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Synthesis, spectral characterisation of 2-(5-methyl-1*H*-benzimidazol-2-yl)-4-bromo/nitro-phenols and their complexes with zinc(II) ion, and solvent effect on complexation

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Abstract

2-(5-Methyl-1*H*-benzimidazol-2-yl)-4-bromo/nitro-phenols (HLBr and HLNO₂) and their Zn(II) complexes with ZnX₂ (X = Cl, I, NO₃) were synthesized and characterized by elemental analysis, molar conductivity, IR, ¹H and ¹³C NMR spectra. The OH proton appears near the NH protons in the ¹H NMR spectra of the ligands because of the strong intramolecular hydrogen bonding between the OH hydrogen and the C=N nitrogen atoms. The complexation is investigated in ethanol and isopropanol and it is observed that isopropanol is a better solvent than ethanol for the complex forming. HLBr gives harder complexation reaction with Zn(II) according to HLNO₂ because of the stronger intramolecular hydrogen bonding in HLBr, and the both ligands react easier with Zn(NO₃)₂ than ZnCl₂ and ZnI₂. The Zn(II) complexes of HLBr have 1:1 M:L ratio and ionic character, however, HLNO₂ give a non-ionic complex that has 1:2 M:L ratio. In the complexes the phenolic hydrogen is eliminated and a chelate structure is formed.

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Keywords: Zinc(II) complexes; 2-(5-Methyl-1H-benzimidazol-2-yl)-4-bromo/nitro-phenols; Solvent effect

1. Introduction

It is known that solvent plays a considerable role in controlling the dynamics of chemical reaction. In the literature, the influence of the solvent on the structure was reported [1–4]. Several reviews have underlined the importance of the essential role played by solvents in many chemical reactions, and especially in reactions involving charge transfer, with particular relevance to chemistry and biochemistry [5–7].

The solvent plays a fundamental role in the relative stabilization of different ground-state rotameric and tautomeric structures, and determines the nature of the proton transfer processes in the excited state [8]. Intra- or intermolecular hydrogen bonding is very importance factor in the solvation, reaction and stabilization of the compounds. In the last few years, the study of ground state intramolecular proton transfer

* Tel.: +90 212 473 70 70; fax: +90 212 473 70 26. *E-mail address:* atavman@istanbul.edu.tr. events has received increasing attention aiming at the characterization of a large number of compounds.

According to Prieto et al., 2-(2-hydroxyphenyl)-1Hbenzimidazole (HBI) has different behaviour in water and different solvents. In both water and ethanol, ground state HBI exhibits conformational equilibrium between a *cis*-enol form with an intramolecular hydrogen bond and a *trans*enol form that is hydrogen-bonded to the solvent; the ground state keto tautomer is also present in water. The excited *cis*enol conformer always undergoes ultra-fast intramolecular proton transfer to afford the excited keto tautomer (Fig. 1) [5].

It is known that zinc(II) is essential for human health and plays a key role in human metabolism. In this paper, the ligands, 2-(5-methyl-1*H*-benzimidazol-2-yl)-4-bromo- (HLBr) and nitro-phenols (HLNO₂) (Fig. 2), and their complexes with Zn(II) were synthesized and characterized. The complexation ability of the ligands with Zn(II) ion in ethanol and isopropanol is investigated, and the substituent, solvent and Zn(II) salt effects on complexation is observed.

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Fig. 1. Different behaviours of 2-(2-hydroxyphenyl)-1H-benzimidazole in solvent.



Fig. 2. Chemical structure of the ligands.

2. Experimental

2.1. Apparatus

IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer. ¹H and ¹³C NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. The residual DMSO-d₆ signal was also used as an internal reference. Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyser 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 (2-hydroxy-5-nitro/bromo benzaldehydes) with NaHSO₃ and 4-methyl-1,2-phenylenediamine [9,10]. 6 mmol of aldehyde (1.0 g 2-hydroxy-5-nitrobenzaldehyde or 1.2 g 2-hydroxy-5-nitrobenzaldehyde) and 0.65 g NaHSO₃ (6 mmol) were stirred at room temperature in ethanol (25 ml) and a precipitate is formed after 4 h reaction. 0.74 g 4-methyl-1,2-phenylenediamine (6 mmol) and 25 ml DMF were added to this mixture. After 2 h reflux the solution was poured into 10-fold water. The benzimidazole compound precipitated was filtered, dried and crystallised from ethanol.

