

involving the Cu^{2+} $d_{x^2-y^2}$ and oxygen p_x orbitals is important, distortion from planarity toward tetrahedral geometry would reduce overlap of the orbitals and weaken antiferromagnetic exchange.²⁶⁻²⁸

In this tetranuclear series a larger R produces a stronger antiferromagnetic interaction, and thus it would seem that variations in spectral and magnetic properties must be explained as a systematic variation in the dimer-dimer interaction. The change in central atom geometry from four- to five-coordinate by the introduction of a fifth donor in the apical position of the vinyl acetate dimer also occurs in the aggregation of two imino-alkoxy dinuclear units to form a tetranuclear species. Since, in general, short bond distances lead to greater overlap of metal d orbitals with orbitals of bridging oxygens leading to stronger interactions, a decrease in overlap of the copper d orbitals and sp hybrid orbitals on the bridging oxygens must occur with an increase in the bulk of R.

Therefore, as the bulk of R increases and the Cu-O (axial) overlap decreases, we see an increase in the antiferromagnetic

behavior of the complex (Figure 2). This may be ascribed to less distortion of the dinuclear exchange system due to less dimer-dimer interaction and a dominance of the intradimer exchange pathway over the interdimer exchange pathway. Although coupling constants are small and small structural changes could easily affect their values, we believe this systematic variation of the magnitude of the coupling constants with the nature of R demonstrates that, in an imino complex of this type, the nature of a substituent group in the chelate ring containing the bridging oxygen atom has an important effect on the degree and type of magnetic interaction between the four Cu^{2+} ions. The effect is clearly steric in nature, in agreement with earlier results in which the size and confirmation of this ring has been varied.^{12,13} In particular, we show that even such an apparently trivial change as the use of resolved rather than racemic ligands may have a significant effect on interactions in the solid state.

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Registry No. 2, R = H, 77744-95-7; 2, R = CH_3 , 77744-96-8; 2, R = C_2H_5 , 77744-97-9; 2, R = C_6H_5 , 77744-98-0; 2, R = $(\text{CH}_3)_2\text{CH}$, 77744-99-1; 2, R = CH_3 (racemic), 77841-55-5.

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Contribution from the Department of Chemistry,
Banaras Hindu University, Varanasi 221005, India

Magnetic and Spectroscopic Studies on *N*-(Picolinamido)salicylaldimine Complexes of Some Bivalent 3d Metal Ions

R. C. AGGARWAL,* N. K. SINGH, and R. P. SINGH

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Adducts as well as deprotonated complexes of *N*-(picolinamido)salicylaldimine (H_2PIS) of the types $\text{MCl}_2 \cdot 2\text{H}_2\text{PIS}$ [$\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$], $\text{M}(\text{HPIS})_2$ [$\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II})$], and $\text{M}(\text{PIS}) \cdot n\text{H}_2\text{O}$ [$\text{M} = \text{V}^{\text{IV}}\text{O}$, $\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II})$; $n = 1$ for $\text{V}^{\text{IV}}\text{O}$, 2 for other metal ions] have been prepared. In the case of $\text{Cu}(\text{II})$ a partially deprotonated $\text{Cu}(\text{HPIS})\text{Cl} \cdot \text{H}_2\text{O}$ has also been obtained. Molar conductivities indicate nonelectrolytic behavior of deprotonated complexes and some ionic dissociation of the adducts in 10^{-3} M DMF solution. Magnetic and electronic spectral studies suggest octahedral geometry for all the complexes except those of $\text{Cu}(\text{II})$, which are distorted octahedra. The distorted octahedral geometry for $\text{Cu}(\text{II})$ complexes is further shown by the solid-state ESR spectra. X-ray powder diffraction studies of $\text{Cu}(\text{PIS}) \cdot 2\text{H}_2\text{O}$ suggest that this complex belongs to the tetragonal crystal system with $a = 8.6059$ Å, $c = 17.7$ Å, and $Z = 4$. The infrared spectral studies indicate that H_2PIS acts as a bi-, ter-, or quadridentate ligand in the complexes.

