

Studies on 2-acetylpyridineisonicotinoyl hydrazone complexes of some bivalent 3d-metal ions

PARITI S S J SASTRY and T R RAO*

Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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Abstract. 2-Acetylpyridineisonicotinoyl hydrazone (Hapinh) complexes of OV(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) having 1:1 metal–ligand stoichiometry have been prepared and characterised by elemental analyses, molar conductance, magnetic susceptibility, electronic, infrared, ESR and NMR (^1H and ^{13}C) studies. Octahedral/distorted octahedral geometry has been assigned for the OV(II), Mn(II), Ni(II), Cu(II) and Zn(II) complexes while tetrahedral and trigonal bipyramidal configurations have been suggested for the Co(II) adduct and deprotonated complexes respectively. IR and NMR spectral studies suggest a tridentate behaviour of Hapinh and apinh^- species in the adducts and deprotonated complexes respectively.

Keywords. 2-Acetylpyridineisonicotinoyl hydrazone complexes; 3d-metal complexes; unsymmetrical Schiff-base complexes.

1. Introduction

Apart from the importance of isonicotinic acid hydrazide and its derivatives due to their well known antitubercular activity (Sorkin *et al* 1952), the chelating Schiff-base derived from pyridoxal and isonicotinic acid hydrazide (H_2pih) has attracted considerable attention in the search for high affinity iron chelators due to its high activity in mobilising cellular iron in a variety of cellular and animal-based bioassays (Martell *et al* 1981; Modell and Berdoukas 1984). Recent studies (Ponka *et al* 1984) have shown that the analogue, Hapinh is as active as H_2pih in reticulocyte cells. Further investigations on protonation constants of H_2pih and related Schiff-bases (Richardson *et al* 1990), their formation constants with iron(III) (Vitolo *et al* 1990) and their interesting behaviour in forming zwitterions (Heinert and Martell 1959) and consideration of the high-activity of Hapinh have prompted us to undertake systematic studies on the complexation tendency of 2-acetylpyridineisonicotinoyl hydrazone (Hapinh). Hence, in continuation of our previous studies on metal-complexes of pyridine carboxylic acid hydrazides and hydrazones (Rao and Khan 1986; Rao and Singh 1990, 1991; Rao and Srivastava 1992; Rao *et al* 1992), this paper describes the results of investigations on the synthetic and spectral studies of 2-acetylpyridineisonicotinoyl hydrazone (Hapinh) (figure 1) complexes with OV(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).

*For correspondence

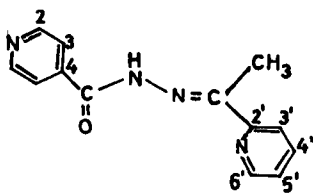


Figure 1. Structure of Hapinh.

2. Experimental

2.1 Starting materials

All the chemicals and metal salts were from BDH or E. Merck. 2-Acetylpyridine and isonicotinic acid hydrazide obtained from Sigma Chemical Company, USA were used as supplied. 2-Acetylpyridineisonicotinoyl hydrazone was prepared as reported (Rao and Singh 1990).

2.2 Preparation of the complexes

Adduct complexes were prepared by mixing together solutions of the appropriate metal salt (2 mmol/0.48 g in 20 cm³ EtOH) and Hapinh (2 mmol/~0.50 g, in 40 cm³ EtOH) and keeping the reaction mixture under stirring for ~ 1 h. The complexes thus formed were filtered off, washed repeatedly with ethanol to remove the excess of starting material, if any, and dried at room temperature.

Deprotonated complexes were prepared by mixing together aqueous solutions of the appropriate metal salt (2 mmol/0.48 g in 20 cm³) and potassium salt of the ligand (2 mmol/0.48 g of Hapinh and 2 mmol/0.12 g of KOH taken together in 40 cm³ of H₂O) and adjusting, if necessary, the pH of the solution to ~ 6.8. The complexes thus formed were digested on a water bath for ~ 0.5 h. The resulting complexes were filtered off, washed successively with water and ethanol and finally dried at room temperature.

