

Microwave Irradiative Synthesis, Characterization and Evaluation of Microbial Activity of Co(II), Ni(II) and Cu(II) metal complexes with ligands 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine derivatives.

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ABSTRACT:

Complexes of Co(II), Ni(II) and Cu(II) with 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^1] and 2,4-di(2-hydroxy-5-methoxybenzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^2] have been prepared. All the complexes have been characterized by elemental analyses, conductance measurement, magnetic moment, infrared, NMR, ESR and electronic spectral studies. The complexes were found to have stoichiometry (1:1) ML. On the basis of spectral and magnetic studies octahedral geometry has been assigned for these complexes. The prepared ligands [H_2L^1] and [H_2L^2] and their Co(II), Ni(II) and Cu(II) metal complexes have been tested for antimicrobial activity. All copper complexes $Cu(L^1)H_2O$ and $Cu(L^2)H_2O$ were found to be most active against all the microbes tested, as compared to their ligands,

KEYWORDS: Triazines, Metal complexes, Magnetic moment, Electronic spectra, stoichiometry.

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I. INTRODUCTION

In life science industry and industrial field's related to fine and special chemistry, heterocyclic compounds showed important role [1]. They consist of a class of natural and synthetic products; some of them showed good pharmacological property [2]. Triazines have a unique position in pharmaceutical chemistry. It is worked as protecting groups in natural chemistry. Triazines are reactive groups and flexible for different synthetic transformations [3]. Triazine is a six-membered heterocyclic compound with empirical formula $C_3H_3N_3$. Its structure is analogous to the benzene ring in which three carbons of the ring are substituted by nitrogen atoms. Due to different position of nitrogen atoms in the ring, triazine are found in three isomeric forms 1 (1,2,3-triazine); 2 (1,2,4-triazine); 3 (1,3,5-triazine). 1,3,5-triazine isomer also called as s-triazine due to the symmetry of three nitrogen in the ring. This isomer is an oldest known organic compound. 1,3,5-Triazines represent a broadly used lead structure with remarkable applications in various fields [4]. Ammeline, acetoguanide, acetoguanamine, cyanuric acid, and melamine are the 1,3,5-triazine moiety-containing compounds. Cyanamide or cyanogen chloride was trimerized to 1,3,5-triazines. Benzoguanamine was synthesised from benzonitrile and dicyandiamide in dimethoxyethane with KOH [5]. Due to various applications in different fields, 1,3,5-triazines are a well-known class of compounds from a long time and still continue of considerable interest [6]. Thiazolo-s-triazine nucleobases were formed by reaction of -amino-4-arylthiazoles, $ArCHO$ and NH_4SCN in microwave irradiation [7]. Under microwave irradiation when primary alcohols or aldehydes reacted with iodine in ammonia water to give intermediate nitriles, which interact with cyandiamide and N_3Na to form corresponding s-triazines with good yield [8].

The coordinating centers and structures of the metal complexes play a vital role in almost all biological activities. It is reasonable to expect suppression or enhancement of herbicide activity when active heterocyclic centers are bound to metal ions [9]. Due to the electronegativity difference between nitrogen and carbon, the electrons in the ring S-triazines are located in the vicinity of nitrogen centers that enable coordination to metal ions [10].

On the basis of literature survey and in continuation of our previous studies on characterization of new triazine ligands and their transition metal complexes, 14–15 the present investigation deals with the syntheses, characterization and thermal studies of Co(II), Ni(II) and Cu(II) complexes of some Schiff bases derived from 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^1] and 2,4-di(2-hydroxy-5-methoxybenzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^2] (Fig. 1).

II. MATERIALS AND METHODS

All the chemicals used in this investigation were of Analytical grade. The metal contents were estimated using standard gravimetric methods; cobalt was estimated as cobalt pyridine thiocyanate, nickel as nickel dimethyl glyoximate, copper as cuprous thiocyanate and zinc as zinc ammonium phosphate [11].

Instrumentation

Melting points were determined in open capillaries in electrical melting point apparatus Perfit and are uncorrected. Carbon, hydrogen and nitrogen were estimated using Perkin-Elmer 2400 Elemental Analyzer at Punjab University, Chandigarh. The water of hydration was included in micro analysis data of the metal complexes. Electronic spectra of metal complexes were recorded in DMF on a Hitachi U-2000 spectrophotometer in the region 1100–200 nm. IR spectra were recorded in Beckman IR-20 Spectrophotometer in KBr/Nujol mulls in the range 4000–250 cm^{-1} . Proton NMR spectra were recorded in DMSO- d_6 on a Bruker ACF 300 spectrometer at 300 MHz using ‘tetramethyl silane’ as the internal standard. Magnetic moments were measured at IIC, IIT Roorkee on vibrating sample magnetometer (Model 155).

