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Synthesis and structural studies of new Ni(II) complexes with carboxyamides

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ABSTRACT

Synthesis of nickel(II) complexes with nine amide ligands viz. 4-(2-acetylhydrazino)-4-oxobut-2-enoicacid (AOBEH), 4-(2-acetylhydrazino)-4-oxobutanoic acid (AOBAH), 2-[(2-acetyl hydrazino)carbonyl]benzoicacid (AHCBH), 4-[(2-cyanophenyl)amino]-4-oxobut-2-enoicacid (COBEH), 4-[(2-cyanophenyl)amino]-4-oxo butanoicacid (COBAH), 2-{[(2-cyano phenyl)amino]carbonyl}benzoicacid (CACBH), 4-(1*H*-benzimidazol-2-ylamino)-4-oxobut-2-enoicacid (BOBEH), 4-(1*H*-benzimidazol-2-ylamino)-4-oxobutanoicacid (BOBAH) and 2-[(1*H*-benzimidazol-2-ylamino) carbonyl]benzoicacid (BYCBH) have been described. These complexes were characterized by elemental analysis, magnetic moments, molar conductivity measurements, thermal studies, infrared, and electronic spectra.

Key words: Ni(II) complexes, carboxyamides.

INTRODUCTION

The complexation of metal ions to amide group ligands has been a subject of increasing interest over the past two decades because many of these reactions provide good models such as metal peptides and enzymes[1-2]. Recent investigations in the field of coordination chemistry clearly indicate that the research is mainly centered in developing model structures. Ni(II) complexes especially with amide ligands is given more importance because of their usefulness as catalysts. The interaction of different metal ions with diversely substituted amides has been intensively studied[3-4]. We have extensively in studied the coordinating properties of an amide group with different metal ions and the biological activities[5-10] and in the present investigations we have succeeded in synthesizing Ni(II) complexes with nine carboxy amide ligands.

EXPERMENTAL

Materials

All the chemicals used in the study were of AR grade. The ligands used in complexation were prepared by following reported methods[3]. The solvents diethyl ether and methanol were distilled by standard procedures before use. The nine amide ligands, their complexes were synthesized and characterized by elemental analyses, IR, NMR and mass spectral data. The melting points of all the macrocyclic ligands and macrocyclic metal compounds were obtained on a Buchi- 510 melting point apparatus. The percentages of carbon, hydrogen, nitrogen in macrocyclic metal compounds were determined using a Perkin-Elmer CHN analyzer at 240C. Gouy balance calibrated with $Hg[Co(NCS)_4]$ was used for the determination of magnetic susceptibilities of complexes in solid state at room temperature. Conductance measurements were done on 10^{-3} M solution of compounds in dichloromethane at room temperature using Digisun Digital conductivity meter model DL-909. TG-DSC thermograms were recorded on Mettler-TA-2000C model. The IR spectra were recorded in KBr pellets on Perkin Elmer-283 spectrophotometer. The scanning rate was 6 min. in the range of 4000-200 cm^{-1}. UV-Visible spectra were recorded with Shimadzu UV-160A, a UV-Visible double beam spectrophotometer with matched quartz cells of path length 1 cm.

Synthesis of Ni(II) complexes

Selected amide ligand (5 mmol) was dissolved in 30 ml of methanol. Nickel acetate (2.5 mmol) in 25 ml methanol was added to this solution with constant stirring. The reaction mixture was refluxed on a water bath for 2-3 hr at 70 °C. The micro crystals formed were filtered and washed several times with methanol followed by repeated washing with 1:1 diethyl ether, methanol mixture and dried in vacuo over anhydrous calcium chloride (Yield: 82-89%).

RESULTS AND DISCUSSION

Physical and analytical data

All the nickel (II) complexes are non-hygroscopic and stable at room temperature. All the complexes are soluble in DMF, DMSO and insoluble in organic solvents. According to the elemental analysis the metal, ligand ratio is found to be 1:2 and the experimental values are in good agreement with calculated values.

All the metal complexes have magnetic moments in the range 3.00-3.30 B.M. [58]. In an attempt to correlate the spectral and magnetic data μ_{eff} has been calculated[11] using 10 Dg. The calculated values are found to be in good agreement with the experimental values indicating small orbital contribution due to spin orbit contribution of the ground state with first excited state.

The molar conductance values of all the complexes in DMSO at 10^{-3} M concentration are in the range of 8.8.-15.0 ohm^{-1} $mole^{-1}$ cm^2 suggesting that they are non-electrolytes[12].

