

Synthesis and Characterization of Transition Metal(II) Schiff Bases Complexes Derived from 2,5-Dihalosalicylaldehyde and 4-Methyl-3-thiosemicarbazide

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The metal complexes of cobalt(II), nickel(II) copper(II) and zinc(II) with Schiff bases [HL¹⁻²] derived from 2,5-dichlorosalicylaldehyde/ 2,5-dibromosalicylaldehyde and 4-methyl-3-thiosemicarbazide were synthesized. The structure of all the compounds have been evaluated on the basis of elemental analysis, molar conductance measurements and spectroscopic studies like FT-IR, UV-visible, NMR, ESR and mass. The Schiff base ligands existed as NOS donor coordinating to metal ion through azomethine nitrogen, sulphur of thiosemicarbazide and oxygen of deprotonated phenolic group forming complexes of the type [M(L¹⁻²)₂] in 1:2 molar ratio. The spectroscopic data and physical measurement techniques suggested octahedral geometry around metal centres.

Keywords: Dibromosalicylaldehyde, Spectroscopic studies, Thiosemicarbazide, Octahedral.

INTRODUCTION

Schiff-base ligands are versatile compounds synthesized by condensation between carbonyl compounds and primary amines. Schiff-base ligands can coordinate with different transition metal ions [1-3] and stabilize in various oxidation states. Schiff-base complexes show excellent catalytic activity [4] and exhibit broad range of biological activity [5,6]. Schiff-base complexes containing Co(II), Ni(II), Cu(II) and Zn(II) have been studied for enzymatic reactions [7], thermal analysis [8], magnetic properties [9,10] and used in coordination chemistry of transition metal ions [11].

Thiosemicarbazide based Schiff bases have been widely studied since 1950 due to their tendency to bind with metal centers [12] and also due to the fact that these molecules and their complexes have been used as therapeutics and imaging agents [13]. Also, literature shows that the transition metal complexes of nitrogen-sulfur chelating agents, mainly those formed from thiosemicarbazide show variety of medicinal properties such as anticancer, antibacterial, antiviral, anti-tumour, antifungal, antimalarial *etc.* [14-18]. Thiosemicarbazides has also been used due to their variable applications in industry and analytical chemistry [19]. The molecules containing a chromophore based on the thiosemicarbazide moiety

has imported in increasing the light fastness [20]. With this view, we are reporting here the synthesis and characterization of Co(II), Ni(II), Cu(II) and Zn(II) complexes of Schiff base derived from 4-methyl-3-thiosemicarbazide and dihalosalicylaldehydes.

EXPERIMENTAL

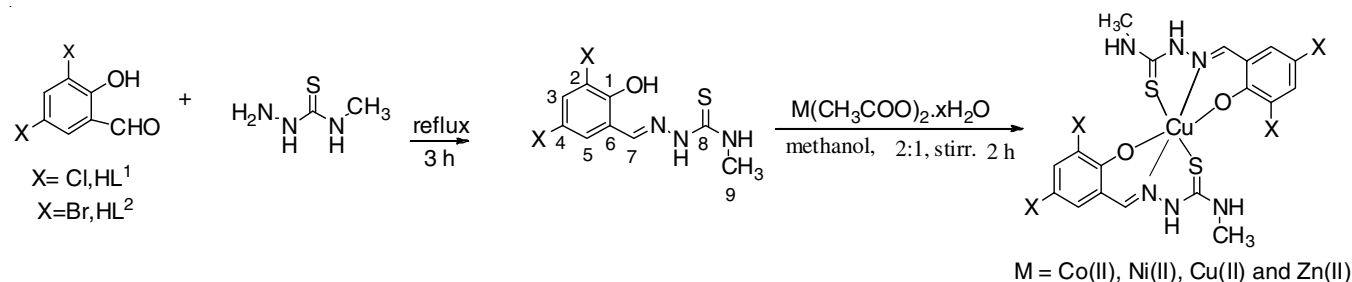
All chemicals were of analytical reagent grade having high purity, purchased from Sigma Aldrich and solvents methanol, ethyl acetate, chloroform, DMSO, DMF and diethyl ether [21]. Spectrograde solvents were used for spectral and conductance measurements. The CHN elemental analysis was performed using a Perkin-Elmer CHN 2400 elemental analyzer. Molar conductance measurements of compounds with concentration 10⁻³ mol L⁻¹ in DMSO were carried out using a Jenway 4010 conductivity meter. ¹H NMR spectra were measured using a Bruker 400 MHz spectrometer with DMSO as solvent; chemical shifts are given in parts per million (ppm) relative to tetramethylsilane. Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometer. IR spectra (4000-400 cm⁻¹) were recorded as KBr pellets on a Bruker FT-IR spectrophotometer. ESR spectra of Cu(II) complexes were carried on a Varian E112X band spectrometer.

