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STUDIES OF METAL COMPLEXES OF 2-(2-PYRIDINYL)-, 2-(6-METHYL-2-PYRIDINYL)-, 2-(3-PYRIDINYL)-1H-BENZIMIDAZOLES WITH SOME d^{8-10} IONS

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ABSTRACT

2-R-1H-Benzimidazoles [L^1, R = 2-pyridinyl; L^2, R = 6-methyl-2-pyridinyl; L^3, R = 3-pyridinyl] and their complexes with Ni(II), Pd(II), Zn(II), Cd(II), Hg(II) chloride were prepared. The complexes, having 1:1 and 1:2 metal:ligand ratios, were characterized by elemental analyses, magnetic susceptibility and molar conductance measurements, IR and ^{1}H NMR spectroscopy. The Ni(II) complexes are paramagnetic. The metal:ligand ratio are 1:1 in the Pd(II) and Hg(II) complexes of the ligands, and these complexes are non-ionic. In the IR spectra the band character and vibrational frequencies of the groups participating in coordination changed on complexation. In the ^{1}H NMR spectra, considerable changes were found in the chemical shifts of protons neighboring to the coordinated nitrogen atoms. The ligands L^1 and L^2 give chelates easily with the metal ions, but L^3 does not.

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RESULTS AND DISCUSSION

Physical and Chemical Properties of the Compounds

The reaction of the ligands L^1, L^2 and L^3 with MCl_2 in 1:2 metal:ligand molar ratio in ethanol yielded stable solid complexes corresponding to the general formulas $[M(L)Cl_2]$ and $[M(L)_2Cl_2]$ ($M = Ni^{2+}$, Pd^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}). There are no coordinated water molecules in the metal complexes. Tentative formulas, elemental analyses, some physical properties (color, molar conductance and melting points) of the compounds were given in TABLE I.

Typical reactions for forming the complexes are given below.

$$L + MCl_2 \cdot 6H_2O \longrightarrow M[L]Cl_2 + 6H_2O \quad (1)$$

$M = Ni^{2+}, Pd^{2+}, Cd^{2+}, Hg^{2+}$; $L = L^1$; $M = Pd^{2+}, Cd^{2+}, Hg^{2+}$; $L = L^2$

$M = Ni^{2+}, Pd^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}$; $L = L^3$.

$$2\,L + MCl_2 \cdot 6H_2O \longrightarrow M[L]_2Cl_2 + 6H_2O \quad (2)$$

$M = Zn^{2+}$, $L = L^1, L^2, L^3$; $M = Ni^{2+}$, $L = L^2$.

The complexes of the ligands with Pd(II), Cd(II) and Hg(II) have 1:1 metal:ligand molar ratio. This ratio was 1:1 in Ni(II) complexes of L^1, L^3 and 1:2 in that of L^2. The ligands have a tendency to form complexes with Zn(II) ion in 1:2 metal:ligand ratio. Only L^3 formed two complexes with Zn(II) in 1:1 and 1:2 metal:ligand ratio, at room temperature and under reflux, respectively.

The ligands are soluble in the polar solvents, however, their metal complexes are soluble only in DMSO, DMF and acetic acid. The solubility of $Ni[L^1]Cl_2$, $Ni[L^2]_2Cl_2$ and $Pd[L^1]Cl_2$ is different from that of the others, these complexes are also soluble in alcohol.

INTRODUCTION

Benzimidazoles have a wide range of biological activity. The ligands, 2-(2-pyridinyl)- (L^1), 2-(6-methyl-2-pyridinyl)- (L^2), 2-(3-pyridinyl)-1H-benzimidazole (L^3), have various antimicrobial activities. L^1 and L^2 showed antifungal, antinematocide, antihelmintic, antiinflammatory and tuberculostatic effects; L^2 has only antiinflammatory activity[1-8].

In the literature, many metal complexes of L^1 were investigated since they were used in the spectrofluorimetric determination of Ga, In, Zn[9] and in a spectrophotometric study of the extraction of Fe(II) by isoamylalcohol[10]. It was reported that L^1 formed complexes with Co(II), Zn(II) and Ni(II) of the composition $M(L^1)_3X_2$[11]. The ligand L^1 gave complexes of the metal:ligand ratio 1:3 with Fe(II)[12] and formed dimeric complexes with $FeSO_4$, bridged by oxygen[13]. The metal:ligand ratio is 1:4 in the $[Th(L^1)_4](ClO_4)_4$ complex[14]. L^1 is a classical ligand and has been used in many complexes, for example, in $[Mo(CO)_4(L^1)]$[15], in some trinuclear Cu(II) complexes[16], and in mixed-ligand complexes with acetylacetonato[17], biguanide[18], 2,2'-bipyridine[19], and Schiff bases[20].

