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# **Graphical Abstract**

Experimental and theoretical studies on isatin-Schiff bases and their copper(II)-complexes: Syntheses, spectroscopy, tautomerism, redox potentials, EPR, PXRD and DFT/TDDFT

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The isatin-Schiff bases 3-(o/p-tolylimino)indolin-2-one (HL1 and HL2) react with the copper(II) acetate or nitrate to give the *bis*[3-(o/p-tolylimino)indole-2-olato- $\kappa^2$ N,O]copper(II) (1 and 2) *via* lactam (L)- to enol (E)-tautomerism in solution.



# Experimental and theoretical studies on isatin-Schiff bases and their copper(II)-complexes: Syntheses, spectroscopy, tautomerism, redox potentials, EPR, PXRD and DFT/TDDFT

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#### Abstract

The isatin-Schiff bases 3-(*o*/*p*-tolylimino)indolin-2-one (HL1 and HL2) react with the copper(II) acetate or nitrate to give the *bis*[3-(*o*/*p*-tolylimino)indole-2-olato- $\kappa^2$ N,O]copper(II) (**1** and **2**) *via* lactam (L)- to enol (E)-tautomerism in solution. IR spectra show solely the L-tautomer at solid state, while both tautomers in solution. <sup>1</sup>H NMR results indicate a dynamic tautomerism equilibria between the L- and E-tautomers in solution with varying ratios of *ca.* 83/17, 60/40, 54/46 (L/E) within 0.5, 5, 24 h, respectively. Cyclic voltammogram demonstrate two quasi reversible one electron charge transfer processes for Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in acetonitrile, respectively. PXRD patterns at 5-50 ° (2 $\theta$ ) correspond well to the crystalline nature with various degrees of crystallinity for the ligands and complexes. X-band EPR spectrum shows an intense broad band at high field region with isotropic nature. Magnetic moment values ( $\mu_{eff.} = 1.56 - 1.63 \mu$ B) indicate paramagnetic nature of the copper(II)-complexes with one unpaired electron in methanol. Optimized structures by DFT show the L-form relatively stable than E-form by 19.76 Kcal/mol, while compounds HL2 and **2** are slightly stable than HL1 and **1** by 0.35 and 0.79 Kcal/mol, respectively. Electronic spectra by TDDFT strongly support the experimental results in methanol.

*Keywords*: Isatin-Schiff bases; Copper(II)-isatin Schiff bases; Lactam-Enol tautomerism; Redox potentials; DFT/TDDFT.

#### 1. Introduction

The indoline-2,3-dione (Isatin), a cheap starting material for drug syntheses, and isatin-Schiff bases are particularly important because of their pharmacological activities including anticancer, antibacterial, antifungal, antiviral, antileukemic and antiprotozoal agents [1,2,3]. In this connection, many isatin-Schiff bases and their derivatives were synthesized from condensation of isatin with arylamine [4], hydrazine [5] semicarbazide [6], thiosemicarbazide [7,8,9,10] and dithiocarbazate [11], respectively. Indeed, because of biological applications and dependences of many enzymes reactivities on copper, a large number of copper(II)-isatin Schiff bases complexes have been reported [7-9,11,12,13].

As part of our recent studies on transition metal complexes with *chiral/achiral*-Schiff bases ligands [14-25], we reported syntheses, spectroscopic characterizations, chiroptical properties and X-ray structural analyses of the enantiopure isatin-Schiff bases of 3-{(*R*)-(Ar)-ethylimino}-1,3-dihydro-indol-2-one (Ar = C<sub>6</sub>H<sub>5</sub>, *o-/p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-BrC<sub>6</sub>H<sub>4</sub> and 1-naphthyl) [26]. <sup>1</sup>H NMR studies demonstrate a time dependent dynamic tautomerism equilibrium between the lactam (L)and enol (E)-forms of the isatin-Schiff bases in solution [12b,26]. Whereas, solid state X-ray structures show solely the lactam-form [26]. Our results further explore several intermolecular hydrogen bonding interactions and/or short contacts, a common feature of isatin-Schiff bases, at solid state [4,5,6,10,26]. However, isatin-Schiff bases readily react with the dinuclear [Rh( $\mu$ -O<sub>2</sub>CMe)( $\eta$ <sup>4</sup>-cod)]<sub>2</sub> (cod = 1,5-cyclooctadiene) to give the mononuclear [Rh( $\eta$ <sup>4</sup>-cod){3-((*R*)-(Ar)ethylimino)-3*H*-indol-2-olato}] complexes *via* tautomerism in solution [26].

The present endeavor, in continuation, reports the results of syntheses, spectroscopy, lactamenol tautomerism, redox potential, EPR, paramagnetism and PXRD studies on isatin-Schiff bases 3-(o/p-tolylimino)indolin-2-one (HL1 and HL2) and their complexes bis[3-(o/p-tolylimino))indole-2-olato- $\kappa^2$ N,O]copper(II) (1 and 2), respectively. Theoretical calculations by DFT/TDDFT are employed to rationalise the experimental results.

