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Synthesis and characterization of copper(II), nickel(II), cadmium(II), cobalt(II) and zinc(II) complexes with 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on

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Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes of 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on, which is a derivative of carboxamide, were prepared and characterized by elemental, spectral and magnetic methods. Based on the analytical results, electronic and infrared spectral data and magnetic susceptibility measurements, suitable structures have been proposed. The formation of the complexes in solution was investigated conductometrically. 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on was found to be a bidentate ligand coordinating through enolic oxygen and amide nitrogen. The complexes of Co(II) and Ni(II) are proposed to have an octahedral structure, while Cd(II), Cu(II) and Zn(II) are suggested to possess a square-planar environment in the complexes.

Introduction

The binding of metal ions to amide groups has been a subject of increasing interest over the past two decades largely because many of these reactions provide simple models for much more complex metal-peptide systems and enzymes[1]. The interaction of different metal ions with diversely substituted amides has been intensively studied[2–5]. We are interested in studying the coordinating properties of an amide group containing compounds and the biological activity of their complexes[6–9]. In this paper we report the preparation and characterization of 2-Benzoyl-3-hydroxy-1-naphthylamino-3-phenyl-2-propen-1-on complexes with Cu(II), Ni(II), Co(II), Zn(II) and Cd(II).

Experimental

The chemicals used were all of Merck and Aldrich or chemically pure grade.

Preparation of ligand. Dibenzoylaceticacit-N-carboxymethylamide was synthesized according to the literature method.[10] The ligand was prepared from Dibenzoylaceticacit-N-carboxymethylamide with 1-naphthylamin (1:1) under reflux in the presence of toluene for 3h. The product was crystallized from hot ethanol. The structure of the ligand was characterized by elemental analysis, IR, NMR and X-ray studies[11].

In the ligand, the hydroxy groups are involved in O-H....O intramolecular hydrogen bonds[11]. Yield was 161 mg (41%).

Anal Calcd for ligand ($C_{26}H_{19}NO_3$): C, 79.42; H, 4.83; N, 3.56; Found C, 79.73; H, 5.04, N, 3.40 ^{1}H-NMR ($CDCl_3$): δ 11.57 (s, NH), 7.07-8.25(m, arom.H) ^{13}C-NMR ($CDCl_3$): δ 188.99, 200.61 (C=O), 172.32-105.95 (arom.C).

Synthesis of complexes. The metal acetate salt (2 mmol) in the case of Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) was dissolved in 10-15 ml of methanol. To this, 4 mmol of ligand in chloroform (30 ml) was added slowly, with constant stirring. The mixture was refluxed for 1-2h. The Cu(II), Ni(II), Co(II), Zn(II) and Cd(II) complexes separated out were filtered and washed thoroughly with water, ethanol and hexane and then air-dried.

Physical measurements. IR spectra were recorded on a Shimadzu 435V-04 spectrophotometer using KBr pellets in the 4000-400 cm^{-1} range. The electronic spectra were recorded on a Pye-Unicam u.v.-vis spectrophotometer model UV2-100 over the 200-900 nm range. A Gouy balance was used to determine the magnetic moments of the powdered samples, employing Hg(II) tetrathiocyanatocobaltate(II) as a calibrant. Diamagnetic corrections were made from the Pascal's constants. Molar conductances of all the compounds were determined in $CHCl_3$ (10^{-3} M) at room temperature using a Jenway Model 4070 conductivity meter. Elemental analyses were performed at the Microanalytical Laboratory, University of Erciyes, Kayseri. NMR spectra were recorded on a Varian A-60 ^{1}H-NMR spectrophotometer.

Results and Discussion

All the complexes are non-hygroscopic and stable at room temperature. The Co(II), Cu(II), Ni(II), Cd(II) and Zn(II) complexes are insoluble in common organic solvents but are soluble in DMSO, DMF and $CHCl_3$. The analytical data of the complexes are presented in Table 1. The molar conductances of the solutions of the compounds in $CHCl_3$ (1 mM) are in the range (Table 1) 3.3-4.3 Ω^{-1} cm^2 mole^{-1}. These values are lower than those expected for an electrolyte[12]. These observations suggest that all the compounds are non-electrolytes in $CHCl_3$ (1.10^{-3}M) at room temperature.