2.3. Synthesis of the complexes

2.3.1. $Zn(LBr)ipa(NO_3)$

HLBr (80 mg, 0.26 mmol) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (77 mg, 0.26 mmol) is solved in isopropanol (20 ml) and the mixture refluxed with stirring. After 5 h reaction a precipitate is

obtained. The precipitate is filtered, washed with isopropanol and ether and dried at 80 °C.

$$Zn(NO_3)_2 + HLBr + ipa \rightarrow Zn(LBr)ipa(NO_3) + HNO_3$$

2.3.2. $Zn_2(LBr)_2I_2$

HLBr (80 mg, 0.26 mmol) and ZnI_2 (83 mg, 0.26 mmol) is solved in isopropanol (20 ml) and the mixture refluxed with stirring. After 7 h reaction a precipitate is obtained. The precipitate is filtered, washed with isopropanol and ether and dried at 80 °C.

$$2ZnI_2 + 2HLBr \rightarrow Zn_2(LBr)_2I_2 + 2HI$$

2.3.3. Zn(LNO₂)₂

HLNO₂ (75 mg, 0.28 mmol) and ZnCl₂· $6H_2O$ (69 mg, 0.28 mmol) or Zn(NO₃)₂· $6H_2O$ (83 mg, 0.28 mmol) is solved in isopropanol (20 ml) and the mixture refluxed with stirring. After 6 h (with ZnCl₂) and 4 h reactions (with Zn(NO₃)₂) the precipitate is filtered and washed with isopropanol and ether and dried at 80 °C. The reaction equations are the following:

 $Zn(NO_3)_2 + 2HLNO_2 \rightarrow Zn(LNO_2)_2 + 2HNO_3$

 $ZnCl_2 + 2HLNO_2 \rightarrow Zn(LNO_2)_2 + 2HCl$

3. Results and discussion

3.1. General properties

The analytical data and some physico-chemical properties of the ligands and the complexes are given in Table 1.

HLBr has good solubility and its complexes with Zn(II) have moderate solubility in polar solvents such as ethanol. However, HLNO₂ and Zn(LNO₂)₂ have lower solubility than the HLBr and its Zn(II) complexes. Reason of this is strong intermolecular hydrogen bonding between nitro and OH, NH groups of HLNO₂ (NO₂···HO; NO₂···HN).

Zn(II) complexes of HLBr are yellow colored compounds whereas the ligand itself colourless. This shows that there is a charge transfer transition from the ligand to Zn(II) ion $(L \rightarrow M)$. Zn(LNO₂)₂ has 1:2 M:L ratio and non-ionic character. However, the HLBr complexes have 1:1 ratio and show

Table 1	
Analytical data and some properties of the ligands and the complexes	

Compound	Found (calcd	. %)		Yield (%)	m.p. (°C) ^a	Λ^{b}	Color	
	C	Н	N	Zn				
HLBr C ₁₄ H ₁₁ BrN ₂ O	55.3 (55.5)	3.8 (3.7)	9.1 (9.2)	_	80	303	0	Color-less
Zn(LBr)ipa(NO ₃) C ₁₇ H ₁₈ BrN ₃ O ₅ Zn	41.8 (41.7)	3.8 (3.7)	8.3 (8.6)	13.0 (13.3)	60	285	62	Yellow
$Zn_2(LBr)_2I_2 C_{28}H_{22}Br_2I_2N_4O_2Zn_2$	34.2 (33.9)	1.9 (2.2)	5.4 (5.6)	13.1 (13.2)	55	265	25	Light yellow
HLNO ₂ C ₁₄ H ₁₁ N ₃ O ₃	62.3 (62.4)	4.0 (4.1)	15.4 (15.6)		75	295-310	0	Yellow
$Zn(LNO_2)_2 C_{28}H_{20}N_6O_6Zn$	55.7 (55.9)	3.1 (3.3)	13.9 (14.0)	11.2 (10.9)	90	>350	2.0	Khaki-yellow

^a Decomposed.

^b Molar conductivity, measured in DMSO, Ω^{-1} cm² mol⁻¹, at 25 ± 1 °C.

high molar conductivity in DMSO, namely they have ionic character.

3.2. Solvent effect on complexation

HLBr did not react with ZnX_2 (X = Cl, I, NO₃) in both ethanol and isopropanol for 15 h and, it did not react with $Zn(NO_3)_2$ in ethanol for approximately 12 h. However, a reaction is occurred between HLBr and Zn(II) ion for 5 h (with $Zn(NO_3)_2$) and 7 h (with ZnI_2) in isopropanol, respectively.

