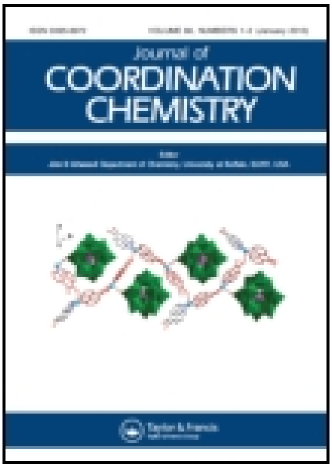

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Zinc(II) complexes with an imidazolylpyridine ligand: luminescence and hydrogen bonding

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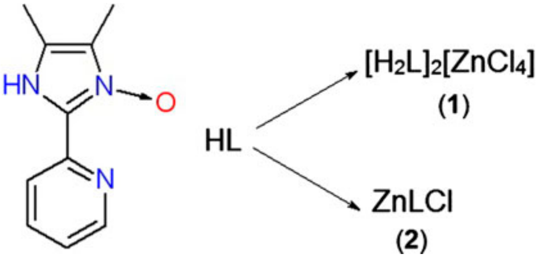

ZnLCl and $[H_2L]_2[ZnCl_4]$, based on 2-(1-hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine (HL), have been synthesized. There is a short intraionic O–H···N hydrogen bond between the hydroxyimidazolyl and pyridyl of H_2L^+ cations (N···O 2.608(2) Å) in the structure of $[H_2L]_2[ZnCl_4]$. The formation of this rather strong hydrogen bond is confirmed by IR spectroscopy through a broad band at 3200–2200 cm^{-1} and a band at 1655 cm^{-1}. HL crystallizes in the form of a hemihydrate, $HL{\cdot}0.5H_2O$. HL assemble into infinite helical chains due to N–H···O intermolecular hydrogen bonds between the NH of imidazole and O of the N-oxide (O···N 2.623(2) Å). An unusual mid-IR pattern with three broad bands at 3373, 2530, and 1850 cm^{-1} is typical for strong hydrogen bonds, explained by resonance-assisted hydrogen bonding occurring in the helical chains. On cooling to 5 K, noticeable changes in the IR spectra of $[H_2L]_2[ZnCl_4]$ and $HL{\cdot}0.5H_2O$ were observed. ZnLCl and $[H_2L]_2[ZnCl_4]$ exhibit bright photoluminescence with maxima of emission at 458 nm (for ZnLCl) and 490 nm (for $[H_2L]_2[ZnCl_4]$).

Keywords: Zinc(II); N-ligands; Synthesis; Hydrogen bond; Supramolecular chemistry; Luminescence

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1. Introduction

Among nitrogen-containing heteroaromatic compounds, 2-(1*H*-imidazol-2-yl)pyridines have attracted attention as ligands for synthesis of transition metal complexes [1–35]. However, little is available on coordination behavior of N-hydroxyimidazolylpyridines; there are only two articles dealing with the synthesis of transition metal complexes with N-hydroxyimidazolylpyridines [36, 37]. McCann and colleagues synthesized a series of copper(II) complexes with 2-(1-hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine (HL) and 2-(1-hydroxy-4,5-diphenyl-1*H*-imidazol-2-yl)pyridine, and studied their supramolecular structures [37]. In addition, zinc(II) complexes with bis(N-hydroxyimidazole) ligands have been synthesized. All N-hydroxyimidazole ligands are in the zwitterionic, or N-oxide, form [37]. Taking into account that zinc(II) and cadmium(II) complexes with heteroaromatic ligands are main groups of luminescent compounds [38–43], we synthesized two compounds with the deprotonated form of HL, i.e. $ZnL_2{\cdot}2H_2O$ and CdL_2, and studied their luminescent properties [37]. Luminescence intensity for these compounds increased with respect to very weak intensity of HL luminescence [37]. Luminescent zinc(II) complexes have attracted interest for biological applications [44, 45]. As a logical continuation of our research, we endeavored to synthesize zinc(II) compounds with the N-oxide form of HL and with its protonated form, and to study their luminescent properties.

2. Experimental

2.1. *General*

2-(1-Hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine ($HL{\cdot}0.5H_2O$) has been prepared according to the reported procedure [37]. Anal. Calcd for $C_{10}H_{12}N_3O_{1.5}$ (%): C, 60.6; H, 6.1; N, 21.2. Found: C, 60.6; H, 6.3; N, 21.2. Single crystals of $HL{\cdot}0.5H_2O$ suitable for X-ray single crystal analysis have been obtained by slow crystallization from EtOH. All other reagents and solvents were commercially available and used without additional purification. Elemental analysis (C, H, and N) was performed on a Carlo–Erba analyzer using standard technique. Zinc content was determined by complexometric titration; the samples were mineralized in H_2SO_4/HNO_3 mixture. The emission spectra were recorded on a Cary Eclipse spectrophotometer, $\lambda_{exc} = 350$ nm, ex. slit 5 nm, em. slit 5 nm, PMT voltage 500 V.

