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COPPER COMPLEXES OF NOVEL ARYL AZO SCHIFF BASES: SYNTHESIS, SPECTRAL, THERMAL AND FUNGICIDAL STUDY

ABSTRACT:

Novel aryl azo Cu^{II} complexes containing tridentate NON donor ligands derived from 3-acetyl-6-methyl pyran-2,4(3H)-dione (dehydroacetic acid) and aromatic substituted amines, have been synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic, IR, 1H NMR, UV-VIS, X-ray diffraction and fungicidal study. The ligands react with Cu^{II} ion to yield binuclear complexes. Distorted octahedral geometry for Cu^{II} complexes is proposed. The Kinetic parameters, (E , A , ΔS and ΔG) from thermal analysis, of Cu^{II} complex have been estimated. The X-Ray diffraction suggests monoclinic crystal system for Cu^{II} complexes. The ligand and their metal complexes have been screened in vitro for their antifungal activities against *Aspergillus niger*.

KEYWORDS: Dehydroacetic acid, Aryl Azo Schiff bases, Copper complexes, Thermal analysis, Powder X-ray diffraction.

INTRODUCTION:

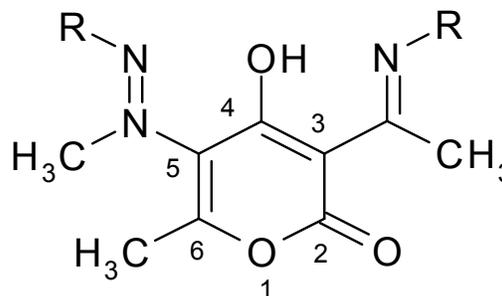
Metal complexes of azo compounds containing ring system finds various applications. Azo compounds are known to be involved in a number of biological reactions such as inhibition of DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation¹. These types of molecules have several advantages, such as azo group in photocromic, redox responsive, pH sensitive; stabilizes low valent metal oxidation states due to the presence of a low lying azo centered π^* molecular orbital, serves as a molecular switch, is used as a metal ion indicator in complexometric titration, dyes and pigments in textile industries²⁻⁴. Dehydroacetic acid (3-acetyl-6-methyl-2H-

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pyran-2,4(3H)-dione), an important biologically active compound and finds many biological and industrial applications. It has shown to have good antibiotic and antifungal effects, besides showing strong antiseptic properties. It has also been used to enhance vitamin 'C' stability in vegetable, food processing and as a preservative. The aqueous solution of dehydroacetic acid even at very low concentrations (0.02 to 0.2%) exhibits a strong antiseptic effect⁵. In continuation of our research on the studies of metal complexes of biologically active dehydroacetic acid and various aromatic amines and aldehydes⁶⁻¹², we report herein the synthesis and characterization of various new aryl azo Schiff bases and their Cu^{II} complexes.



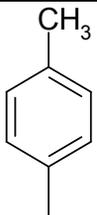
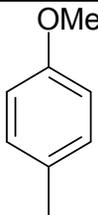
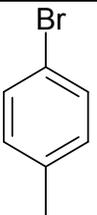
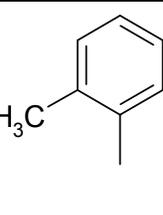
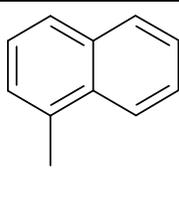
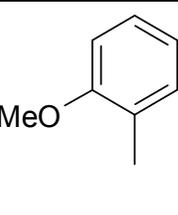
	HL ¹	HL ²	HL ³	HL ⁴	HL ⁵	HL ⁶
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Figure 1: Proposed structure of Ligand

RESULTS AND DISCUSSION:

All the azo Schiff base metal complexes are coloured solids, stable at room temperature, air and moisture and decompose at higher temperature. They are insoluble in water, but soluble in DMF, DMSO. The low molar conductance value (Table 1) of these complexes in 10^{-4} M solution in DMSO indicates non-electrolytic nature. The elemental analysis (Table 1) show 1:1 (metal : ligand) stoichiometry in a dimeric structure for all the complexes (Fig 2).