Synthesis of the Schiff base ligands: The Schiff bases (HL^1) and (HL^2) were formed by condensation of 4-methyl-3-thiosemicarbazide (0.012 g, 1 mmol) with 2,5-dichlorosalicylaldehyde (0.019 g, 1 mmol) and 2,5-dibromosalicylaldehyde (0.027 g, 1 mmol) in methanol solution. The reaction mixture was refluxed for 3 h and the solution was filtered. The yellow precipitate was washed several times with hot methanol and dried under vacuum and all organic impurities were then extracted by washing with diethyl ether. The purity of the ligands was confirmed by thin layer chromatography and the compositions of the ligands were confirmed by elemental analysis and spectroscopic techniques.

Synthesis of metal complexes: The metal complexes were prepared by adding Schiff base (HL^1/HL^2 , 0.622/0.798, 2 mmol) to the appropriate metal salt, $Cu(CH_3COO)_2 \cdot 3H_2O$ (0.198 g, 1.0 mmol), $Ni(CH_3COO)_2 \cdot 7H_2O$ (0.240 g, 1.0 mmol) $Co(CH_3COO)_2 \cdot 4H_2O$ (0.242 g, 1.0 mmol) and $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.201 g, 1.0 mmol) in 20 mL aqueous methanol in 2:1 molar ratio. The reaction mixture was stirred in and heated on a hotplate at 60 °C for 100 min. The solid precipitate was obtained and volume of the obtained solution was reduced to one half by evaporation and after this the coloured complexes formed were purified by washing with hot ethanol and diethyl ether and finally dried under vacuum (**Scheme-I**).

RESULTS AND DISCUSSION

Condensation of the 2,5-dihalosalicylaldehyde with 4-methyl-3-thiosemicarbazide readily gives the Schiff base ligands which were identified by UV, IR, NMR, ESR and mass spectra. Six-coordinate metal complexes were obtained from 2:1 molar ratio of Schiff base ligand with $Cu(CH_3COO)_2 \cdot 3H_2O$, $Ni(CH_3COO)_2 \cdot 7H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$.



Scheme-I: Synthesis of ligands and their metal complexes

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF COMPOUNDS

Compd.	m.f.	m.w.	Colour	Yield (%)	Elemental analysis (%): Calcd. (found)				$\Omega \times 10^{-3}$
					C	H	N	M	
HL^1	$C_9H_9N_3OSCl_2$	278.16	Yellow	75	38.86 (38.78)	3.26 (3.17)	15.11 (15.07)	–	13
$Co(L^1)_2$	$C_{18}H_{16}N_6O_2S_2Cl_4Co$	613.33	Red brown	73	35.25 (35.17)	2.63 (2.57)	13.70 (13.65)	9.61 (9.55)	16
$Ni(L^1)_2$	$C_{18}H_{16}N_6O_2S_2Cl_4Ni$	615.15	Green	64	35.27 (35.19)	2.63 (2.57)	13.56 (13.48)	9.57 (9.52)	18
$Cu(L^1)_2$	$C_{18}H_{16}N_6O_2S_2Cl_4Cu$	618.80	Brown	78	34.99 (35.92)	2.61 (2.55)	13.60 (13.53)	10.29 (10.22)	14
$Zn(L^1)_2$	$C_{18}H_{16}N_6O_2S_2Cl_4Zn$	620.34	White	76	34.89 (35.82)	2.60 (2.54)	13.56 (13.49)	10.55 (10.49)	19
HL^2	$C_9H_9N_3OSBr_2$	367.00	Yellow	75	29.45 (29.38)	2.47 (4.87)	11.45 (4.87)	–	11
$Co(L^2)_2$	$C_{18}H_{16}N_6O_2S_2Br_4Co$	791.33	Red brown	73	27.33 (27.21)	2.04 (2.01)	10.62 (10.55)	7.45 (7.38)	15
$Ni(L^2)_2$	$C_{18}H_{16}N_6O_2S_2Br_4Ni$	793.15	Green	64	27.33 (27.23)	2.04 (1.97)	10.62 (10.54)	7.42 (7.35)	12
$Cu(L^2)_2$	$C_{18}H_{16}N_6O_2S_2Br_4Cu$	795.00	Brown	78	27.17 (27.11)	2.03 (1.96)	10.56 (10.51)	7.99 (7.92)	14
$Zn(L^2)_2$	$C_{18}H_{16}N_6O_2S_2Br_4Zn$	796.34	White	76	27.11 (27.07)	2.02 (1.95)	10.54 (10.49)	8.20 (8.13)	17

