

Equilibrium and spectral studies on ligational behaviour of N,N'-diformylhydrazine

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MS received 26 April 2002; revised 16 October 2002

Abstract. The ligand N,N'-diformylhydrazine (DFH) is a resonance hybrid of its keto- and enol-forms. The resonance structures indicate enolisation of one as well as both the carbonyl groups. This indicates the presence of dissociable protons in the molecule. Equilibrium studies carried out with DFH indicate the presence of one dissociable proton. The solid complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pb(II) with DFH have been synthesized, and have been characterized by elemental analysis, magnetic susceptibility, IR, Far-IR, ¹H NMR, TGA, FAB and reflectance spectra. IR and ¹H NMR spectra of the complexes indicate deprotonation of both the enol protons upon complexation. Elemental and TG analyses of Mn(II), Ni(II), Zn(II) DFH complexes indicate 1 : 1 metal to ligand composition. The dimeric nature of the Mn(II)–DFH complex is supported by its FAB spectrum.

Keywords. N,N'-diformylhydrazine; ligational behaviour; resonance hybrid; keto-enol forms.

1. Introduction

N,N'-Diformylhydrazine (DFH) molecule has a planar S-shape with both –HNCHO groups in the trans form^{1,2}, its relevant symmetry being *C₂h*. The electronic structure of the molecule was studied by use of the molecular orbital method, and also its resonance structures¹. The compound consists of three rotamers viz., *ZZ*, *ZE*, and *EE*. Its ¹H, ¹³C, and ¹⁵N NMR data and rotamer distribution were thoroughly investigated earlier³. The vibrational assignment of the observed frequencies was proposed based upon dichroism of single crystals². As DFH comprises important functional groups in biochemistry and potential binding sites such as 'N' and 'O' in the molecule, it is interesting to study its ligational tendencies. A survey of the literature revealed that no work appears to have been done on the complexing ability of DFH, therefore we took up the study of the ionization process of the ligand and characterization of its metal complexes.

2. Experimental

2.1 Preparation of the ligand

All chemicals used were of AR grade. The ligand was prepared in our laboratory following the reported procedure⁴. DFH was synthesized by refluxing a solution of hydrazine

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hydrate and formic acid in 1 : 2 molar ratios for 30 min. The product was recrystallised from water and the purity of compound was checked by TLC (m.p. 160°C).

2.2 Potentiometric titrations

Potentiometric titrations were carried out for the determination of dissociation constant, adopting the Irving–Rossotti pH titration technique⁵. The following solutions were titrated potentiometrically against standard carbonate-free 0.1 M NaOH containing (i) only acid (4×10^{-3} M), and (ii) acid (4×10^{-3} M) + ligand (1×10^{-3} M), at $m = 0.1$ M (KNO₃) under N₂ atmosphere.

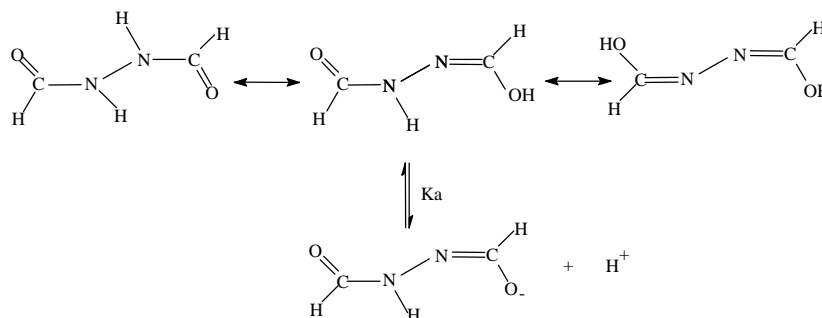
2.3 Synthesis of complexes and physical measurements

