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Reactions of Zinc Salts with bis(Benzimidazolyl) Derivatives

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ABSTRACT

Zinc complexes of the formulae $ZnX_2L \cdot nH_2O$ [$X = Cl$ or Br , $n = 2$, $X = I$, $n = 1$, $L = L^1$, 1,3-bis(benzimidazol-2-yl)benzene; $X = Cl$, Br or I , $n = 0$, $L = L^2$, 1,3-bis(1-methylbenzimidazol-2-yl)benzene] and $Zn(L)_2(ClO_4)_2 \cdot 2H_2O$ ($L = L^1$ and L^2) were obtained by the reactions of zinc halides/perchlorate with N-heterocycles in ethanol. The complexes have been characterized based on elemental analyses, molar conductance measurements, IR, 1H and ^{13}C NMR spectral studies and thermal analysis.

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INTRODUCTION

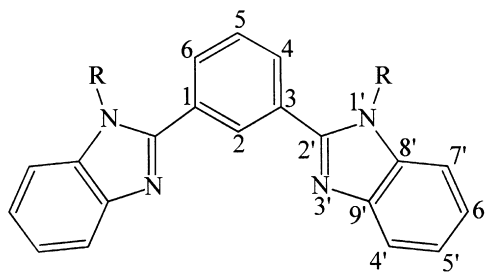
Benzimidazolyl derivatives and their transition metal complexes have been extensively investigated. Substituents of the benzimidazolyl derivatives could significantly modify their reactivity towards metal ions. Further, several of their metal complexes may serve as models to mimic the active centers of metallobio-molecules.^[1,2] Divalent zinc is responsible for the function of carboxy-peptidase A and carbonic anhydrase in biological systems.^[3] Thus, the coordination behaviour of N-heterocycles with zinc is of considerable importance.

In continuation of our studies on copper(II) complexes with the aforesaid ligands,^[4] we herein report the synthesis and characterization of complexes of zinc stabilized by bis(benzimidazolyl) derivatives (Figure 1), 1,3-bis(benzimidazol-2-yl)-benzene (L^1) and its N-methyl derivative, 1,3-bis(1-methylbenzimidazol-2-yl)-benzene (L^2).

RESULTS AND DISCUSSION

Reactions of the zinc salts with N-heterocycles in 1:1 mole ratio in ethanol produced three series of complexes of zinc of the formulae $[ZnX_2(L^1)(H_2O)] \cdot nH_2O$ ($X = Cl$ or Br , $n = 1$, $X = I$, $n = 0$), $[ZnX_2(L^2)]$ ($X = Cl$, Br or I) and $[Zn(L)_2(H_2O)](ClO_4)_2 \cdot H_2O$ ($L = L^1$ or L^2). The physical properties and analytical results of the complexes are listed in Table 1.

The chloro and bromo complexes are insoluble in common organic solvents but are soluble in dimethyl formamide, the solutions of which are



	R	Name
L^1	H	1,3-bis(benzimidazol-2-yl)benzene
L^2	CH ₃	1,3-bis(1-methylbenzimidazol-2-yl)benzene

Figure 1. The structure of the ligands.

Table I. Physical properties and analytical data of the complexes.

