ZINC(II) COMPLEXES OF 2-(2-HYDROXY-5-BROMO/NITRO-PHENYL)-5-METHYL/CHLORO/NITRO-1H-BENZIMIDAZOLES

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Abstract

2-(2-Hydroxyphenyl)-5-R_1-1H-benzimidazoles [R_1=H (L^1H), CH_3 (L^2H), Cl (L^3H), NO_2 (L^4H)], 2-(2-Hydroxy-5-R_2-phenyl)-1H-benzimidazoles [R_2=Br (L^5H), NO_2 (L^6H)] and their $Zn(NO_3)_2$ complexes were synthesized, characterized by elemental analysis, molar conductivity, IR and ^{1}H-NMR spectra. L^1H, L^2H, L^4H and L^6H give a complex with $Zn(NO_3)_2$ in general formula $Zn(L^n)_2$; however, L^3H and L^5H complexes are in $[Zn(L^n)_2](HNO_3)_2$ form. The substituent effect on the characteristic of the ligands and the complexes was investigated.

1. Introduction

2-(2-Hydroxyphenyl)-1H-benzimidazole (L^1H) is an important compound and a classical ligand. It is antifungal against *Botrytis cinerea*[1], and antinematodic towards *Trichinella spiralis*[2], *Syphacia obvelata*[3], *Nippostrongylus brasiliensis*[4]. In addition, it showed antihelmintic[5,6] and antipoliovirus activity[7]. On the other hand, Ag(I) complex of L^1H has antibacterial and antifungal effect[8].

In the literature, many metal complexes of L^1H were studied. For example, complexes of L^1H with Cu(II), Ni(II), Co(II), Zn(II) [9,10]; $VOSO_4$ [11], $Cu(OAc)_2$ [12], Pd(II) and Pt(II) [13] were investigated. Also with some of the rare earth elements[14,15], UO_2^{2+} [16] Mo and W complexes [17] were obtained. On the other hand, analytical stability constants of some metal complexes of L^1H were determined[18-21], and L^1H coordinated to Cr(I) [22] and Mo(VI) [23,24] as a secondary ligand in the mixed complexes.

The purpose of this study is to synthesize and characterize various 5- (R_1) and 5'- (R_2) substituted derivatives of L^1H and their complexation with Zn(II), an oligo element, using spectroscopic methods, analytical data and molar conductivity.

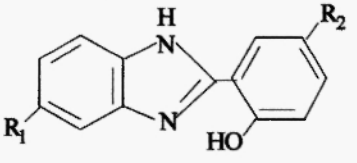
2. Materials and Methods

2.1. Apparatus

^{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 Varian SpectrAA 220/SS atomic absorption spectrometer. The molar conductance of the compounds was measured in DMSO on a WPA CMD 750 conductivity meter. All the chemicals used were reagent grade.

2.2. Synthesis of the Ligands

The ligands were prepared by the reaction of the addition product of aldehydes with $NaHSO_3$ and 4-R-1,2-phenylenediamines[9]. 4-R-1,2-phenylenediamines (R=H, CH_3, Cl, NO_2) and salicylaldehyde were used for synthesis of $L^{1-4}H$. In synthesis of L^5H and L^6H, 5-bromo- and 5-nitro-salicylaldehyde were used, respectively.



R_1=R_2= H; (L^1H). R_1=CH_3; R_2= H; (L^2H). R_1=Cl; R_2= H; (L^3H)
R_1=NO_2; R_2= H; (L^4H). R_1=H; R_2= Br; (L^5H). R_1=H; R_2= NO_2; (L^6H)

Figure 1. 2-(2-Hydroxy-5-bromo/nitro-phenyl)-5-methyl/chloro/nitro-1H-benzimidazoles

2.3. Synthesis of the Complexes

$Zn(L^1)_2$ and $Zn(L^2)_2$: 150 mg L^1H or 157 mg L^2H (*ca.* 0.7 mmole ligand) and 110 mg $Zn(NO_3)_2 \cdot 6H_2O$ (*ca.* 0.35 mmole) were dissolved in 20 ml alcohol. The mixture was reacted with stirring under reflux for 4 h, and

then allowed to stand at room temperature overnight. The precipitate was filtered off, washed with 5 ml alcohol, 5 ml ether and dried under vacuum over anhydrous $CaCl_2$.