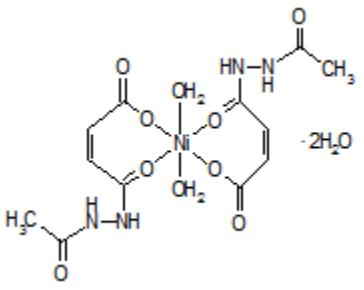
Table - 1: Physical and analytical data of Ni(II) complexes

Complex/ Color	Decomp. Temp (°C)	Found (Calcd) % C	H	N	M	μ_{eff} (BM)	Λ M
$[Ni(AOBEH)_2(H_2O)_2]2H_2O$	350	32.65	4.98	12.69	13.37	3.10	11.0
Green		(32.55)	(5.01)	(12.71)	(13.40)		
$[Ni(AOBAH)_2(H_2O)_2]$	330	32.65	4.98	12.69	13.37	3.10	11.0
Pale green		(32.60)	(5.01)	(12.70)	(13.40)		
$[Ni(AHCBH)_2(H_2O)_2$	370	44.69	4.09	10.42	10.98	3.15	8.8
Blue		(44.72)	(4.01)	(10.45)	(10.90)		
$[Ni(COBEH)_2(H_2O)_2]H_2O$	360	50.28	3.42	10.66	11.23	3.14	14.0
Green		(50.30)	(3.41)	(10.60)	(11.20)		
$[Ni(COBAH)_2(H_2O)_2]2H_2O$	340	49.90	4.15	10.58	11.15	3.20	15.0
Pale green		(50.01)	(4.12)	(10.60)	(11.11)		
$[Ni(CACBH)_2(H_2O)_2]$	390	57.60	3.56	8.96	9.44	3.15	10.5
Purple		(57.70)	(3.60)	(8.90)	(9.51)		
$[Ni(BOBEH)_2]$	380	50.86	3.08	16.18	14.36	3.20	14.5
Green		(50.80)	(3.01)	(16.10)	(14.35)		
$[Ni(BOBAH)_2]$	385	50.47	3.82	16.06	11.28	3.20	13.5
Pale green		(50.50)	(3.91)	(16.00)	(11.31)		
$[Ni(BYCBH)_2]$	360	56.69	3.14	13.22	9.29	3.00	9.0
Pale green		(56.71)	(3.13)	(13.11)	(9.21)		

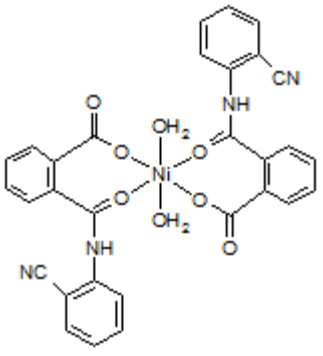
The thermograms of complexes of AOBEH, COBEH and COBAH exhibit three stages of decomposition. The initial weight loss in the region of 80-130 ^{0}C corresponds to the loss of water molecules in lattice sphere[13]. It is further evidenced by an endothermic peak in the same range in DTA curve. The second stage shows loss of water molecules in the range of 150-220 ^{0}C, corresponding to the loss of water molecules in coordinated sphere[14]. The presence of an endothermic peak at 180-200 ^{0}C in DTA curve of the complex further supports the presence of coordinated water molecules. The third stage about 390 ^{0}C corresponds to the loss of ligands. The thermograms of Ni(II) complexes with AOBAH, AHCBH and CACBH show only two clear cut stages. The first corresponds to the dehydration of water molecules in temperature range of 140-220 ^{0}C and the second being decomposition of the ligand. The presence of water molecules in the complexes is further supported by DTA curves which give endothermic peaks in the temperature range of 160-200 ^{0}C. The expulsion of water molecules in the above temperature range indicates that they are coordinated. The Ni(II) complexes of BOBEH, BOBAH and BYCBH show only a single stage decomposition devoid of any water molecules and are found to be thermally stable up to 375 ^{0}C, and the absence of water molecules in these complexes is further confirmed by the absence of an