#### 2. Experimental

#### 2.1. Materials and measurements

IR spectra were recorded on Nicolet iS10 (Thermo Scientific) spectrometer as KBr discs at ambient temperature. Electronic spectra were obtained with the Shimadzu UV 1800 spectrophotometer in methanol at 25 °C. Elemental analyses were performed on a VarioEL from the Elementaranalyensysteme. <sup>1</sup>H NMR-spectra were recorded on Bruker Avance 400 spectrometer operating at 400 MHz in CDCl<sub>3</sub> or dmso-d<sub>6</sub> at 20 °C. ESI mass (positive mode) spectrum for compound 1 was recorded on Shimadzu LCMS-2020. The isotopic distributions patterns for the <sup>63/65</sup>Cu containing ions are visible in the mass spectrum. Epsilon<sup>TM</sup> instruments (BASi) electrochemical analyser was used for running cyclic voltammograms experiments containing tetra-N-butyl-ammonium-hexaflorophosphate (TBAP) as supporting electrolyte in acetonitrile at 25 °C. A three-electrode measurement system was used, which composed of a platinum disc working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode, respectively. The solution containing the sample and TBAP was deoxygenated with purging nitrogen gas for 10 minutes prior to use. Working electrode was cleaned with supplied solution and dried prior to use in each scan to avoid any contamination caused by deposition of the metal. The reproducibility of CV pattern was checked out at a scan rate of 0.10 Vs<sup>-1</sup> in acetonitrile. The X-band EPR spectrum was recorded on ECS-EMX (Bruker) spectrometer in dmso at 120 K using the diphenylpicrylhydrazine (DPPH) as reference compound. The magnetic moments values ( $\mu_{eff}$ / $\mu$ B) for the complexes were measured, based on the Evans method [27], in methanol at 20 °C. For measurement, <sup>1</sup>H NMR spectra were run using a sealed coaxial insert containing TMS in acetone- $d_6$  (0.5%, v/v) as an external standard and Instrument lock. Cyclohexane in methanol (1.0%, v/v) was used as an internal reference compound, and methanol peaks (i.e., CH<sub>3</sub> and OH) were used for temperature calibration [27c-f].

#### 2.2. Syntheses of the 3-(o/p-tolylimino)indolin-2-one (HL1 and HL2)

An equimolar amount of Indoline-2,3-dione (Isatin) (0.294 g, 2.0 mmol) and o/p-toludine (0.214 g, 2.0 mmol) were dissolved in 10 mL methanol. Added 3-4 drops of concentrated H<sub>2</sub>SO<sub>4</sub> into this reaction mixture and refluxed the solution for 6-8 hours. Colour of the solution changed from red-orange to orange-yellow. Afterwards, reduced the volume of the solvent to *ca*. 50% in *vacuo* and left standing the solution for crystallization *via*. slow evaporation of the solvent at room temperature. Orange-yellow microcrystals were precipitated out after 2-3 days, filtered off

and washed the crystals with methanol for three times (2 ml in each). Dried the microcrystals in air for 3-4 days and obtained the Schiff bases 3-(o/p-tolylimino)indolin-2-one (HL1 and HL2).

3-(*o*-tolylimino)indolin-2-one (HL1): Yield: 0.385 g (82%). IR (KBr, cm<sup>-1</sup>): 3451vs/br. (vH<sub>2</sub>O), 3241vs (vN-H), 3067w (vC-H<sub>Ar</sub>), 1748vs (vC=O) and 1615 (vC=N). IR (in CHCl<sub>3</sub>, cm<sup>-1</sup>): 3693s, 3688s, 3683s and 3609w (vO-H), 3439s (vN-H), 1746s (vC=O), 1734s (vC–O) and 1619s, 1603sh (vC=N). IR (ATR, cm<sup>-1</sup>): 3234vs (vN-H), 3066w (vC-H<sub>Ar</sub>), 1745vs (vC=O) and 1610, 1593vs (vC=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 2.18$  (s, 3H, CH<sub>3</sub>-L, *ca*. 83%), 2.46 (s, 3H, CH<sub>3</sub>-E, *ca*. 17%), 6.53 (d, J = 7.6 Hz, 1H, H<sub>14</sub>-L), 6.77 (t, J = 7.6 Hz, 1H, H<sub>13</sub>-L), 6.86 (d, J = 7.6 Hz, 1H, H<sub>1</sub>-L), 6.94 (d, J = 7.0 Hz, 1H, H<sub>14</sub>-E), 7.10-7.15 (m, 2H, H<sub>11,13</sub>-E), 7.19 (t, J = 7.6 Hz, 1H, H<sub>12</sub>-L), 7.26 (t, J = 7.2 Hz, 1H, H<sub>6</sub>-L), 7.31-3.33 (m, 4H, H<sub>6,12</sub>-E, H<sub>5,7</sub>-L), 7.34 (d, J = 7.6 Hz, 1H, H<sub>8</sub>-E), 7.59 (t, J = 7.6 Hz, 1H, H<sub>7</sub>-E), 7.65 (d, J = 7.2 Hz, 1H, H<sub>5</sub>-E), 8.24 (br, 1H, OH-E, 20%), 8.46 (br, 1H, NH-L, 80%) (L = Lactam-form and E = Enol-form, for proton numbering see the Scheme 1).