The characterization of metal complexes of L^2 and L^3 was aimed to clarify the structures of the ligands and of their complexes with Ni(II), Pd(II), Zn(II), Cd(II) and Hg(II) chlorides.

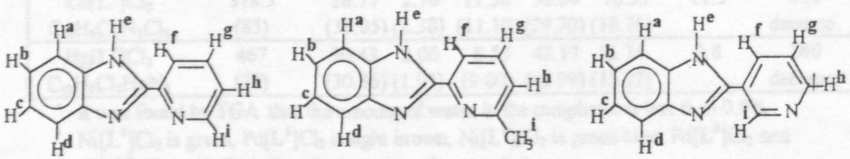


Fig. 1. Structure of the Ligands

Magnetic Susceptibility

The Ni(II) complexes are paramagnetic (high-spin) and the μ_{eff} values of $Ni[L^1]Cl_2$, $Ni[L^2]_2Cl_2$, $Ni[L^3]Cl_2$ are 2.22, 2.87 and 2.38 BM, respectively. The magnetic susceptibility of the 1:1 Ni(II) complexes are lower than the 1:2 complex. These values are corresponding to approximately two unpaired electrons. In light of these data, it is suggested that the Ni(II) complexes are tetrahedral, the others are tetragonal or distorted-octahedral.

It was impossible to obtain useful data about *d-d* electronic transitions by UV/visible spectra because the metal complexes have very poor solubility in common organic solvents, such as chloroform, methanol, acetone, dioxan, toluene.

Molar Conductance

The low molar conductance values (0.8–1.9 $\Omega^{-1}cm^2\ mol^{-1}$) of the Pd(II) and Hg(II) complexes of the ligands indicates their non-ionic character. The 1:2 Zn(II) complexes have a lower molar conductance, but the $Zn[L^3]Cl_2$ complex, obtained at room temperature, has a high conductivity. Chloride ions in the 1:2 Zn(II) complexes were coordinated to the Zn(II) ions, forming an octahedral or distorted-octahedral structure. The compound $Ni[L^2]_2Cl_2$ has a higher value of conductance (88.1 $\Omega^{-1}cm^2mol^{-1}$) than the other Ni(II) complexes. The molar conductivities of the complexes of L^1, L^2, L^3 with $PdCl_2$ and $HgCl_2$ are lower than those of the others (TABLE I).

IR Spectra

Lane *et al.* studied L^1 and its metal chelates with $CuBr_2$, $NiBr_2$, $CoBr_2$ and ZnI_2 by IR spectroscopy and found the pyridine and the imidazole C=N frequencies at around 1575 and 1603 cm^{-1} as medium bands in the IR spectra of L^1. The bands with different intensities between 1450-1550 cm^{-1} were assigned to the NH bending, the *o*-substituted pyridine and the *o*-disubstituted benzene rings vibrations. In additon,

TABLE I. Analytical Data and Some Physical Properties of L^1, L^2, L^3 and Their Metal Complexes.

