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Synthesis and characterization of 3-(2-hydroxy-1-naphthylhydrazinylidene)pentane-2,4-dione and its metal chelates

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ABSTRACT

The coupling of diazotized 2-aminonaphthalene with acetylacetone yielded a new type of tridentate ligand (Hhnh). Analytical, IR, ^{1}H NMR and mass spectral data indicate that the compound exists in the intramolecularly hydrogen bonded keto-hydrazone tautomeric form. Dibasic tridentate coordination of the compound in its [ML(H_2O)] complexes [M = Ni(II), Cu(II), Zn(II) and Pd(II)] has been established on the basis of analytical and spectral data. The Ni(II), Zn(II) and Pd(II) chelates are diamagnetic while Cu(II) complex showed normal paramagnetic moment.

KEYWORDS

Hydroxynaphthylhydrazones;
Keto-hydrazone form;
Metal complexes;
IR spectra;
^{1}H NMR spectra;
Mass spectra.

INTRODUCTION

Metal complexes of arylhydrazones occupy a central role in the development of coordination chemistry as manifested by the huge number of publications ranging from purely synthetic to modern physically and biochemically relevant studies[1]. The coupling of diazonium salts, containing additional metal binding sites at *ortho* position, with the active methylinic carbon of 1,3-dicarbonyl compounds result in the formation of multidentate azo/hydrazone ligand systems[2]. Aryl hydrazones have been used for analytical purposes[3], in the determination of metal ions[4], and some of their derivatives have been used in bacteriological and histological investigations[5]. However structural aspect of many of these products and their metal derivatives do not received as much attention as they deserve. In continuation of our studies on arylhydrazones of 1,3-dicarbonyl compounds and their metal complexes[6-11], we report herein the synthesis and characterization of a new type of tridentate hydroxynaphthylhydrazone obtained by coupling diazotized 1-amino-2-naphthol with acetylacetone. Typical metal complexes of the compound were also synthesized and characterized.

EXPERIMENTAL

Methods, instruments and materials

Carbon, hydrogen and nitrogen percentages were determined by microanalyses (Heraeus Elemental analyzer) and metal contents of complexes by AAS (Perkin Elmer 2380). The IR spectra (KBr discs) were recorded on a 8101 Shimadzu FTIR spectrophotometer, ^{1}H NMR spectra in $CDCl_3$ orDMSO-d_6 on a Varian 300 NMR spectrometer and mass spectra on a Jeol / SX-102 mass spectrometer (FAB using Argon and meta-nitrobenzyl alcohol as the matrix). Molar conductance of the complexes was determined in DMF at 28±1^{0}C using solution of about 10^{-3} M concentration. Magnetic susceptibilities were determined at room temperature on a Guoy type magnetic balance at room temperature (28±1^{0}C) using $Hg[Co(NCS)_4]$ as standard. Corrections for diamagnetism of the constituents were made using Pascal's constants[12]. The chemicals used were of AR grade, purchased from Merck, Germany.

Synthesis of 3-(2-hydroxy-1-naphthylhydrazinylidene)pentane-2,4-dione (Hhnh)

An aqueous solution of 2-hydroxynaphthyldiazonium ion was prepared by standard method[13]. 1-Amino-2-naphthol (1.59 g, 0.01 mol) and $CuSO_4$ (10 mg) were made into an aqueous paste. To this a solution of $NaNO_2$ (0.7 g) was added and then acidified with 5N HCl (50 mL). The temperature was kept below 0^{0}C. After destroying the excess nitrous acid with urea, the diazonium salt solution was added drop by drop with stirring to an ice-cold (<5^{o}C) solution of acetylacetone (0.01 mol, 50 mL methanol). Sodium acetate was added to maintain the pH around 6. The mixture was stirred for about 1 h below 5^{o}C and then filtered, washed with water and recrystallized twice from hot ethanol to get chromatographically (TLC) pure compound.

Synthesis of Ni(II), Cu(II), Zn(II) and Pd(II) complexes

An aqueous solution of metal(II)acetate (0.01 mol) in minimum amount of water was added to a solution of the ligand (0.27 g, 0.01 mol) in methanol (50 mL). The mixed solution was refluxed for about 24 h on a water bath. The volume was reduced to half and the solution cooled in an ice-bath. The precipitated complex was filtered, washed with water and recrystallized from hot chloroform to get chromatographically (TLC) pure compound.

RESULTS AND DISCUSSION

The observed elemental analytical data of hydroxynaphthylhydrazone indicate that the diazo-coupling reaction has occurred in the 1:1 ratio (TABLE 1). The compound is crystalline in nature and is soluble in common organic solvents. It formed stable complexes with Ni(II), Cu(II), Zn(II) and Pd(II) ions. The analytical data (TABLE 1) together with non-electrolytic nature in DMF (specific conductance <10Ω^{-1}cm^{-1}; 10^{-3} M solution) suggest $[ML(H_2O)]$ stoichiometry of the complexes. The Ni(II), Zn(II) and Pd(II) chelates are diamagnetic while Cu(II) complex showed normal paramagnetic moment. The observed IR, ^{1}H NMR and mass spectral data are in conformity with Figure 1 of the hydroxynaphthylhydrazone and Figure 2 of the complexes.