3-(*p*-tolylimino)indolin-2-one (HL2): Yield 0.376 g (80%). IR (KBr, cm<sup>-1</sup>): 3453vs/br. (vH<sub>2</sub>O), 3261vs (vN-H), 3046w (vC-H<sub>Ar</sub>), 1742vs (vC=O) and 1613vs (vC=N). IR (in CHCl<sub>3</sub>, cm<sup>-1</sup>): 3689s, 3675s, 3610w (vO-H), 3439s (vN-H), 1745s (vC=O) and 1616s, 1595sh (vC=N). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.32 (s, 3H, CH<sub>3</sub>-E, *ca*. 15%), 2.43 (s, 3H, CH<sub>3</sub>-L, *ca*. 85%), 6.79 (t, *J* = 7.6 Hz, 1H, H<sub>6</sub>-L), 6.83 (t, *J* = 7.2 Hz, 1H, H<sub>5</sub>-L), 6.94 (t, *J* = 8.0 Hz, 4H, H<sub>11-12,14-15</sub>-E), 6.97 (d, *J* = 8.0 Hz, 4H, H<sub>11-12</sub>-L), 7.06 (d, *J* = 7.6 Hz, 1H, H<sub>8</sub>-E), 7.14 (t, *J* = 7.6 Hz, 1H, H<sub>8</sub>-L), 7.26 (d, *J* = 8.0 Hz, 3H, H<sub>14-15</sub>-L+H<sub>6</sub>-E), 7.33 (t, *J* = 7.6 Hz, 1H, H<sub>7</sub>-L), 7.58 (t, *J* = 7.6 Hz, 1H, H<sub>7</sub>-E), 7.64 (d, *J* = 7.2 Hz, 1H, H<sub>5</sub>-E), 8.41 (br, 1H, OH-E, *ca*. 15%), 8.66 (br, 1H, NH-L, *ca*. 85%).

# 2.3. Syntheses of the bis[3-(o/p-tolylimino)indole-2-olato- $\kappa^2 N$ ,O]copper(II) (1 and 2)

Two equivalents of the Schiff base 3-(o/p-tolylimino) indolin-2-one (HL1 or HL2) (1.0 mmol) were dissolved in 10 mL methanol and stirred the solution for 10 min at room temperature. Added one equivalent of copper(II) acetate or nitrate solution (0.5 mmol, dissolved in 10 mL methanol) into the solution of Schiff base. The solution mixture was then stirred for *ca*. 8 hours at room temperature and colour changed from orange-yellow to dark brown. Reduced the volume of solvent to *ca*. 70 % in *vacuo* and left standing this solution for precipitation at room

temperature. After 4-5 days, dark brown precipitate was formed, filtered off and washed two times with diethyl ether (2 mL in each) followed by methanol. The precipitate was dried for 3-4 days and obtained dark brown microcrystals of  $bis[3-(o/p-tolylimino)indole-2-olato-\kappa^2N,O]copper(II)$  (1 and 2).

 $Bis[3-(o-tolylimino)indole-2-olato-\kappa^2N,O]copper(II), [Cu(L1)_2] (1): Yield: 0.220 g (75\%). IR (ATR, cm<sup>-1</sup>): 3170, 3065w (vC-H<sub>aromatic</sub>), 1728vs (vC-O) and 1612, 1591vs (vC=N). MS (ESI+):$ *m/z* $(%) = 602 (20) [M(HCO_2H)+Na]<sup>+</sup>, 556 (10) [M+Na]<sup>+</sup>, 473 (100) [(HL1)_2+H]<sup>+</sup>, 382 (25) [(HL1)_2-C_6H_4(CH_3)+H]<sup>+</sup>, 361 (10) [(CuL1)(CH_3CO_2)+2H+H]<sup>+</sup>, 298 (17) [CuL1]<sup>+</sup>, 237 (40) [HL1+H]<sup>+</sup> and 208 (12) [CuL1-C_6H_4(CH_3)+H]<sup>+</sup> {M = Cu(L1)_2 = C_{30}H_{22}N_4O_2Cu; HL1 = C_{15}H_{12}N_2O\}. - C_{30}H_{22}N_4O_2Cu \cdot 3H_2O (588.11): Calcd C 61.27, H 4.80, N 9.53; found C 60.90, H 4.62, N 9.41.$ 

 $Bis[3-(p-tolylimino)indole-2-olato-\kappa^2 N,O]copper(II), [Cu(L2)_2] (2): Yield 0.210 g (71\%). IR (ATR, cm^{-1}): 3188, 3061w (vC-H_{aromatic}), 1726vs (vC-O) and 1614vs, 1595sh (vC=N). - C_{30}H_{22}N_4O_2Cu\cdot 3H_2O (588.11): Calcd C 61.27, H 4.80, N 9.53; found C 61.00, H 4.65, N 9.35.$ 

#### 2.4. Computational method

To rationalize the experimental results, a through computational procedure was performed with the Gaussian 09 software [28]. The gas phase equilibrium geometries for both the Lactam (L)and Enol (E)-forms for HL1 or HL2 were optimized with DFT using the functional B3LYP and the basis set LANL2DZ, respectively (Fig. S1). Optimizations were also carried out in chloroform with Polarization Continuum Model (PCM) at B3LYP/LANL2DZ, respectively. It has been reported that four-coordinated metal(II)-N^O Schiff bases complexes in tetrahedral to distorted square-planar geometry exhibit induced chirality at-metal center, and provide two possible  $\Delta$ (right)-Cu and  $\Lambda$ (left)-Cu handed isomers (i.e., opposite configuration at-metal center) along the  $C_2$ -symmetry of the molecule [15-24]. Thus, we optimized both the  $\Delta$ -Cu and  $\Lambda$ -Cu configured structures for **1** or **2** using the functional B3LYP and the basis set 6-31G(d), respectively (Fig. 2).

