ORIGINAL PAPER

Structures and Characterization of [Zn(*n*-chlorosalicylato)$_2$ (*N*-methylnicotinamide)$_2$(H$_2$O)$_2$] (*n* = 4 or 5) Ligand Isomers

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Abstract Two ligand isomers [Zn{4-ClC$_6$H$_3$-2-(OH) COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**I**) and [Zn{5-ClC$_6$H$_3$-2-(OH) COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**II**) (Menia = *N*-methylnicotinamide) were prepared and characterized by elemental analysis, IR spectroscopy and thermal analysis. The X-ray crystal structures of complexes (**I**) and (**II**) were determined. Compound (**I**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.105(1)$ Å, $b = 10.036(2)$ Å, $c = 10.545(2)$ Å, $\alpha = 109.088(9)°$, $\beta = 91.416(8)°$, $\gamma = 102.757(9)°$, $V = 786.2(2)$ Å^3, $Z = 1$. Compound (**II**) crystallizes in the triclinic space group $P\bar{1}$. Its cell parameters are: $a = 8.133(1)$ Å, $b = 10.119(2)$ Å, $c = 10.428(1)$ Å, $\alpha = 66.44(1)°$, $\beta = 74.32(1)°$, $\gamma = 80.16(1)°$, $V = 755.5(2)$ Å^3, $Z = 1$. The molecular structure of both isomers is monomeric. Each Zn(II) atom is hexacoordinated by three pairs of unidentate ligands in *trans*-positions (ZnO$_4$N$_2$). The 5-Clsal complex is somewhat less distorted than 4-Clsal complex (Cl-sal = chlorosalicylate). The structural data are compared with those found in similar [Zn(RCOO)$_2$(NL)$_2$(H$_2$O)$_2$].

Introduction

Zinc is an element of strong interest in biology, medicine, materials and catalysis. It forms zinc finger proteins with key function in gene expression and also plays important roles in the central nervous system and neurodegenerative disorders, and it is a critical cofactor for many cellular functions [1]. Coordination numbers of zinc are most commonly four to six, with three not quite so common, and two, seven and eight less often observed and more dependent on donor or ligand types [2–5]. Four-coordinate zinc plays a structural role in zinc finger proteins and enzymes [6]. Of particular interest is the coordination environment of zinc in complexes with carboxylic acids and N-, O- and S-donor ligands. It is well known that the presence of ligand in the zinc complex can increase its bioactivity. Therefore the variety of zinc(II) carboxylate complexes with heterocyclic ligands e.g. nicotinamide, isonicotinamide, methyl-3-pyridylcarbamate, etc. [7, 8] attract the attention of many authors. Except for the above mentioned bioactive ligands, one of the major primary metabolites of nicotinamide, *N*-methylnicotinamide is often chosen for the study of synthesis and physicochemical properties of the complex compounds. It has been shown at in vitro study to be a potent anti-inflammatory agent [9–12].

In our previous papers we dealt with the synthesis, spectral and thermal properties of zinc(II) salicylates and

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5-chlorosalicylates with bioactive ligands (urea, thiourea, nicotinamide, caffeine, theobromine and theophylline) [13–15]. In this paper the study of the structural, spectroscopic and thermal properties of ligand isomers 4-chlorosalicylato- and 5-chlorosalicylatozinc(II) complexes with N-methylnicotinamide is presented.

Experimental

Preparation of Complexes

Preparation of [Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$ (Menia)$_2$(H$_2$O)$_2$] (I)