To the hot ethanol solution of DFH aqueous MCl₂ (M(II) = Mn, Co, Ni, Cu, Zn)/MSO₄ (M(II) = Fe)/M(NO₃)₂(M(II) = Pb) solution was added in 1 : 2 (M : L) molar ratio. The mixture was refluxed for 12–16 h. The pH of the solution was maintained by adding a few drops of dilute ethanolic ammonium hydroxide solution. The solid complexes that separated were filtered hot, washed with hot ethanol and then with water to remove unreacted ligand and metal, and finally dried under vacuum. IR spectra of the ligand and complexes were recorded as KBr pellets in the range (4000–500 cm⁻¹) on a Perkin-Elmer model 435; the far-IR data were recorded on a Bruker IFS-66v FT-IR. Proton NMR spectra were scanned on a Bruker WH 270 MHz NMR spectrometer. Thermogravimetric analyses (TGA) of the complexes were carried on a Mettler Toledo Star System in the temperature range 0–1000°C. FAB spectra were recorded on a Jeol SX 102/DA-6000 mass spectrometer. The EPR spectrum of the copper complex was recorded on an EPR Varian-E-112 at room temperature and the diffuse reflectance spectrum (d.r.s.) was recorded on a Shimadzu UV 3101BC. Magnetic susceptibilities of the metal chelates were measured at room temperature on a Faraday balance, Model 7550.

3. Results and discussion

3.1 Equilibrium studies

The potentiometric titrations were carried out in aqueous medium at constant temperature of 303 K and 0.1 M (KNO₃) ionic strength. The results revealed that there is only one dissociable proton corresponding to p*K*_a value of 9.1. The dissociation process can be explained, considering keto–enol tautomerism (figure 1). Though the resonance structures indicated enolisation at two carbon atoms, the results of potentiometric titrations clearly indicated dissociation of only one proton in solution. Thus the ligand DFH is a monobasic ligand. To study the effect of temperature on the dissociation constant, potentiometric titrations were carried out with DFH in aqueous medium at various constant temperatures i.e. 303, 313, 323 and 333 K (table 1). Comparison of data reveals that an increase of temperature results in the decrease of p*K*_a values, due to the endothermic nature of the dissociation process. To study the effect of solvent, potentiometric titrations were also carried out in 70% *v/v* ethanol–water medium at temperature of 303 K. The p*K*_a value is found to be greater in ethanol–water medium (table 1). This is due to the low dielectric constant of ethanol as compared to water.

**Figure 1.** Reaction showing dissociation of DFH.**Table 1.** Proton dissociation constant of DFH at constant 0.1 M (KNO₃) ionic strength.

Medium	Temperature (K)	p <i>K</i> _a (enolic OH)
Water	303	9.10
Water	313	8.80
Water	323	8.30
Water	333	7.96
Ethanol-water 70% <i>v/v</i>	303	9.20

Table 2. Physical and analytical data of DFH and its metal complexes.

Compound	Colour	m.p. (°C)	<i>m</i> _{ff} (BM)	Analysis – found (calc.) %			
				C	H	N	M
DFH	White	160	–	27.19 (27.27)	4.54 (4.50)	32.36 (31.81)	–
Mn(II)-DFH	Light brown	Dp	6.42	16.65 (17.03)	1.42 (1.41)	18.04 (19.87)	37.26 (38.96)
Fe(II)-DFH	Reddish brown	Dp	–	14.33 (13.48)	3.12 (3.37)	16.65 (15.73)	31.34 (31.46)
Co(II)-DFH	Brown	Dp	3.24	14.18 (13.28)	3.13 (3.32)	15.97 (15.49)	33.31 (32.48)
Ni(II)-DFH	Light blue	Dp	2.91	13.64 (13.26)	3.78 (3.31)	14.73 (15.47)	31.40 (32.55)
Cu(II)-DFH	Bluish green	Dp	1.19	12.14 (12.93)	3.40 (3.23)	15.36 (15.09)	34.62 (34.24)
Zn(II)-DFH	White	Dp	dia	12.62 (12.81)	3.30 (3.20)	14.65 (14.94)	34.23 (34.86)
Pb(II)-DFH	White	Dp	dia	8.05 (8.18)	0.58 (0.68)	8.45 (8.45)	71.12 (70.66)

dia = diamagnetic

3.2 Characterization of complexes

Elemental analyses show 1 : 1 (metal : ligand) stoichiometry for all the complexes. The analytical data of C, H, N and M for the complexes is given in table 2. The complexes are insoluble in polar and non-polar organic solvents, indicating their polymeric nature. The absence of chloride is evident from Volhard's test⁶. The melting points of all the complexes are above 300°C.