Compound	F. W. (g/mole)	Color	M.p./D.p. (°C)	Λ^a ($\Omega^{-1} \text{ cm}^2$ mol^{-1})	Analytical data, % calculated (found)			
					Zn	C	H	N
$L^1 \cdot H_2O$ ($C_{20}H_{16}N_4O$)	328.3	White	> 250	25	13.54 (13.33)	49.77 (49.28)	3.75 (3.63)	11.60 (11.74)
$[ZnCl_2L^1(H_2O)] \cdot H_2O$ ($C_{20}H_{18}Cl_2N_4O_2Zn$)	482.6	White	> 250	40	11.43 (11.07)	42.02 (41.86)	3.17 (2.87)	9.80 (9.94)
$[ZnBr_2L^1(H_2O)] \cdot H_2O$ ($C_{20}H_{18}Br_2N_4O_2Zn$)	571.5	White	> 250	84	10.09 (10.43)	37.09 (37.57)	2.49 (2.65)	8.65 (8.52)
$[ZnI_2L^1(H_2O)]$ ($C_{20}H_{16}I_2N_4OZn$)	629.5	White	> 250	138	7.09 (7.07)	52.16 (52.26)	3.50 (3.45)	12.15 (12.05)
$[Zn(L^1)_2(H_2O)](ClO_4)_2 \cdot H_2O$ ($C_{40}H_{32}Cl_2N_8O_{10}Zn$)	920.9	White	247–250*					
L^2 ($C_{22}H_{18}N_4$)	338.4	Violet						
$[ZnCl_2L^2] (C_{22}H_{18}Cl_2N_4Zn)$	474.634	Bluish grey	> 250	22	13.77 (13.03)	55.67 (56.06)	3.82 (4.30)	11.80 (12.05)
$[ZnBr_2L^2] (C_{22}H_{18}Br_2N_4Zn)$	563.6	Bluish grey	> 250	33	11.60 (11.39)	46.88 (46.42)	3.22 (3.12)	9.93 (9.84)
$[ZnI_2L^2] (C_{22}H_{18}I_2N_4Zn)$	657.5	Green	> 250	122	9.94 (10.11)	40.18 (39.91)	2.76 (2.76)	8.51 (8.05)
$[Zn(L^2)_2(H_2O)](ClO_4)_2 \cdot H_2O$ ($C_{44}H_{40}Cl_2N_8O_{10}Zn$)	997.0	Blue	> 250	136, 226 ^b , 41 ^c	6.69 (6.72)	54.09 (54.34)	4.12 (4.11)	11.46 (11.56)

^aMolar conductance of ca. 10^{-3} M solution in DMF;^bin MeCN;^cin $PhNO_2$.

*D.p.

non-conducting while the iodo complexes seem to decompose in dimethyl formamide as evidenced by their conductivity data. The perchlorate complexes exhibit uni-bivalent electrolytic behaviour in dimethyl formamide, nitrobenzene and acetonitrile.^[5]

IR Spectra

The IR spectra of the complexes are comparable to those of the uncoordinated N-heterocycle ligands except for minor shifts in the position of some bands. The spectra of the halo complexes containing L^1 display $\nu(\text{NH})$ around 3200 cm^{-1} which, has shifted by 40 cm^{-1} to lower frequency as compared to that of the uncoordinated ligand L^1 . A close similarity in the spectra of all complexes suggests the same coordination environment around the metal ion. The positions of $\nu(\text{NH})$ and $\nu(\text{CN})$ in the spectra of the complexes are suggestive of coordination of the heterocycle via the tertiary nitrogen of the imidazole moiety.^[6,7] The absorption bands around 3360 and $3460\text{--}3610\text{ cm}^{-1}$ are attributable to coordinated and lattice water, respectively.^[8,9] In the case of the perchlorate complex of L^1 , the spectrum exhibits a band at 3300 cm^{-1} which is assignable to both $\nu(\text{NH})$ and $\nu(\text{OH})$, the latter due to coordinated water. A similar observation has been made in the spectrum of the copper isolog. In the case of the L^2 containing complexes, $\nu(\text{CN})$ shifts from 1612 cm^{-1} for the free heterocycle to $1615\text{--}1618$ and 1595 cm^{-1} for the halo and perchlorate complexes, respectively. The spectra of the perchlorate complexes exhibit strong, unsplit bands at 1095 (ν_3) and 620 cm^{-1} (ν_4) and are typical of uncoordinated perchlorate.^[10] This is further corroborated by the uni-bivalent electrolytic behaviour of the complexes in dimethyl formamide, acetonitrile or nitrobenzene.

Far-IR spectra of the halo complexes recorded in polyethylene powder exhibit some additional, medium-intensity absorption bands, which are not observed in the corresponding spectra of the uncoordinated ligand N-heterocycles. The bands observed in the frequency ranges $294\text{--}290$, $237\text{--}226$ and $195\text{--}174\text{ cm}^{-1}$ are assigned to $\nu(\text{Zn-Cl}_{(t)})$, $\nu(\text{Zn-Br}_{(t)})$ and $\nu(\text{Zn-I}_{(t)})$ respectively. They are consistent with those reported in the literature for terminal halogen-metal stretches.^[11-13] For a given metal, $\nu(\text{M-X})$ decreases in the order $\nu(\text{M-Cl}) > \nu(\text{M-Br}) > \nu(\text{M-I})$. In addition, the frequency ratios, $[\nu(\text{Zn-Br})/\nu(\text{Zn-Cl})]$ and $[\nu(\text{Zn-I})/\nu(\text{Zn-Cl})]$ being 0.78 and 0.66 , respectively, are in the accepted range.^[14,15]