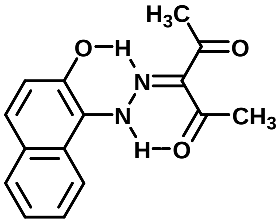
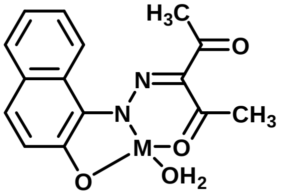


Figure 1 : Structure of Hhnh



M = Cu(II), Ni(II), Zn(II), Pd(II)

Figure 2 : Structure of the metal complexes of Hhnh

TABLE 1 : Physical and analytical data of Hhnh and its metal complexes

Compound/ Empirical formula	Yield %	m.p. ^{0}C	Elemental Analysis: Found (Calculated)% C	H	N	M
Hhnh $C_{15}H_{14}N_2O_3$	55	270	66.80 (66.67)	5.20 (5.19)	10.45 (10.37)	-
$[Ni(hnh)(H_2O)]$ $C_{15}H_{14}N_2NiO_4$	60	282	52.26 (52.22)	4.03 (4.06)	8.03 (8.12)	17.15 (17.03)
$[Cu(hnh)(H_2O)]$ $C_{15}H_{14}CuN_2O_4$	50	305^d	51.38 (51.50)	3.99 (4.01)	7.95 (8.01)	18.24 (18.18)
$[Zn(hnh)(H_2O)]$ $C_{15}H_{14}N_2O_4Zn$	54	290	51.28 (51.23)	3.98 (3.98)	7.90 (7.97)	18.75 (18.61)
$[Pd(hnh)(H_2O)]C_{15}H_{14}N_2PdO_4$	60	298	45.76 (45.87)	3.53 (3.57)	7.13 (7.14)	27.02 (27.12)

d = decompose

Infrared spectra

The IR spectrum of Hhnh in the 1600-1800 cm^{-1} region showed strong bands at 1670 and 1628 cm^{-1} due to the stretching of free conjugated and intramolecularly hydrogen bonded acetyl carbonyls respectively[8,9]. The spectrum also showed a medium intensity band at 1618 cm^{-1} assignable to C=N vibration[14,15]. The broad band in the range 2500-3400 cm^{-1} indicates the existence of strong intramolecular hydrogen bonding in the compound. The spectrum showed several medium intensity bands in the range 1580-1600 cm^{-1} due to various C=C vibrations. Absence of any band assignable to N=N in the region 1400-1500 cm^{-1} and the presence of a medium intensity band at 1525 cm^{-1} due to deformation vibration of NH group further support the hydrazone form of the compound. Thus the IR spectrum strongly support the existence of the compound in the intramolecularly hydrogen bonded keto-hydrazone form as in Figure 1.

In the spectra of all the metal complexes the free acetyl carbonyl and C=N bands remained almost unaffected indicating their non-involvement in complexation. However the band due to the hydrogen bonded acetyl carbonyl at 1628 cm^{-1} of the ligand disappeared and instead a new strong band appeared at ~1560 cm^{-1} assignable to the stretching of metal bonded carbonyl group as in Figure 2. The broad band in the range 2500-3400 cm^{-1} of the ligand disappeared in the spectra of all the complexes and bands due to various νC-H vibrations appeared in the region. A prominent band present in the spectrum of the ligand at 1525 cm^{-1} due to νN-H vibration also disappeared in the spectra of all the complexes. These indicate that the metal ion replaced the phenolic OH and hydrazone NH protons. The spectra of the complexes show bands due to coordinated water at ~3450 cm^{-1}. That the hydrazone nitrogen, phenolate oxygen and the intramolecularly hydrogen bonded carbonyl oxygen are involved in complexation is clearly evident from the appearance of two additional bands at ~450 and ~530 cm^{-1} assignable of νM-O and νM-N vibrations[16]. Thus the IR spectra of the complexes are in agreement with the formulation of C_2N_2OM chelate ring as in Figure 2. Important bands that appeared in the spectra are given in TABLE 2.