$\Omega \times 10^{-3}$ = molar conductivity ($Ohm^{-1} cm^2 mol^{-1}$)

$2H_2O$. The Schiff-base ligands and their metal complexes are stable at room temperature in solid state and these compounds are generally soluble in DMF and DMSO. The colour, yield, elemental analysis and molar conductance value of all the compounds are presented in Table-1. The analytical data are in agreement with the proposed stoichiometry of the complexes. The metal:ligand ratio in the complexes was found to be 1:2. The molar conductivity values for all the compounds in DMSO was in the range 11-19 $ohm^{-1} cm^2 mol^{-1}$, suggesting non-electrolyte nature ligand and complexes (Table-1) [22]. IR, NMR, UV-visible and ESR data indicate the complexes of the formation of tridentate ligands.

IR spectra: The IR spectra of compounds were recorded in the range of 4000-400 cm^{-1} and band assignments are reported in Table-2. The most characteristic vibrations are selected by comparing the IR spectra of the ligands with those of their metal complexes. The strong bands at 1595-1585 cm^{-1} for free ligand is due to the azomethine vibration mode, $\nu(C=N)$ which gets shifted to the higher frequency in the range of 1630-1608 cm^{-1} on complexation to metal atom. Ligands display band at 3250-3238 cm^{-1} which are assigned to OH vibration modes and this bands gets disappeared after complexation [23]. The sharp and distinct bands present in the far infrared spectra of all complexes at 541-522 cm^{-1} and 457-427 cm^{-1} , 393-365 cm^{-1} provide a compelling evidence for the presence of metal-oxygen, metal-nitrogen and metal-sulphur bond, respectively [24].

NMR spectra: 1H NMR spectra of Schiff bases and their complexes were recorded in $CDCl_3$ and DMSO. All chemical shifts were reported in parts per million relative to TMS as internal standard (Table-3). The free ligands showed singlet at δ 8.03-8.05 ppm due to azomethine proton which gets shifted

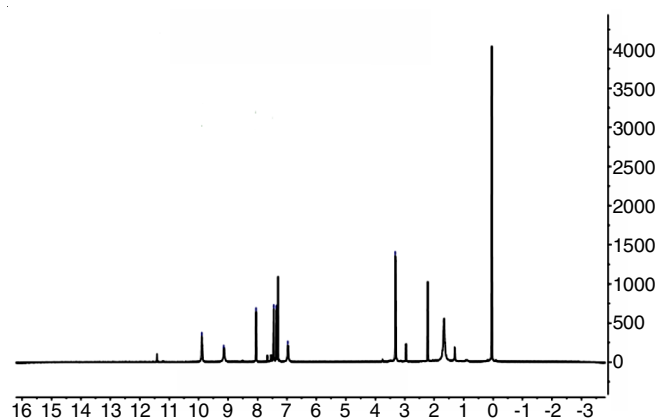
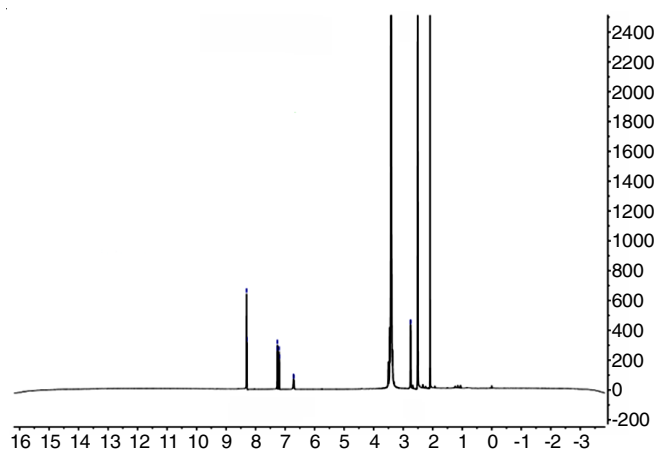
TABLE-2
 IR SPECTRAL DATA (cm⁻¹) OF LIGANDS AND THEIR METAL COMPLEXES

