Synthesis, Characterization and Antimicrobial Activity of Cu(II), Co(II) and Ni(II) Complexes with O, N, and S Donor Ligands

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Abstract: The complexes of the type ML_2 [where M = Cu(II), Co(II), and Ni(II)] L = 1-phenyl-1-ene-3-(2-hydroxyphenyl)-prop-2-ene with 3- substituted-5-mercapto-4-amino-1,2,4-triazoles. Schiff base ligands have been prepared by reacting 3-(2-hydroxyphenyl)-1-phenylprop-2-en-1-one and 3-phenyl/pyridyl-4-amino-5-mercapto-1,2,4-triazoles in an alcoholic medium. The complexes are non-electrolytes in DMF. The resulting complexes were characterized by elemental analysis, magnetic measurements, conductivity measurements and spectral studies. The Schiff base acts as a tridentate dibasic and coordinating through the deprotonated oxygen, thioenolic sulphur and azomethine nitrogen atoms. It is found that Cu(II), Co(II), and Ni(II) complexes exhibited octahedral geometry. The antimicrobial activities of ligands and its complexes were screened by cup plate method.

Keywords: Chalcones, Triazoles, Metal complexes, Spectral, Magnetic moment and Antimicrobial activity

Introduction

There is great interest in synthesis and characterization of ligands which contain O, N, S-sequence and their metal complexes. Chalcones were synthesized by the condensation of acetophenones with aromatic aldehyde in the presence of acidic¹ and basic² media. Chalcones were found to be pharmacologically and physiologically active³. Chalcone derivatives are associated with some important biological activities such as antitubercular, anthelmintic⁴, fungicidal⁵, antitumor⁶ and antibacterial activity⁷. The presence of a reactive α,β unsaturated keto in chalcones is found to be responsible for their antimicrobial activity. The tridentate Schiff bases with heterocyclic amines containing O, N, S donor sequence have been tried for complexation with transition metals⁸. The search for a new sequence has resulted by the condensation of chalcone and triazoles. The neutral tridentates are shown to form octahedral complexes with transition metal, where two ligands encompass the metal ion in an octahedral array⁹. In this paper we wish to report the synthesis and characterization of

Cu(II), Co(II) and Ni(II) complexes with the Schiff bases obtained from the condensation of 1-phenyl-1-ene-3-(2-hydroxyphenyl)-prop-2-ene with 3-Substituted-5-mercapto-4-amino-1,2,4-triazoles resulted as shown in Figure 1.

R = Phenyl, pyridine

Figure 1. 2-[(1*E*,3*Z*)-3-[(5-mercapto-3-Phenyl/Pyridyl-4*H*-1,2,4-triazol-4-yl)imino]-3-phenylprop-1-en-1-yl]phenol.

Experimental

All the chemicals are reagent grade. Solvents were dried and distilled before use according to standard procedures¹⁰. The metal salts used were in their hydrated form.

Synthesis of ligands

One mole of chalcone in 30 mL of ethanol was taken in round bottom flask, to this one mole of 3-phenyl/pyridyl- 5-mercapto-4-amino 1, 2, 4 triazoles were added. The reaction mixture was refluxed for 6-7 hours, evaporated the solvent on water bath and solid separated was collected, the product was washed with absolute alcohol, the product was crystallized from rectified spirit to obtain yellow coloured crystals.