For excited state properties, time-dependent density functional theory (TDDFT) was employed using the functionals B3LYP, M06 and the basis sets SDD, TZVP, 6-31G(d) on the

optimized structures with B3LYP/6-31G(d) or B3LYP/SDD, respectively for **1**. Polarization Continuum Model (PCM) was incorporated using methanol as solvent and 72 excited states (roots) were considered for calculations (Table S1). The calculated electronic spectra, from different combinations of the functionals and the basis sets, are similar in nature with little shifting of the band maxima ( $\lambda_{max}$ ) (Figs. 3, S2), strongly support the reliability and validity of the methods used for calculations. The best fitted calculated spectra to the experimental spectra are obtained with B3LYP/6-31G(d)//B3LYP/6-31G(d) (Fig. 3). The spectra for both  $\Delta$ - and  $\Lambda$ configured structures of **1** were calculated. TDDFT was further employed on the Lactam- and Enol-forms of HL1 at B3LYP/LANL2DZ, respectively (using PCM in methanol) (Fig. S3). Assignments of excited state properties and molecular orbitals (MOs) calculations were carried out at the same level of theory. The electronic spectra were generated using the program SpecDis [29] by applying Gaussian band shape with exponential half-width  $\sigma = 0.24$  eV.

#### 3. Results and discussion

Reaction of indoline-2,3-dione (Isatin) with the *o/p*-toludine in presence of 3-4 drops of concentrated H<sub>2</sub>SO<sub>4</sub> under reflux affords the isatin-Schiff bases 3-(o/p-tolylimino) indolin-2-one (HL1 or HL2) in methanol. The isatin-Schiff bases undergo tautomerism between the lactam (L)-and enol (E)-forms in solution, and hence react with the copper(II) acetate or nitrate to give the *bis*[3-(o/p-tolylimino) indole-2-olato- $\kappa^2$ N,O]copper(II), {Cu(L1)<sub>2</sub>] (**1**) or [Cu(L2)<sub>2</sub>] (**2**)} (Scheme 1). ESI mass spectrum shows the molecular ion peaks at m/z 556 ([M+Na]<sup>+</sup>) for **1** (Fig. 1). Indeed, the spectrum is dominated by several ions peaks for the protonated Schiff base ligand at m/z 473 {[(HL1)<sub>2</sub>+H]<sup>+</sup>} and 237 ([HL1+H]<sup>+</sup>), and fragmented complex species at m/z 602 ([M(HCO<sub>2</sub>H)+Na]<sup>+</sup>), 298 ([CuL1]<sup>+</sup>) and 208 ([CuL1-C<sub>6</sub>H<sub>4</sub>(CH<sub>3</sub>)+H]<sup>+</sup>).



Scheme 1. Synthetic route to the  $bis[3-(o/p-tolylimino)indole-2-olato-\kappa^2N,O]copper(II)$  (1 or 2).



Fig. 1. ESI-mass spectrum for compound 1.

#### 3.1. Vibrational spectra and optimized structures

The vibrational spectra for the isatin-Schiff bases (KBr disc) show main characteristics bands at 3246 (HL1)/3261 (HL2) for vN-H, and at 1748 (HL1)/1742 (HL2) cm<sup>-1</sup> for vC=O, suggesting solely the lactam (L)-tautomer at solid state (Fig. S4, top). The spectra taken in chloroform solution show bands at *ca*. 3439 cm<sup>-1</sup> (vN-H) and 1745 (vC=O) cm<sup>-1</sup> for the lactam (L)-tautomer, and bands at *ca.*  $3690/3608 \text{ cm}^{-1}$  (vO-H) and  $1734 \text{ cm}^{-1}$  (vC-O) for the enol (E)-tautomer (Fig. S4, bottom). The ratio of peaks areas for L/E-tautomers is ca. 60/40 within ca. 2 h of dissolution in solution. The results suggest the existences of both the L- and E-tautomers simultaneously in solution (Scheme 1), as evidenced by <sup>1</sup>H-NMR studies (discussed below). The vibrational spectrum for HL1 (with lactam-form) from optimized structure at B3LYP/LANL2DZ shows the characteristics bands at 3672, 1728 and 1665 cm<sup>-1</sup> due to vN-H, vC=O and vC=N, respectively (Fig. S5). While the spectrum for HL1 (with enol-form) shows bands at 3654 and 1593 cm<sup>-1</sup> due to vO-H and vC=N, respectively (where vN-H/vC=O bands are absent). As the complexes are formed via deprotonation of the enolic-proton (resulting from tautomerism in solution), the vN-H, vC=O and/or vO-H bands are obviously absent in their spectra (Fig. S6). Indeed, the complexes show strong band at *ca.* 1728 (1) and 1726 (2) cm<sup>-1</sup> for vC-O (Fig. S6). The Schiff bases further show strong bands at *ca*. 1615 cm<sup>-1</sup> (KBr disc) and *ca*. 1620, 1603 cm<sup>-1</sup> (in CHCl<sub>3</sub>) for vC=N, which are found at *ca*. 1612, 1591 cm<sup>-1</sup> (1) and *ca*. 1614, 1595 cm<sup>-1</sup> (2) in complexes. Several weak bands/shoulders are observed at 2950-3070 cm<sup>-1</sup> for vC-H both in the Schiff bases and complexes (Figs. S4, S6).

