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Synthesis and Studies of some Bivalent Transition Metal Complexes with Acylhydrazones

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Abstract

Complexes of 3-hydroxy-2-naphthaldehyde benzoylhydrazone (H_2nabh) and 3-hydroxy-2-naphthaldehyde salicyloylhydrazone (H_3nash) of the empirical composition $M(L-2H)\cdot nH_2O$ [M = manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), mercury(II), L = H_2nabh, H_3nash and $n = 0, 1, 2$] were prepared and characterized by elemental analyses, magnetic susceptibility, electronic and infrared spectral data. Zinc(II) and cadmium(II) complexes were also studied by ^{13}C, ^1H NMR and the Cu(nabh)·H_2O complex by transmission electron microscopy. The complexes are coloured and highly insoluble in common organic solvents. Absence of the original anion in the complexes indicates deprotonation of the ligands (H_2nabh and H_3nash) which bind the metal ions from the –OH and the C=N groups.

Introduction

Acylhydrazones RCONHN=CR′R″ are potential flexidentate ligands and in the recent past have assumed considerable importance. Narang *et al.* [1, 2] have reported solid-solution reactions of metal ions with insoluble solid salicylaldehyde benzoylhydrazone and salicylaldehyde salicyloylhydrazone and solid polymers derived from glyoxal and organic acid dihydrazides. Monoamine oxidase (MAO) enzyme inhibition by acylhydrazines has been suggested to take place via a metal–acylhydrazine Schiff base complex [3]. Copper(II) salicylaldehyde benzoylhydrazone complex [4] and copper(II) pyridine-2-carboxaldehyde-2-pyridyl hydrazonate [5] have been reported to produce significant inhibition of tumor growth. In continuation of our work on the complexes of acylhydrazones [6], we report here the synthesis and characterization of several bivalent transition metal complexes with two of the acylhydrazones derived from 3-hydroxy-2-naphthaldehyde and benzoyl or salicyloyl hydrazine.

Experimental

All the chemicals were of BDH (AnalaR) or equivalent grade. 3-Hydroxy-2-naphthaldehyde, Koch Light Laboratories, U.K., was used as such. Benzoyl and salicyloyl hydrazine were prepared by the literature methods [7, 8].

The complexes were analysed for their metal content employing a standard literature method [9], after destroying the organic matter with a HNO_3 + HCl mixture and then evaporating the acid mixture with concentrated H_2SO_4. Nitrogen was estimated microanalytically using a Coleman nitrogen analyzer. Room temperature magnetic susceptibility measurements were carried out on a Gouy type balance (Cahn magnetic susceptibility apparatus), using $CoHg(SCN)_4$ as calibrant and the experimental magnetic susceptibilities were corrected for diamagnetism [10]. The electronic and infrared spectra of the ligands and their complexes were recorded in nujol on Cary-14 and Perkin-Elmer-621 Spectrophotometers respectively. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX 90Q multinuclear spectrophotometer equipped with a variable temperature controller in DMSO-d_6 at 35 °C using TMS as an internal reference standard. Transmission electron microscopic photographs of the Cu(nabh)·H_2O complex were obtained on a TEM JEOL 200 CX model with resolving power of 2 Å.

Preparation of the Ligands

3-Hydroxy-2-naphthaldehyde benzoylhydrazone (H_2nabh) or salicyloylhydrazone (H_3nash) was prepared by refluxing a mixture of 0.1 mol benzoyl hydrazine or salicyloyl hydrazine (dissolved in 50 ml ethanol) and 0.2 mol of 3-hydroxy-2-naphthaldehyde (dissolved in 30 ml ethanol) for ~4 h. The yellow products were suction filtered, washed with ethanol and dried over anhydrous calcium chloride.