An aqueous solution of ZnCl$_2$ (2.17 g; 15.9 mmol) was added under continual stirring to an aqueous solution of NaHCO$_3$ (2.68 g; 31.9 mmol) and stirred together for an hour. A hot methanol/aqueous solution of 4-chlorosalicylic acid (2.75 g; 15.9 mmol) was added to an excess of the freshly prepared suspension of ZnCO$_3$ and stirred for 90 min. The excess of ZnCO$_3$ was filtered off. Then N-methylnicotinamide (2.17 g; 15.9 mmol) was added to the filtrate and stirred together for 2 h. Reaction mixture was reduced in volume to the half in a water bath at 80 °C and left to crystallize. After a few days light brown crystals precipitated. Calculated for C$_{28}$H$_{28}$Cl$_2$N$_4$O$_{10}$Zn (MW: 716.81): C 46.92, H 3.94, N 7.82, Cl 9.89, Zn 9.12. Found C 46.50, H 3.41, N 7.21, Cl 9.61, Zn 9.67%. IR (KBr pellet, cm^{-1}): 3323 v(N–H), 3109 v(C–H)$_{ar}$, 2974 v(C–H), 1657 v(C=O), 1628 δ(O–H)$_{H_2O}$, 1572 v_{as}(COO$^-$), 1485 v(C–C)$_{ar}$, 1431 δ_{as}(C–H)$_{-CH_3}$, 1369 v_s(COO$^-$), 1315 δ_s(C–H)$_{-CH_3}$, 1236 v(C–OH), 1201 v(C–N), 1149 δ(N–H), 1034 v(C–C), 866 δ(C–H), 783 v(C–Cl), 750 γ(C–H), 704 γ(N–H), 447 v(Zn–O).

Preparation of [Zn{5-ClC$_6$H$_3$-2-(OH)COO}$_2$ (Menia)$_2$(H$_2$O)$_2$] (II)

A hot methanol solution of 5-chlorosalicylic acid (1.45 g; 8.4 mmol) was added to the freshly prepared aqueous suspension of ZnCO$_3$, which was in a higher amount than the calculated stoichiometric one. They were stirred together for an hour and the excess of ZnCO$_3$ was filtered off. Then a solution of N-methylnicotinamide (1.14 g; 8.4 mmol) was added to the filtrate of zinc(II) 5-chlorosalicylate in a molar ratio 2:1 and stirred for 1½ h. The reaction mixture was reduced to the half of the volume in a water bath at 80 °C and left to crystallize at room temperature. In a few days white crystalline product precipitated. Calculated for C$_{28}$H$_{28}$Cl$_2$N$_4$O$_{10}$Zn (MW: 716.81): C 46.92, H 3.94, N 7.82, Cl 9.89, Zn 9.12. Found C 46.81, H 3.93, N 7.79, Cl 9.80, Zn

9.02%. IR (KBr pellet, cm^{-1}): 3430 v(O–H)$_{H_2O}$, 3288 v(N–H), 3043 v(C–H)$_{ar}$, 2939 v(C–H), 1659 v(C=O), 1610 δ(O–H)$_{H_2O}$, 1564 v_{as}(COO$^-$), 1483 v(C–C)$_{ar}$, 1433 δ_{as}(C–H)$_{-CH_3}$, 1367 v_s(COO$^-$), 1313 δ_s(C–H)$_{-CH_3}$, 1252 v(C–OH), 1205 v(C–N), 1149 δ(N–H), 1034 v(C–C), 904 δ(C–H), 798 v(C–Cl), 744 γ(C–H), 715 γ(N–H), 463 v(Zn–O).

Analysis, Spectral and Thermal Characterization

Elemental analyses were performed on a Perkin Elmer 2400 CHN analyser. The content of zinc was determined complexometrically using Complexone III as an agent and Eriochrome black T as an indicator.

Infrared spectra of prepared compounds were recorded on AVATAR 330 FT-IR Thermo Nicolet using KBr pellets (2 mg/200 mg KBr) in the range 4,000–400 cm^{-1}.

TG/DTG measurements were performed in nitrogen atmosphere on a Perkin Elmer TGA 7 Thermoanalyser with a heating rate 10 °C min^{-1}.

X-ray Diffraction Data Collection and Refinement

Intensity data for [Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$ (H$_2$O)$_2$] (I) and [Zn{5-ClC$_6$H$_3$-2-(OH)COO}$_2$ (Menia)$_2$(H$_2$O)$_2$] (II) were collected using a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation at 293 K [16]. The diffraction intensities were corrected for Lorentz and polarization effects. Absorption corrections were applied using the program XEMP [17]. The structures were solved by direct methods using the program SHELXS-97 [18] and refined by the full matrix least-squares method on all F^2 data using the program SHELXL-97 [19]. Geometrical analyses were performed using SHELXL-97. The structures were drawn by ORTEP-3 for Windows. The Single Crystal Suite WinGX was used as an integrated system for all crystallographic programs and software for preparing material for publication [20]. Crystal data and conditions of data collection and refinement are reported in Table 1.

