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Switching from 4 + 1 to 4 + 2 zinc coordination number through the methyl group position on the pyridyl ligand in the geometric isomers *bis*[*N*-2-(4/6-methyl-pyridyl)salicylaldiminato-κ^2*N*,*O*]zinc(II)

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ABSTRACT

The Schiff bases *N*-2-(4/6-methyl-pyridyl)salicylaldimine (HL) which are geometric isomers differing in the para- or ortho-position of the methyl group to the pyridyl nitrogen atom react with zinc(II) acetate to give the bis-ligand chelate complexes *bis*[*N*-2-(4/6-methyl-pyridyl)salicylaldiminato-κ^2*N*,*O*]zinc(II) {4-methyl or para (**1**), 6-methyl or ortho (**2**)}. The zinc complexes feature an N_2O_2 chromophore from the two salicylaldiminato moieties with one or two additional weak Zn–N(pyridyl) contacts to give a 4 + 1 or 4 + 2 coordination in **1** or **2**, respectively. The difference in metal coordination is traced to competitive alternative C–H···π interactions of the non-coordinated methyl-pyridyl ring in compound **1** which are absent in **2**. Instead, the weakly zinc-coordinated methyl-pyridyl rings in **1** and **2** are at the same time engaged in π···π interactions. The latter compound features two C–H···O contacts. DFT calculation produces the similar structural features for **1** and **2**. The excited state properties calculated by TDDFT reveal that the complexes have distinctive ligand–ligand (LL) and metal-to-ligand (ML) charge transfer bands. Hirshfeld surface analysis also discloses similar C–H···π and C–H···O interactions in crystals **1** and **2**, respectively.

1. Introduction

Zinc is highly versatile in its coordination geometry and number. Zinc centers can be pseudo-tetrahedrally four-coordinated [1–7], five-coordinated [7–11], and octahedrally [3,6,7,10,12–14] to trigonal prismatic six-coordinated [3]. In all coordination modes the zinc atom can also adapt to different degrees of distortion from the ideal tetrahedral, square-pyramidal [10] or trigonal–bipyramidal [9] to octahedral coordination polyhedron. Because of the relevance of Zn in enzymes and proteins this is of fundamental importance. The flexibility and adoptability of variable coordination geometry at the zinc ion is essential for the enzyme or protein function as the molecular basis for the numerous biological effects [14]. Zinc complexes are highly abundant in biological systems, being essential for the functionalities of a number of metalloproteins, expressing both catalytic and structural roles [14–16]. In the cases of enzymes and zinc finger proteins, the cation is usually tetrahedrally coordinated [17] leading to a defined asymmetric geometry involving the zinc atom in their active site. Further, the variable coordination leads the chemical properties of the zinc ion to be either metabolically active or inert [14d–e]. The phenomenon also plays a key role for catalytic turnover *via* structural rearrangement of the metal sites, and affords strong interaction with a variety of substrates [14f].

We are investigating the coordination chemistry of modified Schiff base ligands and have recently given attention to achiral and in particular chiral *N*,*O*-chelate Schiff base ligands (HL) of the salicylaldimine and naphthaldimine type, and their complexes with transition metal ions such as $[Rh(\eta^4\text{-cod})(L)]$, $[Rh(\eta^4\text{-cod})(HL)]^+$ and $[Cu/Ni(L)_2]$ [18–25]. Solid state X-ray analyses show that the deprotonated Schiff base anion (L^-) coordinates to the $Rh(\eta^4\text{-cod})$-fragment as six-membered *N*,*O*-chelate in distorted-tetrahedral geometry. More recently, we reported the syntheses, diastereoselectivity, molecular structures, solution CD and DFT studies on chiral four-coordinated, distorted-tetrahedral $[M(R/S\text{-}N\text{\^{}}O)_2]$ {M = Cu or Zn , *N*^*O* = deprotonated Schiff base

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ligand = L$^-$} [26–28]. The *R*- or *S*-ligand chirality induces metal-centered Λ- or Δ-chirality at the metal atom in these C_2-symmetric complexes.

The present paper utilizes the Schiff base ligands *N*-2-(4/6-methyl-pyridyl)salicylaldimine [29–31] and describes the effect of the pendant isomeric para- or ortho-methyl pyridyl group in the Schiff base ligands (**HL1** and **HL2)** on the zinc coordination polyhedra in *bis*[*N*-2-(4/6-methyl-pyridyl)salicylaldiminato-κ^2*N*,*O*] zinc(II) (**1**, **2**) (Scheme 1). Structural and photophysical properties of the complexes are also studied by DFT (Density Functional Theory) and TDDFT (Time Dependent Density Functional Theory) calculations.