Preparation of complex

Warm ethanolic solutions of metal(II)chloride (0.01M) were added to ethanolic solution of ligands H_2L^1 and H_2L^2 (0.02M) in about 30 mL of ethanol. The resulting solutions were refluxed for about 6 hours. The complex thus formed was filtered and washed with alcohol and dried in vacuum over fused $CaCl_2$. The metal estimation was carried out by standard methods, nitrogen by Kjeldahl method and sulphur¹¹ in the complexes estimated as $BaSO_4$. The CHN analyses were carried out by STIC Cochin. The conductance was measured in DMF and DMSO solvent on an Elico CM-82 conductivity bridge. The magnetic susceptibility measurements at room temperature were made on Gouy balance at room temperature using $HgCo(NCS)_4$ as calibrant. The IR spectra of ligand and its complexes were recorded on a Perkin-Elmer instrument in KBr pellets in the range of $4000-350\text{ cm}^{-1}$. UV-Visible spectra were recorded on an Elico SL 164 double beam UV-Visible spectrometer in the range 200-1200nm. ¹HNMR spectra were recorded on an AMX-400 NMR spectrometer using TMS as internal standard and DMSO as a solvent. Electron spin resonance spectra complexes in polycrystalline state were recorded on Varian E-4x-band ESR spectrometer using DPPH free radical as 'g' marker ($g=2.0027$) at room temperature.

Results and Discussion

The elemental analysis shown in Table 1 indicates that, all the metal complexes have 1:2 stoichiometry and are dark colored amorphous substances, soluble in DMF and DMSO.

The molar conductance values obtained for these complexes at the concentration of 10^{-3} M are in the range of $20\text{--}30\text{ ohm}^{-1}\text{ mol}^{-1}\text{ cm}^2$. These values are too low to account for any dissociation of the complexes in DMF. Hence these complexes can be regarded as non-electrolytes.

Table 1. Physical, analytical, magnetic susceptibility and molar conductance data of the ligand H_2L^1 and H_2L^2 and its complexes

Ligand / Complex	Empirical Formula	Mol. Wt.	M.P. $^{\circ}\text{C}$	Yield %	M	C	H	N	S	μ_{eff} .M.	Molar Conductance $\Lambda_m^{\text{Ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}}$
H_2L^1	$\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2\text{S}$	398.12	180	70		69.31 (69.32)	4.15 (4.55)	14.01 (14.00)	8.06 (8.05)	–	–
$\text{Cu}(\text{L}^1)_2$	$\text{C}_{46}\text{H}_{32}\text{N}_8\text{O}_2\text{CuS}_2$	855.14	295	70	7.41 (7.42)	64.50 (64.51)	3.41 (3.77)	13.10 (13.08)	7.44 (7.41)	1.6	17.15
$\text{Co}(\text{L}^1)_2$	$\text{C}_{46}\text{H}_{32}\text{N}_8\text{O}_2\text{CoS}_2$	851.14	280	65	7.00 (6.98)	64.84 (64.86)	3.42 (3.79)	13.17 (13.15)	7.54 (7.53)	5.05	17.38
$\text{Ni}(\text{L}^1)_2$	$\text{C}_{46}\text{H}_{32}\text{N}_8\text{O}_2\text{NiS}_2$	850.14	275	68	6.90 (6.89)	64.85 (64.88)	3.72 (3.79)	13.15 (13.16)	7.51 (7.53)	2.8	19.89
H_2L^2	$\text{C}_{22}\text{H}_{17}\text{N}_4\text{O}_2\text{S}$	399.46	242	60	–	67.52 (67.54)	5.92 (5.89)	15.73 (15.75)	7.25 (7.21)	–	15.13
$\text{Cu}(\text{L}^2)_2$	$\text{C}_{44}\text{H}_{30}\text{N}_{10}\text{O}_2\text{CuS}_2$	857.17	265	65	7.41 (7.42)	53.41 (61.56)	3.56 (3.52)	16.35 (16.32)	6.49 (7.47)	1.85	18.26
$\text{Co}(\text{L}^2)_2$	$\text{C}_{44}\text{H}_{30}\text{N}_{10}\text{O}_2\text{CoS}_2$	853.10	272	75	6.93 (6.92)	61.90 (61.89)	3.53 (3.54)	16.41 (16.40)	7.52 (7.51)	5.14	19.00
$\text{Ni}(\text{L}^2)_2$	$\text{C}_{44}\text{H}_{30}\text{N}_{10}\text{O}_2\text{NiS}_2$	852.10	293	70	6.866 (6.88)	61.90 (61.92)	3.52 (3.54)	16.43 (16.41)	14.01 (7.51)	3.20	11.10