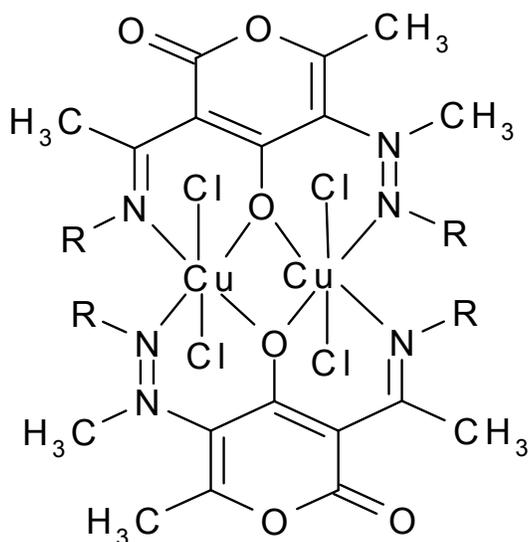


Figure 2: The proposed structure of the complexes

Table 1: Analytical, molar conductance, Magnetic and electronic spectral data of the ligands and its metal complexes.

Compound	colour	Found (Calculated) %						Mol.Wt.	M.P/ Decom. Temp.°C	λ_{m} Mho $\text{cm}^2\text{mol}^{-1}$	μ_{eff} BM	Electronic spectral bands(cm^{-1})		Dq cm^{-1}	LFSE (Kcal mol^{-1})
		C	H	N	Cl	Br	M					${}^2E_g \rightarrow {}^2T_{2g}$	charge transfer		
HL ¹ C ₂₂ H ₂₁ O ₃ N ₃	Reddish Brown	70.21 (70.38)	5.98 (5.63)	11.02 (11.19)	-	-	-	375.42	180	-	-	-	-	-	-
HL ² C ₂₂ H ₂₁ O ₃ N ₃	Dark brown	64.71 (64.85)	4.87 (5.19)	9.99 (10.31)	-	-	-	407.42	250	-	-	-	-	-	-
HL ³ C ₂₀ H ₁₅ O ₃ N ₃ Br ₂	Dark brown	46.97 (47.55)	2.79 (2.99)	8.33 (8.31)	-	31.22 (31.67)	-	505.16	166	-	-	-	-	-	-
HL ⁴ C ₂₂ H ₂₁ O ₃ N ₃	Light brown	70.93 (70.38)	5.95 (5.63)	11.09 (11.19)	-	-	-	375.42	160	-	-	-	-	-	-
HL ⁵ C ₂₀ H ₂₁ O ₃ N ₃	Dark violet	75.48 (75.15)	4.94 (4.72)	9.29 (9.38)	-	-	-	447.49	161	-	-	-	-	-	-
HL ⁶ C ₂₂ H ₂₁ O ₃ N ₃	red	65.30 (64.85)	5.57 (5.19)	10.17 (10.31)	-	-	-	407.42	141	-	-	-	-	-	-
[(Cu) ₂ (L ¹) ₂ (Cl) ₄]	Greenish Brown	51.05 (51.93)	3.52 (3.96)	8.38 (8.26)	13.45 (13.93)	-	12.38 (12.49)	1397	39.80	20.15	1.65	13966	27932	1397	39.80
[(Cu) ₂ (L ²) ₂ (Cl) ₄]	Grey	47.56 (48.86)	4.72 (3.73)	7.77 (7.77)	13.05 (13.11)	-	11.25 (11.75)	1389	39.58	19.74	1.67	13889	30864	1389	39.58
[(Cu) ₂ (L ³) ₂ (Cl) ₄]	Pale Green	37.14 (37.62)	2.18 (2.21)	6.12 (6.58)	11.05 (11.10)	24.76 (25.02)	10.59 (9.95)	1344	38.30	21.55	1.63	13441	31447	1344	38.30
[(Cu) ₂ (L ⁴) ₂ (Cl) ₄]	Greenish yellow	52.73 (51.93)	4.86 (3.96)	8.06 (8.26)	13.35 (13.93)	-	12.21 (12.49)	1567	44.67	23.40	1.69	15674	30675	1567	44.67
[(Cu) ₂ (L ⁵) ₂ (Cl) ₄]	Violet	57.12 (57.89)	3.14 (3.47)	8.05 (7.23)	11.96 (12.20)	-	10.16 (10.94)	1333	37.99	19.64	1.63	13333	31056	1333	37.99
[(Cu) ₂ (L ⁶) ₂ (Cl) ₄]	brown	50.38 (48.86)	4.65 (3.73)	8.60 (7.77)	12.65 (13.11)	-	12.09 (11.75)	1490	42.47	19.25	1.73	14903	26316	1490	42.47

IR Spectra:

Important spectral bands for the ligand and their metal complexes are presented in Table 2. The IR spectrum of the ligands shows bands at 2581-2705, 1694-1704, 1567-1668, 1458-1567, 1244-1358, 1174-1251 cm^{-1} assignable to νOH (intramolecular hydrogen bonded), $\nu\text{C}=\text{O}$ (lactone carbonyl), $\nu\text{C}=\text{N}$ (azomethene), $\nu\text{N}=\text{N}$, $\nu\text{C}-\text{N}$ (aryl azomethene) and $\nu\text{C}-\text{O}$ (phenolic) respectively. In the IR spectra of all the metal chelates, no band is observed in the region 2581-2705 cm^{-1} , suggesting the cleavage of intramolecularly hydrogen bonded (O-H---N) and subsequent coordination of enolic oxygen with metal ion forming M-O bond¹³. This is supported by an upward shift in $\nu\text{C}-\text{O}$ (phenolic)⁷ to the extent 20 – 40 cm^{-1} . A significant downward shift of the ligands band due to enolic $\nu\text{C}=\text{N}$ stretching vibration mode by 20-80 cm^{-1} on complexation indicates that, the C=N group of the ligand is coordinated to the metal ion via its azomethine nitrogen¹⁴. This is further supported by an upward shift of bands by 25-30 cm^{-1} of aromatic C-N frequency. The shift of aryl azo (N=N) frequency to lower side by 20-40 cm^{-1} on complexation suggests the involvement of one of the azo nitrogen atom in bonding with the metal ion¹⁵. The presence of new bands in the region 651-511 cm^{-1} and 553-443 cm^{-1} can be assigned to $\nu\text{M}-\text{O}$ and $\nu\text{M}-\text{N}$ vibrations¹⁶⁻¹⁷ respectively.

Table 2: Characteristic IR frequencies (cm⁻¹), and Mycelial dry weight in mg (% inhibition) of ligands and their complexes.

Compound	νOH	νC=O (lactone)	νC=N (azo methine)	νN=N (aryl azo)	νC-N (aryl azomethine)	νC-O (enolic)	νM-O	νM-N	Mycelial dry weight in mg (% inhibition)		
									control	250 ppm	500 ppm
HL ¹ C ₂₂ H ₂₁ O ₃ N ₃	2600(b)	1700(s)	1657(m)	1567(s)	1328(m)	1245(w)	-	-	82	72(12)	37(54)
HL ² C ₂₂ H ₂₁ O ₃ N ₃	2605(b)	1687(m)	1652(m)	1503(m)	1244(s)	1174(m)	-	-	82	69 (16)	19(77)
HL ³ C ₂₀ H ₁₅ O ₃ N ₃ Br ₂	2590(b)	1690(w)	1567(m)	1478(s)	1300(m)	1233(s)	-	-	82	73(11)	34(58)
HL ⁴ C ₂₂ H ₂₁ O ₃ N ₃	2581(b)	1701(s)	1668(m)	1458(s)	1354(m)	1243(w)	-	-	82	63(23)	43(47)
HL ⁵ C ₂₈ H ₂₁ O ₃ N ₃	2582(b)	1704(s)	1662(m)	1479(m)	1358(m)	1212(w)	-	-	82	73(11)	69(15)
HL ⁶ C ₂₂ H ₂₁ O ₃ N ₃	2705(b)	1694(s)	1661(m)	1502(m)	1327(m)	1251(s)	-	-	82	82(17)	58(29)
[(Cu) ₂ (L ¹) ₂ (Cl) ₄]	-	1695(s)	1622(m)	1521(m)	1358(m)	1284(m)	555(w)	475(w)	82	61(25)	24(71)
[(Cu) ₂ (L ²) ₂ (Cl) ₄]	-	1692(s)	1615(m)	1485(m)	1275(m)	1202(m)	575(m)	470(w)	82	54(34)	03(96)
[(Cu) ₂ (L ³) ₂ (Cl) ₄]	-	1690(s)	1540(m)	1463(m)	1335(m)	1251(m)	513(w)	512(m)	82	60(26)	13(84)
[(Cu) ₂ (L ⁴) ₂ (Cl) ₄]	-	1678(s)	1641(s)	1444(s)	1378(s)	1247(m)	511(m)	443(m)	82	-	19(77)
[(Cu) ₂ (L ⁵) ₂ (Cl) ₄]	-	1700(s)	1624(m)	1449(m)	1375(m)	1235(m)	600(w)	523(w)	82	53(34)	40(51)
[(Cu) ₂ (L ⁶) ₂ (Cl) ₄]	-	1696(w)	1581(m)	1459(m)	1356(m)	1271(m)	651(w)	553(m)	82	67(19)	49(40)

¹H-NMR spectrum: The ¹H-NMR spectrum of the ligands was recorded in CDCl₃. The spectrum of ligand HL² shows sharp peaks at δ = 2.16(S, 3H, C₆-CH₃), 2.57(S, 3H, CH₃ of azomethine), 3.84(S, 6H, OCH₃ of phenyl ring), δ = 6.94-7.11(m, 8H) for aromatic protons and δ = 15.7(S, 1H, phenolic OH).