Optimized structures (gas phase) for the lactam (L)- and enol (E)-tautomers for HL1 or HL2 show the L-tautomer relatively more stable than E-tautomer by *ca*. 19.76 Kcal/mol (Fig. S1). Similarly, optimized structures in chloroform also reveal the L-form more stable by *ca*. 21.33 Kcal/mol. The optimized structures at B3LYP/6-31G(d) show both the  $\Delta$ -Cu and  $\Lambda$ -Cu configured isomers are equi-energetic (i.e., same electronic and thermal free energy) for **1** or **2**. The optimized structure for HL2 (or **2**) with *p*-tolyl group is slightly stable by *ca*. 0.35 (or *ca*. 0.79) Kcal/mol than HL1 (or **1**) with *o*-tolyl group due to less steric hindrance (Fig. 2). Some selected bond lengths and angles for the ligands and complexes are listed in Table 1, which are comparable to X-ray structural data for HL1 with lactam-form [30]. The computed C8-N2-C9

bond angle (*ca.* 127.7 °) is higher by *ca.* 10 ° than the X-ray value (117.7 °) in HL1 due to existing intermolecular hydrogen bonding interactions and short contacts in the crystals [26,30]. The bond angles are lowered by 5-7 ° in **1** or **2** due to steric constraints experienced in the coordination sphere. In fact, the two ligands differ in their relative orientations of the aryl- and lactam-rings, which is reflected by the dihedral angles ( $\theta$ /° = angle between the two planes of the aryl- and lactam-rings) of 57.1 ° (HL1) and 54.4 ° (HL2) because of uneven steric hindrances induced by the *o*- or *p*-methyl groups on the aryl-ring (Table 1). However, these  $\theta$  values are significantly lowered by 11-14 ° than the X-ray value (68.6 ° in HL1) due to intermolecular hydrogen bonding and short contacts in the crystals as mentioned above. The N2-C8 bond lengths (1.27-1.29 Å) indicate carbon-nitrogen double bond, while C8-N2-C9 bond angles (117.7-127.8 °) represent sp<sup>2</sup>-hybridization of the imino-nitrogen atom (Figs. 2, S1) [26]. Further, the bond angles for O-Cu-O' (*ca.* 100 °) and N2-Cu-N2' (*ca.* 104 °) comply well with the distorted tetrahedral geometry for the complexes.



**Fig. 2.** DFT optimized structures for the ligands (HL1 and HL2) at B3LYP/LANL2DZ and complexes (**1** and **2**) at B3LYP/6-31G(d), respectively.

Bond lengths (Å)/	HL1 (X-ray	HL1 (cal.) <sup>1</sup>	HL2 (cal.) $^{1}$	1 (cal.) <sup>2</sup>	<b>2</b> (cal.) $^{2}$
angles (°)	structure) <sup>a</sup>				
C7-0	1.212(2)	1.2423	1.2422	1.2838	1.2833
C7-N1	1.362(2)	1.4001	1.4006	1.3055	1.3058
C1-N1	1.412(3)	1.4114	1.4107	1.4100	1.4084
C7-C8	1.503(3)	1.5392	1.5395	1.5325	1.5342
C8-N2	1.276(2)	1.2925	1.2935	1.2955	1.2964
N2-C9	1.431(6)	1.4125	1.4121	1.4259	1.4206
Cu-O/O'				1.9153	1.9138
Cu-N2/N2'				2.0105	2.0056
C8-N2-C9	117.7(3)	127.78	127.62	122.65	124.13
N2-Cu-N2'				104.13	103.76
O-Cu-O'			0	98.93	100.20
O-Cu-N2'/N2-Cu-O'		5		149.00	148.17
N2-Cu-O/N2'-Cu-O'				86.67	86.69
Dihedral angles $(\theta/^{\circ})^{3}$	68.62	57.12	54.38	66.00	56.29/52.63

Table 1. Some selected bond lengths (Å) and angles (°) in HL1 and HL2.

<sup>a</sup> From ref. 30; <sup>1</sup> Calculated at B3LYP/LANL2DZ, <sup>2</sup> at B3LYP/6-31G(d) for  $\Delta$ -isomer.

<sup>3</sup>  $\theta/^{\circ}$  = Dihedral angles between the two planes of the aryl- and lactam-rings.