^1H NMR Spectra

^1H NMR spectral data of the free heterocycles and their complexes are presented in Table 2. The spectra of the free N-heterocycles display a doublet at δ 8.28 (L^1) or 8.04 (L^2) for H-4 and H-6. Further, the spectra are

Table 2. ¹H NMR chemical shifts (ppm) for the free ligands and complexes.^a

Compound ^b	Benzene ring						Benzimidazole ring					
	H-2	H-4, 6	H-5	H-4'	H-5'	H-6'	H-6'	H-5'	H-4'	H-5'	H-6'	NH/CH ₃
L ¹	9.07 s	8.28 d (1.4)	7.75 t (7.8)	7.64 s	7.24 m	7.24 m	7.24 m	7.24 m	7.24 m	7.24 m	7.24 m	13.14 b
[ZnCl ₂ L ¹ (H ₂ O)]·H ₂ O	9.06 s	8.27 d (1.5)	7.73 t (3.4)	7.58 d (2.1)	7.25 m	7.25 m	7.25 m	7.25 m	7.25 m	7.25 m	7.25 m	13.15 s
[ZnBr ₂ L ¹ (H ₂ O)]·H ₂ O	9.07 s	8.27 d (1.5)	7.73 t (2.1)	7.58 d (1.5)	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	13.15 s
[Zn(L ¹) ₂ (H ₂ O)](ClO ₄) ₂ ·H ₂ O	9.07 s	8.28 d (1.6)	7.75 t (7.8)	7.65 d (3.1)	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	7.26 m	13.15 b
L ²	8.31 s	8.04 dd (1.7)	7.80 t (7.6)	7.73 d (1.2)	7.30 m	7.30 m	7.30 m	7.30 m	7.30 m	7.30 m	7.30 m	3.96 s
[ZnCl ₂ L ²]	8.29 s	8.05 d (7.7)	7.79 t (7.7)	7.79 d (7.6)	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	3.96 s
[ZnBr ₂ L ²]	8.31 s	8.06 d (7.7)	7.80 t (7.7)	7.75 d (7.2)	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	7.32 m	3.98 s
[Zn(L ²) ₂ (H ₂ O)](ClO ₄) ₂ ·H ₂ O	8.30 s	8.05 d (1.5)	7.79 t (7.7)	7.73 d (7.7)	7.32 t (7.0)	7.32 t (7.0)	7.32 t (7.0)	7.32 t (7.0)	7.32 t (7.0)	7.32 t (7.0)	7.32 t (7.0)	3.97 s

^aCoupling constants expressed in Hz are in parentheses.^bSpectra recorded in DMSO-d₆.

illustrative of the two benzimidazole groups being equivalent. The resonance due to H-4' and H-7' is observed as a singlet at δ 7.64 for L¹ while the resonances corresponding to H-4' and H-7' of L² are located, as doublets at δ 7.73 and 7.65 respectively. The signal due to H-5' and H-6' is centered as a multiplet at δ 7.24 (L¹) and δ 7.30 (L²). A broad singlet displayed at δ 13.14 arises due to the imine proton. The N-CH₃ resonance is located at δ 3.96 as a singlet. The spectra of the complexes show all the ligand peaks, which are barely shifted, compared to those of the uncoordinated ones. A similar observation has been made earlier in the spectra of the zinc complexes containing 2,6-bis(benzimidazol-2-yl)pyridine and its N-methyl derivative, 2,6-bis(1-methylbenzimidazol-2-yl)pyridine.^[16] A singlet observed for H-4' and H-7' in the free ligand L¹ is resolved into a doublet on complexation.