Table 1. Elemental Analysis and Some Physical Properties of the Chelates.

Complexes	Colour	Λ_{m*} in $CHCl_3$	M.P. (Dec.)°C	Yield (%)	Found (Calc.) %		
					C	H	N
$[Cu(L)_2]H_2O$	Olive green	4.3	219	87	71.84 (72.09)	4.30 (4.39)	3.24 (3.30)
$[Co(L)_2 2H_2O]$	Light yellow	3.3	220	78	68.61 (68.18)	4.69 (4.80)	2.90 (3.05)
$[Ni(L)_2 2H_2O]$	Light green	3.5	120	81	66.83 (66.89)	4.71 (4.92)	3.24 (3.00)
$[Zn(L)_2]3H_2O$	Dull white	4.1	192	64	68.71 (69.06)	4.80 (4.64)	3.11 (3.09)
$Cd(L)_2]3H_2O$	Yellow	3.6	167	78	68.26 (67.88)	4.41 (4.15)	3.03 (3.06)

*Ω^{-1} cm^2 mole^{-1}

The IR values of the complexes studied are presented in Table 2. The IR spectrum of the ligand shows three strong bands at 3250 ν(NH), 1620-1680 ν(C=O) and 1560 cm$^{-1}\nu$(C-N) +δ(N-H) amide vibrations.

The IR spectra of the complexes do not show the characteristic stretching frequency of the NH group at 3250 cm^{-1}. The ν(C=O) groups and enolic carbonyl oxygen (C=O) at 1620-1680 cm^{-1} frequency found in the IR spectra of the ligand show a shift in the spectra of complexes. The following evidence supports the coordination through the enolic carbonyl oxygen (C=O) and the (NH) amide.

Table 2. Important IR bands (cm^{-1}) and Magnetic Moments (μ_{eff}: B.M.)

Compounds	ν (H_2O)/ ν (OH)	ν (NH)	ν (C=O)	ν (CN)	ν (C-O)	ν (M-N)	ν (M-O)	μ_{eff} (B.M.)
L		3250	1620-1680	1140	1560			
$[Cu(L)_2]H_2O$	3500		1600	1070	1560	495	440	1.93
$[Co(L)_2 2H_2O]$	860		1590	1090	1540	500	420	4.75
$[Ni(L)_2 2H_2O]$	850		1600	1085	1520	480	470	3.10
$[Zn(L)_2]3H_2O$	3480		1580	1070	1530	470	420	Diam.
$[Cd(L)_2]2H_2O$	3510		1600	1100	1540	510	450	Diam.

The IR spectra of all the complexes show two absorption bands in the far infrared region, 420-440 cm^{-1} and 480-520 cm^{-1}, which are assignable to ν(M-O)and ν(M-N) vibrations, respectively[13]. The IR spectra of all the complexes show new absorption bands in the region 3300-3500 cm^{-1}indicating the presence of water molecules. The existence of the water molecules inside the coordination sphere of the complexes Co(II) and Ni(II) is suggested on the basis of IR studies. In addition, the band at 860 cm^{-1} in the IR spectra of Co(II) and Ni(II) complexes suggests that water molecules are coordinated to metal ions[13].

DMSO was used as a deuterated solvent to measure the ^{1}H NMR spectra of the metal chelates except those of Cu(II), Co(II) and Ni(II). The ^{1}H NMR spectra show multiplets observed at δ 6.82-8.38 for phenyl protons in the ligand and its complexes. In the ligand, a broad signal for –NH proton appears at δ 11.57, which, however, disappears in the corresponding complexes indicating the removal of –NH proton during the course of chelation.

Listed in Table 3 are the electronic spectra and magnetic susceptibilities for the ligand and its metal complexes measured in the $CHCl_3$ solutions. The ligand spectrum consists of a maximum at ~350 nm which can be assigned to the n-π^* transition of the carbonyl groups. Further, two medium intensity bands at 300 nm and 260 nm due $\pi - \pi^*$ transitions in the ligand remain as such in the spectrum of the metal complexes.