Results and Discussion

IR Spectra

The IR spectrum of **I** indicates the typical carboxylate stretching frequencies for the antisymmetric stretching vibration v_{as}(COO$^-$) at 1,572 cm^{-1} and for the symmetric stretching vibration v_s(COO$^-$) at 1,369 cm^{-1}. Similarly in the IR spectrum of **II** the absorption bands at 1,564 and 1,367 cm^{-1} are assigned to v_{as}(COO$^-$) and v_s(COO$^-$). The existence of water in complexes **I** and **II** is approved by the

Table 1 Crystal data and structure refinement for $[Zn\{4\text{-ClC}_6H_3\text{-}2\text{-}(OH)COO\}_2(Menia)_2(H_2O)_2]$ (**I**) and $[Zn\{5\text{-ClC}_6H_3\text{-}2\text{-}(OH)COO\}_2(Menia)_2(H_2O)_2]$ (**II**)

	(I)	(II)
Identification code	mk40	mk39
Empirical formula	$C_{28}H_{28}Cl_2N_4O_{10}Zn$	$C_{28}H_{28}Cl_2N_4O_{10}Zn$
Formula weight	716.81	716.81
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Tricline, $P\bar{1}$	Tricline, $P\bar{1}$
Unit cell dimensions	$a = 8.105$ (1) Å	$a = 8.133$ (1) Å
	$b = 10.036$ (2) Å	$b = 10.119$ (2) Å
	$c = 10.545$ (2) Å	$c = 10.428$ (1) Å
	$\alpha = 109.088$ (9)°	$\alpha = 66.44$ (1)°
	$\beta = 91.416$ (8)°	$\beta = 74.32$ (1)°
	$\gamma = 102.757$ (9)°	$\gamma = 80.16$ (1)°
Volume	786.2 (2) Å^3	755.5 (2) Å^3
Z, calculated density	1, 1.514 mg/m^3	1, 1.576 mg/m^3
Absorption coefficient	1.012 mm^{-1}	1.054 mm^{-1}
$F(000)$	368	368
Crystal size	$0.40 \times 0.42 \times 0.6$ mm^3	$0.06 \times 0.38 \times 0.24$ mm^3
θ range for data collection	4.43–26.37°	4.10–26.37°
Limiting indices	$-1 < h < 10, -12 < k < 12, -13 < l < 13$	$-1 < h < 10, -12 < k < 12, -13 < l < 13$
Reflections collected/unique	3790/3124 [$R_{(int)} = 0.0473$]	3741/3069 [$R_{(int)} = 0.0657$]
Completeness to Θ	26.37–97.3%	26.37–99.6%
Absorption correction	XEMP program	XEMP program
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3124/0/207	3069/0/206
Goodness-of-fit on F^2	0.939	0.857
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0337$, $wR_2 = 0.0811$	$R_1 = 0.0468$, $wR_2 = 0.1169$
R indices (all data)	$R_1 = 0.0397$, $wR_2 = 0.0846$	$R_1 = 0.0776$, $wR_2 = 0.1337$
Largest diff. peak and hole	0.468 and -0.447 e Å^{-3}	0.388 and -0.324 e Å^{-3}

characteristic deformation vibration $\delta(O-H)_{H_2O}$ at 1,628 and 1,610 cm^{-1}. The strong absorption band of stretching vibration $v(C=O)$ of the ligand *N*-methylnicotinamide in complex **I** appears at 1,657 cm^{-1} and in complex **II** at 1,659 cm^{-1}. They are shifted to higher wavenumbers as compared with the free *N*-methylnicotinamide (1,644 cm^{-1}). It can be explained by the fact, that the pyridine nitrogen of the ligand *N*-methylnicotinamide is involved in coordination with zinc, therefore the electron density in the ligand is shifted towards the pyridine nitrogen leading to the increase in the double bond character of the carbonyl group.