Preparation of the Complexes

The complexes were prepared by solid-solution reactions by taking the metal(II) salt (0.01 mol) solution (in 50 ml ethanol) and the finely powdered ligand (0.01 mol) in a 1:1 mol ratio. The mixtures

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TABLE I. Analytical, Magnetic and Electronic Spectra of the Complexes

Compounds[a]	Found (Calc.) (%)		μ_{eff}[b] (BM)	Yield (%)	Colour	Electronic spectral bands (nm)
	M	N				
Fe(nabh)·H_2O	14.52 (15.31)	7.62 (7.74)	5.10 (5.48)	78	brown	230, 256, 350, 600
Fe(Hnash)	15.31 (15.40)	7.20 (7.79)	5.00 (4.38)	74	black	280, 300, 340, 390, 650
Mn(nabh)·H_2O	14.92 (15.21)	6.99 (7.75)	3.05 (5.72)	62	light yellow	250, 320, 380
Mn(Hnash)·H_2O	14.27 (14.57)	7.24 (7.42)	4.12 (5.72)	50	yellow	240, 415
Co(nabh)·$2H_2O$	15.26 (15.39)	7.23 (7.31)	2.07 (2.90)	76	light brown	230, 260, 290, 312, 420, 1180
Co(Hnash)	16.10 (16.23)	7.00 (7.11)	2.42 (2.90)	78	brown	238, 263, 285, 306, 360, 425, 700, 1200
Ni(nabh)·H_2O	16.12 (16.09)	6.36 (7.67)	3.34 (3.00)	70	brown	220, 335, 370, 600, 950
Ni(Hnash)	17.19 (16.18)	7.36 (7.72)	3.32 (3.00)	70	light brown	225, 300, 365, 590, 980
Cu(nabh)·H_2O	18.02 (17.20)	6.59 (7.57)	1.31 (1.73)	80	green	230, 275, 325, 375, 640
Cu(Hnash)	16.99 (17.29)	7.36 (7.61)	1.30 (1.73)	82	green	220, 330, 390, 655
Zn(nabh)·H_2O	17.50 (17.60)	7.38 (7.53)	dia[c]	74	yellow	235, 260, 362, 420
Zn(Hnash)	17.52 (17.69)	7.38 (7.58)	dia	70	light yellow	230, 270, 350, 430
Cd(nabh)	28.06 (28.07)	6.49 (6.99)	dia	60	dark yellow	220, 240, 330
Cd(Hnash)	25.99 (26.89)	6.68 (6.72)	dia	62	yellow	290, 330
Hg(nabh)	40.19 (41.05)	5.40 (5.73)	dia	60	yellow	210, 270
Hg(Hnash)	38.94 (39.75)	5.36 (5.54)	dia	50	dark yellow	215, 272, 290

[a] All the complexes are decomposed above 300 °C. [b] μ_{eff} values in parentheses are expected values for number of unpaired electrons. [c] dia = diamagnetic.

were refluxed for 5–6 h with shaking at regular intervals. The products were filtered and re-refluxed with a fresh lot of metal salt solution (0.01 mol in 50 ml ethanol) and refiltered, washed with ethanol and dried over anhydrous calcium chloride. Since the complexes were insoluble and non-crystallizable in common organic solvents, they were purified by washing thoroughly with ethanol to free them from the unreacted metal salt.

Results and Discussion

The analytical data of the complexes, given in Table I, indicate 1:1 metal to ligand stoichiometry and show that the complexes can be represented by the general formula $M(L-2H)\cdot nH_2O$ where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L = H_2nabh, H_3nash and n = 0, 1, 2.

The complexes are insoluble in water as well as common organic solvents like ethanol, diethylether, chloroform, benzene etc., but soluble in polar coordinating solvents such as DMF, DMSO and decompose above 300 °C without melting. The absence of anions of the original metal salt in the resulting complexes indicates deprotonation of the ligands to the extent of two protons. The ease with which formation of the deprotonated complexes takes place is, probably, due to the greater aromaticity of the naphthalene ring stabilizing the enolic form of the ligands, H_2nabh and H_3nash as under, and resulting in the deprotonated complexes.

$$C_6H_4(R).CO.NH\,N{:}CHC_{10}H_6 \rightleftharpoons C_6H_4(R).C(OH){:}N.N{:}CHC_{10}H_6$$

R = H, OH
(keto form) (enol form)

The loss of water molecules at 110 °C without any change in colour of the complexes suggests that the water molecules are in the lattice.