3.2a *IR spectra*: The broad bands centred at 3100 cm⁻¹ and 2917 cm⁻¹ in the IR spectrum of DFH^{2,7} are attributed to ν NH and ν CH respectively. A band at 1607 cm⁻¹ is attributable to C=O stretching vibration. The broad IR bands, and the ν NH and ν C=O absorptions that are lower than expected, are due to the existence of strong inter- and intra-molecular hydrogen bonding in the ligand molecule^{2,8}. The IR spectra⁹ of all the complexes were recorded and compared with that of the ligand to study the structural changes in the ligand upon complexation. IR spectra of the complexes distinctly showed absence of ν NH and ν C=O peaks. The spectra also showed a strong peak in the region of 1540 to 1575 cm⁻¹ in the complexes, attributable to C=N stretching vibration. It is difficult to observe the disappearance of the band due to ν NH on complexation, due to the presence of coordinated water molecules in the complexes. However, the IR spectra of Mn(II) and Pb(II)-DFH complexes clearly showed the absence of ν NH peak as coordinated water molecules are absent in these complexes. The absence of ν NH and ν C=O peaks and appearance of a new ν C=N peak in the complexes indicates enolisation of both the carbonyl groups and subsequent loss of both the protons upon complexation. The Far-IR spectra of the complexes indicated presence of M-O and M-N bonds. Thus the complexes formed in solution are totally different from the solid complexes.

3.2b *¹H NMR spectra*: The ¹H NMR spectrum of DFH in DMSO-*d*₆ recorded a broad singlet peak at δ 10.09, attributable to two amide protons, which is identified by its ready exchange with D₂O. Another signal recorded at δ 7.92– δ 8.2 is due to two formyl protons, the split nature of the signal explains the existence of ligand in three conformations. The ¹H NMR of Pb(II)-DFH in a mixture of CDCl₃-CF₃COOD showed a singlet at δ 7.35, which may be assigned to two protons of formyl groups. The singlet nature of the peak supports the deprotonation of two NH protons through the enol form of the ligand upon complexation, which retards the rotation of the C-N bond due to formation of a double bond. This leads to ligand acquiring sterically preferred *trans* configuration in the complex, resulting in the same chemical environment for two formyl protons.

3.2c *TGA and DTA*: Thermal behaviour of M(II)-DFH (M(II) = Mn, Ni, Zn) complexes were studied¹⁰ in the temperature range of 0–1000°C, using a combined thermogravimetric analyzer and differential thermal analyser.

Thermograms of Mn(II)-DFH indicate weight loss corresponding to decomposition of ligand moiety in two steps in temperature range of 440–450°C and 810–840°C. The residue left at 1000°C is about 44%, and corresponds to the weight of the metal oxide, indicating 1 : 1 composition of the complex. The DTA curve indicates two endothermic peaks at 495 and 810°C. Thermograms of Ni(II)-DFH complex show a total weight loss of 71.6% in two steps in temperature ranges of 100–165°C and 320–420°C, indicating loss of water molecules and decomposition of ligand moiety around the metal ion in the complex. The final residue corresponds to weight of metal oxide indicating composition

of complex as 1 : 1. The DTA curve shows four endothermic peaks at 170, 300, 390 and 435°C, attributable to energy absorptions due to loss of water molecules and total decomposition of complex. Thermograms of zinc complex indicate weight loss corresponding to loss of water molecules and total decomposition of ligand moiety in temperature ranges 100–160°C, 410–460°C and 710–800°C. The residue left at 790°C is about 33%, and corresponds to weight of metal oxide supporting 1 : 1 metal to ligand composition. A gradual weight loss is further observed in the temperature range 800 to 900°C, which is due to the melting and vaporization of zinc metal, as its m.p. is 792.6°C. The corresponding DTA curve also shows four endothermic peaks.