Compound	$\nu(\text{-OH})$	$\nu(\text{-C=N})$	$\nu(\text{-C=S})$	$\nu(\text{-NH})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$	$\nu(\text{M-S})$
HL ¹	3250	1585	805	3220	—	—	—
Co(L ¹) ₂	—	1630	845	3265	457	541	393
Ni(L ¹) ₂	—	1608	827	3275	431	525	375
Cu(L ¹) ₂	—	1618	823	3271	429	527	371
Zn(L ¹) ₂	—	1616	838	3258	441	535	365
HL ²	3238	1595	810	3260	—	—	—
Co(L ²) ₂	—	1640	848	3323	452	538	397
Ni(L ²) ₂	—	1618	831	3338	437	522	383
Cu(L ²) ₂	—	1627	828	3319	427	525	375
Zn(L ²) ₂	—	1625	841	3327	439	531	370

 TABLE-3
¹H NMR AND ¹³C NMR SPECTRAL CHARACTERISTICS (δ , ppm) OF SCHIFF BASES AND ITS ZINC METAL COMPLEXES

¹ H NMR	(O-H), (N-NH), (R-NH)	-CH=N- (azomethine)	Aromatic	-CH ₃ -
HL ¹	9.87 (s, 1H, -OH), 9.12 (s, 1H, -N-NH) 6.95 (s, 1H, R-NH)	8.03 (s, 1H, -CH=N-)	7.43 (d, 1H, C ₃ , Ar-H), 7.34 (d, 1H, C ₅ , Ar-H)	3.30 (d, 3H)
HL ²	9.89 (s, 1H, -OH), 9.15 (s, 1H, -N-NH) 6.97 (s, 1H R-NH)	8.05 (s, 1H, -CH=N-)	7.45 (d, 1H, C ₃ Ar-H), 7.36 (d, 1H, C ₅ , Ar-H)	3.32 (d, 3H)
Zn(L ¹) ₂	8.31 (s, 1H, -N-NH), 6.72 (s, 1H R-NH)	8.29 (s, 1H, -CH=N-)	7.27 (d, 1H, C ₃ , Ar-H), 7.20 (d, 1H, C ₅ , Ar-H)	2.75 (d, 3H)
Zn(L ²) ₂	8.33 (s, 1H, N-NH), 6.74 (s, 1H -NH)	8.31 (s, 1H, CH=N-)	7.28 (d, 1H, C ₃ Ar-H), 7.21 (d, 1H, C ₅ , Ar-H)	2.78 (d, 3H)
¹³ C NMR	(C=S)	-CH=N- (azomethine)	Aromatic	-CH ₃ - (methyl)
HL ¹	178.02	152.58	138.58 (-C-OH, C ₁), 135.40 (-CH-, C ₃), 129.17 (-CH-, C ₅), 125.62 (C ₆), 113.42 (CBr, C ₄), 112.08 (-C-Br, C ₂)	30.38
HL ²	178.07	155.43	138.22 (-C-OH, C ₁), 135.42 (-CH-, C ₃), 129.19 (-CH-, C ₅), 125.14, (-C-, C ₆), 113.42 (-C-Br, C ₄), 112.08 (-C-Br, C ₂)	30.33
Zn(L ¹) ₂	178.42	152.21	138.22 (-C-OH, C ₁), 135.42 (-CH-, C ₃), 129.19 (-CH, C ₅), 125.14 (-C-, C ₆), 113.82 (-C-, Br, C ₄), 112.08 (-C-Br, C ₂)	30.98
Zn(L ²) ₂	178.53	155.32	138.22 (-C-OH, C ₁), 135.42 (CH, C ₃), 129.19 (-CH-, C ₅), 125.14 (-C-, C ₆), 113.42 (-C-Br, C ₄), 112.38 (-C-Br, C ₂)	30.87