2.2. *Synthesis of $[H_2L]_2[ZnCl_4]$ (1)*

A solution containing $Zn(OAc)_2{\cdot}2H_2O$ (0.20 mmol, 43.9 mg), HL (0.40 mmol, 75.7 mg), and KOH (0.40 mmol, 22.4 mg) in 1 mL of MeOH was heated to reflux. Water (2 mL) was added to the solution. In 1–2 min, light-yellow precipitate was formed. The reaction was carried out in an open flask, thus allowing most of the solvent to evaporate. When the volume of mixture became ca. 1 mL, $ZnL_2{\cdot}2H_2O$ was filtered off, washed with water, and dried in air. Yield: 81.7 mg. The precipitate was suspended in EtOH (4 mL) and a solution of HCl in EtOH was added dropwise to dissolve the precipitate (pH 4–5). The resulting solution was stirred for three days with gentle heating. When the volume of the solution became ca. 1–2 mL, yellowish precipitate was formed. The precipitate was filtered off, washed with EtOH, and dried in air. Yield: 47.6 mg (40%). Anal. Calcd for $C_{20}H_{24}Cl_2N_6O_2Zn$ (%): C, 40.9; H, 4.1; N, 14.3. Found: C, 40.8; H, 4.4; N, 14.3. Single crystals suitable for X-ray single crystal analysis have been obtained by slow crystallization from EtOH.

2.3. *Synthesis of ZnLCl (2)*

Method A: A solution containing HL (0.40 mmol, 75.7 mg) and $ZnCl_2$ (0.20 mmol, 27.3 mg) in EtOH/H_2O (2 mL/2 mL) mixture was heated to reflux. In 2–3 h, white precipitate appeared. It was left in contact with the mother liquor for several days. After that, precipitate was filtered off, washed with water and dried in air. Yield: 31.4 mg (54% based on Zn). Anal. Calcd for $C_{10}H_{10}ClN_3OZn$ (%): C, 41.6; H, 3.5; N, 14.5; Zn, 22.6. Found: C, 41.6; H, 3.7; N, 14.5; Zn, 22.4.

Method B: The procedure was performed in the same way as that for Method A. The quantities of reagents were: 0.30 mmol (56.8 mg) of HL and 0.30 mmol (40.9 mg) of $ZnCl_2$. Yield: 29.0 mg (33% based on Zn). Anal. Calcd for $C_{10}H_{10}ClN_3OZn$ (%): C, 41.6; H, 3.5; N, 14.5. Found: C, 41.6; H, 3.6; N, 14.6.

2.4. *X-ray data collection and structure determination*

Intensity data were collected at 298 K on a Bruker Nonius X8Apex CCD diffractometer equipped with graphite monochromated Mo-K_α ($\lambda = 0.71073$ Å) radiation. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT [46, 47] and SADABS [46, 47] for absorption correction. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software [46, 47]. All the non-H atoms were refined in the anisotropic approximation. Hydrogens were placed in idealized positions and refined using a riding model to the atom to which they are attached.

Table 1. Crystallographic data and refinement details for $HL\cdot0.5H_2O$ and $[H_2L]_2[ZnCl_4]$.

	$HL\cdot0.5H_2O$	$[H_2L]_2[ZnCl_4]$
Empirical formula	$C_{10}H_{12}N_3O_{1.50}$	$C_{20}H_{24}Cl_4N_6O_2Zn$
Formula weight	198.23	587.62
Crystal system	Tetragonal	Monoclinic
Space group	$P4_32_12$	$P2/n$
Unit cell dimensions (Å, °)		
a	11.3891(3)	8.178(1)
b	11.3891(3)	11.581(2)
c	16.1753(4)	13.088(2)
β		96.956(2)
Volume (Å^3), Z	2098.12(9), 8	1230.3(3), 2
D_{Calcd} (mg m^{-3})	1.255	1.586
F (0 0 0)	840	600
μ (Mo-K_α) (mm^{-1})	0.088	1.463
θ Range (°)	2.19–26.37	1.76–26.27
Collected reflections	13579	8717
Independent reflections	2155	2453
R_{int}	0.0227	0.0244
Observed reflections	2022	2071
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0307/0.0821	0.0545 / 0.1548
R_1 / wR_2 (all data)	0.0340 / 0.0845	0.0635 / 0.1584
Goodness-of-fit on F^2	1.044	1.138
Largest diff. peak and hole (eÅ^{-3})	0.141, −0.172	1.652, −0.294

Table 2. Bond lengths (Å) and angles (°) for HL·0.5H_2O and $[H_2L]_2[ZnCl_4]$.