Thermal Properties

The thermogravimetric analyses of the prepared compounds **I** and **II** were carried out in nitrogen atmosphere up to 800 °C. The thermal decomposition of complex **I** is shown in Fig. 1. In the first step of the thermal decomposition the release of water takes place at 70 °C. Then the

organic ligand *N*-methylnicotinamide and 4-chlorosalicylic acid are liberated in the temperature range 120–320 °C. In the temperature range 320–800 °C carbon monoxide and 3-chlorophenol are released. The final solid product of the thermal decomposition is zinc oxide. On the basis of the mass loss, the following equation is proposed for the thermal decomposition:

$$[Zn\{4\text{-ClC}_6H_3-2-(OH)COO\}_2(Menia)_2(H_2O)_2] \rightarrow$$
$$2H_2O + 2Menia + 4\text{-ClC}_6H_3-2-(OH)COOH + CO$$
$$+ 3\text{-ClC}_6H_4OH + ZnO$$
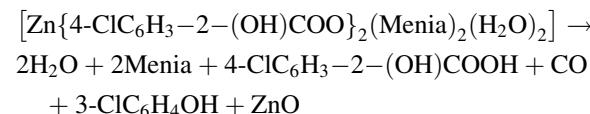
The thermal decomposition of complex **II** is similar to **I**.

Crystal Structure Description

The structures of the ligand isomers **I** and **II** are very similar and the structure of the former complex is shown in Fig. 2. The zinc(II) atoms in both isomers are octahedrally
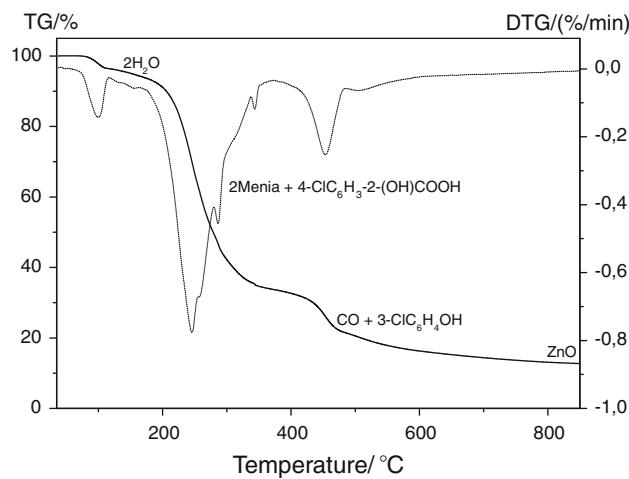
Fig. 1 TG/DTG curves of [Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**I**)

coordinated. The rhombic D$_{2h}$ stereochemistry around each zinc(II) atom is created by three pairs of unidentate ligands in *trans*-positions. Selected bond distances and bond angles are given in Table 2. As can be seen, the Zn–O$_{(\eta1\text{-}RCOO)}$, Zn–O$_{(H_2O)}$ and Zn–N bond distances are differing. The mean value of the respective bond distances **I** versus **II**, are elongated in the sequence: 2.081 versus 2.098 Å < 2.128 versus 2.142 Å < 2.219 versus 2.167 Å. The maximum deviation of the *cis*-L–Zn–L bond angles from 90 are 1.7° and 2.3°, respectively. The *trans*-L–Zn–L bond angles are exactly 180°. The sum of all six (Zn–O(×4) plus Zn–N(×2)) bond distances are 12.858 and 12.818 Å respective. This indicates that the isomer **I** is somewhat less crowded than the isomer **II**.

The *trans*-[Zn(n-Clsal)$_2$(Menia)$_2$(H$_2$O)$_2$] are clearly hypervalent. The central Zn(II) cation is surrounded by a total of 22 electrons (10 electrons of Zn^{2+} and 6 electron pairs of ligand atoms). The coordination polyhedron of Zn^{2+} displays O$_h$ site symmetry. Those deformations are

Table 2 Selected bond distances (Å) and bond angles (°)

	[Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**I**)	[Zn{5-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**II**)
Zn1–O1	2.128 (2)	2.142 (2)
Zn1–O11	2.082 (1)	2.098 (2)
Zn1–N21	2.219 (2)	2.167 (3)
O1–Zn1–O11	88.27 (6)	92.28 (10)
O1–Zn1–N21	89.27 (6)	88.39 (10)
N21–Zn1–O11	91.60 (6)	88.71 (10)