on complexation to metal atom (Fig. 1). The phenolic-OH proton showed singlet at δ 9.87-9.89 ppm which gets disappeared in the spectra of zinc complexes suggested coordination of phenolic-OH group to metal ion (Fig. 2). The (N-NH) proton appeared at δ 9.15-9.12 ppm and δ 6.97-6.95 ppm (-NH-R) which also gets shifted when complexes are formed. The aromatic proton appeared in range of δ 7.45-7.34 ppm which also gets shifted suggested coordination.

Fig. 1. ¹H NMR spectra of Schiff base ligand (HL²)Fig. 2. ¹H NMR spectra of zinc metal complex (Zn(L²)₂)

In ¹³C NMR of Zn complexes shifting of signals of azomethine carbon (-CH=N-) of Schiff base ligands from δ 152.58 to 152.51 ppm (HL¹) and δ 155.43 to δ 155.32 ppm (HL²), signal of carbon attached to thiocarbonyl group shift from δ 178.07-178.02 ppm to δ 178.53-178.42 ppm. When coordinated to Zn(II) ions the other carbon atoms were observed in the range of δ 138.58-112.08 and remains almost unaltered on complexation.

Electronic spectra: The electronic spectra of the complexes were recorded in DMSO solution (Table-4). Electronic spectra of Co(II) complexes are characterized by three bands in the regions 25431-25483 cm^{-1} , 17645-17704 cm^{-1} , 9345-9412 cm^{-1} and these spectral bands are due to $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$, $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}(\text{F})$, $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}(\text{F})$ transitions. Electronic spectra of Ni(II) complexes shows three electronic spectral bands in the range of 28245-28263 cm^{-1} , 19432-19535 cm^{-1} and 11567-11627 cm^{-1} . These bands are due to $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{P})$ (ν_1), $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{1g}(\text{F})$ (ν_2), $^3\text{A}_{2g}(\text{F}) \rightarrow ^3\text{T}_{2g}(\text{F})$ (ν_3) transitions, respectively. The position of bands indicates that these complexes have octahedral geometry. In copper complexes one band at 11653-11697 cm^{-1} is due to $d-d$ transitions and the spectrum also displayed a broad band in the range 22823-22908 cm^{-1} . This band corresponded to the transition $^2\text{B}_{1g} \rightarrow 2\text{A}_{1g}$. The electronic spectra of the zinc(II) complexes showed one high-intensity band at 38453 -38496 cm^{-1} is due to LMCT transition and a band at 28830-28867 cm^{-1} is due to $\pi \rightarrow \pi^*$ transitions. So from the magnetic moment value in Table-4, electronic transitions show that all the complexes are octahedral in nature.

Molar conductivities: Conductivity measurement in non-aqueous solutions is used for testing the degree of ionization of the complexes. The conductivity data reported for 10^{-3} M solution for these complexes are given in Table-1. The conductivity data shows that the complexes are non-electrolytes.

ESR spectra: The X-band EPR spectrum of the Cu(II) complexes were recorded in the solid state at room temperature. The ESR spectral studies of Cu(II) complexes gives information about the distribution of unpaired electron and nature of bonding between the metal ion and its ligands. In the present study, ESR spectra of $[\text{Cu}(\text{L}^1)_2]$ had values $g_{\parallel} = 2.83$; $g_{\perp} = 2.43$ and $[\text{Cu}(\text{L}^2)_2]$ (Fig. 3) had values $g_{\parallel} = 2.69$; $g = 2.33$ and the trend $g_{\parallel} > g_{\perp}$ observed indicated that the unpaired electrons are most likely to be in $d_{x^2-y^2}$ orbital. For complex, the observed g values are $g_{\parallel} > g_{\perp} > 2.0023$ which shows that the complexes has an octahedral geometry and the ground state is $^2\text{B}_{1g}$. In the axial spectra, the g -values are related with the exchange interaction coupling constant G by the expression

$$G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$$

According to Hathaway and Underhill [25] if G value is larger than four, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. In the present $\text{Cu}(\text{L}^1)_2$ complex G value 2.00 and