$[Zn(L^3)_2](HNO_3)_2$: 150 mg **L^3H** (*ca.* 0.6 mmole) was dissolved in 30 ml dichloromethane. 95 mg $Zn(NO_3)_2{\cdot}6H_2O$ (*ca.* 0.3 mmole) was added to this solution and refluxed with stirring for 4 h. After cooling to room temperature the mixture volume was diminished to 15 ml by evaporation, and 10 ml petroleumether:ether (1:1, v:v) was added. The mixture was kept in a refrigerator for a week at ^0C, then the khaki precipitate was filtered off, washed with 10 ml petroleum ether and dried.

$Zn(L^4)_2$: 150 mg **L^4H** (*ca.* 0.6 mmole) and 95 mg $Zn(NO_3)_2{\cdot}6H_2O$ (*ca.* 0.3 mmole) were reacted in 25 ml dichloromethane:alcohol mixture (5:1, v/v) and refluxed with stirring for 4 h. At the room temperature a yellow precipitate was collected by filtration, washed with 10 ml petroleumether:ether (1:1, v/v) and dried.

$[Zn(L^5)_2](HNO_3)_2$: 120 mg **L^5H** (*ca.* 0.4 mmole) and 62 mg $Zn(NO_3)_2{\cdot}6H_2O$ (*ca.* 0.2 mmole) were reacted in 25 ml *iso*-propylalcohol under reflux for 4 h. After then the solution volume was diminished to 10 ml by evaporating and 5 ml petroleum ether was added. This mixture was kept at a refrigerator for a week and the precipitate was filtered off, washed with 5 ml petroleum ether and dried.

$Zn(L^6)_2$: 105 mg **L^6H** (*ca.* 0.4 mmole) was suspended in 25 ml *iso*-propylalcohol and to this mixture 62 mg $Zn(NO_3)_2{\cdot}6H_2O$ (*ca.* 0.2 mmole) was added and refluxed for 4 h. The mixture was kept at room temperature overnight and the precipitate was filtered off, washed with 5 ml petroleumether and dried.

Table 1 Some properties and analytical data of the ligands and their Zn(II) complexes.

Compound	M.p. °C	Yield (%)	Elemental Analysis Found (Calcd.) %C	%H	%N	%M	Molar Cond. *	Color
L^1H	243	85	74.4	4.9	13.2	0	0	Cls.
$C_{13}H_{10}N_2O$			(74.3)	(4.8)	(13.3)			
$Zn(L^1)_2$	>350	65	64.4	3.6	11.4	13.7	1.5	Cls.
$C_{26}H_{18}N_4O_2Zn$			(64.5)	(3.7)	(11.6)	(13.5)		
L^2H	237	90	75.0	5.4	12.4	0	0	Cls.
$C_{14}H_{12}N_2O$			(75.0)	(54.)	(12.5)			
$Zn(L^2)_2$	>350	50	65.6	4.2	10.9	12.9	3.2	Cls.
$C_{28}H_{22}N_4O_2Zn$			(65.7)	(4.3)	(10.9)	(12.8)		
L^3H	233	65	63.9	3.8	11.3	0	0	Cls.
$C_{13}H_9ClN_2O$			(63.8)	(3.7)	(11.4)			
$[Zn(L^3)_2](HNO_3)_2$	>350	45	46.0	2.8	12.8	9.5	76	Khaki
$C_{26}H_{18}N_6O_8Cl_2Zn$			(46.1)	(2.7)	(12.4)	(9.6)		
L^4H	229	75	61.3	3.7	16.3	0	0	Light
$C_{13}H_9N_3O_3$			(61.2)	(3.5)	(16.5)			yellow
$Zn(L^4)_2$	>350	50	54.5	2.9	14.5	11.5	13	Dark
$C_{26}H_{16}N_6O_6Zn$			(54.4)	(2.8)	(14.6)	(11.4)		yellow
L^5H	198	80	54.1	3.2	9.6	0	0	Cls.
$C_{13}H_9BrN_2O$			(54.0)	(3.1)	(9.7)			
$[Zn(L^5)_2](HNO_3)_2$	214	70	40.8	2.5	10.7	8.8	78	Light
$C_{26}H_{18}N_6O_8Br_2Zn$			(40.6)	(2.3)	(10.9)	(8.5)		brown
L^6H	240	85	61.2	3.7	16.4	0	0	Light
$C_{13}H_9N_3O_3$			(61.2)	(3.6)	(16.5)			yellow
$Zn(L^6)_2$	238	75	54.7	3.0	14.3	11.1	11	Dark khaki
$C_{26}H_{16}N_6O_6Zn$			(54.4)	(2.8)	(14.6)	(11.4)		

*measured in DMSO, $\Omega^{-1}cm^2mol^{-1}$, at 25±1°C. Cls. : colorless

3. Results and Discussion

The analytical data, melting point, molar conductivity are given in Table 1.