¹³C NMR Spectra

¹³C NMR spectral data of the uncoordinated heterocycles and the complexes are collected in Table 3. The spectra of the free heterocycles exhibit eleven signals in the range δ 110.0–153.0 except that of N-CH₃ whose resonance is observed at δ 31.69. The assignments of the signals are made with the aid of the off-resonance spectrum of L² as well as in comparison with the reported values for benzimidazole and substituted benzimidazoles.^[17–20] It may be pointed out that the signal due to H-4' (in the ¹H NMR spectra) proximate to the tertiary nitrogens has not experienced any deshielding effect on complexation. On the other hand, the resonances due to C-4' and C-9' in the coordinated heterocycle are shifted upfield (negative coordination induced shifts; coordination induced shifts, c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$) and this parallels the effect of protonation of the benzimidazole ring.^[17,21] The other carbon signals in the complexes experience either upfield or downfield shifts relative to those of the uncoordinated ligand N-heterocycles. The negative c.i.s. observed for the carbon resonances may be attributed to greater metal-to-ligand π -back donation whereas positive c.i.s. values to ligand-to-metal σ -donation.^[22] A reduction in the peak heights for C-8', C-9' and C-4', C-7' is noticed in the complexes containing L¹. Furthermore, four independent peaks observed for the aforesaid carbons in the free ligand coalesce into two short peaks in the complexes, one for bridge-head carbons, C-8' and C-9' and another for C-4' and C-7'.

Thermal Studies

The TG traces of the chloro, bromo and perchlorate complexes associated with L¹ and the perchlorate complex of L² show a weight loss in the range 80–100 °C (Table 4) and this corresponds to the loss of one molecule

Table 3. ^{13}C NMR chemical shifts (ppm) for the free ligands and complexes.

Compound ^a	Benzene ring						Benzimidazole ring					
	C-1, 3	C-2	C-4, 6	C-5	C-2'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	N-CH ₃
L ¹	124.84	129.82	127.65	131.03	150.85	119.03	122.04	122.95	111.67	135.21	143.84	-
[ZnCl ₂ L ¹ - (H ₂ O)]·H ₂ O	125.14 (0.30)	129.83 (0.01)	128.12 (0.47)	130.90 (-0.13)	151.17 (0.32)	115.48 (-3.55)	122.72 (0.68)	122.72 (-0.23)	115.48 (3.81)	139.58 (4.37)	139.58 (-4.26)	-
[ZnBr ₂ L ¹ - (H ₂ O)]·H ₂ O	125.33 (0.49)	129.81 (-0.01)	128.02 (0.37)	131.02 (-0.01)	151.12 (0.27)	115.45 (-3.58)	122.66 (0.62)	122.66 (-0.29)	115.45 (3.78)	139.50 (4.29)	139.50 (-4.34)	-
[Zn(L ¹) ₂ (H ₂ O)]· (ClO ₄) ₂ ·H ₂ O	124.47 (-0.37)	129.27 (-0.55)	127.23 (-0.42)	130.57 (-0.46)	150.44 (-0.41)	118.00 (-1.03)	122.01 (-0.03)	122.01 (-0.94)	111.44 (-0.23)	134.98 (-0.23)	143.17 (-0.67)	-
L ²	129.11	129.82	130.36	130.57	152.33	119.08	122.00	122.50	110.61	136.63	142.46	31.69
[ZnCl ₂ L ²]	128.53 s	129.71 d	129.71 d	131.29 d	150.90 s	119.91 d	122.08 d	123.67 d	109.87 d	136.71 s	143.07 s	31.73 q
[ZnBr ₂ L ²]	129.22 (0.11)	129.73 (-0.09)	130.65 (0.29)	131.26 (0.69)	152.82 (0.49)	119.12 (0.04)	122.81 (0.81)	123.29 (0.79)	111.12 (0.51)	136.21 (-0.42)	141.57 (-0.89)	31.98 (0.29)
[Zn(L ²) ₂ (H ₂ O)]· (ClO ₄) ₂ ·H ₂ O	129.09 (-0.02)	129.42 (-0.4)	130.62 (0.26)	131.25 (0.68)	152.67 (0.34)	118.95 (-0.13)	122.73 (0.73)	123.20 (0.70)	111.03 (0.42)	135.97 (-0.66)	141.21 (-1.25)	31.91 (0.22)
	128.75 (-0.36)	129.67 (-0.15)	129.67 (-0.69)	130.29 (-0.28)	152.10 (-0.23)	118.51 (-0.57)	122.03 (0.03)	122.53 (0.03)	110.34 (-0.27)	135.94 (-0.69)	141.45 (-1.01)	31.32 (-0.37)

^aValues in parentheses are coordination induced shifts, c.i.s. = $\delta_{\text{complex}} - \delta_{\text{ligand}}$. Spectra recorded in DMSO-d₆.