Compound[a,b]	Formula weights (yields %)	Elemental Analysis Found (Calculated) %C	%H	%N	%M	%Cl	Molar cond.[c]	M.p. °C
L^1	195	73.96	4.78	21.38			0	218
$C_{12}H_9N_3$	(37)	(73.84)	(4.61)	(21.54)				decomp.
$Ni[L^1]Cl_2$	325	44.45	2.86	13.08	16.92	21.36	42.1	293
$C_{12}H_9Cl_2N_3Ni$	(65)	(44.31)	(2.77)	(12.92)	(18.15)	(21.87)		decomp.
$Pd[L^1]Cl_2$	372.5	39.09	2.45	11.04	29.11	18.95	1.9	>350
$C_{12}H_9Cl_2N_3Pd$	(65)	(38.67)	(2.42)	(11.28)	(28.57)	(19.06)		
$Zn[L^1]_2Cl_2$	527	54.58	3.34	15.83	12.91	20.75	11.6	>350
$C_{24}H_{18}Cl_2N_6Zn$	(85)	(54.70)	(3.42)	(15.95)	(12.42)	(21.42)		
$Cd[L^1]Cl_2$	378.5	38.18	2.21	10.64	29.92	19.53	14.2	>350
$C_{12}H_9CdCl_2N_3$	(80)	(38.05)	(2.37)	(11.10)	(29.70)	(18.76)		
$Hg[L^1]Cl_2$	467	30.87	1.93	9.00	42.65	14.66	1.8	341
$C_{12}H_9Cl_2HgN_3$	(75)	(31.06)	(1.90)	(8.70)	(42.98)	(15.19)		decomp.
L^2	209	74.67	5.29	20.04			0	222
$C_{13}H_{11}N_3$	(35)	(74.64)	(5.26)	(20.09)				decom
$Ni[L^2]_2Cl_2$	548	57.00	3.80	14.03	11.12	12.68	88.1	>350
$C_{26}H_{22}Cl_2N_6Ni$	(65)	(56.96)	(4.02)	(15.34)	(10.76)	(12.96)		
$Pd[L^2]Cl_2$	387	40.51	2.92	10.81	27.71	18.60	9.3	349
$C_{13}H_{11}Cl_2N_3Pd$	(65)	(40.37)	(2.85)	(10.87)	(27.53)	(18.37)		decomp.
$Zn[L^2]_2Cl_2$	555	45.91	3.07	12.24	19.00	21.06	9.6	>350
$C_{26}H_{22}Cl_2N_6Zn$	(90)	(46.02)	(3.18)	(12.39)	(17.40)	(20.55)		
$Cd[L^2]Cl_2$	393	40.10	2.93	10.56	28.80	18.41	15.3	>350
$C_{13}H_{11}CdCl_2N_3$	(85)	(39.75)	(2.80)	(10.70)	(28.64)	(18.09)		
$Hg[L^2]Cl_2$	481	32.71	2.32	8.60	41.83	15.08	3.8	312
$C_{13}H_{11}Cl_2Hg\ N_3$	(80)	(32.47)	(2.29)	(8.74)	(41.74)	(14.77)		decomp.
L^3	195	73.87	4.69	21.48			0.5	254
$C_{12}H_9N_3$	(55)	(73.84)	(4.61)	(21.54)				decomp.
$Ni[L^3]Cl_2$	325	45.10	3.30	12.45	14.93	21.73	65.8	308
$C_{12}H_9Cl_2N_3Ni$	(85)	(44.31)	(2.77)	(12.92)	(18.15)	(21.87)		decomp.
$Pd[L^3]Cl_2$	372.5	38.69	2.38	10.79	28.86	18.81	1.1	271
$C_{12}H_9Cl_2N_3Pd$	(75)	(38.67)	(2.42)	(11.28)	(28.57)	(19.06)		decomp.
$Zn[L^3]Cl_2$	331.5	43.51	2.76	12.64	18.28	21.03	61.0	>350
$C_{12}H_9Cl_2N_3Zn$	(70)	(43.44)	(2.71)	(12.67)	(19.73)	(21.42)		
$Zn[L^3]_2Cl_2$	527	54.77	3.46	15.92	11.38	13.11	6.4	>350
$C_{24}H_{18}Cl_2N_6Zn$	(70)	(54.70)	(3.42)	(15.95)	(12.42)	(13.49)		
$Cd[L^3]Cl_2$	378.5	38.77	2.76	11.58	30.04	18.55	11.5	325
$C_{12}H_9CdN_3Cl_2$	(85)	(38.05)	(2.38)	(11.10)	(29.70)	(18.76)		decomp.
$Hg[L^3]Cl_2$	467	30.43	2.06	8.55	43.17	15.74	0.8	260
$C_{12}H_9Cl_2HgN_3$	(70)	(30.86)	(1.93)	(9.00)	(42.99)	(15.22)		decomp.

[a] It was found by TGA that the amount of water in the complexes is less than 0.9%

[b] $Ni[L^1]Cl_2$ is green, $Pd[L^1]Cl_2$ is light brown, $Ni[L^2]_2Cl_2$ is green-blue, $Pd[L^2]Cl_2$ and $Pd[L^3]Cl_2$ are yellow, the other compounds are colorless.

[c] measured in DMSO, $\Omega^{-1}cm^2mol^{-1}$, at 25±1°C.