HLNO₂ reacted with $ZnCl_2$ and ZnI_2 in isopropanol in end of 6 h period and with Zn(NO₃)₂ end of 4 h. HLNO₂ did not reacted with Zn(II) for approximately 10h in ethanol. Ethanol is a more polar solvent according to isopropanol and in ethanol the intramolecular and intermolecular hydrogen bonding is stronger. An interaction between the solvent (ethanol) and the ligands may occur and the complex forming is not observed because of the stronger hydrogen bonding and the solvent effect. This is supported by the ¹H NMR spectra of the ligands in CD₃OD: the OH signals are not detected because of the factors mentioned above. However, the OH and NH signals are detectable near 13 ppm in the ¹H NMR spectra in DMSO (NMR Spectra section). On the other hand, Zn(II) ion itself is another factor for harder complexation, because it is a weak Lewis acid because of a d-filler (d¹⁰) ion. Cu(II) and Fe(III) ions are easily reacted with the ligands in alcohol. The complexation of Cu(II) and Fe(III) will be evaluated in another study). According these observations, it can be said that isopropanol is a more suitable solvent than ethanol for synthesis of the Zn(II) complexes, and HLBr gives harder complexation reaction with Zn(II) according to HLNO₂.

The methyl group at 4-position on the benzimidazole section must affected the complexation too. Because the methyl group has an electron deficient group and increase the electronegativity of the C=N nitrogen. Therefore, the C=N nitrogen shows stronger hydrogen bonding with the phenolic OH hydrogen atom.

3.3. IR spectra

The IR spectral data of the ligands and the complexes are given in Table 2.

The broad bands at around the 3450 cm^{-1} are assigned to NH stretching vibrations in the IR spectra of the ligands and the complexes. In the bromo derivative the strong and broad band at 3272 cm^{-1} is attributed to the intramolecular hydrogen bonded ν (OH). In the nitro derivative ν (OH) appears as a weaker band according to HLBr at 3203 cm^{-1} . It is observed that the hydrogen bonding is weakened in the complexes. The 3068 and 3072 cm^{-1} bands are belonging to the aromatic CH groups in HLBr and HLNO₂, respectively. The weak band near 2920 cm^{-1} is due to the stretching vibrations of the methyl group.

The 1632 and 1640 cm⁻¹ medium bands are assigned to the aromatic ν (C=C) group for HLBr and HLNO₂, respectively. Also, the 1582 and 1607 cm⁻¹ bands are belonging to the ν (C=N) groups, for bromo and nitro derivatives, respectively. In the complexes, the ν (C=N) bands show considerable changes shifting to the lower field. The strong peaks near 1490 cm⁻¹ are due to the stretching vibration of the aromatic C=C groups in the ligands and the complexes. The medium and strong bands between 700 and 900 cm⁻¹ are assigned to the out-of-plane of CH bendings of the phenol

IR spectral data of HLBr, HLNO2 and their Zn(II) complexes

Compound	Frequencies, cm ⁻¹ (KBr disks)
HLBr	3460 br, 3272 s, 3068 w, 2918 w, 1632 m, 1582 m, 1532 m, 1486 s, 1389 s, 1374 s, 1320 m, 1274 s, 1251 s, 1139 m, 974 m, 866 m, 800 s, 704 m, 634 m
Zn(LBr)ipa(NO ₃)	3438 s,br, 3322 s, 3068 w, 2972 w, 2914 w, 1632 m, 1601 m, 1532 m, 1478 s, 1386 s, 1339 m, 1289 m, 1247 m, 1139 m, 1043 m, 997 m, 943 m, 827 m, 804 m, 700 m, 643 m
$Zn_2(LBr)_2I_2$	3265 s,br, 3053 m,br, 2914 w, 1621 m, 1605 m, 1543 m, 1478 s, 1370 m, 1293 m, 1247 s, 1139 m, 1100 m, 874 m, 804 s, 747 m, 708 m, 635 m
HLNO ₂	3441 m,br, 3203 m, 3072 m, 2922 w, 2610 w, 1851 w, 1640 m, 1607 m, 1555 s, 1497 s, 1479 s, 1320 s, 1304 s, 1293 s, 1158 m, 1235 m, 1135 s, 927 m, 881 m, 834 m, 808 m, 770 m, 739 m, 639 m, 612 m
$Zn(LNO_2)_2$	3303 s, 3083 w, 2918 w, 1636 m, 1605 s, 1563 m, 1493 s, 1312 s, 1128 s, 916 m, 831 m, 800 m, 750 m, 723 m, 646 m, 527 m

and the benzimidazole benzene rings in the spectra of the compounds.