Table 3 Hydrogen bonds in the structures of the ligand isomers

	[Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**I**)	[Zn{5-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**II**)
O13···H131	0.820 Å	0.811 Å
O12···H131	1.798 Å	1.858 Å
O12···O13	2.528 Å	2.543 Å
O13···H131···O12	147.45°	141.36°
O1···H1	0.810 Å	0.901 Å
O12···H1	1.957 Å	1.859 Å
O1···O12	2.722 Å	2.679 Å
O1···H1···O12	157.23°	150.40°
O1···H2	0.813 Å	0.879 Å
O21*···H2	1.975 Å	1.908 Å
O1···O21*	2.778 Å	2.758 Å
O1···H2···O21*	169.60°	162.37°

then stabilized in the solid state e.g. by hydrogen bonding networks. The observed diminishing of symmetry in the zinc(II) isomers, which have D$_{2h}$ site symmetry could be due to hydrogen bonds. The *n*-chlorosalicylate anions have two carboxylate oxygens ready to form both coordination and hydrogen bonds. In the isomers each n-chlorosalicylate

**Fig. 2** ORTEP drawing of [Zn{4-ClC$_6$H$_3$-2-(OH)COO}$_2$(Menia)$_2$(H$_2$O)$_2$] (**I**). *Thermal ellipsoids* are drawn at the 50% probability level
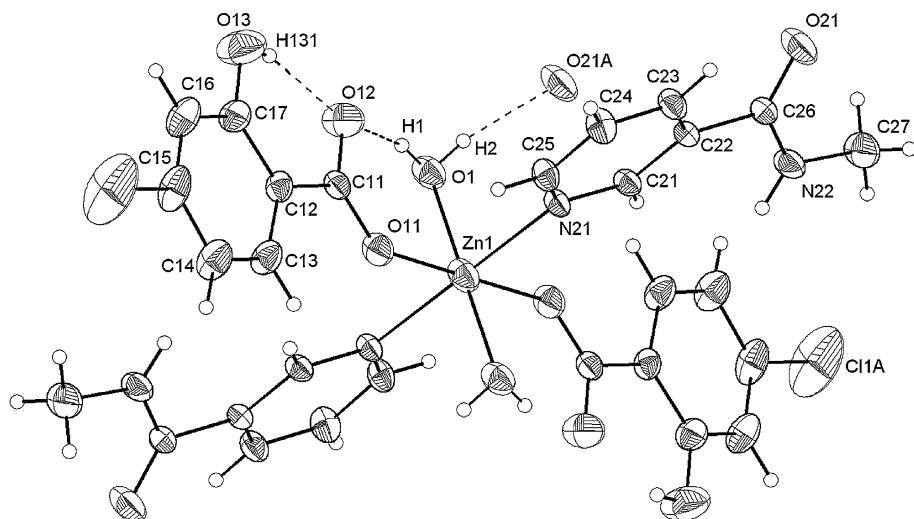
Table 4 Summary of the Zn–L bond distances (Å) of $Zn(\eta^1\text{-RCOO})_2(NL)_2(H_2O)_2$ complexes