2.3 Analysis

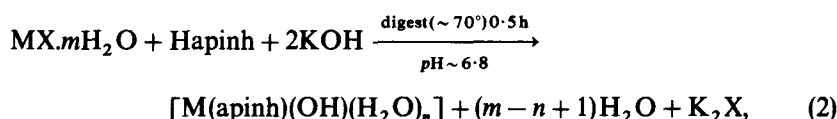
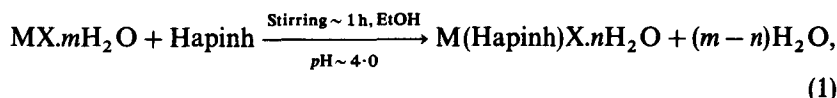
The complexes were analysed for their metal contents using literature procedures (Vogel 1973). The chloride and the sulphate were estimated gravimetrically as AgCl and BaSO₄ respectively (Vogel 1973). Hydrazine was estimated (Vogel 1973) volumetrically by titrating KIO₃ after subjecting the complexes to acid hydrolysis. Nitrogen was microanalysed.

2.4 Physical measurements

The molar conductances of the complexes were measured at room temperature on a WTW conductivity meter. The IR spectra (4000–400 cm⁻¹) were recorded on a JASCO FT/IR-5300 spectrophotometer and the UV-visible spectra on a Cary-2390 and Shimadzu (model-160A) spectrophotometers. The room temperature magnetic susceptibility measurements were carried out on a Cahn-Faraday electrobalance using Hg[Co(NCS)₄] as the calibrant. The ESR spectra were recorded on a Bruker X-band ESP-300 spectrometer and the NMR spectra on a Jeol FX 90Q multinuclear and Bruker VM-40C (400 MHz FT/NMR) spectrometers.

3. Results and discussions

Hapinh reacts with the metal salts in its non-deprotonated and deprotonated forms yielding two types of complexes as indicated by the analytical data (table 1). Elemental analyses of the complexes show a 1:1 metal–ligand ratio and the reaction presumably proceeds as follows:



where M = OV(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); $n = 2, 1$ or 0; and X = Cl₂ or SO₄.

All the complexes are stable at room temperature but get decomposed on heating beyond 240°C. They are soluble in DMF, DMSO and pyridine while the adduct complexes are also soluble in water. Molar conductances in 0.001 M DMF solutions show a 1:1 electrolytic nature of the Co(II) adduct complex and a nonionic behaviour of all the other complexes (Geary 1971). Insolubility in non-coordinating solvents and decomposing behaviour presumably suggest polymeric nature (Hua *et al* 1972; Lorenzini *et al* 1983) of the present complexes.

3.1 Magnetic moments and electronic spectra

The room temperature magnetic moments corrected for diamagnetism are given in table 1 while the electronic spectral data along with the assignments are included in table 2. The slightly low magnetic moment of the Cu(II) deprotonated complex may presumably be due to antiferromagnetic coupling phenomenon that usually occurs in polymetallic Cu(II) systems by virtue of a superexchange interaction (Narang and Aggarwal 1974). The single band observed at 14 084 and 14 858 cm⁻¹ respectively in the adduct and the deprotonated Cu(II) complexes may be assigned to a distorted octahedral geometry (Sacconi 1969). The $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ ratios (1.46 for the adduct and 1.30 for the deprotonated complex) suggest a considerable distortion in the octahedral geometry (Jorgensen 1955). The magnetic moments of the Ni(II) complexes and the electronic spectral bands observed in the 9652–12 406, 15 527–19 851 cm⁻¹ and at $\sim 32\,258$ cm⁻¹ regions are independently assignable to an octahedral geometry around the metal ion (Lever 1968). The μ_{eff} value of the Co(II) adduct complex and the electronic spectral bands at 8196, 15 503 and 16 666 cm⁻¹ may be assigned to a tetrahedral geometry (Cotton *et al* 1961; Figgis and Lewis 1964). High-spin, five-coordinate Co(II) complexes normally exhibit magnetic moments in the range 3.50–4.40 BM and produce two major visible bands at $(5.0\text{--}6.5) \times 10^3$ cm⁻¹ and $(14.0\text{--}16.0) \times 10^3$ cm⁻¹ (Sacconi and Bertini 1966; Boge *et al* 1977). The present Co(II) deprotonated complex shows a magnetic moment of 3.62 BM suggesting a five-coordinate geometry in analogy to that of penta-coordinate Co(benacPhDPT) (3.50 BM) reported by Chen *et al* (1981). Further, the corresponding electronic spectrum shows two bands at 6793 and 13 888 cm⁻¹ suggesting most likely a trigonal bipyramidal geometry (Chen *et al* 1981). The room temperature magnetic moment of the OV(II) adduct complex is close to the spin-only value of a d^1 system indicating the absence of