#### 3.2. Experimental and computed electronic spectra (UV-Vis.)

Electronic spectra (UV-Vis.) for the Schiff bases and complexes in methanol are identical in nature (Fig. 3) and feature several bands/shoulders below 500 nm due to the ligand-centered  $n\rightarrow\pi^*/\pi\rightarrow\pi^*$  (LL) transitions. A weak broad band, in addition, is found at visible region (500-800 nm) in the complexes (Fig. 3, inset), results from overlapping of metal-ligand (ML) charge transfer and metal-centered d-d transitions (MM) of copper(II)-core electrons [15,19,26,30]. Excited state properties by TDDFT for the complexes, from different combinations of the functionals and the basis sets, provide similar spectra with little shifting of the bands maxima ( $\lambda_{max}$ ), which are comparable to the experimental spectra (Figs. 3, S2). The computed spectra for L- and E-tautomers of isatin-Schiff bases are almost identical and fit well to the experimental spectra (Fig. S3). Similarly, spectra for  $\Delta$ - and  $\Lambda$ -configured structures are essentially identical for **1** or **2**. [15,17-23]. However, there are some discrepancies in the bands positions ( $\lambda_{max}$  values) between experimental and calculated spectra (Figs. 3, S3 and Table 2) due to certain

drawbacks of TDDFT protocol including overestimation of excitation energies, presence of low energy states with low oscillator strengths, improper description and/or long distance of charge-transfer processes, etc. [31]. " In addition, lacking of proper choices of the functionals and basis sets, gas phase DFT optimizations and limitations of experimental spectra including unavoidable (a) solute and solvent interactions and (b) dissociation-equilibria as found for the labile tetrahedral/square-planar complexes in solution [16-19,22-25,32-33] may contribute to these discrepancies."

Some selected and simplified assignments on computed spectrum, relevant to the experimental data, are made based on the orbital and population analyses for **1** ( $\Delta$ -Cu isomer) (Table 2) [15,19,26,30]. A combined band resulting from metal d-d, metal-ligand (ML) and intra-ligand (LL) transitions (for example) is found at 593 nm, close to the experimental band/shoulder at *ca*. 600 nm (Table 2), for HOMO to LUMO and HOMO-14 to LUMO transitions with MOs contributions of 54 and 14 %, respectively. Frontier molecular orbitals HOMO, HOMO-14 and LUMO, calculated at B3LYP/6-31g(d)//B3LYP/6-31G(d) in methanol, are shown in Fig. 4. The HOMO orbital is localized on the  $\pi$ -electrons moieties of the lactam- and aryl-ring plus metal d-moieties, while the LUMO is localized mainly on the  $\pi$ -moieties of the ary-ring with a very little d-moieties. The energy gap between these two MOs are very narrow ( $\Delta$ Eg = 2.7x10<sup>-4</sup> eV), involves maximum transitions in the excitations (MOs >54%) [31f]. On the other hand, the HOMO-14 is localized only on the  $\pi$ -electrons moieties of the lactam-ring (no metal d-moieties), which transits to LUMO with a high energy gap ( $\Delta$ Eg = 6.10 eV) and involves low transitions in the excitations (MOs <14%).



**Fig. 3.** Experimental electronic spectra for HL1 (0.07 mmol/L) and **1** (0.15 mmol/L) in methanol at 25 °C, and calculated spectrum for **1** ( $\Delta$ -Cu isomer) at B3LYP/6-31G(d)//B3LYP/6-31G(d) in methanol.

#### Table 2.

Some selected and simplified assignments on 1 ( $\Delta$ -Cu isomer), calculated at B3LYP/6-31G(d)//B3LYP/6-31G(d) in methanol.

$\lambda/nm^{a}$	Oscillator	MOs	Assignments <sup>c,#</sup>
	strength (f)	contributions (%) <sup>b</sup>	
628	0.0007	$\text{H-23} \rightarrow \text{L} (47), \text{H-16} \rightarrow \text{L} (31)$	MM, ML
593 (600sh)	0.0113	$\text{H-14} \rightarrow \text{L} \text{ (14), H} \rightarrow \text{L} \text{ (54)}$	MM, ML, LL
535	0.0153	$H-1 \rightarrow L+2$ (55), $H \rightarrow L+1$ (68)	MM, ML, LL
446 (380sh)	0.1319	$\text{H-3} \rightarrow \text{L} (78)$	MM, ML, LL
323 (300sh)	0.2094	$\text{H-7} \rightarrow \text{L+2 (45), H-3} \rightarrow \text{L+2 (10)}$	MM, ML, LL
282 (245)	0.0951	$H-14 \rightarrow L$ (29), $H-10 \rightarrow L$ (41)	ML, LL
269	0.1431	$\text{H-12} \rightarrow \text{L+1}$ (12), $\text{H-10} \rightarrow \text{L+2}$ (32)	ML, LL

<sup>a</sup> Experimental values are in parentheses; <sup>b</sup> H = HOMO and L = LUMO; <sup>c</sup> MM = metal-centered (d-d), ML = metal-ligand, LL= ligand-centered transitions; <sup>#</sup>  $\beta$ -spin MOs are considered.



Fig. 4. Frontier molecular orbitals (HOMO, HOMO-14 and LUMO) for 1 ( $\Delta$ -Cu isomer), calculated at B3LYP/6-31g(d)//B3LYP/6-31G(d) in methanol (Isovalue 0.02).