Table 4. TGA data of the complexes.

Complex	Stage	Temp. (°C)	Weight loss, % calculated (found)	Species lost	Residue, ZnO % calculated (found)
[ZnCl ₂ L ¹ (H ₂ O)]·H ₂ O	1	100	3.73 (4.00)	Lattice water	15.24 (14.00)
	2	140	3.73 (3.40)	Coordinated water	
	3	495	14.69 (14.85)	2 Cl	
	4	660	64.3 (63.75)	L ¹	
[ZnBr ₂ L ¹ (H ₂ O)]·H ₂ O	1	95	3.15 (2.60)	Lattice water	12.84 (13.20)
	2	227	3.15 (3.65)	Coordinated water	
	3	495	13.98 (12.50)	1 Br	
	4	655	64.3 (63.75)	1 Br + L ²	
[Zn(L ¹) ₂ (H ₂ O)](ClO ₄) ₂ ·H ₂ O	1	95	1.95 (1.70)	Lattice water	a
	2	270	1.95 (2.00)	Coordinated water	a
[Zn(L ²) ₂ (H ₂ O)](ClO ₄) ₂ ·H ₂ O	1	80	1.84 (1.75)	Lattice water	a
	2	290	1.84 (1.75)	Coordinated water	

^aTGA analysis carried up to 350 °C as the perchlorate complexes are explosives.

of water of crystallisation. The other water molecule is lost in the temperature range 100–290 °C implying that it is present as coordinated water.^[23] The halo complexes undergo decomposition in the temperature range 140–660 °C, suggesting that they are thermally more stable than the uncoordinated heterocycle. The final product in these complexes is zinc oxide.

Stereochemistry

The N-heterocycles (L^1 and L^2) are planar and each would serve as chelating bidentates via the tertiary nitrogens. For the halo complexes containing L^1 , a square-pyramidal geometry with a bidentate coordinating heterocycle, anions and a water molecule may be proposed (Figure 2). Such a geometry has been reported for the related bis-benzimidazolyl zinc complexes.^[12] The bis-heterocycle complexes are also suggested to have a similar geometry (Figure 3). The halo complexes of L^2 are proposed to have a tetrahedral structure (Figure 4).

EXPERIMENTAL

Reagents and Measurements

Zinc halides (hydrated zinc chloride and anhydrous zinc bromide and zinc iodide) used were procured from BDH. Hydrated zinc(II) perchlorate

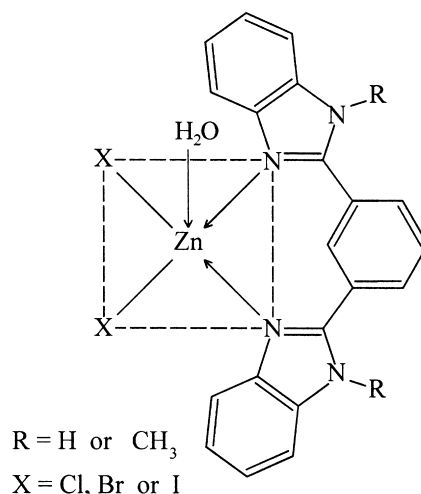


Figure 2. Proposed structure of the halo complexes of L^1 .



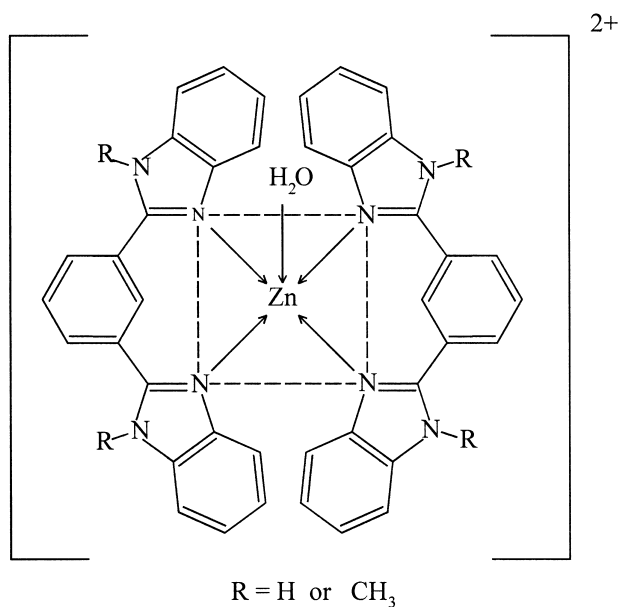


Figure 3. Proposed structure of the perchlorate complexes of L¹ and L².