3.1. General Properties

It has been determined that the benzimidazole ring substituents reduce the melting point of **$L^{1-4}H$**. On the other hand, the melting point of the **L^{1-4}** complexes is greater than 350°C. However, **L^5** and **L^6** complexes with phenol ring substituents, have lower melting point compared to the others.

The complexes including NO_2, Cl and Br substituents are colored. The color of the complexes including nitro group, $Zn(L^4)_2$, $Zn(L^6)_2$, is deeper than the others due to the charge transfer transition.

L^1H, L^2H, L^3H and **L^5H** are very slightly soluble in apolar solvents such as CCl_4, benzene, toluene *etc.* and water, ether; but they are easily soluble in polar solvents such alcohol. **L^4H** and **L^6H** have lower solubility because of the hydrogen bonding of the nitro group.

The electronegative groups, Cl, Br, NO_2, increase the solubility of the complexes, on the contrary, hydrogen and methyl substituents decrease it. It was observed that, the electronegative groups, Cl, Br, NO_2, also increased the acidity of the ligands [25].

3.2. Molar Conductivity

The lower molar conductance values of $Zn(L^1)_2$, $Zn(L^2)_2$, $Zn(L^4)_2$ and $Zn(L^6)_2$ in the range 1.5–13 $\Omega^{-1}cm^2mol^{-1}$ indicate that these complexes are non-ionic. $[Zn(L^3)_2](HNO_3)_2$ and $[Zn(L^5)_2](HNO_3)_2$ have a ionic structure; because their molar conductance values are 77 and 78 $\Omega^{-1}cm^2mol^{-1}$, respectively. The NO_3^- stretching vibrations in the IR spectra of these complexes support this observation.

3.3. IR Spectra

The IR spectrum of **L^1H** was studied in the literature. **L^1H** and its complexes with Cu(II), Ni(II), Co(II), Zn(II) iodide, bromide[9] , and acetate salts[10] were obtained and found to be $M(L^1)_2$. In addition, it was reported that, in the Hg(II) [26], $VOSO_4$ [11], $PbCl_4$ complexes[27], the coordination occurred through the nitrogen atom with double bond, and the oxygen atom by the elimination of the OH hydrogen. It was determined that **L^1** gave square planar complexes with Cu(II), Ni(II) [28], Pd(II) and Pt(II) ions [13]; and tetrahedral with the Co(II) ion [29]. On the other hand, the complexes in which **L^1H** acted as a monodentate ligand, were obtained with rare earth elements [30] and UO_2^{2+} [16].

The important IR spectra frequencies are given in Table 2. In the spectra of the ligands, the N–H stretching vibration frequencies appear at *ca.* 3300 cm^{-1} as a sharp band, and change to a broad band in the complexes. The O–H stretching vibration bands lie in the 3200-2700 cm^{-1} region as a rather broad band due to hydrogen bonding. The ν(C=N) frequencies are seen around 1600 cm^{-1} as a medium band. The sharp or medium bands in the 1460 - 1495 cm^{-1} region are assigned to the aromatic ν(C=C). The C–O stretching vibration frequencies appear between 1250-1280 cm^{-1} as medium or sharp bands. The sharp or medium bands around 740 and 830 cm^{-1} are due to the out-of-plane deformation bands for the aromatic C–H.

Table 2 The IR spectral data of the ligands and their Zn(II) complexes.