Introduction

Recently a number of papers^{1,2} have been published from our laboratories on 3d metal complexes of acetone isonicotinoyl-, nicotinoyl-, and picolinoylhydrazones and salicylaldehyde isonicotinoylhydrazone. This work has now been extended to the hitherto uninvestigated *N*-(picolinamido)- and *N*-(nicotinamido)salicylaldimine complexes of 3d metal ions because there are as many as five potential donor sites and a possibility of keto-enol tautomerism in these ligands, which may be expected to lead to varied bonding and stereochemical behavior in the complexes. The present paper describes the results of our investigation on the synthesis and structural studies of *N*-(picolinamido)salicylaldimine complexes of $\text{V}^{\text{IV}}\text{O}$,

$\text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}),$ and $\text{Zn}(\text{II})$.

Experimental Section

Materials. All the chemicals used in this study were of BDH or equivalent quality. *N*-(Picolinamido)salicylaldimine was prepared as described by Sacconi;³ mp 172 °C (lit.³ mp 173-75 °C).

Synthesis and Analysis of the Complexes. Dichlorobis(*N*-picolinamido)salicylaldimine)metal(II) complexes, $\text{M}(\text{H}_2\text{PIS})_2\text{Cl}_2$ [$\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$], were obtained by mixing ethanolic solutions of H_2PIS and the appropriate metal chloride in ~2:1 molar ratio and refluxing the reaction mixture for about 6 h. The resulting solution was concentrated to incipient crystallization.

Aquo(*N*-(picolinamido)salicylaldiminato)oxovanadium(IV), $\text{VO}(\text{PIS}) \cdot \text{H}_2\text{O}$, and chloroaquo(*N*-(picolinamido)salicylaldiminato)copper(II), $\text{Cu}(\text{HPIS})\text{Cl} \cdot \text{H}_2\text{O}$, were prepared by mixing the methanolic or ethanolic solutions of H_2PIS and vanadyl sulfate or cupric chloride in a 1:1 molar ratio. The complexes precipitated almost immediately.

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Table I. Analytical Data and General Behavior of H₂PIS Complexes^a

complex	color	% metal	% N	% Cl	% H ₂ O	μ_{eff}, μ_B	mp, °C
Mn(H ₂ PIS) ₂ Cl ₂	yellowish brown	8.69 (9.08)	13.12 (13.88)	11.52 (11.72)		6.03	288
Co(H ₂ PIS) ₂ Cl ₂	reddish brown	9.82 (9.63)	13.70 (13.72)	11.47 (11.58)		4.73	288
Ni(H ₂ PIS) ₂ Cl ₂	light green	9.45 (9.59)	13.48 (13.73)	11.65 (11.59)		3.14	290 dec
Cu(HPIS)Cl·H ₂ O	green	18.05 (17.79)	12.13 (11.76)	9.74 (9.93)	5.30 (5.04)	1.89	204
Mn(HPIS) ₂	light brown	10.61 (10.27)	16.06 (15.70)			5.70	>250
Co(HPIS) ₂	reddish brown	10.80 (10.93)	14.95 (15.58)			3.93	>250
Ni(HPIS) ₂	light brown	10.83 (10.89)	15.47 (15.59)			3.20	>250
Cu(HPIS) ₂	green	12.04 (11.69)	14.84 (15.45)			1.80	>250
Zn(HPIS) ₂	yellow	11.23 (11.98)	15.15 (15.40)			diamag	>250
VO(PIS)·H ₂ O	reddish brown	15.10 (15.72)	13.25 (12.96)		6.02 (5.55)	1.68	>250
Mn(PIS)·2H ₂ O	light brown	16.32 (16.65)	12.60 (12.72)		10.50 (10.91)	5.73	>250
Co(PIS)·2H ₂ O	dark brown	16.93 (17.64)	12.88 (12.57)		10.70 (10.78)	3.50	>250
Ni(PIS)·2H ₂ O	brown	16.97 (17.59)	13.01 (12.58)		10.28 (10.78)	2.97	>250
Cu(PIS)·2H ₂ O	green	18.70 (18.76)	12.29 (12.40)		10.56 (10.63)	1.90	>250
Zn(PIS)·2H ₂ O	yellow	19.30 (19.20)	12.71 (12.33)		10.35 (10.57)	diamag	>250

^a Calculated values are given in parentheses.