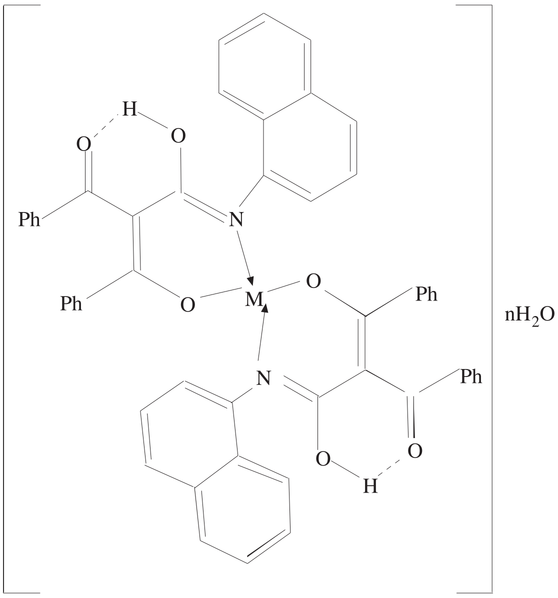
Room temperature magnetic susceptibility measurements of these complexes (Table 2) show that the Cu(II) complexes have μ_{eff} values (1.93 B.M.) corresponding to the presence of one unpaired electron. The reflectance spectrum of the Cu(II) chelate, $[Cu(L)_2].H_2O$, exhibits a broad band centred at 15640 cm^{-1}, which is assigned to $^2B_{1g\rightarrow}{}^2A_{1g}$ transition in a square-planar configuration.[14] Also, the band observed at 23840 cm^{-1} may be assigned to a charge transfer. The magnetic moment value and the ligand field parameters confirmed the square-planar configuration.

The electronic spectrum of Ni(II) complexes showed peaks characteristic of octahedral geometry. The reflectance spectra of Ni(II) complex consist of the transition bands at 9980, 16800 and 26350 cm^{-1} assignable to the transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$[15] respectively. The Ni(II) complex possesses magnetic moment in the range μ_{eff}=3.10 B.M. in agreement with octahedral geometry.[15] Magnetic moments of octahedral Ni(II) complexes are thus expected to be well in excess of the spin only value, and typically lie in the range 3.2-4.0 B.M.[15]

Table 3. Electronic Spectra (cm^{-1}) of the ligand and their metal complexes

Compounds	Mode	d-d transitions and intraligand and charge transfer
L	$CHCl_3$	38363,33364, 28255
$[Cu(L)_2]H_2O$	$CHCl_3$	15640, 23840, 28800
$[Co(L)_2 2H_2O]$	$CHCl_3$	8250, 16220, 20360
$[Ni(L)_2 2H_2O]$	$CHCl_3$	9980, 16800, 26350
$[Zn(L)_2]2H_2O$	$CHCl_3$	19540, 31800
$[Cd(L)_2]2H_2O$	$CHCl_3$	20920, 26650

The Co(II) complex possesses magnetic moment in the range μ_{eff}=4.75 B.M. in agreement with octahedral geometry.[15] The tree transitions observed in the electronic spectra of the Co(II) complex indicate the octahedral environment around the metal ion. The electronic spectrum of the Co(II) complexes show strong peaks at 8250, 16220 and 20360 cm^{-1} assignable to the transitions $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$. [14] The other characteristic bands for d-d transitions appear at 16220 cm^{-1}.



M=Cu(II), Zn(II) and Cd(II)

Figure 1. Coordination spheres of the compounds.

In general, it can be seen that the spectra consist of a band in the near infrared which is assigned to $^4T_{1g} \rightarrow ^4T_{2g}$ and a band in the visible near 20000 cm^{-1} which is assigned to $^4T_{1g} \rightarrow ^4T_{1g}(P)$. The magnetic properties of high spin octahedral cobalt(II) complexes are governed by the orbitally degenerate ground term $^4T_{1g}$; this provides an orbital contribution to the magnetic moment so that room temperature moments are experimentally found to be in the range 4.7-5.2 BM.[15]

Finally, the magnetic moments of the Zn(II) and Cd(II) complexes were found to be diamagnetic, while all other complexes were paramagnetic with magnetic moment values close to the spin only values.[15] Cd(II) and Zn(II) are suggested to possess a square-planar environment in the complexes.

Considering the spectral data and elemental analysis, the following structure (Figure 1) for Cu(II), Zn(II) and Cd(II) complexes is proposed. In each fundamental ML_2 unit, the metal ion is bonded to two ligand molecules through nitrogen and oxygen.

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