HL·0.5H_2O			
O(1)–N(1)	1.343(1)	C(3)–N(2)–C(2)	109.9(1)
N(1)–C(3)	1.344(2)	C(6)–C(5)–C(4)	118.3(1)
N(1)–C(1)	1.375(2)	C(2)–C(1)–N(1)	106.3(1)
N(2)–C(3)	1.342(2)	C(2)–C(1)–C(11)	132.5(1)
N(2)–C(2)	1.367(2)	N(1)–C(1)–C(11)	121.2(1)
C(5)–C(6)	1.379(2)	C(1)–C(2)–N(2)	107.3(1)
C(5)–C(4)	1.393(2)	C(1)–C(2)–C(21)	130.2(1)
C(1)–C(2)	1.360(2)	N(2)–C(2)–C(21)	122.4(1)
C(1)–C(11)	1.488(2)	N(2)–C(3)–N(1)	106.5(1)
C(2)–C(21)	1.490(2)	N(2)–C(3)–C(4)	124.6(1)
C(3)–C(4)	1.460(2)	N(1)–C(3)–C(4)	128.7(1)
C(4)–N(3)	1.341(2)	N(3)–C(4)–C(5)	123.0(1)
N(3)–C(8)	1.334(2)	N(3)–C(4)–C(3)	114.2(1)
C(8)–C(7)	1.382(2)	C(5)–C(4)–C(3)	122.8(1)
C(7)–C(6)	1.376(2)	C(8)–N(3)–C(4)	116.9(1)
O(1)–N(1)–C(3)	126.6(1)	N(3)–C(8)–C(7)	124.4(2)
O(1)–N(1)–C(1)	123.4(1)	C(6)–C(7)–C(8)	117.7(2)
C(3)–N(1)–C(1)	110.0(1)	C(7)–C(6)–C(5)	119.7(1)
$[H_2L]_2[ZnCl_4]$			
Zn(1)–Cl(1)	2.239(1)	Cl(1)–Zn(1)–Cl(2)#1	111.33(5)
Zn(1)–Cl(1)#1	2.239(1)	Cl(2)–Zn(1)–Cl(2)#1	101.65(6)
Zn(1)–Cl(2)	2.307(1)	C(3)–N(1)–O(1)	126.8(4)
Zn(1)–Cl(2)#1	2.307(1)	C(3)–N(1)–C(1)	111.7(4)
N(1)–C(3)	1.336(5)	O(1)–N(1)–C(1)	121.5(4)
N(1)–O(1)	1.361(5)	C(3)–N(2)–C(2)	110.2(3)
N(1)–C(1)	1.366(6)	N(1)–C(3)–N(2)	105.6(4)
N(2)–C(3)	1.340(6)	N(1)–C(3)–C(4)	125.3(4)
N(2)–C(2)	1.374(5)	N(2)–C(3)–C(4)	129.1(4)
C(3)–C(4)	1.453(6)	N(3)–C(4)–C(5)	123.4(4)
C(4)–N(3)	1.346(6)	N(3)–C(4)–C(3)	113.2(4)
C(4)–C(5)	1.375(6)	C(5)–C(4)–C(3)	123.4(4)
N(3)–C(8)	1.337(6)	C(8)–N(3)–C(4)	117.1(5)
C(2)–C(1)	1.365(6)	C(1)–C(2)–N(2)	106.9(4)
C(2)–C(10)	1.490(6)	C(1)–C(2)–C(10)	130.5(4)
C(1)–C(9)	1.478(6)	N(2)–C(2)–C(10)	122.6(4)
C(5)–C(6)	1.391(7)	C(2)–C(1)–N(1)	105.6(4)
C(8)–C(7)	1.377(8)	C(2)–C(1)–C(9)	132.1(4)
C(6)–C(7)	1.363(8)	N(1)–C(1)–C(9)	122.3(4)
Cl(1)#1–Zn(1)–Cl(1)	113.83(8)	C(4)–C(5)–C(6)	118.0(5)
Cl(1)#1–Zn(1)–Cl(2)	111.33(5)	N(3)–C(8)–C(7)	123.0(5)
Cl(1)–Zn(1)–Cl(2)	109.02(5)	C(7)–C(6)–C(5)	119.1(5)
Cl(1)#1–Zn(1)–Cl(2)#1	109.02(5)	C(6)–C(7)–C(8)	119.3(5)