Complex	Zn–O$_{(RCOO^-)}$ (Å)	Zn–O$_{(H_2O)}$ (Å)	Zn–N (Å)	ΣZn–L($\times$6) (Å)	Space group	Reference
Zn(3,5-(NO$_2$)bz)$_2$(ptio)$_2$(H$_2$O)$_2$	2.088 (1)	2.109 (1)	2.150 (2)	12.694	tr $P\bar{1}$	[21]
Zn(4-Brbz)$_2$(Et$_2$nia)$_2$(H$_2$O)$_2$	2.097 (3)	2.143 (3)	2.157 (3)	12.794	tr $P\bar{1}$	[23]
Zn(2-OHbz)$_2$(Et$_2$nia)$_2$(H$_2$O)$_2$	2.098 (3)	2.153 (4)	2.154 (4)	12.808	tr $P\bar{1}$	[24]
Zn(4-NO$_2$bz)$_2$(Et$_2$nia)$_2$(H$_2$O)$_2$	2.115 (1)	2.137 (2)	2.153 (2)	12.810	tr $P\bar{1}$	[25]
Zn(4-Fbz)$_2$(Et$_2$nia)$_2$(H$_2$O)$_2$	2.090 (2)	2.143 (2)	2.169 (3)	12.810	tr $P\bar{1}$	[26]
Zn(4-Clbz)$_2$(Et$_2$nia)$_2$(H$_2$O)$_2$	2.097 (2)	2.143 (2)	2.168 (2)	12.816	tr $P\bar{1}$	[27]
Zn(5-Clsal)$_2$(Menia)$_2$(H$_2$O)$_2$	2.098 (2)	2.142 (2)	2.167 (3)	12.818	tr $P\bar{1}$	This work
Zn(4-Clsal)$_2$(Menia)$_2$(H$_2$O)$_2$	2.082 (1)	2.128 (2)	2.219 (2)	12.858	tr $P\bar{1}$	This work
Zn(phtbz)$_2$(py)$_2$(H$_2$O)$_2$	2.088 (16)	2.203 (17)	2.16 (2)	12.898	m $P2_1$/c	[22]

3,5-(NO$_2$)bz = 3,5-dinitrobenzoate; ptio = 2-(4-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxy-3-oxide; 4-Brbz = 4-bromobenzoate; Et$_2$nia = N,N-diethylnicotinamide; 2-OHbz = 2-hydroxybenzoate; 4-(NO$_2$)bz = 4-nitrobenzoate; 4-Fbz = 4-fluorobenzoate; 5-Clsal = 5-chlorosalicylate; 4-Clsal = 4-chlorosalicylate; phtbz = (bis(2,3,4,5,6-pentachlorophenyl)methanido)2,3,5,6-tetrachlorobenzoate-; py = pyridine

anion is coordinated to zinc(II) atom only by one oxygen atom of the respective carboxylate group. In both isomers the non-coordinated oxygen O12 participates in the hydrogen bonds (Table 3; Fig. 2). As can be seen, the hydrogen bonds are differing in these two isomers, with somewhat narrower angles in the 5-Clsal, than those in the 4-Clsal isomer.

A search of the Cambridge Crystallographic Database revealed a total of seven [Zn(RCOO)$_2$(NL)$_2$(H$_2$O)$_2$] complexes with similar molecular structures to the ligand isomers studied (Table 4). The Zn–O$_{(RCOO^-)}$, Zn–O$_{(H_2O)}$ and Zn–N bond distances range from 2.082–2.115, 2.109–2.199 and 2.150–2.219 Å with the mean values increased in the sequence: 2.095 < 2.144 < 2.167 Å. The sum of all six (Zn–O($\times$4) plus Zn–N($\times$2)) bond distances elongated from 12.694 Å [21] to 12.898 Å [22], indicating that from top to bottom (Table 4) the inner coordination sphere around Zn(II) atom (ZnO$_4$N$_2$) magnify. Noticeable, except for example [Zn(phtbz)$_2$(py)$_2$(H$_2$O)$_2$] which belongs to the monoclinic $P2_1$/c crystal class, all the others are triclinic $P\bar{1}$. The mean Zn–N bond distances reflect the "bulky" as well as π-bonding system of respective N donor atom ligand elongated in the order: 2.150 Å (ptio) < 2.160 Å (Et$_2$nia) < 2.162 Å (py) < 2.193 Å (Menia). The T parameter ($T = R_S/R_L$) for ZnX$_2$(NL)$_2$(H$_2$O)$_2$ complex indicating the degree of tetragonal distortion about the Zn(II) centers decreases in the sequence: 0.991 (X = phtbz [22]) > 0.987 (4-NO$_2$bz [25]) > 0.986 (2-OHbz [24]) > 0.983 (4-Brbz [23]) > 0.978 (4-Clbz [27], 5-Clsal [this work]) > 0.976 (4-Fbz [26]) > 0.948 (4-Clsal [this work]).

Supplementary Material

CCDC 753017 and 761392 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: data_request@ccdc.cam.ac.uk.

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