TABLE II. Some Selected IR Bands of L^1, L^2, L^3 and of the Their Metal Complexes (cm^{-1}, in KBr disc).

Compound	ν(NH)	$\nu(C{=}N)_{im}$	$\nu(C{=}N)_{py}$	δ(NH)	=CH [a]	=CH [b]
L^1	[c]	1592 m	1569 m	1546 w	746 s	708 m
$Ni[L^1]Cl_2$	3384 br	1638 m	1607 m	1569 w	754 s	700 w
$Pd[L^1]Cl_2$	3454 br	1638 m	1608 m	1569 w	754 s	692 w
$Zn[L^1]_2Cl_2$	3261 br	1638 m	1608 m	1577 w	754 s	700 sh
$Cd[L^1]Cl_2$	3192 br	1607 m	1600 m	1538 w	754 s	669 m
$Hg[L^1]Cl_2$	3238 br	1607 m	1600 m	1538 w	754 s	646 m
L^2	[c]	1600 m	1577 m	1538 w	746 s	677 w
$Ni[L^2]_2Cl_2$	3369 br	1615 m	1584 m	1546 w	754 s	684 w
$Pd[L^2]Cl_2$	3323 br	1615 m	1592 m	1546 w	754 s	677 sh
$Zn[L^2]_2Cl_2$	3231 br	1608 m	1577 m	1538 w	754 s	684 w
$Cd[L^2]Cl_2$	3238 br	1607 m	1577 sh	1538 w	754 s	669 m
$Hg[L^2]Cl_2$	3223 br	1600 m	1577 sh	1538 w	761 s	684 m
L^3	[c]	1628 m	1584 m	1546 w	754 s	708 m
$Ni[L^3]Cl_2$	3107 br	1654 m	1592 m	1546 w	738 s	708 m
$Pd[L^3]Cl_2$	3300 br	1661 m	1608 m	1538 w	754 s	696 m
$Zn[L^3]Cl_2$	3200 br	1623 m	1592 m	1538 w	761 s	708 s
$Zn[L^3]_2Cl_2$	3107 br	1623 m	1592 m	1546 w	777 s	708 s
$Cd[L^3]Cl_2$	3384 br	1653 m	1623 m	1546 w	738 s	708 m
$Hg[L^3]Cl_2$	3192 br	1600 m	1577 m	1538 w	761 s	708 m

[a] The out-of-plane C–H bending vibrations of the *o*-disubstituted benzene ring.

[b] The out-of-plane C–H bending vibrations of the substituted pyridine ring.

[c] This band did not appear because of hydrogen bonding. The aromatic CH stretching and overtone/combination of the *o*-disubstituted benzene ring are appear weakly between 3050-3060 cm^{-1} and 1700-2000 cm^{-1}, respectively.

im: imidazole, py: pyridine, br: broad, m: medium, sh: shoulder, w: weak, s: sharp.

they suggested that the bands at around 744 (weak) and 770 cm^{-1} (medium) are due to the C–H out-of-plane deformation vibrations of the *o*-substituted pyridine and the *o*-disubstituted benzene rings, respectively. An increasing was observed at frequencies on complexation[21].

The ligands show their characteristic pyridine and imidazole C=N frequencies at around 1570 and 1628 cm^{-1}. The weak band around 1540 cm^{-1} in the IR spectra of the ligands is probably due to δ(NH). The sharp band between 746-754 cm^{-1} is assigned to the out-of-plane C–H bending vibrations of the *o*-disubstituted benzene ring. The medium bands in the IR spectra of L^1 and L^3 at 708 cm^{-1} and the weak band in L^2 at 677 cm^{-1} are assigned to the out-of-plane C–H bending vibrations of the substituted pyridine ring. The IR data in this study is fitting to the literature[21, 22].

The imidazole and the pyridine nitrogens in L^1, L^2 and L^3 are strong chelators and the coordination of metal ions can be observed by means of IR spectra[21, 22]. The characteristic bands in the coordination region of the ligands are shifted towards the higher frequency region in the spectra of their metal complexes. In addition to this, differences were observed in the band character due to the perturbing effect of metal ions on complexation (TABLE II).

The out-of-plane C–H bending vibrations band of the substituted pyridine ring in the IR spectra of $Pd[L^3]Cl_2$ appears at 696 cm^{-1} as a difference than the other metal complexes of L^3. Because of this, it can be suggested that the coordination between Pd(II) and L^3 occurs through the imidazole C=N and also the pyridine ring.