Table 1. Analytical data and general behaviour of the 3d-metal complexes of Hapinh.

Complex	Colour	M.P. (<i>d</i>) (°C)	Analysis - Found (Calcd.) %					μ_{eff} (BM)	Molar conductance (ohm ⁻¹ cm ² mol ⁻¹)
			M	Cl/SO ₄	N ₂ H ₄	N	N		
[Cu(Hapinh)Cl ₂ (H ₂ O)]	Green	240	15.90 (16.18)	17.96 (18.08)	—	14.20 (14.26)	1.96	34.9	
[Ni(Hapinh)Cl ₂ (H ₂ O)]	Light green	300	14.98 (15.15)	18.25 (18.31)	8.15 (8.25)	14.34 (14.44)	3.21	27.2	
[Mn(Hapinh)Cl ₂ (H ₂ O)]	Yellow	338	14.24 (14.31)	18.35 (18.49)	8.30 (8.33)	14.52 (14.58)	5.95	8.2	
[Zn(Hapinh)Cl ₂ (H ₂ O)]	Light Yellow	333	16.50 (16.58)	17.91 (18.00)	8.04 (8.11)	14.10 (14.19)	Diamag.	39.6	
[Co(Hapinh)Cl]Cl	Green	265	15.85 (15.93)	18.98 (19.19)	8.57 (8.65)	15.07 (15.13)	4.41	108.7	
[OV(Hapinh)SO ₄]	Greenish yellow	320	12.42 (12.64)	23.68 (23.82)	—	13.75 (13.89)	1.82	23.9	
[Cu(apinh)(OH)(H ₂ O) ₂]	Green	252	17.71 (17.82)	—	—	15.70 (15.75)	1.68	7.6	
[Ni(apinh)(OH)(H ₂ O) ₂]	Yellowish brown	345	16.51 (16.69)	—	(9.07) (9.09)	15.96 (15.96)	3.17	36.5	
[Mn(apinh)(OH)(H ₂ O) ₂]	Grey	345	15.60 (15.78)	—	9.09 (9.19)	16.09 (16.14)	5.84	18.6	
[Zn(apinh)(OH)(H ₂ O) ₂]	Light Yellow	333	18.12 (18.24)	—	8.82 (8.93)	15.66 (15.67)	Diamag.	7.8	
[Co(apinh)(OH)(H ₂ O) ₂]	Yellowish brown	320	17.51 (17.64)	—	9.42 (9.58)	16.79 (16.82)	3.62	17.5	
[OV(apinh)(OH)]	Yellowish Green	315	15.61 (15.77)	—	—	17.21 (17.34)	Diamag.	12.9	

d = decomposition temperature

Table 2. Electronic spectral bands (cm^{-1}) and their assignments.

Complex	Bands (cm^{-1})	Assignments
[Cu(Hapinh)Cl ₂ (H ₂ O)]	14084	${}^2E_g \rightarrow {}^2T_{2g}$
[Ni(Hapinh)Cl ₂ (H ₂ O)]	9652, 15527	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F)$
[Co(Hapinh)Cl]Cl	8196, 15503, 16666	${}^4A_2 \rightarrow {}^4T_1(F), {}^4T_1(P)$
[OV(Hapinh)SO ₄]	12500, 16666	$d_{xy} \rightarrow d_{xz}, d_{yz}; d_{x^2-y^2}$
[Cu(apinh)(OH)(H ₂ O) ₂]	14858	${}^2E_g \rightarrow {}^2T_{2g}$
[Ni(apinh)(OH)(H ₂ O) ₂]	12406, 19851, 32258	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$
[Co(apinh)(HO)(H ₂ O)]	6793, 13888	$d_{xz}, d_{yz} \rightarrow d_{zy}, d_{x^2-y^2}, d_{z^2}$