Magnetic moment and Electronic absorption spectra : All the Cu^{II} complexes consists of a broad band at 13333-15674 cm⁻¹ assigned to ²E_g → ²T_{2g} character of distorted octahedral stereochemistry with D_{4h} geometry. Beside, the above band, the band observed at 26316-31447 cm⁻¹ may be assigned due to charge transfer. The LFSE of Cu^{II} complexes are 37.99-44.67 KCalmol⁻¹. The electronic spectra along with magnetic moment value (1.63-1.73 B.M) value at room temperature indicate distorted-octahedral geometry¹⁸. The magnetic moment values are lower than spin only value (1.73 B.M) for one unpaired electron in Cu^{II} ion shows subnormal character of the complexes. The lowering in magnetic moment may be attributed to spin-spin interaction between two Cu^{II} ions in binuclear complexes¹⁶.

Thermal Analysis:

The [(Cu)₂(L²)₂(Cl)₄] complex is chosen for thermal study. In the TG curve, there is no weight loss up to 250°C and this rules out the presence of any water molecule in the complex. It undergoes a decomposition in two steps. The first step is very rapid (250-385°C), 51.3 % weight loss may be due to decomposition of non-coordinated part of the complex. A sharp exotherm is observed in DTA at 299°C. The second step shows slow decomposition (385-895°C), 34.1% weight loss. A broad endotherm is observed for this step. The residue 13.5% weight (theoretical 14.60%) remaining at the end of the second decomposition correspond to CuO. Thus the complex is thermally stable. In order to determining the kinetic parameters i.e., E (energy of activation), A (pre-exponential factor), ΔS (entropy) and ΔG (free energy change), Horowitz-Metzger¹⁵ method is used.

$$\log(\log Wc/Wr) = E\theta / 2.3 RT_m^2 - \log 2.3$$

Where the term have their usual meaning. The E, A, ΔS and ΔG for the first step decomposition were found to be $67.66 \text{ kJ mol}^{-1}$, 263.25 S^{-1} , $-204.05 \text{ JK}^{-1}\text{mol}^{-1}$ and $81.68 \text{ kJ mol}^{-1}$ respectively.

Powder X-Ray diffraction:

The Cu^{II} complexes are also characterized by powder XRD studies with a view to find the type of crystal system. The $[(\text{Cu})_2(\text{L}^4)_2(\text{Cl})_4]$ and $[(\text{Cu})_2(\text{L}^6)_2(\text{Cl})_4]$ complexes are chosen for study. The diffractogram of $[(\text{Cu})_2(\text{L}^4)_2(\text{Cl})_4]$ complex consist of fourteen reflections between 5° and 80° with maximum reflection at $2\theta = 9.465^\circ$ corresponding to the value of $d = 9.3372 \text{ \AA}$, whereas the diffractogram of $[(\text{Cu})_2(\text{L}^6)_2(\text{Cl})_4]$ complex consist of six reflections between 5° and 80° with maximum reflection at $2\theta = 34.130^\circ$ corresponding to the value of $d = 2.6249 \text{ \AA}$. The diffractogram patterns of complexes with respect to their prominent peaks have been indexed by using computer software keeping in mind the characteristics of various symmetry systems, till a good fit could be obtained between observed and calculated d and 2θ values. The above indexed method also yielded miller indices (hkl) values. The unit cell parameters were calculated using the indexed data refined by weight fraction of the sample. In turn using this parameter, volume of unit cell was computed. The relative intensities corresponding to the prominent peaks have been calculated by normalizing them with respect to their maximum. The comparison of value of observed and calculated d and 2θ reveals that there is good agreement between them on the basis of assumption of monoclinic crystal structure. The small differences in the observed 'd' spacing can be attributed to difference in unit cell dimensions. The unit cell of the $[(\text{Cu})_2(\text{L}^4)_2(\text{Cl})_4]$ complex yielded values for lattice constant $a = 12.0269 \text{ \AA}$, $b = 6.4093 \text{ \AA}$, $c = 34.3588 \text{ \AA}$ and unit cell volume $V = 2555.95 \text{ \AA}^3$. The unit cell of the $[(\text{Cu})_2(\text{L}^6)_2(\text{Cl})_4]$ complex yielded values for lattice constant $a = 12.0142 \text{ \AA}$, $b = 6.4173 \text{ \AA}$, $c = 34.3709 \text{ \AA}$ and unit cell volume $V = 2561.02 \text{ \AA}^3$. In conjunction with these evaluated cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \delta = 90^\circ \neq \beta$ required for the samples to be monoclinic were tested and found to be satisfactory. Hence it is concluded that the complexes under study has monoclinic structure. The experimental density values of the complexes were determined by using specific gravity method²⁰. The number of molecules (n) per unit cell were calculated by using equation $\rho = nm/NV$ and was found to be 4 for both Cu^{II} complexes, with this number, theoretical density has been computed. The experimental and theoretical density values of $[(\text{Cu})_2(\text{L}^4)_2(\text{Cl})_4]$ and $[(\text{Cu})_2(\text{L}^6)_2(\text{Cl})_4]$ are 2.1236, 2.2755 and 2.3246, 2.4369 g cm^{-3} . When experimental density value of the complexes compared with the theoretical density value, it is found that there is good agreement within the limits of experimental errors.