TABLE 2 : Characteristic IR stretching bands (cm^{-1}) of Hhnh and its metal complexes

Compound	Free (C=O)	Chelated (C=O)	(C=N)	(M–N)	(M–O)
Hhnh	1670 s	1628 s	1618 m	-	-
[Ni(hnh)(H_2O)]	1668 s	1558 s	1616 m	522 m	468 m, 422 m
[Cu(hnh)(H_2O)]	1672 s	1562 s	1614 m	518 m	470 m, 426 m
[Zn(hnh)(H_2O)]	1670 s	1564 s	1620 m	530 m	466 m, 430 m
[Pd(hnh)(H_2O)]	1666 s	1556 s	1618 m	526 m	460 m, 424 m

^{1}H NMR spectra

The ^{1}H NMR spectrum of Hhnh is characterized by the presence of two low field one proton signals at δ 15.98 and 12.02 ppm due to intramolecularly hydrogen bonded N–H and O–H protons[17,18]. The integrated intensities of all the signals agree well with the Figure 1 of the compound. In the ^{1}H NMR spectra of the diamagnetic Ni(II), Zn(II) and Pd(II) complexes, the low field signals due to the chelated hydrogens disappeared indicating the replacement of hydrazone and phenolic protons by metal ion during complexation[19]. The chelates show two methyl proton signals of equal intensity indicating that the two acetyl groups are in different chemical environment. The position of the methyl proton signals indicates that one of the acetyl carbonyl is involved in complexation. The aryl proton signals appeared in the range δ 6.70-7.50 ppm as a complex multiplet. Integrated intensities of all other protons agree well with the Figure 2 of the complexes. The assignments of various proton signals observed are assembled in TABLE 3.

TABLE 3 : ^{1}H NMR spectral data (δ, ppm) of Hhnh and its Ni(II), Zn(II) and Pd(II) complexes

Compound	CH_3CO	Naphthyl	OH	NH
Hhnh	2.32 (3H, s) 2.57 (3H, s)	6.88 - 7.47 (6H, m)	12.02 (1H, s, br)	15.98 (1H, s, br)
[Ni(hnh)(H_2O)]	2.34 (3H, s) 2.87 (3H, s)	7.02 - 7.48 (6H, m)	-	-
[Zn(hnh)(H_2O)]	2.30 (3H, s) 2.90 (3H, s)	6.98 - 7.47 (6H, m)	-	-
[Pd(hnh)(H_2O)]	2.28 (3H, s) 2.78 (3H, s)	6.76 - 7.44 (6H, m)	-	-

m = multiplet, s = singlet, br = broad

Mass spectra

The formulation of the compound as in Figure 1 is clearly supported from the presence of intense molecular ion peak in the mass spectrum at *m/z* 270. Since peak due to the elimination of ArN_2[20,21], a characteristic feature of the azo tautomer, has not been observed in the mass spectrum indicating its existence in the hydrazone form. The spectrum of the compound shows an intense peak at *m/z* 158 due to the formation of $C_{10}H_6(OH)NH^+$ through the cleavage of N-N bond thereby confirming its keto-hydrazone tautomeric structure. The formation of other important peaks is due to the elimination of one or both CH_3CO groups from the molecular ion or subsequent fragments. The FAB mass spectrum of the Cu(II) complex showed molecular ion peak corresponding to [ML(H_2O] stoichiometry as in Figure 2. However, the most intense peak in the spectrum is due to $[ML]^+$. Peaks corresponding to the elimination of CH_3CO, H_2O, dicarbonyl moieties etc. from the molecular ion are also present in the spectra. The spectrum contains a number of fragments containing copper in the 3:1 natural abundance of ^{63}Cu and ^{65}Cu isotopes (TABLE 4).

TABLE 4 : Mass spectral data of Hhnh and its Cu(II) complex

Compound	Mass spectral data (m/z)
Hhnh	270, 227, 184, 158, 112
[Cu(hnh)(H_2O)]	351, 349, 333, 331, 308, 306, 290, 288, 270, 265, 263, 247, 245, 184, 158, 112

Electronic spectra

The UV spectrum of Hhnh showed two broad bands with maxima at 370 and 260 nm due to various $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions. In complexes these absorption maxima shifted appreciably to low wave numbers. The Cu(II) complex showed a broad band centered at 15,200 cm^{-1}. This, together with the measured μ_{eff} value (1.76 BM) suggests the square-planar geometry[22]. The observed diamagnetism and broad medium-intensity band at 17,600 cm^{-1} in the spectrum of the Ni(II) chelate suggest its square-planar geometry. In conformity, the spectrum of the chelate in pyridine solution (10^{-3} M) showed three bands corresponding to configurational change to octahedral due to the association of pyridine[23].

CONCLUSIONS

2-Hydroxynaphthylhydrazone has been prepared by the coupling of diazotized 1-amino-2-naphthol with acetylacetone. Analytical, IR, ^1H NMR and mass spectral data revealed a 1:1 product in which one of the carbonyl group of the dicarbonyl compound is involved in intramolecular hydrogen bonding with the hydrazone hydrogen. Analytical, physical and spectral data of the [ML(H_2O)] complexes of Cu(II), Ni(II), Zn(II) and Pd(II) showed thedibasic tridentate O_2N coordination involving one of the hydrazone nitrogen, phenolate oxygen and one of the carbonyl oxygen. The Ni(II), Zn(II) and Pd(II) chelates are diamagnetic while Cu(II) complex showed normal paramagnetic moment.

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