Electronic Spectra and Magnetic Susceptibility Measurements

Copper(II) complexes, Cu(nabh)·H_2O (μ_{eff} 1.30 BM) and Cu(Hnash) (μ_{eff} 1.31 BM) show a broad band at ~600 nm and a high energy band at ~400 nm. The magnetic moments are anomalous signifying Cu–Cu interactions in the complexes [11, 12]. The 400 nm band has been reported to arise from the dinuclear nature [13] of the complexes, while the 600 nm band is observed in square planar copper(II) complexes with Schiff bases presenting an O_2N_2 mixed field [14]. Cu(nabh)·H_2O and Cu(Hnash) are, therefore, dinuclear with a square planar disposition of O_2N_2 atoms of the ligands.

Nickel(II) complexes, Ni(nabh)·H_2O and Ni(Hnash), show bands at 600, 950 and 590, 980 nm, respectively, which are fairly close to those observed for octahedral nickel(II) complexes [15]. The observed μ_{eff} values 3.34 and 3.32 BM, respectively, also correspond to a spin free octahedral geometry around nickel(II). Although the composition of copper(II) and nickel(II) complexes are similar in this study the spectral and magnetic data conform to different geometries around the ions. Most of the square planar nickel(II) complexes are diamagnetic or show anomalous magnetic moments due to stacking of molecules one above the other forming M–M chains [2]. But bis-acetylacetonato nickel(II), Ni(acac)$_2$ is a trimer, [Ni(acac)$_2$]$_3$ in the solid state and is normally paramagnetic [16], in which the three nickel(II) have an octahedral O_6 field around them. It is, therefore, reasonable to believe that Ni(nabh)·H_2O and Ni(Hnash) have attained octahedral geometry in the solid state by molecular association.

Cobalt(II) complexes, Co(nabh)·2H_2O and Co(Hnash), show absorption bands at ~1200 nm which have been assigned to the $^2B_{2g} \rightarrow {}^4A_{2g}$ transition in square planar cobalt(II) complexes with Schiff bases [17]. The anomalous magnetic moments, μ_{eff} 2.07 and 2.42 BM respectively, also correspond to those observed in square planar cobalt(II), d^7, complexes [18] having one unpaired electron.

Iron(II) complexes Fe(nabh)·H_2O and Fe(Hnash) show bands at 350, 600 and 390, 650 nm and μ_{eff} values 5.10 and 5.00 BM respectively. Since manganese(II) shows extremely weak bands in the visible region [15], the absorption bands shown by Mn(nabh)·H_2O (μ_{eff} 3.05 BM) and Mn(Hnash)·H_2O (μ_{eff} 4.12 BM) (Table I) are either ligand bands or M–L charge transfer bands.

TABLE II. ^1H NMR Spectral Data[a] for H_2nabh and H_3nash and Their Complexes

Compound	^1H NMR (ppm)
H_2nabh	6.65 (s, 1H, NH) 8.50 (s, 1H, –CH=N) 11.50 (br, 1H, –OH)
H_3nash	8.83 (s, 1H, NH) 8.55 (s, 1H, –CH=N) 12.00 (br, 1H, –OH)
Zn(nabh)	9.50 (s, 2H, =CH–) 7.00–8.50 (m, aromatic H)
Zn(Hnash)	9.50 (s, 2H, =CH–) 7.00–8.50 (m, aromatic H)
Cd(nabh)	9.00 (s, 2H, =CH–) 7.00–8.50
Cd(Hnash)	9.42 (s, 2H, =CH–) 7.50–8.00

[a] Spectra in DMSO-d_6; s = singlet, m = multiplet, br = broad.

NMR Spectra

The ^1H NMR spectra of the ligands (H_2nabh and H_3nash) exhibit the –CH=N– and –OH proton signals at 8.50 and 11.50–12.00 ppm respectively (Table II). A multiplet due to the naphthaldehyde ring and NH protons appears in the range 6.65–8.53 and 10.00 ppm respectively. Both NH and OH protons disappear on D_2O exchange showing deprotonation of the ligands. In the complexes, the proton signal due to the –CH=N– group shows a downfield shift which is probably due to the donation of the lone-pair of electrons by azomethine nitrogen to the metal ion. Thus the –CH=N– proton is deshielded by 0.30–0.35 ppm in the complexes indicating coordination through azomethine nitrogen [19].