Compound	Frequencies, cm^{-1}
L^1H	3323 s ν(NH), 3246 sh ν(OH), 1600 m ν(C=N), 1492 s ν(C=C), 1269 m ν(C-O), 846 m, 738 m, oop (C-H) def.
$Zn(L^1)_2$	3431 br ν(NH), 1607 m ν(C=N), 1485 s ν(C=C), 1315 m, 1254 m ν(C-O), 1138 m, 738 s, oop (C-H) def.
L^2H	3238 s ν(NH), 3438 br ν(OH), 2915 m ν(CH_3), 1600 m ν(C=N), 1492 s ν(C=C), 1269 s ν(C-O), 854 m, 808 m, 761 s, oop (C-H) def.
$Zn(L^2)_2$	3423 br ν(NH), 2969 m ν(CH_3), 1607 m ν(C=N), 1485 s ν(C=C), 1315 m, 1254 m ν(C-O), 1146 m, 807 m, 761 m, oop (C-H) def.
L^3H	3431 br ν(NH), 3246 br ν(OH), 1608 m ν(C=N), 1461 m ν(C=C), 1261 s ν(C-O), 1108 m, 815 m, 761 s, oop (C-H) def., 592 m ν(C-Cl)
$[Zn(L^3)](HNO_3)_2$	3438 br ν(NH), 3223 br ν(OH), 1623 m ν(C=N), 1461 m ν(C=C), 1385 s ν(NO_3^-), 1331 m, 1233 m, 1269 m ν(C-O), 815 m, 769 m, oop (C-H) def. 600 m ν(C-Cl).
L^4H	3484 br ν(NH), 3292 s ν(OH), 1615 m ν(C=N), 1538 m ν(NO_2), 1492 s ν(C=C), 1338 s ν(NO_2), 1261 m ν(C-O), 1069 m, 815 m, 754 s, oop (C-H) def.
$Zn(L^4)_2$	3381 m ν(NH), 1631 m ν(C=N), 1515 m ν(NO_2), 1484 m ν(C=C), 1338 s ν(NO_2), 1253 m ν(C-O), 1069 m, 823 m, 746 m, oop (C-H) def.
L^5H	3346 s ν(NH), 1584 m ν(C=N), 1492 s ν(C=C), 1261 s ν(C-O), 1146 m, 815 s, 731 s, oop (C-H) def., 585 m ν(C-Br)
$[Zn(L^5)_2](HNO_3)_2$	3241 br ν(NH)+ ν(OH), 1605 m ν(C=N), 1482 m ν(C=C), 1386 s ν(NO_3^-), 1304 m, 1251 m ν(C-O), 819 m, 746 m, oop (C-H) def., 650 m ν(C-Br)
L^6H	3280 s ν(NH), 3000-2500 br ν(OH), 1594 m ν(C=N), 1590 s ν(NO_2), 1478 s ν(C=C), 1339 s ν(NO_2), 1266 m ν(C-O), 1135 s, 831 m, 808 m, 743 s, oop (C-H) def.
$Zn(L^6)_2$	3303 m ν(NH), 1605 m ν(C=C), 1563 m ν(NO_2), 1493 m ν(C=C), 1386 m ν(NO_2), 1312 s, 1282 m ν(C-O), 1131 s, 835 m, 735 m, oop (C-H) def.

In the IR spectra of the complexes, noticeable changes are observed according to the ligands, especially in the intensity or frequencies of the ν(NH), ν(OH), ν(C=N), ν(C=C) and ν(C–O) vibrations. For

example, upon complexation the broad band between 3200-2700 cm^{-1} because of the hydrogen bonding diminishes considerably. This indicates that the hyrogen bonding is partially removed in the complexes. The ν(C=N) frequencies shift to the left as 7-20 cm^{-1} and the bands weaken relatively. The ν(C=C) and ν(C–O) bands also shift to the higher or lower field in the IR spectra of the complexes compared to the ligands.

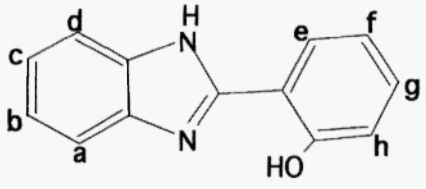
In the spectra of L^4H, the bands at 1538 m, 1338 s, in that of L^6H at 1590 s, 1339 cm^{-1} (s) are assigned to the symmetric and asymmetric ν(NO_2), respectively. The medium band at 2915 cm^{-1} is due to stretching vibration of CH_3 group in the L^2H. The C–Cl and C–Br stretching vibrations are at 592 (m) and 585 cm^{-1} (m) in the spectra of L^3H and L^5H, respectively. This frequencies shift to 600 (m) and 650 cm^{-1} (m) in the complexes, respectively.

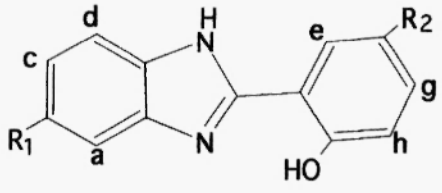
3.4. ^1H NMR Spectra

The ^{1}H-NMR data with coupling constants are given in Table 3.