There are broad bands in the IR spectra of the ligands at 3100-2500 cm^{-1} range corresponding intra- (in L^1 and L^2) and intermolecular (in L^3) hydrogen bonding. The ν(NH) bands of the ligands cannot be seen due to hydrogen bonding.

TABLE III. ^{1}H NMR Chemical Shifts of L^1, L^2, L^3 and Their Metal Complexes (in DMSO-d_6, TMS standard)

Comp.	Chemical shifts, δ (ppm) and coupling constants, J (Hz)
L^1	7.22 (m, 2H, H_b+H_c); 7.53 (m, 2H, H_a+H_d); 7.69 (d-d, 1H, H_g, $J_{g\text{-}f}$ = 8, $J_{g\text{-}h}$ = 6); 7.99 (t, 1H, H_h; J = 6); 8.32 (d, 1H, H_f; J = 8); 8.73 (d, 1H, H_i; J = 6); 12.99 (s,br, 1H, H_e)
$Pd[L^1]Cl_2$	7.60-8.70 (m, 4H, H_a+ H_b +H_c+ H_d); 8.20-8.45 (m, 3H, H_f+H_g+H_h); 9.26 (d, 1H, H_i; J = 6)
$Zn[L^1]_2Cl_2$	(d-d, 2H, H_b+H_c; J = 6); 7.60 (m, 2H, H_a+H_d); 7.63 (s,br, 1H, H_g); 8.11 (t, 1H, H_h; J = 7); 8.37 (d, 1H, H_f; J = 8); 8.65 (s,br, 1H, H_i); 13.47 (s,br, 1H, H_e)
$Cd[L^1]Cl_2$	7.29-7.34 (d-d, 2H, H_b+H_c; J = 6); 7.62-7.68 (d-d, 2H, H_a+H_d; J = 6); 7.88 (s,br, 1H, H_g); 8.15 (t-t, 1H, H_h; J = 7.5); 8.37 (d, 1H, H_f; J = 8); 8.77 (d, 1H, H_i; J = 5); 13.58 (s,br, 1H, H_e)
$Hg[L^1]Cl_2$	7.27-7.32 (d-d, 2H, H_b+H_c, J = 6); 7.62 (t, 1H, H_g; J = 7); 7.71-7.75 (d-d, 2H, H_a+H_d; J = 6); 8.09 (t-t, 1H, H_h; J = 8); 8.37 (d, 1H, H_f; J = 8); 8.74 (d, 1H, H_i; J = 4.5)
L^2	2.62 (s, 3H, H_i); 7.21 (d, 1H, H_b; J = 6); 7.23 (d, 1H, H_c; J = 6); 7.37 (d, 1H, H_h; J = 7.5); 7.63-7.65 (m, 2H, H_a+H_d); 7.87 (t, 1H, H_g; J = 8); 8.13 (d, 1H, H_f; J = 7.5); 12.88 (s,br, 1H, H_e)
$Pd[L^2]Cl_2$	2.66 (s, 3H, H_i); 7.30-7.75 (m, 5H, H_a+ H_b +H_c+ H_d+H_h); 8.00-8.50 (m, H_f+ H_g); 13.84 (s, br, 1H, H_e)
$Zn[L^2]_2Cl_2$	2.69 (s, 3H, H_i); 7.28-7.35 (d-d, 2H, H_b+H_c; J = 6); 7.49 (d, 1H, H_h; J = 7.5); 7.69-7.73 (d-d, 2H, H_a+H_d; J = 6); 8.00 (t, 1H, H_g; J = 7.5); 8.19 (d, 1H, H_f; J = 7.5); 13.42 (s,br, 1H, H_e)
$Cd[L^2]Cl_2$	2.74(s, 3H, H_i); 7.29-7.34 (d-d, 2H, H_b+H_c; J = 6); 7.49 (d, 1H, H_h; J = 6); 7.67 (s,br, 2H, H_a+H_d); 8.01 (t, 1H, H_g; J = 7.75); 8.19 (d, 1H, H_f; J = 7.75); 13.48 (s,br, 1H, H_e)
$Hg[L^2]Cl_2$	2.69 (s, 3H, H_i); 7.31-7.35 (d-d, 2H, H_b+H_c; J = 6); 7.52 (d, 1H, H_h; J = 6); 7.77-7.82 (d-d, 2H, H_a+H_d; J = 6); 8.02 (t, 1H, H_g; J = 7.75); 8.21 (d, 1H, H_f; J = 7.75); 13.57 (s,br, 1H, H_e)
L^3	7.25 (d-d, 2H, H_b+H_c; J = 6); 7.55-7.62 (m, 2H, H_a+H_d); 7.64 (d, 1H, H_f; J = 6.5); 8.49-8.50 (d-d, 1H, H_g; J = 8); 8.68 (d,br, 1H, H_h); 9.35 (s, 1H, H_i); 13.03 (s,br, 1H, H_e).
$Pd[L^3]Cl_2$	7.45 (m, 2H, H_b+H_c); 7.70 (d, 2H, H_a+H_d, J = 6); 8.60 (d, 1H, H_f; J = 6.5); 8.80 (t, 1H, H_g; J = 6); 9.40 (s,br, 1H, H_h); 9.62 (d, 1H, H_i; J = 7); 14.10 (s,br, 1H, H_e)
$Zn[L^3]_2Cl_2$[a]	7.25 (t-t, 2H, H_b+H_c; J = 6); 7.58 (d-d, 2H, H_a+H_d; J = 6); 7.70 (d-d, 1H, H_f; J = 6.5); 8.50 (t-t, 1H, H_g; J = 8); 8.68 (d-d, 1H, H_h; J = 5); 9.35 (s, 1H, H_i); 13.03 (s, 1H, H_e)
$Cd[L^3]Cl_2$	7.24 (m, 2H, H_b+H_c); 7.57 (d, 1H, H_a; J = 6); 7.60 (d, 1H, H_d; J = 6); 7.71 (d,br, 1H, H_f; J = 7); 8.50 (d, 1H, H_g; J = 6); 8.68 (d,br, 1H, H_h; J = 5); 9.35 (s, 1H, H_i); 13.03 (s,br, 1H, H_e).
$Hg[L^3]Cl_2$	7.24 (d-d, 2H, H_b+H_c; J = 6); 7.61(d, 1H, H_a+H_d; J = 6); 7.67 (d, 1H, H_f; J = 6); 8.50 (d, 1H, H_g; J = 8); 8.69 (s, 1H, H_h); 9.36 (s, 1H, H_i); 13.08 (s,br, 1H, H_e).