Table II. Electronic Spectral Data and Various Ligand Field Parameters of H₂PIS Complexes

complex	band max, cm ⁻¹	assignments	10Dq, cm ⁻¹	B', cm ⁻¹	β	$\beta^\circ, \%$	LFSE, kJ mol ⁻¹
VO(PIS)·H ₂ O	13 330, 17 540	$d_{xy} \rightarrow d_{yz}, d_{xz}, d_{x^2-y^2}$	17 540				83.9
Co(H ₂ PIS) ₂ Cl ₂	8230, 19 050	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4T_{1g}(P)$	9329	794	0.816	18.3	89.2
Co(HPIS) ₂	9090, 19 050	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4T_{1g}(P)$	10395	737	0.758	24.2	99.5
Co(PIS)·2H ₂ O	9000, 20 000	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4T_{1g}(P)$	10980	808	0.831	16.9	105.0
Ni(H ₂ PIS) ₂ Cl ₂	9435, 15 380	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F)$	9435	862	0.816	18.4	135.4
Ni(HPIS) ₂	10 750, 17 000	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F)$	10 750	798	0.756	24.4	154.3
Ni(PIS)·2H ₂ O	10 810	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	10 810				155.1
Cu(HPIS)Cl·H ₂ O	14 285	${}^2E_g \rightarrow {}^2T_{2g}$	14 285				102.4
Cu(HPIS) ₂	14 705	${}^2E_g \rightarrow {}^2T_{2g}$	14 705				105.5
Cu(PIS)·2H ₂ O	14 815	${}^2E_g \rightarrow {}^2T_{2g}$	14 815				106.3

Bis(*N*-(picolinamido)salicylaldiminato)metal(II) complexes, M(HPIS)₂, [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)] were precipitated by reacting aqueous solutions of the metal chlorides and ethanolic solutions of the ligand in ~1:2 molar ratio followed by the addition of 1 equiv of aqueous NaOH.

Diquo(*N*-(picolinamido)salicylaldiminato)metal(II) complexes M(PIS)·2H₂O [M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)] were prepared similarly by mixing the metal chloride, ligand, and aqueous NaOH in a 1:1:2 molar ratio.

The adducts and deprotonated complexes prepared as above were filtered, washed with alcohol and 50% ethanol, respectively, and dried in vacuo. Zn-doped copper(II) 1:1 and 1:2 complexes were prepared just as the respective pure copper(II) complexes with a 5:95 molar ratio of copper(II) and zinc(II) chlorides.

The complexes were analyzed for metal, nitrogen, and chloride as described earlier.⁴ The water content of the hydrated complexes was determined by heating them in the range 80–180 °C and finding out the loss in weight. The analytical data are given in Table I.

Instrumentation. The equipment and the methods employed for recording molar conductance, magnetic susceptibility, and electronic and infrared spectra were the same as described in our previous studies.⁴ The values of the various spectral parameters such as 10Dq, B', β , β° , and LFSE were calculated as described by Lever.⁵ The

pertinent experimental data are given in Tables I–III. ESR spectra of Cu(HPIS)₂ and Cu(PIS)·2H₂O doped in the diamagnetic host lattice of Zn(HPIS)₂ and Zn(PIS)·2H₂O were recorded at 77 K on a Varian X-band spectrometer, Model E-4, using DPPH as a *g* marker. The ESR parameters g_{\parallel} , g_{\perp} , g_{av} , A_{\parallel} , and A_{\perp} deduced from the analysis of the spectra are given in Table IV. The in-plane σ - and π -bonding parameters α^2 and β^2 , respectively, calculated according to the method of Neiman and Kivelson⁶ with the assumption of an axial field and consideration of only the Zeeman term with anisotropy in *g*, are given in Table V. The X-ray powder photograph for Cu(PIS)·2H₂O was obtained on a Philips X-ray generator using nickel-filtered Cu K radiation and a Debye–Scherrer camera. The indexing of the X-ray diffraction lines was done by Ito's method.⁷ The observed *Q* values and those calculated for tetragonal symmetry along with the corresponding *hkl* values are included in Table VI.

Results and Discussion

The analytical data given in Table I show that H₂PIS forms two types of complexes, viz., adducts and deprotonated complexes in neutral and alkaline media, respectively; VO(PIS)·H₂O and Cu(HPIS)Cl·H₂O are, however, formed in neutral