# 3.3. <sup>1</sup>H NMR studies: Lactam (L) $\Longrightarrow$ Enol (E) tautomerism

<sup>1</sup>H NMR spectra for the Schiff bases are shown in Figs. 5, 6 and spectral data are summarized in the experimental section. As mentioned above, isatin-Schiff bases undergo a dynamic tautomerization equilibrium between the lactam (L)- and enol (E)-tautomers in solution (Scheme 1), and exhibit peaks for both the tautomers simultaneously [26]. Thus, the methyl protons show two singlets at  $\delta$  2.18 (85%) and 2.46 (15%) ppm in HL1 {or  $\delta$  2.43 (83%) and 2.28 (17%) ppm in HL2} within *ca.* 30 min of dissolution in CDCl<sub>3</sub>, which correspond to the existences of both L- and E-tautomers simultaneously (Figs. 5, 6). The O-*H* (enol) and N-*H* (lactam) protons appear as broad signals at  $\delta$  8.24 and 8.46 ppm in HL1 (or at  $\delta$  8.41 and 8.66 ppm in HL2), respectively. The spectra further show several doublets, triplets and multiplets at the range of  $\delta$ 6.50 - 7.65 ppm, associated to the several aromatic protons for both forms (see experimental section). To study the dynamic tautomerism equilibrium between the lactam (L)- and enol (E)-forms as a function of time, we run <sup>1</sup>H NMR spectra at different time intervals of HL2 dissolution in CDCl<sub>3</sub> (Fig. 6). The results show that both the tautomers co-exit simultaneously at varying ratios with dissolution time. Thus, immediately upon dissolution (within *ca.* 30 min), the major tautomer is lactam-form (*ca.* 83%, based on peak integration value) with the minor enol-form (*ca.* 17%). The lactam-to-enol ratios (L/E) become *ca.* 60/40 within 5 h and *ca.* 54/46 within 24 h of HL2 dissolution in solution. Indeed, no more change is noted upon further standing of this solution, suggesting an equilibrium has been established with almost equal amount of both tautomers in solution. IR spectra at solid state (where solely the lactam-form exits), we assume the major tautomer to be lactam-form and the minor one to be enol-form immediately upon dissolution (i.e., within 30 min). However, <sup>1</sup>H NMR peaks assignments and percentages of the lactam- and enol-forms are made based on corresponding peaks integration values for  $CH_3/N-H$  (lactam) and O-H (enol) protons at different time intervals, respectively (Fig. 6).



**Fig. 5.** <sup>1</sup>H NMR spectrum for HL1 in CDCl<sub>3</sub> at 20 °C (L/E = Lactam-/Enol-form).





**Fig. 6.** <sup>1</sup>H NMR spectra for HL2 at different time intervals in CDCl<sub>3</sub> at 20 °C (L/E = Lactam/Enol-form).

# 3.4. Reaction of 1 with NaCN

To check the presence of the isatin-Schiff bases in paramagnetic  $[Cu(L1)_2]$  (1), we conducted a decomplexation reaction *via* reduction of Cu(II) to Cu(I) in presence of NaCN in dmso-d<sub>6</sub> solution [15,21,23]. This reaction results in the formation of diamagnetic  $[Cu^{I}(CN)_{4}]^{3-}$  and deprotonated Schiff base anion (L1<sup>-</sup>Na<sup>+</sup>) in solution, accompanies a colour change from darkbrown to light-orange (Scheme 2). <sup>1</sup>H NMR spectrum of this solution shows a singlet at  $\delta = 2.11$ ppm for the methyl protons in L1<sup>-</sup>, while no peaks for the O-*H* (enol) and/or N-*H* (lactam) protons, as evidenced in the free HL1 (Fig. 5). However, several peaks associated to the aromatic protons are found at  $\delta$  6.50 - 7.70 ppm in L1<sup>-</sup>.



Scheme 2. Reaction pathway between  $[Cu(L1)_2]$  (1) and NaCN in dmso-d<sub>6</sub>.