3.2d UV-visible diffused reflectance spectra and magnetic moments: The UV-Vis diffused reflectance spectra¹¹ (d.r.s.) of Co(II)-DFH show two bands. Assuming octahedral symmetry, these transitions are assigned as ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g} \rightarrow {}^4T_{2g}$. The d.r.s. of Ni(II)-DFH indicate three bands which are attributed to transitions of ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The observed magnetic moment for Mn(II)-DFH complex is 6.42, which is close to spin only moment. The magnetic moment observed for Co(II)-DFH complex is 3.24 BM. The observed magnetic moment value is in the range expected for high spin octahedral Co(II) complexes. The magnetic moment value for Ni(II)-DFH complex at room temperature is 2.91 BM, which corresponds to presence of two unpaired electrons. The observed magnetic moment value for Cu(II)-DFH complex is 1.19 BM. The observed magnetic moment is less than the expected value. This may be due to anti-ferromagnetic interactions¹² persisting in the complex, where neighbouring magnetic dipoles tend to align in the opposite direction, resulting in zero moment or a decrease in the magnetic moment.

3.2e ESR and FAB spectra: The ESR spectrum of Cu(II)-DFH indicates anisotropy in g values. The g_{\parallel} and g_{\perp} values are 2.171 and 2.039. The fast atom bombardment (FAB) spectrum of the Mn(II)-DFH complex exhibits molecular ion peak at m/z 281, which corresponds to the mass of the binuclear complex.

Thus from the thermal studies it is concluded that the complexes formed are of 1 : 1 (M : L) composition with two moles of coordinated water indicating octahedral geometry, except for Mn(II) and Pb(II)-DFH complexes where tetrahedral geometry is predicted due to the absence of coordinated water. The tentative structures of the complexes

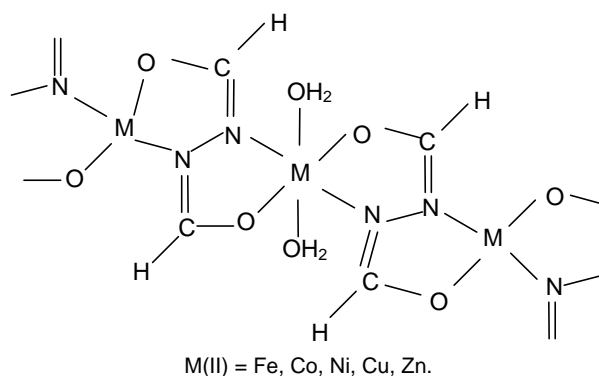


Figure 2. M(II)-DFH complexes.

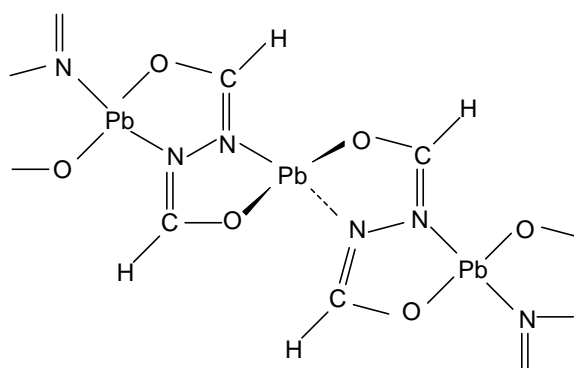


Figure 3. PB(II)–DFH complex.

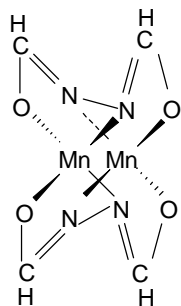


Figure 4. Mn(II)–DFH complex.

(figures 2–4) are given based on the results obtained from IR, ^1H NMR, elemental and thermal studies.

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