any metal-metal interaction and the electronic spectrum yields two bands at 12 500 and 16 666 cm^{-1} which are in accordance with an octahedral geometry around vanadium (Aggarwal *et al* 1979). In contrast, the deprotonated complex of the oxovanadium(II) was found to be diamagnetic at room temperature and accordingly no $d-d$ transition was found in the electronic spectrum. The diamagnetic nature of the complex may presumably be due to a complete magnetic coupling of the lone spins of OV(II) in the adjacent molecules.

3.2 Infrared spectra

The infrared frequencies (KBr pellets) of the structurally important bands along with their assignments are given in table 3. Hapinh shows intense absorption bands at 1670, 1620, 1550 and 1302 cm^{-1} which may be, respectively, assigned to the amide-I, $\nu(\text{C}=\text{N})$, amide-II and amide-III modes (Figgins and Busch 1961; Rana *et al* 1977). The spectra of the adduct complexes show a bathochromic shift of the amide-I, -II and a hypsochromic shift of the amide-III bands suggesting bonding through the carbonyl oxygen and the azomethine nitrogen. However, all the amide bands totally disappear from the spectra of the deprotonated complexes, while a sharp band, diagnostic of $>\text{C}-\text{N}=\text{C}<$ group (Sayed and Iskander 1971), appears at $\sim 1595 \text{ cm}^{-1}$, which indicates *trans*-formation of the carbonyl group to the enolic form through an amide \rightleftharpoons imidol tautomerism and subsequent coordination of the imidol oxygen upon deprotonation. Appearance of new bands characteristic of $\nu(\text{NCO}^-)$ at $\sim 1500, 1365 \text{ cm}^{-1}$ regions further supports the imidolic oxygen coordination (Rao 1963). Coordination of the acetyl pyridyl ring nitrogen is suggested on the basis of the observed changes in the ring skeletal mode (ligand ~ 990 , complexes $\sim 1010 \text{ cm}^{-1}$), in-plane ring deformation mode (ligand ~ 586 , complexes $\sim 640 \text{ cm}^{-1}$) and out-of-plane ring deformation mode (ligand ~ 410 , complexes $\sim 440 \text{ cm}^{-1}$) (Sakamoto 1987). The spectra of the oxovanadium(II) complexes show an additional band at 947/968 cm^{-1} due to the $\text{V}=\text{O}$ stretching mode (Selbin *et al* 1963). Presence of three additional bands at 1244, 1130 and 1047 cm^{-1} in the ν_3 region of the vanadyl adduct complex indicates the chelating sulphate group (Eskenazi *et al* 1966).

3.3 ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra

The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra of Hapinh and the Zn(II) complex were recorded in DMSO- d_6 solutions and the spectral data along with the assignments are given in table 4. The numbering scheme of the carbon atoms is the same as shown in figure 1.

Table 3. IR spectral data (cm^{-1}) of the 3d-metal complexes of Hapinh.

Complex	2-Acetyl pyridyl ring vibrations					
	Amide-I	Amide-II	Amide-III	Ring skeletal	In-plane deformation	Out-of-plane deformation
Hapinh	1670	1550	1302	990	586	410
Cu(Hapinh)Cl ₂ (H ₂ O)]	1633	1533	1330	1000	646	461
[Ni(Hapinh)Cl ₂ (H ₂ O)]	1631	1531	1320	1020	645	430
[Mn(Hapinh)Cl ₂ (H ₂ O)]	1633	1520	1321	1012	634	434
[Zn(Hapinh)Cl ₂ (H ₂ O)]	1637	1518	1329	1018	640	440
[Co(Hapinh)Cl]Cl	1622	1530	1334	1010	638	440
[OV(Hapinh)SO ₄]	1637	1540	1320	1003	640	430
	>C=N-N=C<		$\nu(\text{NCO}^-)$			
[Cu(apinh)(HO)(H ₂ O) ₂]	1601		1500, 1380	1008	635	442
[Ni(apinh)(HO)(H ₂ O) ₂]	1595		1496, 1365	1010	630	448
[Mn(apinh)(HO)(H ₂ O) ₂]	1591		1493, 1380	1010	634	445
[Zn(apinh)(HO)(H ₂ O) ₂]	1593		1502, 1361	1010	636	440
[Co(apinh)(HO)(H ₂ O)]	1593		1500, 1363	1010	640	445
[OV(apinh)(HO)]	1597		1516, 1377	1010	652	450