In the ^{1}H-NMR spectra of the ligands and the complexes the NH resonance appears *ca.* 13 ppm as a broad singlet. The sharp characteristic of the NH resonance is in the following order: $L^1H>L^5H>L^6H>L^2H>L^4H>L^3H$. This means that the substituents increase the fluxionality of the NH proton because of the resonance through the N⁻⁻C⁻⁻N system, or it can be said that the acidity of the NH proton is increased. This increase is relatively higher in case of the δ– effective benzen ring substituents according to the phenol ring substituents. Therefore, it can be said that the δ– effective groups at the R_1 position decrease the electron density of the N⁻⁻C⁻⁻N system while those at R_2 position increase it.

The sharp characteristic of the NH resonance is in the following order in the Zn(II) complexes: $[Zn(L^5)_2](HNO_3)_2 > Zn(L^6)_2 > Zn(L^2)_2 > Zn(L^1)_2 > [Zn(L^3)_2](HNO_3)_2 > Zn(L^4)_2$. This order is almost the same as that of the ligands. As a different, the acidity of the NH proton is relatively decreased in the complexes containing nitrate ion, $[Zn(L^3)_2](HNO_3)_2$ and $[Zn(L^5)_2](HNO_3)_2$





The R_1 substituents make the resonances of the benzimidazole protons clear to identify from each other, and consequentially, protons **a**, **c** and **d** are determined separately in the ^{1}H-NMR spectra of L^2H, L^3H, L^4H and their complexes. For example, **a** proton's resonance appears as a singlet; protons **b** and **c** show a doublet (see Table 3). Determination of protons **f**, **g** and **h** is very difficult in the spectra of $L^{1-4}H$ and their Zn(II) complexes. Because the resonance of **f**, **g** and **h** are complex patterns. However, the resonance of protons e, **g**, h can be seen clearly favor of the phenol ring R_2 substituents in the spectra of L^5H, L^6H and their complexes.

Protons **b** and **c** appear as a complex pattern in the spectra of L^1H, L^2H, L^3H and their complexes. Protons **f** and **g** of $L^{1-4}H$ are also complex patterns but they are separated in the complexes as a doublet or doublet of doublets.

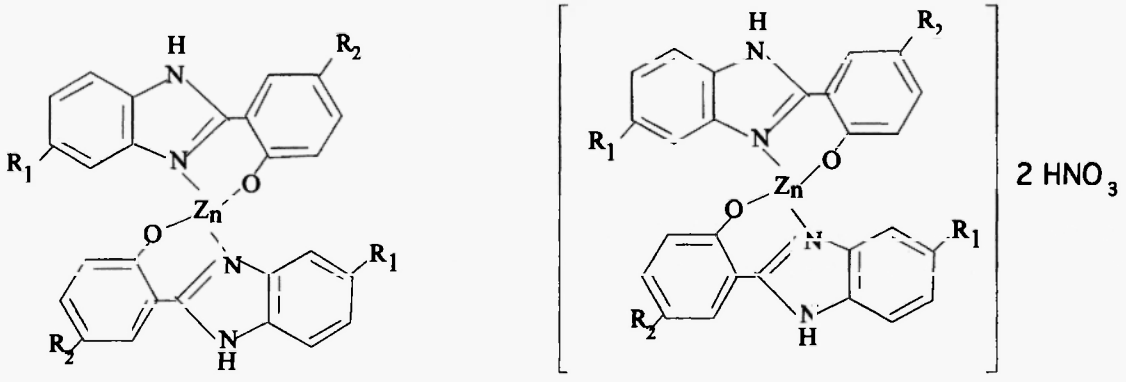
Proton e at the phenol ring give a doublet due to interaction with **g** in the spectra of L^5H and L^6H, (*J* values are 2.0 and 2.8 Hz, respectively). In line with that, proton **g** of L^5H and L^6H give a *d–d* system due to an interaction of **g** with **h** and e. However, in the spectra of $[Zn(L^5)_2](HNO_3)_2$ and $Zn(L^6)_2$, this doublet changes to a singlet.

In the complexes of L^{1-4}, especially phenolic protons' resonance shifts to the right probably due to the L→M charge transfer transition, while it shifts to the left due to the M→L charge transfer in the $[Zn(L^5)_2](HNO_3)_2$ and $Zn(L^6)_2$.

