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Metal Dihydrazide Precursors as Building Blocks for New Macrocyclic Architectures with Tetradentate Octaaza Dibasic Ligands

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A series of 16-membered macrocyclic complexes of cobalt(II) and nickel(II) of the type $[M(H_2Cy^{1-4})]$ have been synthesized and characterized on the basis of spectral, magnetic and conductivity studies. The macrocyclic ligands H_4Cy^{1-4} are tetrabasic having four imido hydrogen but behave in a dibasic manner. Out of eight nitrogens, four imido and four imino, ligands utilize four imido nitrogens for square planar coordination forming four 7:5:7:5 chelate rings giving rise to a 16 membered macrocyclic framework. The red coloured nickel(II) complexes are diamagnetic in nature, whereas cobalt(II) complexes with chocolate brown colour are of low spin type. Low molar conductivity values in the range 3-7 ohm^{-1} cm^2 mol^{-1} suggest complexes to be non-electrolytic in nature. High dilute conditions generally employed in the synthesis of macrocyclic complexes in order to dispense with polymerization reaction have been avoided in the present study and advantage of orientation effect has been taken to have high yield.

Key Words: Oxalodihydrazide complexes, Macrocyclization, Spectral, Electrochemical study, Orientation effect.

INTRODUCTION

It is interesting to note that most of the macrocyclic ligands responsible for important natural phenomena such as photosynthesis by chlorophylls, respiration by hemoglobin and colour production by phthalocynins have four common features: (1) macrocycles are 16-membered, (2) have N_4-donor systems, (3) have conjugated π-electron system and (4) have different peripheral substituents.

Worldwide attentions have been given to studies on macrocyclic complexes with tetraaza system[1-6]. Consequently, we in the present communication, in continuation of our earlier interest[7-10], are reporting a series of cobalt(II) and nickel(II) macrocyclic complexes obtained by macrocyclization between *bis*(oxalodihydrazide)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. Stoichiometry of the

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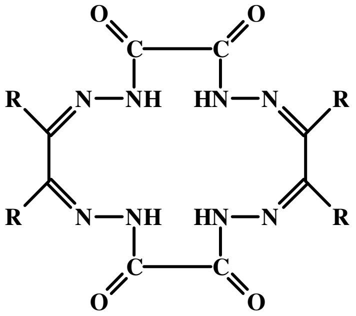
complexes have been found to be of the type [M(H_2Cy^{1-4})]; where M = Co(II) and Ni(II); H_4Cy^1 = 7,16-dimethyl-8,15-diphenyl- 3,4,11,12-tetraoxo-1,2,5,6,9,10,11,14-octaaza-cyclohexadeca-1(16),6,8,13-tetraene; H_4Cy^2 = 7,8,15,16-tetramethyl-3,4,11,12-tetraoxo-1,2,5,6,9,10,11,14-octaaza-cyclohexadeca-1(16),6,8,13-tetraene; H_4Cy^3 = 7,16-dimethyl-8,15-diethyl-3,4,11,12-tetraoxo-1,2,5,6,9,10,11,14-octaaza-cyclohexadeca-1(16),6,8,13-tetraene; H_4Cy^4 = 7,16-dimethyl-8,15-dipentyl-3,4,11,12-tetraoxo-1,2,5,6,9,10,11,14-octaaza-cyclohexadeca-1(16),6,8,13-tetraene.



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

Fig. 1

EXPERIMENTAL

All solvents and chemicals were of reagent grade. Solvents were dried over 4 Å 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. Oxalodihydrazide was prepared according to literature procedure[11] 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.

7,8,15,16-Tetramethyl-3,4,11,12-tetraoxo-1,2,5,6,9,10,11,14- octaaza-cyclohexadeca-1(16),6,8,13-tetraenato nickl(II) [Ni(H_2Cy^2)]: About 2.4 g (0.02 mol) of oxalodihydrazide was dissolved in 200 mL of hot water solution of metal(II) chloride hexahydrate (2.4 g, 0.01 mol) in 100 mL of water was added to oxalodihydrazide solution. A greenish blue solution was formed and it was refluxed for 1 h. Butane-2,3-dione (1.72 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 analyzed. 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) AND COBALT(II) MACROCYCLIC COMPLEXES OF THE TYPE $[M(H_2Cy^{1-4})]$

Compound (colour)	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	Ω^{-1} cm^2 mol^{-1}
	M	C	N	H		
$Co(H_2Cy^1)$ (Brown)	11.34 (11.41)	51.00 (51.06)	21.64 (21.66)	3.34 (3.48)	2.2	3
$Co(H_2Cy^2)$ (Chocolate)	14.45 (15.01)	36.58 (36.64)	28.45 (28.49)	3.52 (3.56)	2.3	7
$Co(H_2Cy^3)$ (Red)	14.00 (14.01)	39.87 (39.90)	26./56 (26.60)	4.25 (4.27)	2.6	5
$Co(H_2Cy^4)$ (Brown)	11.66 (11.68)	47.50 (47.52)	22.15 (22.17)	3.93 (3.94)	2.1	4
$Ni(H_2Cy^1)$ (Pink)	11.35 (11.36)	51.06 (51.09)	21.65 (21.67)	3.45 (3.48)	Diamag.	3
$Ni(H_2Cy^2)$ (Violet)	14.90 (14.94)	36.63 (36.66)	28.50 (28.52)	3.50 (3.56)	Diamag.	4
$Ni(H_2Cy^3)$ (Mauve)	13.91 (13.95)	39.90 (39.93)	26.60 (26.62)	4.21 (4.27)	Diamag.	4
$Ni(H_2Cy^4)$ (Yellow)	11.62 (11.63)	47.53 (47.55)	22.17 (22.19)	5.89 (5.94)	Diamag.	5

RESULTS AND DISCUSSION

Macrocyclic complexes (Fig. 2) containing a pair of α-diimine groups were synthesized by metal ion assisted template condensation of *bis*(oxalodihydrazide) (**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.