### 3.5. Cyclic voltammetry

Cyclic voltammograms for 1 and 2 were taken at the range of -0.8 to 0.4 V vs. Ag/AgCl at varying scan rates in acetonitrile at 25 °C, respectively (Figs. 7, S7). The forward scan shows two strong broad cathodic peaks at ca. -0.40 (Ic1) and ca. -0.57 V (Ic2) at scan rate of 0.10 Vs<sup>-1</sup>, correspond to two electrons charge transfer processes for  $[Cu^{II}(L)_2]^0/[Cu^{I}(L)_2]^-$  and  $[Cu^{I}(L)_{2}]^{-}/[Cu^{0}(L)_{2}]^{2-}$  couples (L<sup>-</sup> = deprotonated Schiff base), respectively [15,19,25,32]. On the other hand, the reverse scan shows two corresponding anodic peaks at ca. 0.03 (Ia1) and ca. -0.45 V (Ia2), due to two electrons charge transfer processes for  $[Cu^{0}(L)_{2}]^{2/}[Cu^{1}(L)_{2}]^{-}$  and  $[Cu^{I}(L)_{2}]^{-}/[Cu^{II}(L)_{2}]^{0}$  couples, respectively. A poor reductive peak on the forward scan at 0.1 to 0.3 V, in particular with higher scan rates, is due to the electrolyte [21,32]. For comparison studies, we run CV for the electrolyte (TBAP) and Schiff base (HL1) plus TBAP solution at the range of -1.0 to 2.0 V vs. Ag/AgCl at scan rates of 0.10 Vs<sup>-1</sup> in acetonitrile at 25 °C, respectively (Fig. S8). The TBAP solution shows two pairs of redox peaks (Ic1'/Ia1' and Ic2'/Ia2') at lower potential (0.5 to 1.0 V) [21,32], while the Schiff base plus TBAP solution shows extra two pairs of redox peaks (Ic1/Ia1 and Ic2/Ia2) at relatively higher potential (1.3 to 2.0 V). The results suggest that the observed redox peaks at the range of -0.05 to -0.60 V (Figs. 7, S7) are solely due to  $[Cu^{II}(L)_2]^0/[Cu^{I}(L)_2]^-$  and  $[Cu^{II}(L)_2]^{-/}[Cu^0(L)_2]^{2-}$  couples in complexes solution, while no peaks at this range in Schiff base (HL1) plus TBAP solution (Fig. S8). Thus CV results indicate two quasi-reversible one electron charge transfer processes for Cu(II)/Cu(I) and Cu(I)/Cu(0) couples, respectively as reported for related copper(II)-Schiff bases complexes [15,19,25,32]. However, analyses of voltammograms for 2 at varying scan rates demonstrate that both the cathodic and anodic peaks become more intense with shifting to higher and lower potentials, respectively with faster scan rates. Indeed, a linear relationship between the cathodic peak current ( $Ic2/\mu A$ ) and square root of scans rate ( $v^{1/2}/Vs^{-1}$ ) (Fig. 8) corresponds to a diffusion-controlled electrochemical process in acetonitrile.



**Fig. 7.** Cyclic voltammograms for **2** (0.5 mmol dm<sup>-3</sup>) containing TBAP (0.1 mol dm<sup>-3</sup>) at varying scans rate (v/Vs<sup>-1</sup>) in acetonitrile at 25 °C.



**Fig. 8.** Plot of peak current (*I*c2/ $\mu$ A) *vs.* square root of scans rate ( $v^{1/2}/Vs^{-1}$ ) for **2** (0.5 mmol dm<sup>-3</sup>) containing TBAP (0.1 mol dm<sup>-3</sup>) in acetonitrile at 25 °C.

#### 3.6. Powder XRD studies

Powder XRD patterns (Fig. 9) for the Schiff base (HL2) and its complex (2) was recorded at the range of 5–50  $^{\circ}$  (2 $\theta$ ) at ambient temperature, which correspond well defined crystalline nature with various degrees of crystallinity [33,34,35]. Comparision studies of spectral patterns show the absences of certain intense peaks at low  $2\theta$  value (<10  $^{\circ}$ ) in HL2, and the presences of several new and/or slightly shifted peaks in the complex. The results suggest coordination of the Schiff bases to the metal(II) ion, and formation of the complex with different structure (phase).



Fig. 9. Powder XRD patterns for the HL2 and 2 at ambient temperature.

### 3.7. EPR spectra and paramagnetism

X-band EPR spectrum of **2** in dmso at 120 K (Fig. 10) shows an intense broad band at high field region, having isotropic pattern due to tumbling motion of the molecules [12a,32,33,36]. There might be some peak broadening effect originated from the dipolar interactions of close paramagnetic centres. The copper(II)-complexes with one unpaired electron are essentially paramagnetic, and show the magnetic moment values,  $\mu_{eff.} = 1.52$  (**1**) and 1.60  $\mu$ B (**2**) in methanol at 20 °C [19,32,33,36c], close to the spin-magnetic moment for a single electron.



Fig. 10. X-band EPR spectrum for 2 in dmso at 120 K.

# 4. Conclusions

The *bis*[3-(*o/p*-tolylimino)indole-2-olato- $\kappa^2$ N,O]copper(II) are synthesized from 3-(*o/p*-tolylimino)indolin-2-one *via* lactam (L)- to enol (E)-tautomerism in solution. Solid state IR spectra show only the L-form, while both L- and E-forms in solution. <sup>1</sup>H NMR results reveal a dynamic tautomerization equilibrium between the L- and E-forms in solution, which changes with time. CV results demonstrate two quasi-reversible one electron charge transfer processes for Cu(II)/Cu(I) and Cu(I)/Cu(0) couples in acetonitrile, respectively. PXRD patterns correspond well define crystalline nature with various degrees of crystallinity for the ligands and complexes. X-band EPR spectrum shows an intense broad band at high field region with isotropic nature. Magnetic moment values ( $\mu_{eff.}$ ) indicate paramagnetic nature of the copper(II)-complexes with an unpaired electron. Optimized structures and excited state properties by DFT/TDDFT correspond well to the experimental results both in solution and at solid state. The results could be interesting for pharmacological and/or biological studies of the isatin-Schiff bases and their copper(II)-complexes.

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#### **Highlights**

- ➤ 3-(o/p-tolylimino)indolin-2-one (HL1 and HL2)
- Copper(II)-3-(*o*/*p*-tolylimino)indole-2-olate complexes (1 and 2)
- Lactam-Enol tautomerism in solution
- Redox potentials
- ➢ DFT/TDDFT calculations

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