Magnetic moment

The magnetic moment values for $\text{Cu}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ complexes of the ligands H_2L^1 and H_2L^2 are shown in Table 1. $\text{Co}(\text{II})$ complexes are in the range of 5.05–5.14 BM indicating that the $\text{Co}(\text{II})$ complexes are typically high spin complexes and having octahedral structure. The $\text{Ni}(\text{II})$ complexes exhibit the magnetic moment values in the range 2.8–3.2 BM, indicating octahedral co-ordination of the ligands around $\text{Ni}(\text{II})$ ion. The $\text{Cu}(\text{II})$ complexes exhibit magnetic moment in the range of 1.61–1.85 BM suggestive of distorted octahedral nature for these complexes¹².

Electronic spectra

The electronic spectral data of $\text{Cu}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ complexes of the ligands H_2L^1 and H_2L^2 were recorded in DMF as shown in Table 2. The electronic spectra of $\text{Co}(\text{II})$ complexes exhibit bands in the region of $8895\text{--}21000\text{ cm}^{-1}$ and $15000\text{--}18000\text{ cm}^{-1}$ are attributed to ${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ (ν_1) and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{p})$ (ν_3) transitions respectively. The bands due to the ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ (ν_2) transition could not be observed because of its very low intensity. However the position of the ν_2 band has been computed (15549 cm^{-1}) by the equation $\nu_2 = \nu_1 + 10\text{Dq}$. The $\text{Co}(\text{II})$ complex under present investigation possesses interelectronic repulsion parameter (B) 749 cm^{-1} . The Racah parameter (B) is less than free ion value (971) suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio (β) for the present $\text{Co}(\text{II})$ complex (0.77). This is less than one, suggesting partial covalency in the metal ligand bond. The values Dq , β %, LFSE and ν_2/ν_1 (Table 2) suggest the octahedral geometry for $\text{Co}(\text{II})$ complex.^{13,14} These observations suggest that $\text{Co}(\text{II})$ complexes have octahedral geometry. $\text{Ni}(\text{II})$ complexes exhibit three bands at $8990\text{--}13810\text{ cm}^{-1}$, $16088\text{--}16335\text{ cm}^{-1}$ and $24964\text{--}25210\text{ cm}^{-1}$ are

assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^4A_{2g}(F) \rightarrow {}^3T_{1g}(p)$ (ν_3) transitions respectively are in conformity with the octahedral geometry for the Ni(II) ion. The Table 2 shows the ligand field parameter such as Dq, B', β , $\beta\%$ and LFSE have been calculated by using Band-fitting equation given by Underhill and Billing¹⁵. Racah parameter B' is less than the free ion value of 1040 cm^{-1} indicating the covalent character of the complex. The ratio ν_2/ν_1 and $\beta\%$ are further support the octahedral geometry around the Ni(II) ion¹⁶. The Cu(II) complexes exhibits three bands in the region 11330 cm^{-1} (ν_1), 17300 cm^{-1} (ν_2) and 19500-21000 cm^{-1} (ν_3) are of equal energy and giving rise to single broad band which may be assigned to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)$, ${}^2B_{1g} \rightarrow {}^2B_{2g}(\nu_2)$, ${}^2B_{1g} \rightarrow {}^2E_g(\nu_3)$ respectively. The broadness of the band is due to the ligand field and the John-Teller effect¹⁷. These observations favor the octahedral geometry for the Cu(II) ion.

