.

The vibrational spectra of complexes show a well-defined band near 1680 cm^{-1}, which posesses the attributes of C$\equiv$O stretching vibrations. A large number of bands are observed in the range 1600-1400 cm^{-1}. The bands appear in close proximity and this is the region, where we expect ring-breathing vibrations of phenyl groups. Although from intensity considerations, we have been able to identify C═N stretching vibrations near 1600 cm^{-1}, for the $Me_2Ph_2O_4$ [16] tetraenato-(2) $N_4(N_4)$-Ni (II) complexes; however, this band is not, distinct.

In the region 900-300 cm^{-1}, additional bands due to out-of-plane deformations for phenyl groups of the macrocyclic complexes were observed besides some of the bands observed for the dihydrazide moieties. The spectra clearly demonstrate template condensation of the bis-(malonodihydrazide) complexes with the α-diketones. The structural features of these complexes involve bonding of amide groups with the metal centres and the macrocyclic ligand exists in a dianionic form. The dianionic from of the ligands for the group of macrocycles appears to be one of the important factors for electrostatic interaction of the metal ion with the macrocyclic ligands, enclosing the metal ion in the macrocyclic cavity forming 6-membered chelate rings with the amide moieties and 7-membered rings involving α-diimine groups. A strong band in the region 460-470 cm^{-1} in the spectra of all the macrocyclic complexes has been assigned to M-N stretching vibration[11].

Electronic spectra and magnetic properties

The nickel (II) macrocyclic complexes $[Ni(H_2Cz)]$ are diamagnetic and their electronic spectra show two intense bands one in the region 19000 to 21000 and another near 27000 cm^{-1}. The transitions are assigned to $^1A_{2g} \leftarrow {}^1A_{1g}$ and $^1B_{1g} \leftarrow {}^1A_{1g}$ under a square planar environment having NiN_4 chromophore. The higher energy band is, however, more intense and the intensity is believed to arise due to metal → ligand π* charge transfer transitions[12].

Table 3: Electronic spectral bands (in cm^{-1}) of the macrocyclic nickel (II) complexes of the type $[Ni(H_2Cz)]$

Complexes	L.F. Bands	C. T. Band	μ_{eff} (B.M.)
$Ni(H_2Cz^1)$	20,000 25,000	28,000	Diamagnetic
$Ni(H_2Cz^2)$	20,800 25,200	28,000	Diamagnetic
$Ni(H_2Cz^3)$	19,300 22,500	27,000	Diamagnetic
$Ni(H_2Cz^4)$	20,500 22,700	27,500	Diamagnetic

Molar conductivity measured in DMF solution lies in the range 7-12 Ω^{-1} cm^2 mol^{-1} and indicate the macrocyclic complexes to be non-electrolytic in nature.

On the basis of information received from spectral, magnetic and conductivity studies, macrocycles have been assigned structure as shown in Fig. 2.

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