Table 4. ^1H and ^{13}C NMR spectral data of Hapinh and the Zn(II) complex.

Proton/carbon atom	Hapinh	[Zn(Hapinh)Cl ₂ (H ₂ O)]
H ₃ C	2.52s	2.60s
-NH-	11.14s	11.41s
HC ₂	8.76d	8.81d
HC ₃ + HC ₅	7.81d	7.73s
HC _{3'}	7.38d	7.45d
HC _{4'}	8.01m	8.13m
HC _{6'}	8.62d	8.65d
>C=O	163.11	168.26
N=C(CH ₃)	150.78	153.73
H ₃ C-	12.74	13.22
C ₂	149.96	149.85
C ₃	122.06	123.53
C _{2'}	154.84	167.02
C _{3'}	120.38	122.85
C _{4'}	136.58	139.76
C _{5'}	124.22	125.09
C _{6'}	148.61	146.81

^{13}C NMR data measured in ppm w.r.t. DMSO-*d*₆ (39-50 ppm).
s = singlet; d = doublet; m = multiplet.

The ^1H NMR spectrum of the Zn(II) complex shows a downfield shift of the -NH- signal suggesting coordination through the carbonyl oxygen and/or azomethine nitrogen (Patil and Kulkarni 1984). Coordination through the azomethine nitrogen is also implied by the observed downfield shift of the -CH₃ signal. Coordination through the ring nitrogen of the acetyl pyridyl group may be suggested on the basis of the downfield shifts of the HC_{4'} and HC_{6'} signals. The unaltered positions of the isonicotinoyl ring proton signals in the complexes rule out coordination through the ring nitrogen.

The proton-noise decoupled ^{13}C NMR spectrum of the Zn(II) complex shows significant downfield shifts of the >C=O and N=C(CH₃) signals suggesting coordination of the carbonyl oxygen and azomethine nitrogen. Further, the observed downfield shifts of the C_{2'}, C_{3'}, C_{4'}, C_{5'} and C_{6'} signals imply coordination through the acetyl pyridyl ring nitrogen (Paolucci *et al* 1980). However, all the isonicotinoyl ring carbon signals show no change suggesting non-coordination through the ring nitrogen.

3.4 ESR spectra

The room temperature DMSO solution spectrum of the oxovanadium(II) adduct complex shows eight lines due to the ^{51}V nucleus ($I = 7/2$) yielding only g_{iso} and A_{iso} values while the DMSO glassy spectrum at LNT shows anisotropic features with g_{\parallel} and g_{\perp} values. The deprotonated complex of the OV(II) (DMSO solution) shows no signals at RT. The g values in the LNT spectra of both the adduct and the deprotonated complexes are found in the order $g_{\parallel} < g_{\perp} < g_e$ (2.0023), which is indicative of the presence of the unpaired electron in the d_{xy} (b_{2g}^*) orbital (Cone and Sharpless 1965).

The EPR spectra of the Cu(II) complexes were recorded in DMSO solution at RT and LNT. The Cu(II) adduct complex at RT shows an isotropic nature due to tumbling

motion of the molecules in solution (Hathaway and Billing 1970), while the DMSO glassy state spectrum was well resolved on the low field side allowing accurate calculation of the g_{\parallel} and A_{\parallel} values. The anisotropic behaviour of the spectrum at LNT suggests typically an elongated octahedron. The corresponding deprotonated Cu(II) complex shows a single and broad isotropic signal yielding only the g_{iso} value which suggests interaction between the adjacent Cu(II) centres (Piquenard and Lautie 1982).

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