^{13}C NMR spectra of the ligands show a cluster of peaks between 133.11–128.97 ppm corresponding to the aromatic carbon atoms of the naphthalene and benzene rings [20]. The number of carbon atoms as judged from the spectra (Fig. 1) correspond well to the number of carbon atoms in the molecules. There is a single peak at 158.46 ppm due to –CH=N– in the ligands. In metal complexes, there is a clear doublet at 158.32 and 159.22 ppm showing the presence of two types of –C=N– group in the complexes (Fig. 1). The peak at 159.22 ppm may be due to $\alpha\alpha'$–C=N– and the one at 158.32 ppm may be due to $\beta\beta'$–C=N– (Fig. 1).

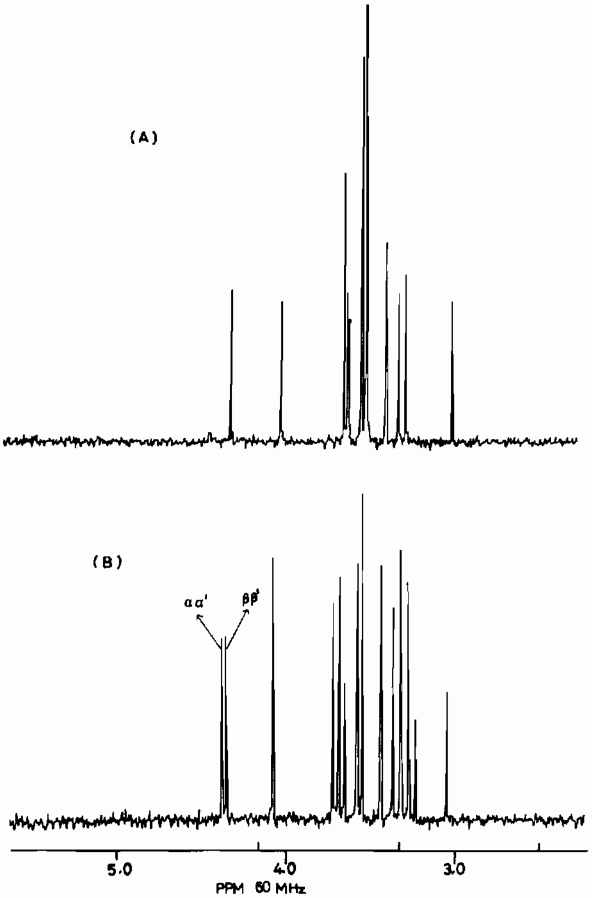

Fig. 1. ^{13}C NMR spectrum in DMSO-d_6 (a) H_2nabh, (b) Zn(nabh).

IR Spectra

IR spectra of the ligands (Table III) show strong bands between 3250–3200 cm^{-1} which are attributed to the ν(OH) vibration of the phenolic group. The bands at ~2770 cm^{-1} suggest intramolecular H-bonding [21]. The bands around 1670–1600, 1560, 1250 and 650 cm^{-1} have been assigned to amide I (ν(C=O)), amide II (CN + δNH), amide III δ(NH) and amide IV (C=O in plane deformation) respectively, suggesting that the ligands exist in the keto form. The strong bands observed between 3050–3000 and 1620–1615 cm^{-1} have been assigned to ν(NH) and ν(C=N) of the azomethine groups.

In some of the complexes a broad band appears between 3640–3200 cm^{-1} due to overlapping ν(OH) of the water molecules in the lattice and ν(OH) (phenolic). The absence of amide I bands (νC=O) between 1670–1660 cm^{-1} and the appearance of a strong band between 1605–1600 cm^{-1} clearly indicates that the ligands undergo keto ⇌ enol tautomerism

$$\text{RCO.NH.N:CHR}' \rightleftharpoons \text{RC(OH):N.N:CHR}'$$

deprotonate in the enol form and coordinate to the metal ion. As a result of enolization the >C=N–N=C< group is formed which absorbs at ~1600 cm^{-1} [22].