[a] The ^{1}H NMR spectrum of $Zn[L^3]_2Cl_2$ is similar to that of $Zn[L^3]Cl_2$.

s: singlet, d: doublet, t: triplet; br: broad, t-t: triplet of triplet, d-d: doublet of doublet, m: multiplet, q: quartet.

The intra- and intermolecular hydrogen bonding was determined by means of the IR spectra at various concentrations of the ligands in KBr pellets (2, 1, 0.5 and 0.25 mg of ligand in 100 mg KBr). It is seen that the ν(NH) band of imidazole of L^3 becomes sharp at 3450 cm^{-1}, but in the spectra of L^1 and L^2 there is no change by diminishing the concentration of the ligands. In the IR spectra of all ligands the imidazole ν(C=N) and the pyridine ν(C=N) bands are of medium intensity, the ν(NH) bands are broad and the δ(NH) bands are weak.

It is also seen, in some of the complexes, that the ν(NH) band that disappeared in the ligands appeared as a broad band at 3000-3500 cm^{-1}. This can be interpreted that H-bonding is removed on complexation. Generally, the evaluation of this band at around 3400 cm^{-1} in, e.g. the $Ni[L^1]Cl_2$, $Pd[L^1]Cl_2$, $Ni[L^2]_2Cl_2$, $Cd[L^3]Cl_2$, $Zn[L^1]_2Cl_2$ complexes, means that H-bonding was removed completely; in the $Cd[L^1]Cl_2$, $Cd[L^2]Cl_2$, $Hg[L^2]Cl_2$ $Zn[L^2]_2Cl_2$, $Hg[L^3]Cl_2$, $Ni[L^3]Cl_2$, $Zn[L^3]_2Cl_2$ complexes a band of 3100-3200 cm^{-1} appeared which means that H-bonding was removed only partially.