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Table III. Important Infrared Spectral Bands (cm^{-1}) and Their Assignments

compd	$\nu(\text{OH})$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	amide I	amide II	amide III	$\nu_{\text{sym}}^-(\text{C}-\text{O})$	$\nu_{\text{asym}}^-(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$	py ring vib	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$
H_2PIS	3400 w	3310 s	1620 s	1695 s	1500	1265	1290		1030	995, 620, 400			
$\text{Mn}(\text{H}_2\text{PIS})_2\text{Cl}_2$	3440	3360	1620 s	1640 s	1510	1275	1290		1025	1010, 630, 410	300	260 ^a	320
$\text{Co}(\text{H}_2\text{PIS})_2\text{Cl}_2$	3400 br	3340 br	1620 s	1630 s	1520	1270	1290		1025	1015, 640, 410	305	240 ^a	340
$\text{Ni}(\text{H}_2\text{PIS})_2\text{Cl}_2$	3400 br		1615 s	1625 s	1510	1270	1290		1025	1015, 650, 418	300	270 ^a	340
$\text{Cu}(\text{HPIS})\text{Cl}\cdot\text{H}_2\text{O}$	3520 br	3350	1600 s	1620 s	1520	1270	1340	1535 s	1050	1010, 645, 420	300	290 ^a	330
$\text{Mn}(\text{HPIS})_2$		3240 m	1590 s	1665 s		1270	1340	1545 s	1050	995, 620, 400	290	342	
$\text{Co}(\text{HPIS})_2$		3240 m	1590 s	1660 s		1270	1340	1530 s	1050	995, 620, 400	300	350	
$\text{Ni}(\text{HPIS})_2$		3245 m	1590 s	1660 s		1270	1340	1535 s	1050	995, 620, 400	300	352	
$\text{Cu}(\text{HPIS})_2$		3240 m	1600 s	1655 s		1280	1350	1525 s	1050	995, 620, 400	310	360	
$\text{Zn}(\text{HPIS})_2$		3250 m	1590 s	1660 s		1270	1340	1535 s	1050	995, 620, 400	300	350	

compd	$\nu(\text{OH})$	$\nu(\text{C}=\text{N})$	$\delta(\text{HOH})$	$\nu(\text{NCO})$	$\nu_{\text{sym}}^-(\text{C}-\text{O})$	$\nu_{\text{asym}}^-(\text{C}-\text{O})$	$\nu(\text{N}-\text{N})$	py ring vib	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	$\text{M}\leftarrow\text{N}(\text{py})^a$
$\text{VO}(\text{PIS})\cdot\text{H}_2\text{O}$	3500 br	1600 s	1650 w	1530	1340	1540 s	1050	1020, 640, 420	490	390	285
$\text{Mn}(\text{PIS})\cdot 2\text{H}_2\text{O}$	3420 br	1600 s	1650 w	1535	1345	1535 s	1050	1020, 635, 410	295	345	270
$\text{Co}(\text{PIS})\cdot 2\text{H}_2\text{O}$	3400 br	1600 s	1650 w	1525	1340	1540 s	1050	1015, 640, 415	300	350	280
$\text{Ni}(\text{PIS})\cdot 2\text{H}_2\text{O}$	3400 br	1600 s	1650 w	1530	1340	1520 s	1050	1020, 640, 420	290	340	280
$\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$	3440 br	1600 s	1650 w	1525	1350	1540 s	1045	1020, 640, 425	300	350	290
$\text{Zn}(\text{PIS})\cdot 2\text{H}_2\text{O}$	3400 br	1600 s	1650 w	1535	1340	1540 s	1045	1020, 630, 410	300	335	280

^a Metal-pyridine nitrogen frequency.

Table IV. ESR Magnetic Parameters^a

compd	g_{\parallel}	g_{\perp}	g_{av}	A_{\parallel}, G	A_{\perp}, G
$\text{Cu}(\text{HPIS})_2$	2.246	2.046	2.113	170	40
$\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$	2.256	2.049	2.188	165	42

^a ESR parameters refer to 77 K; $g_{\text{av}} = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$.

Table V. ESR Bonding Parameters

compd	α	α^2	α'	α'^2	$\beta^2(\text{O})$
$\text{Cu}(\text{HPIS})_2$	0.854	0.729	0.589 (O) 0.606 (N)	0.347	0.838
$\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$	0.863	0.745	0.574 (O) 0.580 (N)	0.330	0.956

media. All the adducts have 1:2 metal to ligand stoichiometry. H_2PIS loses one or two protons to form deprotonated complexes having 1:2 or 1:1 metal to ligand ratios. All the complexes are insoluble in water and organic solvents such as chloroform, ethanol, methanol, acetone, etc. Me_2SO . are slightly soluble in DMF and Me_2SO . The adducts melt in the range 204–290 °C while the deprotonated complexes generally do not melt up to ~250 °C. The low values of molar conductance for deprotonated complexes show their nonelectrolytic behavior. However the molar conductivities of the adducts lying in the range 40–45 $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ are too low for a 1:1 electrolyte but indicate some ionic dissociation in DMF.⁸



Because of the insolubility of these complexes in appropriate solvents it has been possible neither to determine their molecular weights nor to grow a single crystal for X-ray crystallographic studies.