2. Experimental and computational methods

FT-IR-spectra were recorded on Nicolet iS10 (Thermo Scientific) spectrometer as KBr discs at ambient temperature. Electronic spectra were obtained with Shimadzu UV 1800 spectrophotometer in $CHCl_3$ at 25 °C. Elemental analyses were performed on a VarioEL from Elementar. Thermal analysis was performed on a Shimadzu DSC-60 differential scanning calorimeter (DSC), heating range at 303–553 K and rate at 10 K min^{-1}. ^{1}H NMR-spectra were recorded on a Bruker Avance DPX 200 spectrometer operating at 300 MHz (^{1}H) at 20 °C with calibration against the residual protonated solvent signal of $CDCl_3$ (δ 7.25 ppm). MS spectra were taken on Thermo-Finnigan TSQ 700. Isotopic distributions patterns for $^{64/66/68}$Zn(II)-containing ions are clearly visible in the mass spectra.

2.1. General procedure to synthesize the Schiff bases

Salicylaldehyde (1.730 g, 14.18 mmol) was dissolved into 10 mL of methanol, 2–3 drops of H_2SO_4 added and the solution stirred for 10 min. An equimolar amount of 2-amino-4-methyl-pyridyl (1.531 g, 14.18 mmol) was added into this solution. The reaction mixture was then refluxed for 6 h, and the color turned to bright yellow. The solvent was evaporated to 50% in *vacuo*, and the remaining solution left standing for crystallization by slow solvent evaporation at room temperature. Crystals were formed within 4–5 d, filtered off and washed three times with methanol (3 mL in each). The bright yellow crystals were dried in air for 2 d and analyzed as *N*-2-(4-methyl-pyridyl)salicylaldimine (**HL1**). Compound *N*-2-(6-methyl-pyridyl)salicylaldimine (**HL2**) was prepared following same procedure by using 2-amino-6-methyl-pyridyl.

2.1.1. *N-2-(4-methyl-pyridyl)salicylaldimine (**HL1**)*

Yield: 2.450 g (81%). IR (KBr, cm^{-1}): ν = 3053, 2978w (C–H), 1615vs (C=N), and 1570s (C=C). ESI-MS: *m*/*z* 213 (100) [M+H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H, CH_3), 6.99 (dt, J_{HH} = 7.5 Hz, J_{HH} = 0.9 Hz, 1H, $H_{5'}$), 7.05 (d, J_{HH} = 8.0 Hz, 1H, $H_{3'}$), 7.07 (d, J_{HH} = 6.0 Hz, 1H, $H_{6'}$), 7.18 (s, 1H, H_3), 7.42 (ddd, J_{HH} = 7.5, 6.9 Hz, J_{HH} = 1.8, 1.2 Hz, 1H, $H_{4'}$), 7.52 (dd, J_{HH} = 7.8, 7.5 Hz, J_{HH} = 1.8, 1.5 Hz, 1H, H_5), 8.38 (d, J_{HH} = 5.1 Hz, 1H, H_6), 9.46 (s, 1H, *H*CN) and 13.53 (s, 1H, O*H*).

2.1.2. *N-2-(6-methyl-pyridyl)salicylaldimine (**HL2**)*

Yield: 2.550 g (85%). IR (KBr, cm^{-1}): ν = 3053, 2978w (C–H), 1612vs (C=N), and 1578s (C=C). ESI-MS: *m*/*z* 213 (100) [M+H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61 (s, 3H, CH_3), 6.97 (t, J_{HH} = 7.5 Hz, J_{HH} = 0.9 Hz, 1H, $H_{5'}$), 7.05 (d, J_{HH} = 8.1 Hz, 1H, $H_{3'}$), 7.11 (d, J_{HH} = 7.5 Hz, 1H, $H_{6'}$), 7.14 (d, J_{HH} = 7.8, 7.5 Hz, J_{HH} = 1.8, 1.5 Hz, 1H, H_5), 7.41 (dt, J_{HH} = 7.8 Hz, J_{HH} = 1.2 Hz, 1H, $H_{4'}$), 7.53 (dd, J_{HH} = 7.5, 7.8 Hz, J_{HH} = 1.5, 1.7 Hz, 1H, H_3), 7.68 (t, J_{HH} = 7.5, 7.8 Hz, 1H, H_4), 9.46 (s, 1H, *H*CN) and 13.59 (s, 1H, O*H*).