In the complexes the ν(C=N) bands appear at a lower frequency (10 cm^{-1}), indicating the coordination of the nitrogen atom of the azomethine group to the metal atom. The spectra of the ligands show bands around 1520 and 1280 cm^{-1} assigned to ν(NCO) and ν(C–O) [23] respectively. In the complexes these bands appear at higher frequencies

TABLE III. Assignment of Important Bands (cm^{-1}) in the IR Spectra of H_2nabh and H_3nash and Their Complexes[a]

Compounds	ν(OH + NH)	ν(C=O)	ν(C=N)	Amide II + (C–O) phenyl	ν(C–O)	ν(M–O)	ν(M–N)
H_2nabh	3250b	1665s	1620s	1567m	1280m		
H_3nash	3250b	1670s	1625s	1560m	1280m		
Fe(nabh)·H_2O	3420b		1615s	1595m	1310m	500w	380w
Fe(Hnash)	3380b		1610s	1595m	1300s	520w	390w
Mn(nabh)·H_2O	3416b		1610s	1595m	1290m		410w
Mn(Hnash)	3400mb		1610s	1595m	1290m	480m	390w
Co(nabh)·H_2O	3425b		1610s	1595m	1290m	510m	
Co(Hnash)	3420b		1625s	1590s	1300m	530w	345m
Ni(nabh)·H_2O	3400mb		1630m	1590s	1315m		380w
Ni(Hnash)	3430b		1620s	1595m	1315m		
Cu(nabh)·H_2O	3442mb		1605s	1590m	1315m	515w	
Cu(Hnash)	3450b		1615m	1590m	1310s	510m	380w
Zn(nabh)			1610m	1595s	1290m	520w	430m
Zn(Hnash)	3450b		1605m	1595s	1310m	530w	425w
Cd(nabh)			1610s	1590s	1300s		345w
Cd(Hnash)	3460b		1605m	1590m	1290m	500m	340w
Hg(nabh)	3460b		1610s	1595s	1290m	490w	
Hg(Hnash)	3440b		1610m	1590s	1290m	490w	315w

[a] s = strong, b = broad, mb = medium broad, w = weak.

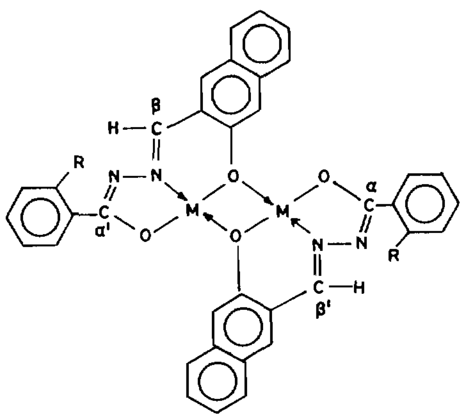

Fig. 2. Structure of M(nabh)·$n$$H_2O$ and M(Hnash)·$n$$H_2O$, M = Cu(II), Ni(II), Co(II); n = 0, 1, 2; R = H, OH.

around 1550–1540 and 1310–1290 cm^{-1} suggesting bonding of the ligands to the metal through O of the C–O group. The upward shift of the ν(C–O) bands is related to the binuclear nature of these complexes involving phenoxide bridging [24, 25]. The non-ligand bands appearing between 530–490 and 340–310 cm^{-1} are assigned to ν(M–O) and ν(M–N) respectively [26]. In Zn(II), Cd(II) and Hg(II) complexes of H_2nabh and H_3nash the bands occurring between 440–420, 350–340 and 330–310 cm^{-1} may be assigned to ν(Zn–N), ν(Cd–N) and ν(Hg–N) vibrations respectively [27].

The general structure proposed for the complexes is given in Fig. 2.

Transmission Electron Microscopic (TEM) Study

Examination of material by electron microscopic study reveals the overall morphology of the substance. The Cu(nabh)·H_2O complex subjected to TEM study was apparently different from the other complexes. Its morphology has been found to be needle shaped.

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