The loss of water molecules around 160–180 °C shows the coordinated nature of these molecules in the hydrated complexes. This is further confirmed by the presence of a band in these complexes in the 720–800- cm^{-1} region characteristic of coordinated water.

Magnetic Properties. The magnetic moment values of all the Ni(II) complexes (2.97–3.20 μ_{B}) and of $\text{Co}(\text{H}_2\text{PIS})_2\text{Cl}_2$ (4.73 μ_{B}) are in agreement with those reported for spin-free octahedral Ni(II) and Co(II) complexes,⁹ respectively. Co-

Table VI. Observed and Computed Q hkl Values for $\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$

powder pattern line	Q_{obsd}	Q_{comp}	hkl	powder pattern line	Q_{obsd}	Q_{comp}	hkl
1	0.0381	0.0398	112	14	0.5002	0.4988	602
2	0.0567	0.0572	201	15	0.5991	0.6012	606
3	0.1078	0.1080	220	16	0.7162	0.7127	704
4	0.1610	0.1638	313	17	0.7561	0.7532	644
5	0.2050	0.2043	323	18	0.7722	0.7767	706
6	0.2287	0.2288	402	19	0.9736	0.9792	806
7	0.2721	0.2700	420	20	0.9842	0.9878	738
8	0.2808	0.2807	414	21	1.0788	1.0800	840
9	0.3820	0.3798	513	22	1.1243	1.1223	903
10	0.3916	0.3915	520	23	1.2577	1.2527	854
11	0.4345	0.4342	515	24	1.3700	1.3718	906
12	0.4647	0.4642	531	25	1.5103	1.5110	955
13	0.4849	0.4860	600	26	1.5700	1.5685	949

(HPIS)₂ and Co(PIS)·2H₂O exhibit anomalous magnetic moments (ca. 3.48–3.93 μ_{B}) that are presumably due to contributions from high- as well as low-spin states of Co(II).¹⁰ The μ_{eff} values for VO(IV) and Cu(II) complexes correspond to one unpaired electron, giving no specific information about their stereochemistry. Mn(II) complexes are spin free as is evident from their magnetic moments.⁹

Electronic Spectra. The UV spectrum of the ligand shows bands characteristic of the picolinamide (45 450 and 33 900 cm^{-1}) and salicylaldimine (40 810, 32 785, and 28 570 cm^{-1}) components present in it. The adducts show three bands at ~41 665, 33 330–32 255, and ~26 665 cm^{-1} . The first two bands may be attributed to the primary and secondary bands of benzene or pyridine while the third one may be assigned to the phenolic OH of the salicylaldimine part. The corresponding bands in the spectra of the deprotonated complexes are observed in the 44 440–40 000-; 33 330–28 570-; and 24 390–22 220- cm^{-1} regions. The significant red shift in the phenolic OH band in all the deprotonated complexes indicates removal of the phenolic proton.¹¹

The visible-region spectrum of VO(PIS)·H₂O shows two bands at 13 330 and 17 540 cm^{-1} assigned to $d_{xy} \rightarrow d_{yz}, d_{xz}$ and

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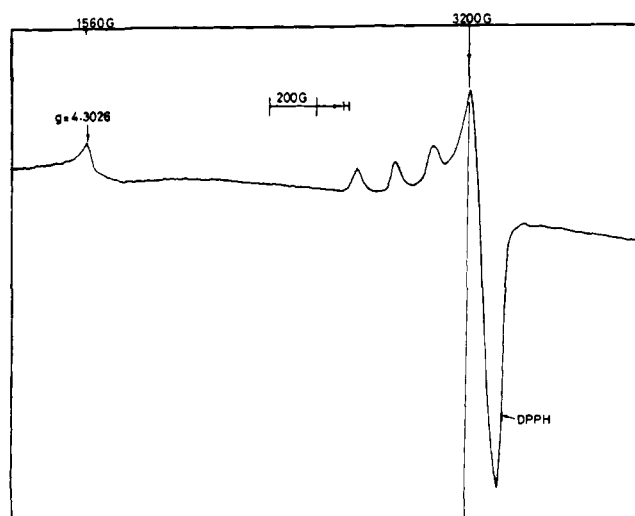


Figure 1. ESR spectrum of $\text{Cu(PIS)} \cdot 2\text{H}_2\text{O}$ at 77 K.