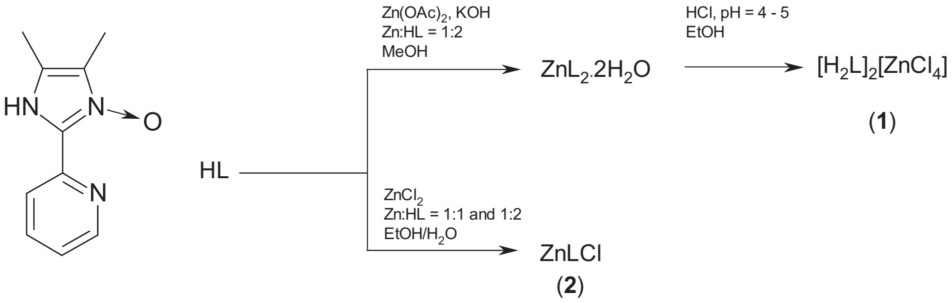
Note: Symmetry transformations used to generate equivalent atoms: for **2**: #1 $-x+1/2$, y, $-z+3/2$.

Crystallographic data and refinement details are displayed in table 1. The bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthetic aspects*

The syntheses of the complexes have been performed as follows. The reaction of Zn $(OAc)_2$, HL, and KOH in a 1 : 2 : 2 molar ratio in MeOH solution yielded $ZnL_2 \cdot 2H_2O$ [37]. In the presence of HCl (pH 4–5), $ZnL_2 \cdot 2H_2O$ dissolves to form $[H_2L]_2[ZnCl_4]$ (**1**) (scheme 1). This complex can easily be obtained as a polycrystalline product and single



Scheme 1. Synthesis of the complexes.

crystals. The driving force for this reaction is protonation of the N^3 of the imidazolyl. The protonation proceeds even in weakly acidified solutions. To synthesize the complex with the zwitterionic form of the ligand, $ZnCl_2$ and HL were reacted in a 1 : 2 metal-to-ligand molar ratio without adding a strong deprotonating agent (KOH); ZnLCl (**2**) was isolated instead of $Zn(HL)_2Cl_2$. Thus, deprotonation of HL occurs even without adding KOH. In fact, since the synthesis in the 1 : 2 metal-to-ligand molar ratio led to the complex having 1 : 1 stoichiometry, the second equivalent of HL may act as a deprotonating agent. Under similar conditions, reaction of $ZnCl_2$ with HL in a 1 : 1 molar ratio led to the same **2**, but in a rather low yield (considerably lower than 50%). Thus, the deprotonation/protonation of HL proceeds even when the stoichiometric molar ratio is applied. To prepare this complex in a reasonable yield, ethanol/water mixture has to be used. The reaction in EtOH gives significantly reduced yields of the product. McCann *et al.* synthesized a copper(II) complex with zwitterionic (or N-oxide) form of HL, $[Cu(HL)_2](ClO_4)_2{\cdot}H_2O$ (in high yield), by reacting $Cu(ClO_4)_2$ with HL in a 1 : 2 metal-to-ligand molar ratio in MeCN or MeCN/H_2O solutions with no deprotonation observed. Unfortunately, all attempts to crystallize **2** failed. The reaction of $ZnCl_2$ with HL (1 : 2 molar ratio) in EtOH, MeOH, and EtOH/H_2O mixture at room temperature yields a white powder, unsuitable for X-ray single crystal analysis.

3.2. *Structure of $HL{\cdot}0.5H_2O$*

The structure of $HL{\cdot}0.5H_2O$ is formed by HL and H_2O (figure 1). For 1-hydroxyimidazoles, the existence of two tautomeric forms (1-hydroxy-1*H*-imidazole and 1*H*-imidazole-3-oxide) has been discussed [48, 49]. It was supposed that a prototropic tautomerism between these forms exists in solution [48, 49]. There are examples of crystal structures of both N-oxide and hydroxy tautomers [50, 51]. We demonstrated that HL exists in the solid state in the N-oxide form. The bond lengths for the heteroaromatic rings of HL are: N–C 1.342(2)–1.375(2) Å, N–O 1.343(1) Å, C–C 1.360(2) Å, $C–C_{Py}$ 1.460(2) Å, $C–C_{Me}$ 1.488(2), 1.490 (2) Å for the imidazole ring; N–C 1.341(2), 1.334(2) Å, C–C 1.376(2)–1.393(2) Å for the pyridine ring. The N–C and C–C bond lengths in the pyridine ring have typical values. The heteroaromatic rings are nearly planar to within 0.006 Å (imidazole ring) and 0.004 Å (pyridine ring) and the torsion angle between the planes of imidazole and pyrimidine rings is 6.3°. There is a moderate intramolecular hydrogen bond between NH of imidazole and N pyridinyl (N(3)···H(2) 2.57, N(3)···N(2) 2.775(2) Å). HL molecules are assembled into infinite helical chains due to N–H···O intermolecular hydrogen bonds between NH of