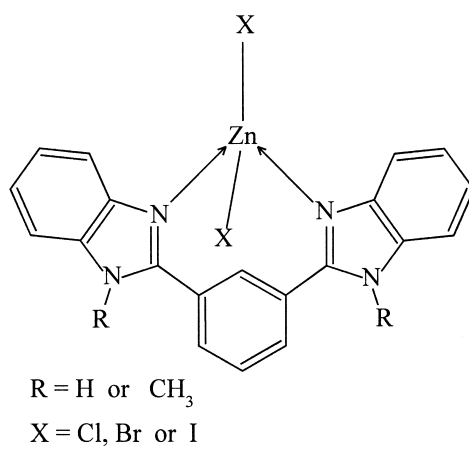


Figure 4. Proposed structure of the halo complexes of L².

was prepared by dissolving zinc carbonate in 1:1 aqueous perchloric acid and evaporating the resulting solutions to almost dryness under reduced pressure. The bis-benzimidazolyl ligands, L^1 and L^2 were prepared according to literature methods.^[24]

Microanalyses were carried out on a Carlo Erba microanalyser. Metal analysis was done using a Spectr AA-30 spectrometer equipped with a Varian DS-15 computer. IR (Nujol mull) and Far-IR (polyethylene powder) spectra were recorded on Shimadzu IR-435 or Bruker IFS 113 V FF spectrophotometers, respectively. Conductivity data were obtained using an Elico-Model CM-82T conductivity bridge. NMR spectra were recorded in DMSO- d_6 on Bruker WH-270 or AMX 400 MHz spectrometers using TMS as the internal standard. Thermal measurements were made on a Mettler TAHE-20 thermal analyzer with a scan rate of 5 °C min⁻¹ in air.

Synthesis of $[\text{ZnX}_2(\text{L}^1)(\text{H}_2\text{O})] \cdot n\text{H}_2\text{O}$ (X = Cl or Br, n = 1, X = I, n = 0) and $[\text{ZnX}_2(\text{L}^2)]$ (X = Cl, Br or I)

To 25 mL of an ethanolic solution of the ligand N-heterocycle (1 mmol; $L^1 = 0.328$ g, $L^2 = 0.338$ g), zinc dihalide (1 mmol; $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O} = 0.1725$ g, $\text{ZnBr}_2 = 0.225$ g, $\text{ZnI}_2 = 0.319$ g) in ethanol (10 mL) was added at ambient temperature when a white or coloured solid separated instantaneously. It was allowed to stand for about an hour and then filtered. The solid was washed with ethanol and dried under vacuum. Yields of the complexes are 0.29 g (60%) for $[\text{ZnCl}_2\text{L}^1(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, 0.354 g (62%) for $[\text{ZnBr}_2\text{L}^1(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$, 0.472 g (75%) for $[\text{ZnI}_2\text{L}^1(\text{H}_2\text{O})]$, 0.308 g (65%) for $[\text{ZnCl}_2\text{L}^2]$, 0.382 g (68%) for $[\text{ZnBr}_2\text{L}^2]$ and 0.46 g (70%) for $[\text{ZnI}_2\text{L}^2]$.

Synthesis of $[\text{Zn}(\text{L})_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (L = L^1 or L^2)

To 20 mL of an ethanolic solution of the N-heterocycle ligand (1 mmol; $L^1 = 0.328$ g, $L^2 = 0.338$ g), 10 mL of an ethanolic solution containing 0.3723 g of hydrated zinc perchlorate (1 mmol) was added. The resulting mixture was refluxed for four hours on a steam bath during which time a white/blue solid separated. The solid was filtered, washed with ethanol and dried in a vacuum. Yields of the complexes (based on N-heterocycles) are 0.391 g (85%) for $[\text{Zn}(\text{L}^1)_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ and 0.398 g (80%) for $[\text{Zn}(\text{L}^2)_2(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.

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