$d_{x^2-y^2}$ transitions, respectively, on the basis of octahedral geometry.¹² The spectra of cobalt(II) complexes show a weak broad band at 8230–9090 cm^{-1} and a strong band at 19050–20000 cm^{-1} , which may be attributed to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1) and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_3) transitions, respectively. The bands are characteristic of octahedral Co(II) complexes.¹³

The spectra of $\text{Ni(H}_2\text{PIS)}_2\text{Cl}_2$ and Ni(HPIS)_2 yield two bands in the 9435–10750- and 15380–17000- cm^{-1} regions, respectively, while that of $\text{Ni(PIS)} \cdot 2\text{H}_2\text{O}$ shows only one band at 10810 cm^{-1} . The low-energy band may be assigned to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$ (ν_1) transition and the high-energy band to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) transition in octahedral geometry.¹⁴

The copper(II) complexes exhibit one broad band at 14285–14815 cm^{-1} due to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition, which is considerably blue shifted compared to the first band maximum of the corresponding Ni(II) complexes, $\nu_{\text{Cu}}/\nu_{\text{Ni}}$ being ~ 1.37 . This suggests appreciable distortion from octahedral geometry in Cu(II) complexes.¹⁵

ESR Spectra. The ESR spectral features of Cu(HPIS)_2 and $\text{Cu(PIS)} \cdot 2\text{H}_2\text{O}$ are characteristic of axial symmetry. The parallel ${}^{63}\text{Cu}$ features are clearly resolved while the perpendicular features are broadened, probably owing to the badly resolved ligand hyperfine interactions. The trend $g_{\parallel} > g_{\perp} > g_e$ (2.0023; free-ion value) observed in the above complexes shows that the unpaired electron is in the $d_{x^2-y^2}$ orbital of Cu(II).¹⁶ The g_{\parallel} and g_{\perp} values in both the complexes deviate considerably from the free-spin value and are close to those reported for a number of distorted-octahedral Cu(II) complexes.^{17,18}

The values of α^2 , 0.729 for Cu(HPIS)_2 and 0.745 for $\text{Cu(PIS)} \cdot 2\text{H}_2\text{O}$, indicate that σ bonding in both cases has considerable covalent character. β^2 values of 0.838 and 0.956 for 1:2 and 1:1 complexes, respectively, show that the extent of in-plane π bonding is greater in the former complex.¹⁹

The additional peak observed at 1560 G (near half-field) in the ESR spectrum of $\text{Cu(PIS)} \cdot 2\text{H}_2\text{O}$ yields a g value of 4.3026, which is due to a singlet-triplet transition ($\Delta M_s = 2$), thereby suggesting the dimeric structure of the complex.^{19–21}

Infrared Spectra. The IR spectrum of H_2PIS in CHCl_3 shows two bands at 3400 (w) and 3310 cm^{-1} , which may be assigned to $\nu(\text{OH})$ and $\nu(\text{N-H})$ modes, respectively. The positions of these bands remain practically unchanged in the spectra of the adducts, indicating that $-\text{NH}$ and $-\text{OH}$ groups of the ligand are not involved in bonding.

The bands occurring at 1695, 1500, and 1265 cm^{-1} in the solution spectrum of the ligand are assigned to amide I, amide II, and amide III modes, respectively. The corresponding bands in the spectra of all the adducts are observed in the 1625–1640-, 1510–1520-, and 1270–1275- cm^{-1} regions, respectively. A negative shift in amide I and a positive shift in amide II²² and amide III bands indicate coordination through the carbonyl oxygen. Ring breathing,²³ in-plane bending, and out-of-plane bending²⁴ vibrations of the pyridine ring occurring at 995, 620, and 400 cm^{-1} , respectively, are appreciably shifted to higher frequencies, viz., 1010–1015, 630–650, and 410–418 cm^{-1} , in the spectra of the adducts, indicating coordination through the ring nitrogen.²³ The coordination through pyridine nitrogen is further supported by the presence of a $\nu(\text{M-N})$ band in the 240–270- cm^{-1} region.²⁵ The same bonding sites, viz., carbonyl oxygen and ring nitrogen, have been reported for the 1:1 addition compound of tin(IV) chloride with a very similar ligand, viz., pyridoxal picolinoylhydrazone, from X-ray crystallographic studies.²⁶