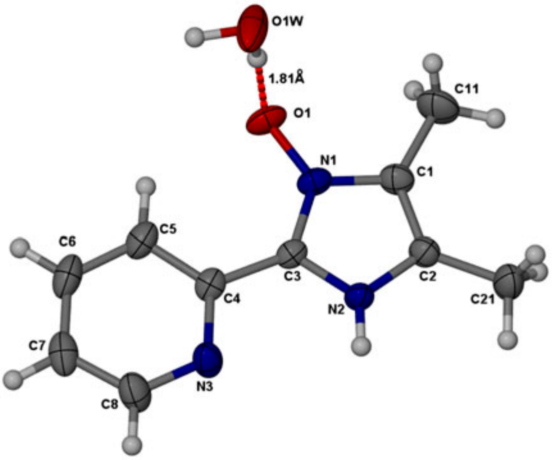


Figure 1. The structure of $HL\cdot0.5H_2O$.

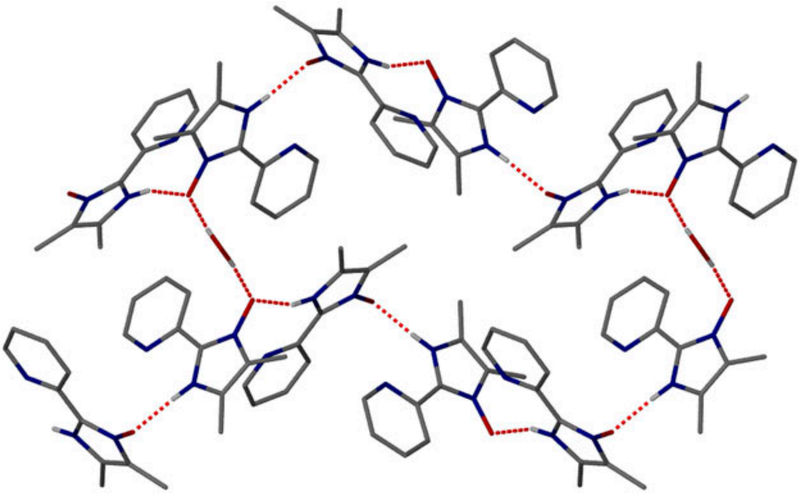


Figure 2. The supramolecular structure of $HL\cdot0.5H_2O$.

imidazole and O of N-oxide (O(1)···H(2)' 1.78 Å, O(1)···N(2) 2.623(2) Å) (figure 2). Thus, each HL is a donor and an acceptor of hydrogen bonds. Achiral HL molecules assemble in chiral helical chains. All chains have the same chirality and the crystal adopts chiral space group $P4_32_12$. In the bulk material, we have a racemic mixture. H_2O is a double hydrogen bond donor, interconnecting HL chains due to O–H···O hydrogen bonds with O of N-oxide groups ((O(1)···H(1A) 1.81 Å, O(1 W)···O(1) 2.787(2) Å) (figures 1 and 2).

3.3. *Structure of $[H_2L]_2[ZnCl_4]$*

The structure of **1** is formed by $[H_2L]^+$ and $[ZnCl_4]^{2-}$ (figure 3). The $[ZnCl_4]^{2-}$ is a distorted tetrahedral geometry. The bond lengths for the heteroaromatic rings of $[H_2L]^+$ are: N–C

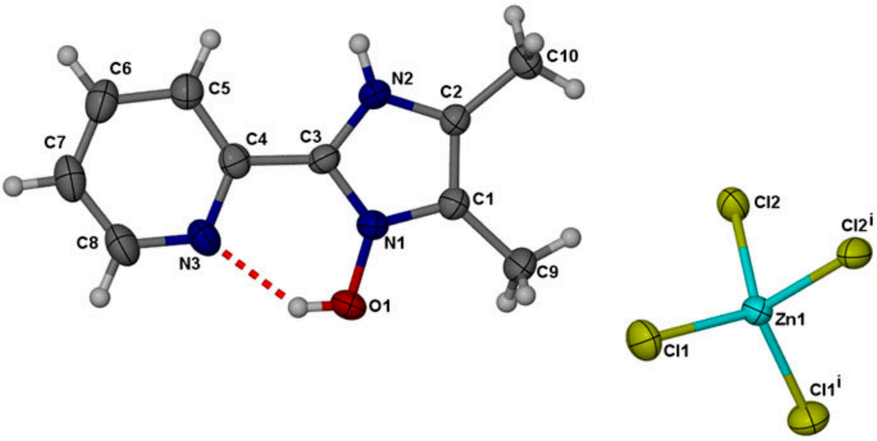


Figure 3. The structures of $[H_2L]^+$ and $[ZnCl_4]^{2-}$.