Table - 2: Selected IR bands of Ni(II) complexes

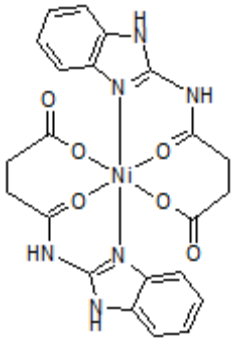
Complexes	ν_{N-H}	ν_{CO} (amide)	ν_{COO^-} (asym)	ν_{COO^-} (sym)	ν_{C-N}	ν_{M-N}	ν_{M-O}
$[Ni(AOBEH)_2(H_2O)_2]2H_2O$	3480-3200 br	1615	1550	1370	1585	-	430
$[Ni(AOBAH)_2(H_2O)_2]$	3400-3200 br	1610	1500	1380	1590	-	350
$[Ni(AHCBH)_2(H_2O)_2$	3400-3250 br	1620	1550	1360	1590	-	370
$[Ni(COBEH)_2(H_2O)_2]H_2O$	3500-3250 br	1630	1530	1350	1570	-	360
$[Ni(COBAH)_2(H_2O)_2]2H_2O$	3500-3200 br	1620	1530	1300	1600	-	350
$[Ni(CACBH)_2(H_2O)_2]$	3400-3200 br	1630	1550	1380	1570	-	360
$[Ni(BOBEH)_2]$	3280	1610	1550	1380	1600	530	350
$[Ni(BOBAH)_2]$	3300	1630	1550	1400	1610	540	360
$[Ni(BYCBH)_2]$	3160	1620	1520	1380	1610	520	370



$[Ni(AOBEH)_2(H_2O)_2]2H_2O$



$[Ni(CACBH)_2(H_2O)_2]$



$[Ni(BOBAH)_2]$

Some representative Ni(II) complexes

endothermic peak in their DTA curve in the temperature range of 180-250 ^{0}C. The sharp decomposition associated with the loss of ligand starts above 350 ^{0}C in the complexes and the final product of decomposition above 500 ^{0}C corresponding to the nickel oxide. The analysis of thermograms gives further support to the composition of the complexes proposed on the basis of elemental analysis. The elemental analysis, magnetic, molar conductivity, thermal data is presented in table-1.

Infrared data

The carboxylic group stretching frequency that appeared in ligand spectra, disappeared in all complexes and showed two new bands around 1550 and 1300 cm^{-1} corresponds to $\nu_{(COO^-asy)}$ and $\nu_{(COO^-sym)}$ respectively, confirming the participation of carboxylate oxygen in coordination[15-16]. In all the complexes the $\nu_{(C=O)}$ band of amide group around 1650 cm^{-1} which was present in the ligands undergone a negative shift by 20-30 cm^{-1} indicating coordination through oxygen of amide group[17]. This was further confirmed by the positive shift in the complexes of $\nu_{(C-N)}$ stretching frequency. In the complexes the $\nu_{(N-H)}$ frequency was shifted positively as compared to its position in the spectra of the ligands indicating non-participation of amide nitrogen in coordination[17]. The ligands of BOBEH, BOBAH and BYCBH showed a band at 1660 cm^{-1} corresponding to $\nu_{(C=N)}$ of benzimidazole moiety and a lower shift about 40–50 cm^{-1} in the complexes due to the coordination of metal ion through nitrogen of C=N[18]. The position of benzimidazole ring vibration was observed around 930 cm^{-1} in ligands and shifted to 990-1000 cm^{-1} in the spectra of complexes[19] supporting the participation of C=N in chelation. A broad band at 3500–3000 cm^{-1} was observed in the complexes of AOBEH, AOBAH, AHCBH, COBEH, COBAH and CACBH indicating the presence of water molecules in these complexes. A presence of a new band around 930–880 cm^{-1} the complexes confirmed the presence of water in coordination[20]. The far infrared spectra of the respective complexes showed non ligand bands corresponding to $\nu_{(M-O)}$ and $\nu_{(M-N)}$ vibration[21-22]. The selected IR data of all Ni(II) complexes is presented in table-2.

Electronic spectra

The electronic spectra of Ni (II) complexes of all ligands have three d-d bands in the regions 9420-10250, 15080-15720 and 25450-26170 cm^{-1} which are assigned to $^3T_{2g} \leftarrow {}^3A_{2g}(\nu_1)$, $^3T_{1g}$ (F) $\leftarrow {}^3A_{2g}$ (ν_2) and $^3T_{1g}$ (P) $\leftarrow {}^3A_{2g}$ (ν_3) transition, respectively. The positions and assignments of these bands suggest octahedral geometry[23]. This is further confirms by the ν_2/ν_1 ratio which is present in the range of 1.52-1.74.

Conclusions

Nine Ni(II) complexes with amide ligands have been synthesized and characterized by elemental analysis, magnetic moments, molar conductivity measurements, thermal studies, infrared, and electronic spectra. Octahedral geometry was tentatively proposed to all the Ni(II) complexes with amide ligands.

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