In the spectra of the complexes of the type M(HPIS)_2 the absence of a $\nu(\text{OH})$ band, a positive shift of 50–60 cm^{-1} in the $\nu_{\text{sym}}(\text{C-O, phenolic})$ band, and the appearance of a new band due to $\nu_{\text{asym}}(\text{C-O-M})$ at 1525–1545 cm^{-1} indicate bonding through the phenolic oxygen by metal ions and monodentate behavior of the C-O group.²⁷ Further, the spectra of these complexes show a negative shift for the $\nu(\text{C=N})$ (20–30 cm^{-1}) and amide I (30–40 cm^{-1}) modes and a positive shift for the amide III (5–15 cm^{-1}) and $\nu(\text{N-N})$ (20 cm^{-1}) modes, indicating coordination through azomethine nitrogen and carbonyl oxygen. The pyridine ring vibrations remain practically unaltered, indicating noninvolvement of pyridine nitrogen in 1:2 deprotonated complexes. The infrared spectral studies thus show mononegative terdentate behavior of H_2PIS in 1:2 deprotonated complexes, the bonding sites being phenolic oxygen, azomethine nitrogen, and carbonyl oxygen. The terdentate behavior of H_2PIS is consistent with the octahedral geometry of these complexes inferred from magnetic and electronic spectral studies discussed earlier. Further, in deprotonated chelates of Schiff bases derived from salicylaldehyde, phenolic oxygen and azomethine nitrogen are always the bonding sites; the third bonding site in deprotonated chelates of H_2PIS may be either carbonyl oxygen, pyridine nitrogen, or imine nitrogen. Out of these three sites, bonding through carbonyl oxygen would be preferred because of the formation of a stable five-membered chelate ring. Thus, bonding sites indicated by the IR spectral studies of 1:2 deprotonated complexes appear to be quite reasonable.

The spectral features of $\text{Cu(HPIS)Cl} \cdot \text{H}_2\text{O}$ are similar to those of 1:2 deprotonated complexes discussed above in the $\nu(\text{C=O})$, $\nu(\text{C=N})$, and $\nu(\text{C-O-M})$ frequency regions, in-

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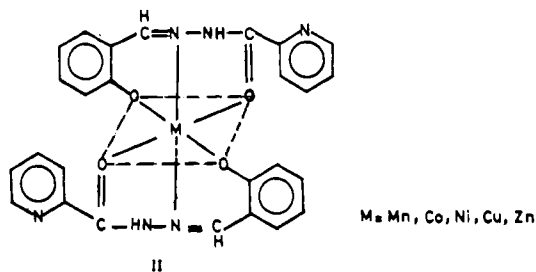
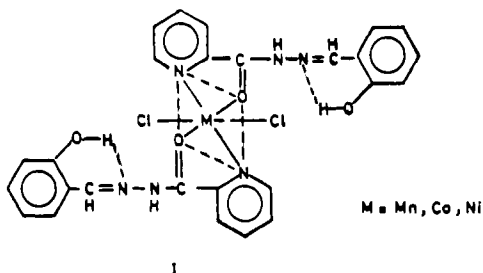
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dicating bonding through the C=O, C=N, and C—O groups, but pyridine ring vibrations are observed in the above complex at higher frequencies (1010, 645, 420 cm^{-1}) as compared to those of the ligand, indicating additional bonding through pyridine nitrogen.^{23,24}

The disappearance of $\nu(\text{OH})$, $\nu(\text{NH})$, amide I, amide II, and amide III bands in the spectra of anhydrous 1:1 deprotonated complexes and appearance of new bands due to $\nu_{\text{asym}}(\text{C—O—M})$ and $\nu(\text{N—C—O})$ in the regions 1520–1540 and 1525–1535 cm^{-1} , respectively, indicate destruction of the keto group through enolization and deprotonation of the enolic as well as phenolic protons as a result of chelation. A negative shift in $\nu(\text{C=N})$ (20 cm^{-1}), a positive shift in $\nu(\text{N—N})$ (15–20 cm^{-1}), and ring-breathing (20–25 cm^{-1}), in-plane bending (10–20 cm^{-1}), and out-of-plane bending (10–25 cm^{-1}) pyridine ring vibrations in the spectra of the 1:1 complexes suggest coordination through azomethine and pyridine ring nitrogens. The infrared studies thus indicate dinegative tetradentate behavior of H_2PIS in 1:1 deprotonated complexes.