Table 2. Electronic spectral data and ligand field parameters of Cu(II), Co(II) and Ni(II) complexes

Complexes	ν_1	ν_2	ν_3	Dq (cm^{-1})	B'	β	$\beta\%$	ν_2/ν_1	ν_3/ν_2	LFSE kcalmol^{-1}
Cu (L^1) ₂	-	17300	21000	1413	-	-	-	-	-	24.50
Co (L^1) ₂	8892	15439	20085	1002	749	0.778	23.03	1.7	2.1	17.17
Ni (L^1) ₂	13810	15151	25316	899	865	0.820	18.00	1.4	1.8	30.82

Infrared spectra

The important infrared frequencies exhibited by the ligands H_2L^1 and H_2L^2 and its complexes are given in Table 3. The ligand molecule exists in both thiol and thione forms due to tautomerism. A medium intensity band around 2560 cm^{-1} due to $\nu(\text{S-H})$ indicates the thiol form of the ligand. A comparison of IR spectra of ligand with those of complexes is based on earlier studies of similar ligand¹⁸. The ligand molecule shows a band at 700-820 due to $\nu(\text{C=S})$. The coordination *via* thioketo sulphur atom causes the decrease in frequency of the $\nu(\text{C=S})$. The complexes show a new band at 650-700 cm^{-1} due to conversion of $\nu\text{C=S}$ into C-S- band indicates the thione $\leftrightarrow$ thiole tautomerism followed by deprotonation of thiol group and consequent coordination of sulphur atom^{19, 20} and is indicated by absence of band at 2560 (due to SH) in the spectra of complexes. The infrared spectra of ligands exhibit high intensity band around 1612 cm^{-1} is due to $\nu(\text{C=N})$ and the band around 3450 cm^{-1} due to phenolic OH. In the complexes, the low frequency shift (15-20 cm^{-1}) are observed around 1594 cm^{-1} are due to $\nu(\text{C=N})$ is suggestive of coordination through nitrogen of the azomethine group²¹ to the metal(II) Chlorides. The band around 3450 cm^{-1} due to phenolic OH, which is observed in ligands, disappears in complexes, this indicates the ligands co-ordinate to the metal ion through phenolic oxygen atom²¹ of OH group *via* deprotonation. The appearance of three new bands 550-520 cm^{-1} , 450-420 cm^{-1} , 380-415 cm^{-1} are due to M-N, M-S and M-O bonds respectively.

¹H NMR spectra

The ¹H NMR spectrums of ligands H_2L^1 and H_2L^2 and its complexes were recorded in DMSO d_6 in the range 0-15 δ (ppm). The multiplets were observed around δ 6.9-8.6 (m, 14, Ar-H) are due to phenyl protons. The protons due to CH=CH are observed around δ 7.4-7.8 (d 2H). In the ligand H_2L^2 Signals due to pyridine ring protons occurs as multiplets between δ 8.03-9.10 (m, 4H Pyridine-H). A proton due to -OH group at 2-position of salicylaldehyde ring has resonated as a singlet at δ 11.20 and δ 11.34 (s, 1H, OH) respectively. Signals in the range of δ 9.6 and 9.5 (s, 1H, SH) are due to SH protons¹⁸. In the ¹H NMR spectrum of Cd (L^1) and Zn (L^2) complexes, the OH moiety of salicylaldehyde and SH which was observed in the ligands disappears in case of complexes indicating the involvement of phenolic oxygen¹⁸ and sulphur in the coordination *via* deprotonation.

Table 3. Characteristic IR bands (cm^{-1}) of the ligand H_2L^1 & H_2L^2 and its complexes

Ligand/ Complexes	ν_{OH}	ν_{SH}	$\nu_{\text{C=S}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-S}}$
H_2L^1	3450	2560	780	1612	1255	-	-	-
$\text{Cu}(\text{L}^1)_2$	-	-	720	1560	1258	380	527	420
$\text{Co}(\text{L}^1)_2$	-	-	732	1594	1262	385	523	427
$\text{Ni}(\text{L}^1)_2$	-	-	738	1583	1267	389	529	432
H_2L^2	3360	2570	770	1610	1260	-	-	-
$\text{Cu}(\text{L}^2)_2$	-	-	726	1570	1272	392	535	439
$\text{Co}(\text{L}^2)_2$	-	-	729	1597	1278	395	542	445
$\text{Ni}(\text{L}^2)_2$	-	-	720	1567	1285	415	555	450