1.336(5)–1.374(5) Å, C–C 1.365(6) Å, C–C_{Py} 1.453(6) Å, C–C_{Me} 1.478(6), 1.490(6) Å for the imidazole ring; N–C 1.337(6) Å, C–C 1.363(8)–1.391(7) Å for the pyridine. The heteroaromatic rings are nearly planar to within 0.004 Å. The imidazole and pyridine rings of $[H_2L]^+$ ions are not coplanar with a torsion angle between the planes of the imidazole and pyridine rings of 5.6°. A noticeable feature of the structure is the formation of a rather short intraionic hydrogen bond between OH of hydroxyimidazolyl and N pyridyl (N(3)···H(1) 1.921(5) Å, N(3)···O(1) 2.607(5) Å).

Each $ZnCl_4$ unit is linked with H_2L units through (i) interionic N–H···Cl hydrogen bonds (Cl(2)···H(2)' 2.285 Å, Cl(2)···N(2) 3.143 Å) and (ii) weak C–H···Cl hydrogen bonds (Cl (1)···H(6)' 2.871 Å, Cl(1)···C(6)' 3.647 Å; Cl(2)···H(9)' 2.846 Å, Cl(2)···C(9)' 3.676 Å). Both heteroaromatic rings of H_2L units are involved in the formation of double π–π stacking interactions, centroid–centroid distance within each imidazole···pyridine unit is

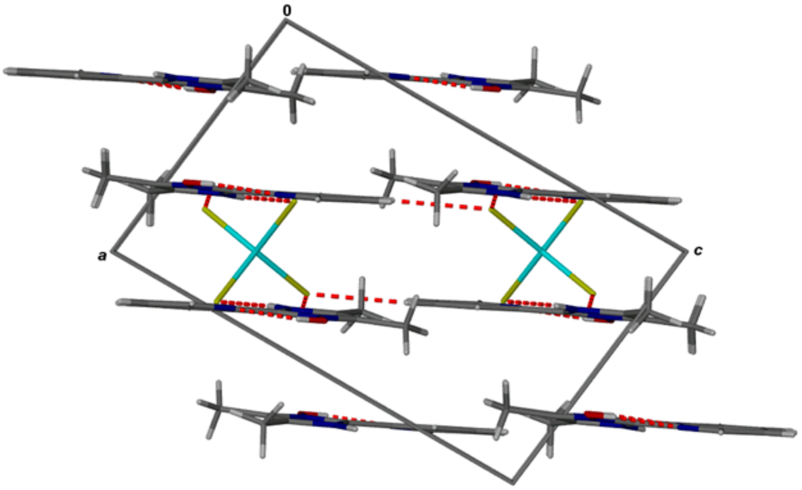


Figure 4. The supramolecular structure of $[H_2L]_2[ZnCl_4]$.

3.746 Å. These interactions result in formation of paired chains aligned along (202) crystallographic planes (figure 4).

3.4. *IR spectroscopy*

IR spectroscopic data for the compounds are given in table 3. The bands of stretching-deformations of the (hetero)aromatic rings in IR spectra of the complexes are shifted in comparison with the spectrum of HL·0.5H_2O. This suggests that rearrangement of the structure of the imidazolylpyridine occurs upon protonation (in the case of **1**) or deprotonation/coordination (in the case of **2**). The low-frequency region of the spectra of the complexes contains bands which can be assigned to stretching vibrations of Zn–Cl bonds, indicating coordination of chloride; their positions are typical for terminal (instead of bridging) chloride. Zn–L vibrations in the spectrum of **2** are ν(Zn–O) and ν(Zn–N) (table 3). The IR spectrum of **1** exhibits a very broad intense band at 3300–2200 cm^{-1} due to ν(NH) and ν(OH). Noticeable band broadening results from formation of rather short N–H···Cl interionic and O-H···N intraionic hydrogen bonds. A band at 1655 cm^{-1} provides additional evidence for formation of a short O–H···N intraionic hydrogen bond. The high-frequency region of **2** contains only ν(CH) and $\nu(CH_3)$ bands; no ν(NH) or ν(OH) bands have been detected. This is consistent with elemental analysis data and indicates that deprotonation of HL occurs upon coordination to Zn^{2+}.