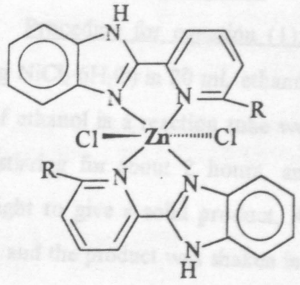
^{1}H NMR Spectra

The ^{1}H NMR chemical shifts of the compounds in DMSO are shown in TABLE III. The data obtained in this study are in line with the findings of the literature, in which the ^{1}H NMR spectra of L^2 were investigated[23].

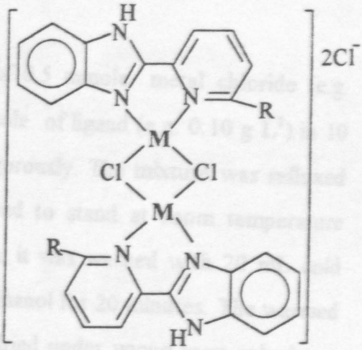
The signals of the protons **a**, **b**, **c** and **d** in Fig. 1 have been seen in the aromatic area as a multiplet. The protons **h**, **g** and **f** are seen at higher field as the benzene ring protons (TABLE III). The proton **e** appears around 13 ppm as a broad singlet and disappears when it is deuterated. The shift values of the proton **i** are quite different for the various ligands. This proton is a doublet (1H, 8.73 ppm, J = 6 Hz), singlet (3H, 2.62 ppm), singlet (1H, 9.35 ppm) in the spectra of L^1, L^2 and L^3, respectively. The proton **e** is seen as a broad singlet in the spectra of L^2 and L^3, but

the pyridine ring is rotated upon complexation. The complexes of L^3 with Zn(II), Cd(II) and Hg(II) ions do not give chelates and coordination occurs through the imidazole ring only. However, all of the protons of the pyridine ring are affected in $Pd[L^3]Cl_2$ (see TABLE III), that is, the coordination between Pd(II) and L^3 takes place through both of the C=N in the imidazole and the pyridine rings.

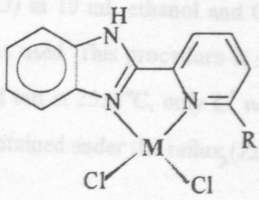
Structures shown in Fig. 2 may be suggested based on the analyses, molar conductivity, IR and ^1H NMR spectral data.



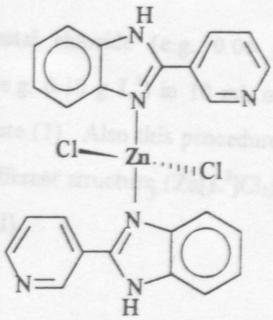
$Zn[L]_2Cl_2$ R = H/CH_3



$Ni[L^1]Cl_2$ R = H
$Cd[L]Cl_2$ R = H/CH_3



$Hg[L]Cl_2$; R = H/CH_3
$Pd[L]Cl_2$; R = H/CH_3



$Zn[L^3]_2Cl_2$

Fig. 2. Suggested Structures of the Some Complexes (L = L^1, L^2).

as a relatively sharp singlet in the spectra of L^1. The proton e of L^2 gives a quite broad peak in the ^1H NMR spectra. Probably, the steric effect of the methyl group slows down the rotation of the pyridine ring in the L^2 molecule. Thus, the intramolecular hydrogen bonding between the imidazole hydrogen and the pyridine nitrogen becomes stronger and the N–H bonding is weakened. This result can be taken as evidence that the NH proton in L^2 is more acidic than that in L^1. A similar explanation may be suggested for L^3. The polarity of L^3 is higher than that of L^1 because the nitrogen atom in the pyridine ring in L^3 is positioned in a location further away than the imidazole ring.

Upon complexation, the chemical shifts of all hydrogens increase due to deshielding of the electrons in the aromatic and heterocyclyc rings of L^1 and L^2. This increase is more apparent in spectra of the Pd(II) complexes than the others because of strong interaction between the ligand and Pd(II) ion. Of course, the protons e and i that are nearer to the coordination regions are most affected by complex formation. Because, when coordination occurs through one of nitrogen atoms of the imidazole ring and the pyridine nitrogen, the shielding is decreased because the electrons in the ring are near to the coordinated nitrogen atoms, consequently the signals of the e and i protons are observed at higher field in the complexes of L^1 and L^2.