X-ray Powder Diffraction Studies. As the observed interplanar spacings in our $\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$ could not be satisfactorily matched with those of any other $\text{Cu}(\text{II})$ complex with Schiff bases similar to H_2PIS for which the X-ray diffraction data are reported in the literature, the trial and error method (Ito's method) was used, and it was found that most of the prominent diffraction lines could be satisfactorily indexed for tetragonal symmetry (Table VI). The lattice parameters computed for the above symmetry are $a = 8.6059 \text{ \AA}$, $c = 17.7 \text{ \AA}$, $\rho = 1.80 \text{ g cm}^{-3}$, and $z = 4$. The powder X-ray diffraction photograph of $\text{Cu}(\text{HPIS})_2$ yields a blurred ring but no specific diffraction lines, indicating that the complex is amorphous.

From composition and physicochemical studies discussed above, structures I and II are tentatively proposed for adducts and 1:2 deprotonated complexes.

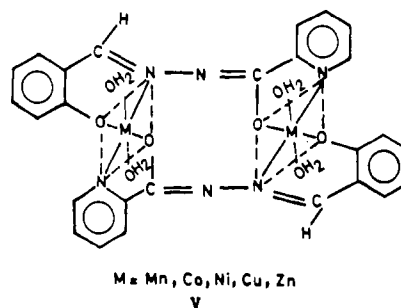
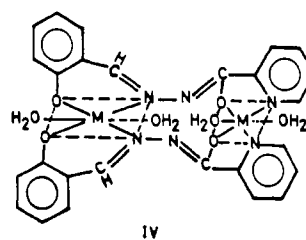
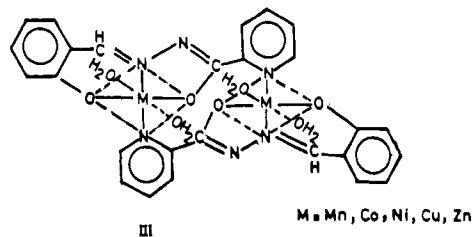


On constructing molecular models for 1:1 deprotonated complexes, we find that the monomeric structure is highly strained. This fact and the ESR evidence that we have for the dimeric nature of the 1:1 deprotonated copper(II) complex rule out the monomeric structures for these complexes. Recently a dimeric structure has been proposed for the oxovanadium(IV) complex of *O*-hydroxyacetophenone picolinoylhydrazone,²⁸ which also supports the dimeric nature of

these complexes.

As pyridine N and C—O groups are adjacent to each other, they would prefer to bond to the same metal center rather than bond to two metal centers, leading to the dimeric and polymeric structures.

Keeping in view this fact and bonding sites and stereochemistry indicated by our experimental evidence discussed above, we feel that the dimeric structures IV and V are possible



while the dimeric structure III and the polymeric structures of these complexes can be ruled out. A construction of molecular models for structures IV and V shows that V involves no strain while structure IV is quite strained. Structure V is therefore proposed for 1:1 deprotonated complexes.

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Registry No. $\text{Mn}(\text{H}_2\text{PIS})_2\text{Cl}_2$, 77846-40-3; $\text{Co}(\text{H}_2\text{PIS})_2\text{Cl}_2$, 77846-41-4; $\text{Ni}(\text{H}_2\text{PIS})_2\text{Cl}_2$, 77846-42-5; $\text{Cu}(\text{HPIS})\text{Cl}\cdot\text{H}_2\text{O}$, 77862-16-9; $\text{Mn}(\text{HPIS})_2$, 77846-43-6; $\text{Co}(\text{HPIS})_2$, 77846-44-7; $\text{Ni}(\text{HPIS})_2$, 77846-45-8; $\text{Cu}(\text{HPIS})_2$, 77846-46-9; $\text{Zn}(\text{HPIS})_2$, 77846-47-0; $\text{VO}(\text{PIS})\cdot\text{H}_2\text{O}$, 77846-48-1; $\text{Mn}(\text{PIS})\cdot 2\text{H}_2\text{O}$, 77846-49-2; $\text{Co}(\text{PIS})\cdot 2\text{H}_2\text{O}$, 77846-50-5; $\text{Ni}(\text{PIS})\cdot 2\text{H}_2\text{O}$, 77846-51-6; $\text{Cu}(\text{PIS})\cdot 2\text{H}_2\text{O}$, 77846-52-7; $\text{Zn}(\text{PIS})\cdot 2\text{H}_2\text{O}$, 77846-53-8.