2.2. General procedure to synthesize the complexes

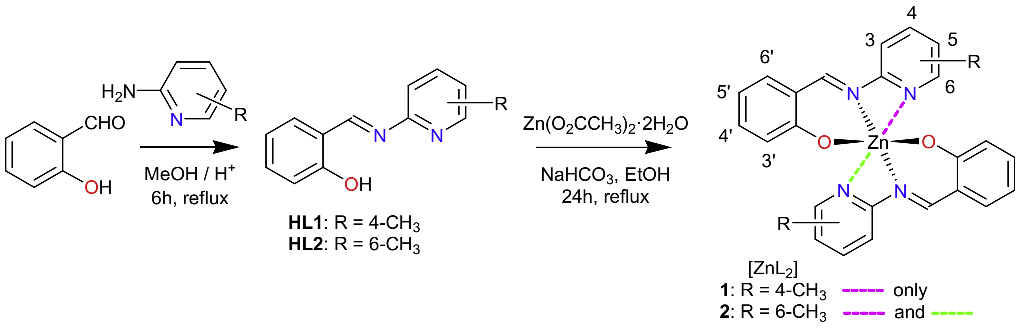
Two equivalents of *N*-2-(4-methyl-pyridyl)salicylaldimine (**HL1**) (0.425 g, 2.00 mmol) dissolved in 10 mL of ethanol were added into 10 mL of an ethanol solution of $Zn(O_2CCH_3)_2{\cdot}2H_2O$ (0.219 g, 1.00 mmol). Into this solution two equivalents of $NaHCO_3$ (dissolved in 5 mL of ethanol) were added and the mixture refluxed for 24 h. The color changes from bright-yellow to orange-yellow. Reduced the volume of solvent to 50% in *vacuo* and left standing this solution for crystallization *via* slow evaporation of solvent at room temperature. Light orange-yellow crystals of *bis*[*N*-2-(4-methyl-pyridyl)salicylaldiminato-κ^2*N*,*O*]zinc(II) (**1**), suitable for X-ray measurement, were obtained within one week. Filtered off, washed the crystals two times with ethanol (3 ml), and dried in *vacuo* at 30 °C. The same procedure was followed for synthesis of **2** using the Schiff base **HL2**.

2.2.1. *Bis[N-2-(4-methylpyridyl)salicylaldiminato-κ^{2}N,O]zinc(II) (**1**)*

Yield: 0.262 g (76%). – IR (KBr, cm^{-1}): ν = 3069, 3050, 3024w (H-C), 1610vs (C=N), and 1586vs (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3H, CH_3), 6.72 (t, J_{HH} = 7.5 Hz, 1H, $H_{5'}$), 6.96 (d, J_{HH} = 7.5 Hz, 1H, $H_{3'}$), 6.99 (d, J_{HH} = 6.5 Hz, 1H, $H_{6'}$), 7.06 (s, 1H, H_3), 7.39–7.44 (m, 2H, $H_{4',5}$), 8.20 (d, J_{HH} = 5.1 Hz, 1H, H_6), and 9.42 (s, 1H, *H*CN). – MS (EI, 70 eV): *m*/*z* (%) = 486 (40) [M]$^+$, 366 (20) [M–C_6H_4(OH)(CHN)]$^+$, 275 (100) [M–L1]$^+$, 212 (20) [HL1]$^+$, and 78 (50) [C_5H_4N]$^+$. – $C_{26}H_{22}N_4O_2Zn$ (487.87). *Anal.* Calc. for C, 64.01; H, 4.55; N, 11.48. Found: C, 63.41; H, 4.71; N, 11.72.

2.2.2. *Bis[N-2-(6-methylpyridyl)salicylaldiminato-κ^{2}N,O]zinc(II) (**2**)*

Yield: 0.288 g (75%). – IR (KBr, cm^{-1}): ν = 3065, 3044, 3020w (H–C), 1615vs (C=N), and 1591vs (C=C). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H, CH_3), 6.74 (t, J_{HH} = 7.5 Hz, 1H, $H_{5'}$), 6.95 (d, J_{HH} = 8.0 Hz, 1H, $H_{3'}$), 7.01 (d, J_{HH} = 7.5 Hz, 1H, $H_{6'}$), 7.05 (d, J_{HH} = 7.8 Hz, 1H, H_5), 7.32 (t, J_{HH} = 7.8 Hz, 1H, $H_{4'}$), 7.45 (d, J_{HH} = 7.5 Hz, 1H, H_3), 7.55 (t, J_{HH} = 7.5 Hz, 1H, H_4), and 9.37 (s, 1H,



Scheme 1. Synthetic route to *bis*[*N*-2-(4/6-methyl-pyridyl)salicylaldiminato-κ^2*N*,*O*]zinc(II) (**1**, **2**).