It was reported that L^1 formed complexes with In(III), Ga(III) and Al(III) having 1:3 metal:ligand ratio and coordination occurred through the C=N nitrogen of the pyridine ring and the deprotonated imidazole nitrogen to result in dimeric or oligomeric structures[24]. However, in our study we did not observe deprotonation of the imidazole ring in the complexes of L^1, L^2 and L^3.

In the complexes of L^3, the protons i and h, compared to the analog proton in L^3, do not shift on complexation except for the Pd(II) complex. However, the signal of the proton f is shifted to higher field because hydrogen bonding is weakened and

temperature (with stirring) for an additional hour. A five-fold volume of water was added to the reaction mixture. The precipitated product was filtered, washed with 20 mL of ether. The crude product was dissolved in 20 mL of ethanol, mixed with charcoal, and then filtered. Recrystalization of this solid product was carried out using water/ethanol in the ratio 1:2 to give crystals of the 2-(2-pyridinyl)-1H-benzimidazole (L^2). The product was then washed with ether and dried under *vacuo* over $CaCl_2$. The ligands L^2 and L^3 were synthesized in a similar manner and the aldehydes used were 6-methylpyridine-2-carboxaldehyde or pyridine-3-carboxaldehyde. Yields of the products were, respectively, 7.21 g (37%) for L^1, 7.31 g (35%) for L^2, 10.72 g (55%) for L^3.

Preparation of Metal Complexes

Procedure for equation (1): Quantities of 0.5 mmole metal chloride (e.g. 0.12 g $NiCl_2 \cdot 6H_2O$) in 20 mL ethanol and 0.5 mmole of ligand (e.g. 0.10 g L^1) in 10 mL of ethanol in a reaction tube were stirred vigorously. The mixture was refluxed with stirring for about 2 hours, and then allowed to stand at room temperature overnight to give a solid product. After filtration, it was washed with 20 mL cold water, and the product was shaken in 20 mL hot ethanol for 20 minutes. The warmed mixture was filtered, washed with 10 mL ether, dried under *vacuo* over anhydrous $CaCl_2$.

Procedure for equation (2): 0.25 mmole metal chloride (e.g. 0.06 g $NiCl_2 \cdot 6H_2O$) in 10 mL ethanol and 0.5 mmole ligand (e.g. 0.10 g L^1) in 10 mL of ethanol was used. This procedure is same as the procedure (1). Also this procedure was carried out at 25±1°C, only L^3 with $ZnCl_2$ gave a different structure, ($Zn[L^3]Cl_2$), than that obtained under the reflux, ($Zn[L^3]_2Cl_2$) (TABLE I).

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The ligands L^1, L^2 and L^3 show fluorescence on radiation with 366 nm wave length light. It has been observed that the fluorescence is retained in their Zn(II) and Cd(II) complexes. It is known that fluorescence results from conjugation, therefore, in the Zn(II) and Cd(II) complexes of the ligands the conjugation was not affected by the coordination bonding.

EXPERIMENTAL

^{1}H NMR spectra (200 MHz) were recorded on a Bruker Ac-200 FT-NMR spectrometer (TUBITAK, Turkey) and chemical shifts were referenced relative to Me_4Si. IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer. Analytical data were obtained with a Carlo Erba 1106 analyzer (TUBITAK, Turkey) and Unicam Solaar 929 atomic absorption spectrometer. The molar conductance of the compounds were measured in DMSO on a WPA CMD 750 conductivity meter. Chloride ions were determined by a Jenway 3040 ion analyzer multimeter. Magnetic measurements were carried out on a Sherwood Scientific apparatus at room temperature by Gouy's method using $CuSO_4 \cdot 5H_2O$ as the calibrant and were corrected for diamagnetism by applying Pascal's constants. Water contents of the compounds were measured by a Schimadzu model TGA. Chemicals used were reagent grade.

Preparation of the Ligands

The ligands L^1, L^2, L^3 were prepared with minor modifications as described in literature[25]. However, this method was used for the first time to obtain the present ligands. A quantity of 10.4 g $NaHSO_3$ (0.1 mol) in 20 mL water was added dropwise to a solution of 10.7 g pyridyne-2-carboxaldehyde (0.1 mol) in 10 mL ethanol at 0° C. Afterwards, this mixture was reacted with 10.5 g (0.1 mol) *o*-phenylenediamine in 15 mL of DMF. The mixture was gently heated to about 70° C and kept at 70° C for an hour; afterwards it was refluxed for 30 minutes and allowed to stand at room

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