Two sharp bands are appeared at ca. 1320 and $1560 \,\mathrm{cm}^{-1}$ for $\nu(NO_2)$ in the IR spectra of HLNO₂ and Zn(LNO₂)₂.

The coordinated isopropanol bands are detectable in the IR spectra of $Zn(LBr)ipa(NO_3)$. The 2972 cm⁻¹ medium band can be attributed to the ν (CH₃) groups of isopropanol. The strong and very broad band between 3500 and $3372 \,\mathrm{cm}^{-1}$ is due to the combinational vibrational stretching of coordinated OH and the NH groups. On the other hand, a shoulder at $1463 \,\mathrm{cm}^{-1}$ is probably due to the methylene groups of coordinated isopropanol. A strong band at 1386 cm^{-1} in Zn(LBr)ipa(NO₃) complex is assigned to ν (NO₃⁻). This band is not detected in $Zn_2(LBr)_2I_2$ and $Zn(LNO_2)_2$ complexes. This observation supports the higher molar conductance and the ionic character of Zn(LBr)ipa(NO₃) complex.

3.4. ¹H and ¹³C NMR-spectra

The ¹H- and ¹³C NMR spectral data are given in Tables 3 and 4, respectively.

There are interesting details in the ¹H NMR spectra of the ligands. For example, proton H6' gives a broad singlet in HLBr while it appears as a doublet in HLNO₂. H7 shows a doublet in HLBr, however it is in a multiplet in the spectra of HLNO₂. H4 gives a broad singlet in HLBr and a sharp singlet in HLNO₂. These observations exhibit that the HLBr ligand has more acidic character than HLNO₂. The acidic character of HLBr may result from high electronegativity of bromide and a strong cis-enol tautomer structure of HLBr. Namely, the cis-enol tautomeric form of HLBr is more stable than that of HLNO₂.

The OH and NH protons appear as a broad singlet at 14.07 ppm in the spectra of HLNO₂ in DMSO. However, in the bromo derivative they give two broad singlets close to each other at 13.13 and 13.33 ppm (Fig. 3). This observation



Fig. 3. ¹H NMR signals of NH and OH protons in (a) HLBr, (b) Zn(LBr)ipa(NO₃), (c) HLNO₂ and (d) Zn(LNO₂)₂.

Compound	The benzimid	azole protons				The phenolic pro	tons		
	H4	H6	H7	HN	CH ₃	H3′	HS'	H6′	НО
HLBr (CD ₃ OD)	7.43 s,br	7.14 d J=7.8	7.51 d J=7.8	1	2.50 s	8.10 d <i>J</i> =2.4	7.45 d-d J=8.8; 2.4	6.97 d J=8.8	a
HLBr (DMSO-d6)	7.45 s,br	7.00 d J = 8.5	7.57 s,br	13.33 s,br	2.45 s	8.26 d $J = 2.4$	7.50 d-d J = 8.8; 2.4	7.12 d J = 8.2	13.13 s,br
Zn(LBr)ipa(NO ₃) ^b (DMSO-d ₆)	7.37 s,br	7.00 d J = 7.8	7.47 d J = 7.8	13.28 s,br	$2.41 \mathrm{s}$	8.11 s.br	7.33 d-d J = 1.9; 8.8	6.74 d J = 8.8	°
Zn ₂ (LBr) ₂ I ₂ (DMSO-d ₆)	7.36 s,br	6.99 d $J = 7.8$	7.47 d J = 7.8	13.55 s,br	2.41 s	8.10 d,br	7.35 d–d J=1.9; 8.8	6.78 d J=8.8	°
HLNO ₂ (in CD ₃ OD)	7.48 d J = 1	7.20 d-d br $J = 8.3$; 1.4	7.57 d J = 8.3	I	2.52 s	8.98 d $J = 2.9$	8.25 d-d J = 9.3; 2.9	7.15 d J = 9.3	_a
HLNO ₂ (DMSO-d ₆)	7.49 s,br	7.15 d-d br J = 8.4; 1.3	7.59 d J = 8.1	14.07 s,br	2.46 s	9.07 d J = 3.0	8.21 d-d J=9.1; 3.0	7.18 d J = 9.1	14.07 s,br
Zn(LNO ₂) ₂ (DMSO-d ₆)	7.41 s	6.78 s,br	7.63 d,br	13.56 s,br	$2.51 \mathrm{s}$	9.04 d J = 2.9	8.10 d–dbr $J=7.3$; 2.9	7.10 d,br	°
The chemical shift values, δ_{H} (ppr	m) with coupling of	constants J (Hz).							