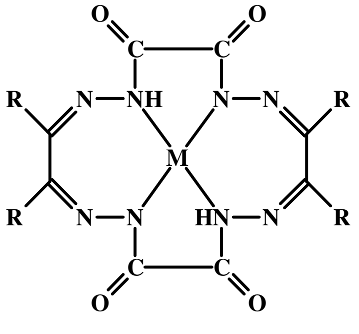


Fig. 2. M = Ni(II) and Co(II); R = CH_3; R' = CH_3, C_2H_5, C_5H_{11}, C_6H_5

The cyclization reactions with diketones takes place readily and was marked by rapid change of colour. 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 recorded in Table-2. The spectra are clearly marked by a strong band in the region 3350-3200 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 the parent dihydrazide complexes have entered into condensation with α-diketones to yield the macrocyclic complexes.

TABLE-2
KEY IR SPECTRAL BANDS (cm^{-1}) OF OXALODIHYDRAZIDE, PRECURSORS [M(DIHYDRAZIDE)$_2$Cl$_2$] AND MACROCYCLES [M(H$_2$Cy$^{1-4}$)]

Compound	ν(N-H)	$\nu_s(NH_2)$	$\nu_{as}(NH_2)$	Amide I	Amide II	Amide III	ν(C-N)	ν(M-X)
Oxalhyd.	3290	3150	3015	1690	1620	1285	1120	1050
[Ni(dihyd)$_2$Cl$_2$]	3350	3155	3010	1630	1615	1260	1100	460
[Ni(H$_2$Cy^1)]	3380	3200	–	1650	1540	1200	1120	465
[Ni(H$_2$Cy^2)]	3385	3205	–	1645	1545	1220	1110	470
[Ni(H$_2$Cy^3)]	3375	3210	–	1640	1540	1215	1115	465
[Ni(H$_2$Cy^4)]	3360	3205	–	1655	1550	1210	1110	460
[Co(dihyd)$_2$Cl$_2$]	3320	3150	3000	1675	1620	1250	1120	470
[Co(H$_2$Cy^1)]	3340	3180	–	1640	1535	1210	1110	455
[Co(H$_2$Cy^2)]	3335	3185	–	1645	1530	1215	1105	450
[Co(H$_2$Cy^3)]	3340	3180	–	1650	1535	1220	1125	460
[Co(H$_2$Cy^4)]	3345	3190	–	1640	1540	1210	1110	465

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 1655-1630, 1620-1530, 1260-1210 and 1120-1105 cm^{-1}, respectively.

The vibrational spectra of complexes show a well-defined band near 1680 cm^{-1} which possesses the attributes of C···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-) $N_4(N_4)$- metal(II) complexes, this band is not, however, distinct.

In the region 900-600 cm^{-1} we observe additional bands due to out-of-plane deformations for phenyl groups of the macrocyclic complexes besides some of the bands observed for the dihydrazide moieties. The spectra clearly demonstrate template condensation of the *bis*(oxalodihydrazide) 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 form 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 5-membered chelate rings with the amide moieties and 7-memebered rings involving α-diimine groups. A strong band in the region 470-460 cm^{-1} in the spectra of all the macrocyclic complexes has been assigned to M-N stretching vibration[12].

Electronic spectra and magnetic properties: The nickel(II) macrocyclic complexes [Ni(H_2Cy^{1-4})] 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[13].

TABLE-3
ELECTRONIC SPECTRAL BANDS (cm^{-1}) OF THE MACROCYCLIC NICKEL(II) AND COBALT(II) COMPLEXES OF THE TYPE [M(H_2Cy^{1-4})]

S. No.	Complexes	L.F. Bands	C.T. Band	μ_{eff} (BM)
1	Ni(H_2Cy^1)	20,000 25,000	28,000	Diamagnetic
2	Ni(H_2Cy^2)	20,800 25,200	28,000	Diamagnetic
3	Ni(H_2Cy^3)	19,300 22,500	27,000	Diamagnetic
4	Ni(H_2Cy^4)	20,500 22,700	27,500	Diamagnetic
5	Co(H_2Cy^1)	19,000	25,000	2.19
6	Co(H_2Cy^2)	19,500	24,800	2.37
7	Co(H_2Cy^3)	19,600	25,600	2.65
8	Co(H_2Cy^4)	19,400	25,300	2.48

The cobalt(II) complexes are of low spin type and are found to possess magnetic moments in the range 2.2 to 2.7 BM. Electronic spectra of the complexes are similar and most of them exhibit two transitions near 20,000 and 25000 cm^{-1}, respectively. The lower energy band has been assigned to the transition $^2A_{1g}$ ground term to one of the higher energy term $^2A_{2g}$ or ^2E_g, the split components of the orbitally triplets $^2T_{1g}$ term. The higher energy band is more intense and indicates its origin due to metal→ligand (π*) charge transfer transition[14,15].

Molar conductivity measured in DMF solution lies in the range 3-7 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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