Formation of a rather short O–H···N intraionic hydrogen bond in the structure of **1** creates helical chains of HL in the structure of HL·0.5H_2O. Although N–H···O hydrogen bonds within a HL chain are longer than O–H···N intraionic hydrogen bond in **1**, the IR spectroscopic pattern for HL·0.5H_2O is more complicated with respect to **1**. Indeed, the IR spectrum of the former contains three broad bands of ν(NH) and ν(OH) at 3373, 2530, and 1850 cm^{-1} [37]. This pattern with three bands is characteristic for strong hydrogen bonds [52]. It was reproduced on different samples of HL·0.5H_2O. Bulk composition of HL·0.5H_2O was confirmed by X-ray powder diffraction. This intriguing IR-pattern can be explained in terms of resonance-assisted hydrogen bonding (or π-bond cooperativity) [53] occurring within the HL chains. Since O of N-oxide of HL accepts a hydrogen bond, the N–H imidazolic group of the same molecule becomes more polarized by charge flow through the imidazolic π-system and becomes a stronger hydrogen bond donor. This effect favors clustering of polar groups and gives energy gain with respect to isolated hydrogen bonds [53]. We suppose that this effect is responsible for the observed IR pattern.

To gain insight into the dynamics of hydrogen bonding, we studied variable temperature mid-IR spectra of these compounds. Cooling the compounds to 5 K is accompanied by noticeable changes in the IR pattern. The intensity of the band at 2530 cm^{-1} in the spectrum of HL·0.5H_2O decreases upon cooling (figure 5). The band at 3373 cm^{-1} becomes narrower and splits into two components as does the band at 1850 cm^{-1}. For **1**, the band at

Table 3. Selected vibration frequencies in IR spectra (cm^{-1}) of the compounds.

Compound	$(\nu+\delta)_{ring}$	ν(NH)	ν(NH) + ν(OH)	ν(Zn–Cl)	ν(Zn–O)	ν(Zn–N)
HL·0.5H_2O	1587, 1564, 1518		3373, 2530, 1850			
$[H_2L]_2[ZnCl_4]$	1591, 1572, 1536, 1498 (including δ(NH))	3200–2200 (ν_{max} 2928)		300, 260		
ZnLCl	1608, 1593, 1567, 1512			341, 328	458, 415	270

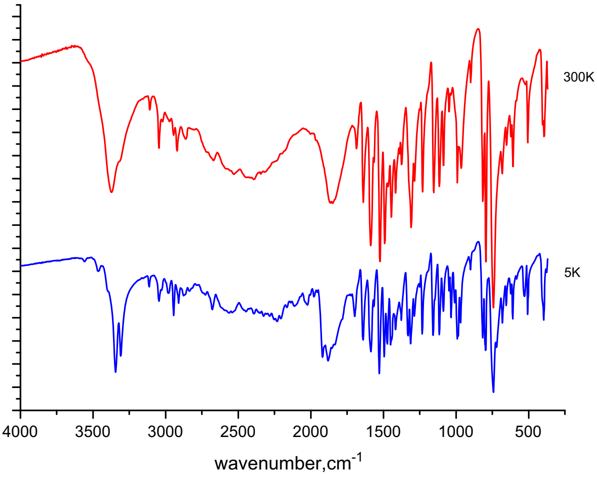


Figure 5. Mid-IR spectra of HL·0.5H_2O at 300 and 5 K.

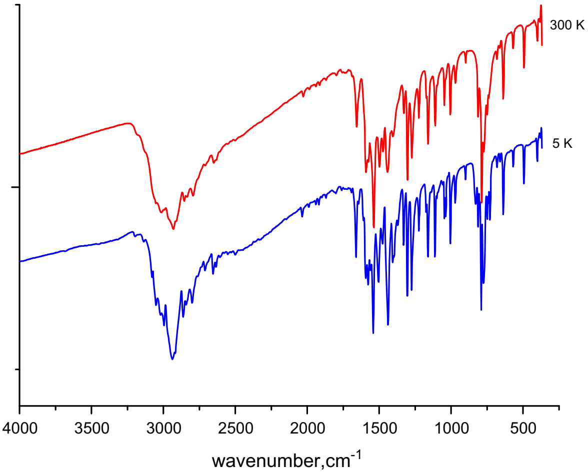


Figure 6. Mid-IR spectra of $[H_2L]_2[ZnCl_4]$ at 300 and 5 K.

2928 cm^{-1} also becomes narrower (figure 6); the relative intensity of the outer components of this band decreases with respect to the central component. These changes at 5 K reflect more localized character of hydrogen bonds. After the samples were heated, the IR pattern at 300 K was reproduced.