Table 3

Not detected.

The proton signals of isopropanol: 4.36 (s, 1H), 3.79 (septet, 1H), 1.05 (d, 6H) ppm

Eliminated

Table 4	
¹³ C NMR spectral data	

Compound	The be	The benzimidazole carbons								The phenolic carbons						
	CH ₃	C2	C4	C5	C6	C7	C8+C9	C1′	C2′	C3′	C4′	C5′	C6′			
HLBr	21.9	150.2	115.4	133.5	125.3	115.4	139.0	157.2	111.0	134.5	118.1	128.8	120.0			
Zn(LBr)ipa(NO ₃) ^a	21.9	152.7	114.5	134.1	126.1	114.5	138.3 140.6	167.6	111.9	135.3	117.0	130.2	117.0			
$Zn_2(LBr)_2I_2$	21.9	152.8	114.6	134.2	126.1	114.6	138.2 140.5	167.5	112.0	135.1	117.1	130.0	117.2			
HLNO ₂	22.0	150.1	115.6	133.8	123.4	114.9	135.6 136.9	164.8	113.3	125.7	139.9	127.5	119.0			
$Zn(LNO_2)_2$	22.0	151.6	113.1	133.4	123.9	113.1	134.2 134.8	174.8	111.8	126.1	138.9	127.9	118.4			

 $\delta_{\rm C}$ (ppm), in DMSO-d₆.

^a The carbon of isopropanol signals: 26.2 and 62.7 ppm.



Fig. 4. Intramolecular hydrogen bonding in the ligands (cis-enol form).

shows that there is very strong intramolecular hydrogen bonding in the both ligands and agree with the literature (Fig. 4).

The OH proton does not appear in the complexes, only the NH proton is detected. In the spectra of the complexes, NH proton signal is sharpened according to the ligands (Fig. 3). This exhibits that the OH hydrogen is eliminated on complex-

ation and a chelate structure is formed through the phenolic oxygen and the C=N nitrogen atoms, and, consequently, the tautomeric equilibrium that make the NH proton fluxional is removed and the NH proton appears as a sharper peak.

An isopropanol molecule that coordinated to Zn(II) ion is detected in the NMR spectra of Zn(LBr)ipa(NO₃) complex. The NMR signals of the coordinated isopropanol molecule are the following (in DMSO-d₆): $\delta_{\rm H}$: 4.36 (s, 1H), 3.79 (septet, 1H), 1.05 (d, 6H) ppm; $\delta_{\rm C}$ 26.2 and 62.7 ppm. The non-coordinated solvent 2-propanol signals were observed as below (in DMSO-d₆): $\delta_{\rm H}$: 1.04 d, 3.01 s, 3.90 sept; $\delta_{\rm C}$: 25.4 and 64.9 ppm. These data are agreed with the elemental analysis results (Table 1).

In the ${}^{13}C$ NMR spectra of the complexes, the chemical shift of C1' (C–OH) is approximately 10 ppm, e.g. from





Fig. 5. The proposal structures of the Zn(II) complexes.

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157.2 to 167.6 in Zn(LBr)ipa(NO₃). This change is an important indication for the elimination of the phenolic hydrogen and coordination of the phenolic oxygen to the Zn(II) ion. On the other hand, a considerable shift of the C=N carbon (C2) atom shows that the C=N nitrogen atom coordinate to the Zn(II) ion and a chelate structure is formed (Table 4). C8 and C9 carbon atoms appear in one signal in the spectra of HLBr. However, they are observed as two signals separately in the spectra of the complexes. This observation is the most important evidence for the C=N nitrogen atom coordination (this shows that the tautomerism is stronger in HLBr according to HLNO₂). Because the tautomeric system is removed in the benzimidazole part as a result of the C=N nitrogen atom coordination.

4. Conclusions

HLBr and HLNO₂ ligands have strong intramolecular hydrogen bonding in polar solvents. The intramolecular hydrogen bonding is stronger in HLBr and consequently, its complexation reaction with zinc(II) is harder according to that of HLNO₂. HLBr and HLNO₂ gave the different complexes with ZnX₂. Considering the elemental analysis results, molar conductivity values, IR and NMR spectral data, the structures in Fig. 5 are proposed for the zinc(II) complexes of HLBr and HLNO₂ ligands.

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