All of the complexes have 2:1 M:L ratio, and in all of the complexes coordination occurs through the C=N and OH groups. Considering molar conductivity, IR and ^{1}H-NMR spectral data, the formulas in Figure 2 are proposed for the Zn(II) complexes of L^{1-6}.

Table 3 ^{1}H NMR data of the ligands and their Zn(II) complexes (in DMSO-d_6)

	The chemical shift values (δ_H, ppm) with coupling constants (J, Hz) (TMS standard)									
Compound	The benzimidazole protons					The phenolic protons				
	NH	a	b	c	d	OH	e	f	g	h
L^1H	13.11 s	7.66 s,br	7.27 m		7.66 s,br	Dis.	in 7.27 m	7.00 m		8.05 d J=8.0
$Zn(L^1)_2$	13.43 s	in 7.24 m	7.07 d,br		in 7.24 m	---	7.58 d J=8.0	6.72 m		7.98 d J=7.9
L^2H	13.02 s	7.36 s	2.43 s	6.84 d J=7.9	7.42 d J=8.6	5.41 s	7.10 d J=8.8	7.02 m		8.01 d J=7.9
$Zn(L^2)_2$	13.26 br,s	7.36 s	2.37 s	6.90 d J=7.5	7.29 d J=8.2	---	7.07 d J=8.1	6.67 d-d J=7.4; 8.4	6.80 d-d J=7.4; 8.1	7.95 d J=7.9
L^3H	12.75 s,br	8.03 s	---	7.68 d J=8.1	7.39 d J=8.2	---	in 7.25 m	7.03 m		in 7.25 m
$[Zn(L^3)](HNO_3)_2$	13.27 s	7.94 s	---	7.77 d J=8.1	7.50 d J=8.2	5.49 s	in 7.28 m	6.86 d-d J=8.1; 8.0	7.28 m	8.02 d J=7.9
L^4H	13.22 s	8.53 s	---	8.13 d J=7.4	7.93 d J=7.6	Dis.	7.42 d J=6.5	7.06 m		7.67 d J=7.0
$Zn(L^4)_2$	Dis.	8.75 s,br	---	8.13 d J=8.3	7.73 d J=8.3	---	7.28 d J=6.4	6.71 m,br	6. 91 d J=7.7	7.98 d,br J=7.6
L^5H	13.20 s	in 7.58 m,br	7.25 m		in 7.58 m	5.31 s	8.24 d J=2.0	---	7.41 d-d J=8.8, 2.0	6.85 d J=8.8
$[Zn(L^5)_2](HNO_3)_2$	13.29 s	7.69 s,br	7.30 m		7.69 s,br	Dis.	8.29 s	---	7.51 d J=8.8	7.02 d J=8.9
L^6H	14.12 s	in 7.71 m	7.35 m		in 7.71 m	Dis.	9.12 d J=2.8	---	8.23 d-d J=9.3, 2.8	7.21 d J=9.0
$Zn(L^6)_2$	13.66 s	7.81 d,br	7.28 s,br		7.60 d,br	---	9.04 s	---	8.09 d,br	6.77 s,br



$Zn(L^n)_2$;
n= 1,2,4 and 6;
R_1/R_2= H/H; CH_3/H; NO_2/H and H/NO_2

$[Zn(L^n)_2]\cdot 2HNO_3$;
n= 3 and 5;
R_1/R_2= Cl/H and H/Br

Figure 2. The proposed structural formula for Zn(II) complexes of $L^{1-6}H$.