Fungicidal Activity:

To evaluate fungicidal activity of the ligands and their corresponding metal complexes, their effect on the growth of *Aspergillus niger* was studied. The ligand and their corresponding metal chelates in DMSO were screened by mycelia dry weight method²¹ in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 11-23 and 15-77 % inhibition for 250 and 500 ppm concentration respectively. The order of inhibition with respect to ligands at 250 ppm is $\text{L4} > \text{L6} > \text{L2} > \text{L1} > \text{L3} = \text{L5}$ and at 500 ppm is $\text{L2} > \text{L3} > \text{L1} > \text{L4} > \text{L6} > \text{L5}$. It is observed that the metal complexes show enhanced antifungal activity as compared to the ligand. The inhibition by metal complexes has been increased by 19 – 34% and 40 – 96 % for 250 and 500 ppm concentration respectively (Table 2).

Experimental:

Dehydroacetic acid and substituted amines used for the preparation of ligand were from Merck and Aldrich respectively. Metal chlorides used for the complex preparation were from BDH. The carbon and hydrogen content in each sample were measured on Perkin Elmer (2400) CHNS analyzer. IR spectra in the range of $4000\text{--}450 \text{ cm}^{-1}$ were recorded on Perkin Elmer-882 IR spectrometer using KBr pellet technique. The AAS, TGA-DTA and XRD were recorded on PerkinElmer PE-Analyst 300, TA/SDT-2960 and Philips 1701 respectively. The UV-VIS spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer. Magnetic susceptibility measurements of the complexes were carried out using a Gouy

balance at room temperature using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant. Molar conductivity was measured on an Elico CM180 conductivity meter with a dip-type cell using 10^{-3} M solution of complexes in DMSO.

Synthesis of Schiff bases:

A solution of 0.05 mole of dehydroacetic acid, and 0.05 mole of substituted aromatic amines in 25 ml ethanol was refluxed for 4-6 hours. After cooling, the product was filter and crystallized from ethanol.

Synthesis of diazonium chloride:

To an ice cold solution of 0.02 mole of primary aromatic and 10 ml conc. HCl, an ice cold solution of sodium nitrate (0.02 mole) was added until the reaction mixture gives a positive test with starch iodide paper. A clear solution of diazonium chloride is obtained. This was filtered and immediately used for synthesis of aryl azo Schiff bases.

Synthesis of aryl azo Schiff bases:

To an ice cold solution ($0-5^\circ\text{C}$) of Schiff bases (0.02 mole) and 10 ml of 10% of NaOH, an ice cold solution of diazonium chloride was added very slowly with vigorous stirring. The mixture was allowed to stand in ice bath for 1 hour with stirring. The solid compound separated was filtered and washed with dilute HCl and distilled water. The crude product was recrystallized from ethanol.

Synthesis of metal complexes:

To hot methanolic solution (30 ml) of aryl azo Schiff bases (5 mmol), methanolic solution (20 ml) of copper chloride (5 mmol) was added drop wise with stirring. The pH of the reaction mixture was maintained around 7.5 by adding 10 % methanolic solution of ammonia. It was then refluxed for 2 hours. The resulting metal complex was filtered in hot condition and washed with methanol, pet-ether and dried over calcium chloride in vacuum desiccator.

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