3.5. *Luminescence*

Photoluminescent properties of the compounds were studied in the solid state. To compare the relative intensities of the emission, the measurements were carried out under the same experimental conditions for all samples at room temperature. To compare luminescent properties of $[H_2L]_2[ZnCl_4]$ and ZnLCl with those of $ZnL_2·2H_2O$ [37], we recorded also the

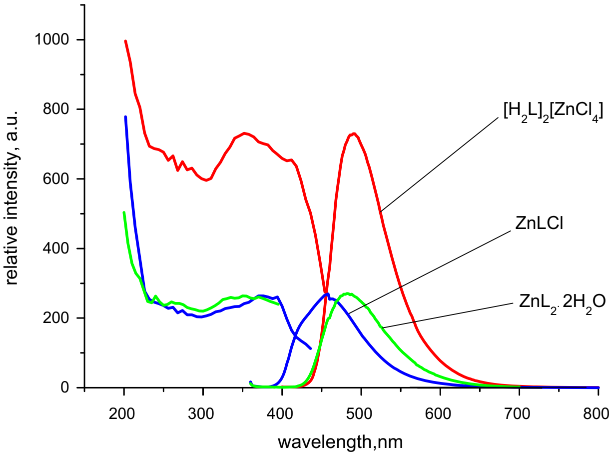


Figure 7. The excitation and emission spectra of the complexes.

excitation and emission spectra of freshly prepared sample of $ZnL_2{\cdot}2H_2O$. The excitation spectra of the complexes contain a broad band at 300–430 nm with a maximum at 350–360 nm. Thus, to obtain the emission spectra under optimal conditions, we applied $\lambda_{exc} = 350$ nm in all cases. While $HL{\cdot}0.5H_2O$ is practically luminescent silent, the complexes have bright-blue or blue–green luminescence; the excitation and emission spectra of the complexes are displayed in figure 7. The maxima of emission are observed at 490 nm for $[H_2L]_2[ZnCl_4]$, 460 nm for ZnLCl, and 482 nm for $ZnL_2{\cdot}2H_2O$. Thereby, the bands of emission for $[H_2L]_2[ZnCl_4]$ and $ZnL_2{\cdot}2H_2O$ are red shifted with respect to the position of the band in the spectrum of ZnLCl. For this series of complexes, the Stokes shift for $[H_2L]_2[ZnCl_4]$ is the largest. The relative intensities of emission for complexes with deprotonated ligand, $ZnL_2{\cdot}2H_2O$, and ZnLCl, are practically identical. Emission intensity of $[H_2L]_2[ZnCl_4]$ exceeds emission intensity of the two other compounds. The observed emissions can be attributed to intra-ligand transitions.

4. Conclusion

Two zinc(II) complexes based on HL, $[H_2L]_2[ZnCl_4]$, and ZnLCl, have been synthesized. Ionic complex $[H_2L]_2[ZnCl_4]$ can be prepared by demetallating $ZnL_2{\cdot}2H_2O$ by HCl in EtOH. Structural and IR-spectroscopic studies of $[H_2L]_2[ZnCl_4]$ show formation of a short intraionic O–H···N hydrogen bond (N(3)···O(1) 2.607(5) Å). 1-D supramolecular structure of the complex is built by N–H···Cl and C–H···Cl hydrogen bonds between H_2L^+ and $ZnCl_4^{2-}$ and by π–π-stacking interactions between adjacent H_2L^+ units. Surprisingly, attempts to synthesize zinc(II) complex with zwitterionic form of the ligand, e.g. Zn$(HL)_2Cl_2$, by reacting $ZnCl_2$ with HL in 1 : 2 and 1 : 1 metal-to-ligand molar ratios in EtOH/H_2O mixture failed and another complex, ZnLCl, containing the deprotonated form of the ligand, was isolated as an alternative. It should be noted that there is a possibility for formation of polynuclear structures in this case. Although chloride seems to be terminal, the deprotonated imidazolylpyridine may act as a linker. Examples of zinc(II) coordination polymers with related hybrid imidazole-based ligands have been reported [54–56]. Some of these compounds show luminescence [54–56]. HL crystallizes as the hemihydrate,

$HL\cdot 0.5H_2O$ in infinite helical chains due to N–H···O intermolecular hydrogen bonds (N···O 2.623(2) Å). This produces rather unusual mid-IR pattern typical for strong hydrogen bonds. This pattern can be explained by resonance-assisted hydrogen bonding (π-bond cooperativity) occurring within HL chains. On cooling to 5 K, noticeable changes in the bands assigned to the hydrogen bond vibrations were observed. The luminescent properties of the compounds were studied in the solid state. $HL\cdot 0.5H_2O$ is practically luminescent silent while the complexes reveal bright photoluminescence.

Supplementary material

CCDC 920587 and 920588 contain the supplementary crystallographic data for the compounds. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44)1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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