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4. References

[1] A. Shinohara, S. Kusano, S. Matsui, N. Muramatsu, S. Kawada, *Japan Kokai,* 78 29,934 (1979); *C.A.*, 89, 101871c (1979).
[2] T. Kharizanova, I. Torlakov, L. Zhelyankov, N. Todorova, N. Sheikov, *Advan. Antimicrob. Antineoplastic Chemother., Proc. Int. Congr. Chemother., 7th*, 1 (1971) 449-51; *C.A.*, 79, 38436r (1972).
[3] T. Kharizanova, I. Torlakov, L. Zhelyankov, N. Todorova, N. Sheikov, *Tr. Nauchnoized. Khim.-Farm. Inst.,* 8 (1972) 347-52; *C.A.*, 79, 38526v (1972).
[4] I. Torlakov, T. Kharizanova, L. Zhelyankov, N. Todorova, *Tr. Nauchnoized. Khim.-Farm. Inst.,* 9 (1974) 325-31; *C.A.*, 83, 90863z (1975).
[5] L. I. Denisova, V. M. Kosareva, K. E. Lotukhova, I. G. Solonenka, *Khim-Farm. Zh.*, 9 (1975) 18-21; *C.A.*, 84, 12469g (1976).
[6] T. P. Veselova, M. V. Doroshina, M. A. Belousova, N. N. Gudkova, *Byull. Vses. Inst. Gel'mintol,* 20 (1977) 7-8; *C.A.*, 90, 97509s (1978).
[7] D. G. O'Sullivan, P. W. Sadler, *Nature,* 192 (1961) 341-3.
[8] B. Ülküseven, A. Tavman, G. Otük, *Metal-Based Drugs,* 6 (1999) 163-7.
[9] T. J. Lane, I. Nakagawa, J. L. Walter, A. J. Kandathil, *Inorg. Chem.,* 1 (1962) 267-76.
[10] D. H. Verkhovodova, N. R. Kal'nitskii, V. I. Minkin, A. D. Garnovskii, O. A. Osipov, *Zh. Neorg. Khim.*, 12 (1967) 3385-7; *C.A.*, 68, 83943n (1968).
[11] S. K. Gupta, L. K. Mishra, *J. Inorg. Nucl. Chem.*, 41 (1979) 890-91.
[12] S. P. Ghosh, S. K. Gupta, L. K. Mishra, *J. Indian Chem. Soc.*, 56 (1979) 206-8.
[13] L. K. Mishra, *J. Indian Chem. Soc.*, 59 (1982) 408-9.
[14] A. Mishra, V. K. Singh, *J. Indian Chem. Soc.*, 58 (1981) 122-4.
[15] A. Mishra, M. P. Singh, J. P. Singh, *J. Indian Chem. Soc.*, 57 (1980) 246-51.
[16] P. S. Mansingh, R. R. Mohanty, S. Jena, K. C. Dash, *Indian J. Chem.*, 35A (1996) 479-82.
[17] M. R. Maurya, S. A. Bhakare, *J. Chem. Res., Synop.*, 8 (1996) 390-91; *C.A.*, 125, 264182e (1996).
[18] A. K. Murthy, P. Lingaiah, *Indian J. Chem. Sci.*, 1 (1987) 17-18; *C.A.*, 111, 84924a (1989).
[19] Z. M. Akhrimenko, V. T. Panyushkin, *Koord. Khim.*, 16 (1990) 863-4; *C.A.*, 113, 104229z (1990).
[20] A. K. Murthy, P. Lingaiah, *Indian J. Chem.*, 23A (1984) 969-71.
[21] A. V. El'tsov, L. I. Rudaja, E. D. Samartseva, I. Ya. Kvitko, A. V. Tret'yakov, *Deposited Doc., VINITI,* 1984, 3275-84; *C.A.*, 103, 28147x (1985).
[22] R. C. Maurya, S. Jaiswal, R. Verma, *Indian J. Chem.*, 35A (1996) 998-1000.
[23] B. Piggott, S. D. Thorpe, R. N. Sheppard, *Inorg. Chim. Acta,* 103 (1985) 3-4.
[24] M. V. Capparelli, B. Piggott, S. D. Thorpe, R. N. Sheppard, *Inorg. Chim. Acta,* 98 (1985) 53-5.
[25] B. Ülküseven, I. Kizilcikli, A. Tavman and B. Akkurt, *Rev. Inorg. Chem.* in press.
[26] R. L. Dutta, S. K. Satapati, *J. Inorg. Nucl. Chem.*, 43 (1981) 1533-9.
[27] N. S. Biradar, N. N. Sirmokadam, *J. Inorg. Nucl. Chem.*, 35 (1973) 3639-41.
[28] H. Ojima, K. Noyonama, *Aichi Kyoiku Daigaku Kenkyu Hokoku, Shizen Kagaku,* 41 (1992) 17; *C.A.*, 118, 93135r (1993).
[29] S. K. Gupta, L. K. Mishra, *J. Nepal Chem. Soc.*, 1 (1981) 57-67; *C.A.*, 103, 11501Is (1985).
[30] V. T. Panyushkin, A. A. Dedyukhin, *Koord. Khim.*, 15 (1989) 1000-3; *C.A.*, 111, 186282g (1989).

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