ESR spectra

The ESR spectra of the polycrystalline sample of the complexes were recorded at room temperature (Table 4). The observed value for the Cu(II) complex for the ligand H_1L^1 are $g_{\parallel} = 2.22$, $g_{\perp} = 2.05$ and $G = 4.4$, while for H_2L^2 $g_{\parallel} = 2.23$, $g_{\perp} = 2.05$ and $G = 4.6$. The anisotropic G values have been calculated by Kneubuhl's method²². $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$ which measures the exchange interaction between copper(II) centers. According to Hathaway²³ if the G value is greater than 4, the exchange interaction is negligible, while a value of less than 4 indicates a considerable exchange interaction in the complexes. As $G = 4.4$ and 4.6 for the present complexes indicates that there is no spin exchange interaction in the copper complexes and hence distorted octahedral geometry proposed for the Cu(II) complex.

Table 4. ESR data of the Cu (II) complex of the ligands H_2L^1 and H_2L^2

Complexes	ESR spectral data			
	$g_{\perp}$	$g_{\parallel}$	g_{av}	G
$\text{Cu}(\text{L}^1)_2$	2.22	2.05	2.053	4.4
$\text{Cu}(\text{L}^2)_2$	2.23	2.04	2.054	4.6

Antimicrobial activity

The biological and medicinal potency of coordination compounds has been established by their antitumor, antiviral and antimalarial activities. This characteristic property has been related to the ability of the metal ion to form complexes²⁴ with ligand containing sulfur, nitrogen and oxygen donor atoms. The synthesized ligands and its complexes were screened for their antibacterial activity²⁵ against *E.coli* and *S.aureus* and antifungal activity against²⁶ *A.niger* and *A.flavous* at $100 \mu\text{g}/0.1 \text{ cm}^3$ concentration. The standard drugs streptomycin and chlotrimazole were also tested for their antibacterial and antifungal activity at the same concentration under the conditions similar to that of the test compounds concentration. The zones of inhibitions of the antimicrobial activity have been presented in Table 5. The results of antibacterial activity of ligands and its complexes Cu(II), Co(II) and Ni(II) shows weak activity against *E.coli* and *S.aureus* when compared with standard streptomycin. The antifungal activity results revealed that the ligands and its Cu(II), Co(II) and Ni(II), complexes have exhibited weak to good activity against *A.niger* and *A.flavous*. The ligand and its Cu(II) and Co(II) complexes shows weak activity when compared to the standard drug chlotrimazole.

Table 5. Antimicrobial activity of the ligands H_2L^1 & H_2L^2 and its complexes

Compound	Antibacterial Activity of zone of inhibition, mm		Antifungal Activity of zone of inhibition, mm	
	<i>E. coli</i>	<i>S. aureus</i>	<i>A. niger</i>	<i>A. falvours</i>
Ligand H_2L^1	14	14	12	13
Cu (L^1) ₂	17	13	13	12
Co (L^1) ₂	15	12	11	14
Ni (L^1) ₂	16	11	18	17
Ligand H_2L^2	15	12	13	15
Cu (L^1) ₂	18	16	16	14
Co (L^1) ₂	17	12	12	18
Ni (L^1) ₂	12	13	15	16
Streptomycin	24	21	-	-
Chlorometazole	-	-	24	23
DMF (Control)	0	0	0	0
Bore size	08	08	08	08

Conclusion

The elemental analysis, magnetic susceptibility, electronic, IR, 1H NMR and ESR spectral observations suggest the octahedral geometry for the Cu(II), Co(II) and Ni(II) complexes and exhibit coordination number six.

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