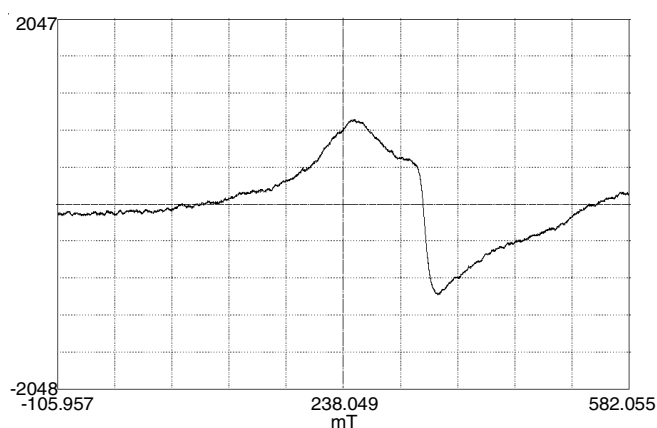


Fig. 3. ESR spectra of $\text{Cu}(\text{L}^1)_2$ complex at room temperature

$\text{Cu}(\text{L}^2)_2$ complex G value is 2.0057, which shows exchange interaction in solid Cu(II) complexes.

Mass spectra: The mass spectra of Schiff base and their complexes were recorded and are reported in Table-1. The mass spectrum of HL^1 shows a well-defined molecular ion peak at m/z 278.16, which matches with a formula weight of Schiff base ligand. Likewise its mass spectrum of $\text{Ni}(\text{L}^1)_2$ complex shows a molecular ion peak at m/z 615.12.

Conclusion

The metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) containing tridentate ONS chelating ligands obtained from substituted salicylaldehyde with thiosemicarbazide have been prepared and characterized by elemental analysis, molar conductance, spectroscopic studies (infrared, mass, NMR and ESR). Under experimental conditions employed, only 1:2 (M:L) complexes have been found. Characterization shows that complexes are hexadentate in nature by coordinating in oxygen of phenolic group, nitrogen of azomethine group and sulphur of thiocarbonyl group to metal ions with octahedral geometry.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-4
ELECTRONIC ABSORPTION SPECTRAL DATA AND MAGNETIC MOMENT OF COMPLEXES

Ligand/Complex	Absorption (cm^{-1})	Band assignment	μ_{eff} (BM) (HL^1 , HL^2)	Geometry
$[\text{HL}^1, \text{HL}^2]$	30845, 31645 29347, 29735	$\pi \rightarrow \pi^*$ transitions $n \rightarrow \pi^*$ transitions	—	—
$\text{Co}(\text{L}^1)_2$, $\text{Co}(\text{L}^2)_2$	25431, 35483 17645, 17704 9345, 9415	$\pi \rightarrow \pi^*$ transitions $n \rightarrow \pi^*$ transitions $d-d$ transitions	5.18, 5.88	Octahedral
$\text{Ni}(\text{L}^1)_2$, $\text{Ni}(\text{L}^2)_2$	28245, 28283 19432, 19539 11567, 11627	$\pi \rightarrow \pi^*$ transitions $n \rightarrow \pi^*$ transitions $d-d$ transitions	3.73, 3.87	Octahedral
$\text{Cu}(\text{L}^1)_2$, $\text{Cu}(\text{L}^2)_2$	22823, 22908 11653, 11793	$n \rightarrow \pi^*$ transitions $d-d$ transitions	1.79, 1.83	Octahedral
$\text{Zn}(\text{L}^1)_2$, $\text{Zn}(\text{L}^2)_2$	28830, 28867 38456, 38496	$\pi \rightarrow \pi^*$ transitions LMCT	Diamagnetic	Octahedral

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