Preparation 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^1]

The compound 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine (2) was prepared by irradiating the mixture of 2,4-diamino-6-methyl-[1,3,5]-triazine (1) (0.01 mol) and salicylaldehyde (0.02 mol) for 3.5 min using microwave under solvent free conditions. The crude solid mass obtained was crystallized from hot ethanol, (92%), m.p. 165 °C. Preparation of the compound was monitored by TLC using silica gel-G plates and the pure compound was separated using the technique of column chromatography.

Preparation 2,4-di(2-hydroxy-5-methoxy benzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^2]

The compound 2,4-di(2-hydroxy-5-methoxy benzylideneamino)-6-methyl[1,3,5]-triazine (2) was prepared by irradiating the mixture of 2,4-diamino-6-methyl-[1,3,5]-triazine (1) (0.01 mol) and methoxy salicylaldehyde (0.02 mol) for 3.0 min using microwave under solvent free conditions. The crude solid mass obtained was crystallized from hot ethanol, (89 %), m.p. 156 °C [17,18]. Preparation of the compound was monitored by TLC using silica gel-G plates and the pure compound was separated using the technique of column chromatography.

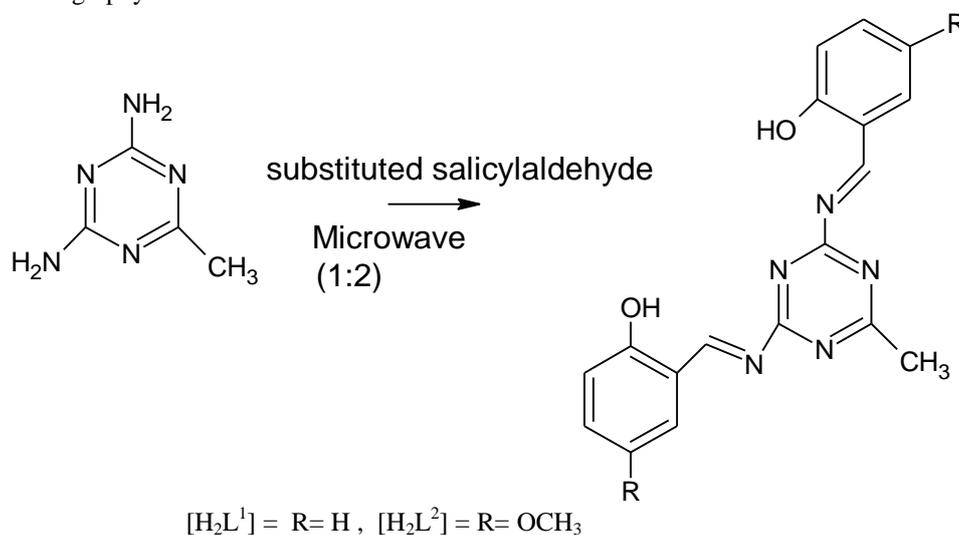


Fig.1. Triazine derivatives Schiff base ligands

Microwave Irradiated Synthesis of Co(II), Ni(II) and Cu(II) metal complexes with ligands [H_2L^1] and [H_2L^2]

A hot solution of a respective metal chloride (0.001 mol) in ethanol was added to a hot solution of 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^1] / 2,4-di(2-hydroxy-5-methoxybenzylideneamino)-6-methyl[1,3,5]-triazine [H_2L^2] (0.001 mol) in ethanol, the reaction mixture was refluxed in microwave irradiation for 4 to 5 minutes, then the colour of the mixture was turned, it was treated with sodium acetate (0.5 g) the resultant reaction mixture was further refluxed in microwave irradiation for 2 more minutes, and then it was decomposed by pouring to distilled water (80 to 100 ml) with stirring. The separated solid (complex) was allowed to settle and collected by filtration, washed several times with distilled water and then with hot ethanol. The solid complex obtained was dried in desiccators over anhydrous calcium chloride.

Table-1. Analytical data of ligands and their metal complexes with 2,4-di(2-hydroxy benzylideneamino)-6-methyl[1,3,5]-triazine [H₂L¹] and 2,4-di(2-hydroxy-5-methoxybenzylideneamino)-6-methyl[1,3,5]-triazine [H₂L²]

Ligands / Complexes	C	H	N	M	Molar conductance (Scm ² mol ⁻¹)	Magnetic Moment μ_{eff} (BM)
H ₂ L ¹	65.00 (64.86)	4.45 (4.50)	21.08 (21.02)	-	--	--
H ₂ L ²	61.02 (61.06)	4.87 (4.83)	17.74 (17.81)	-	--	--
Co(L ¹)H ₂ O	52.91 (52.95)	4.20 (4.16)	17.21 (17.15)	14.50 (14.44)	93.5	4.85
Ni(L ¹)H ₂ O	52.92 (52.98)	4.22 (4.17)	17.12 (17.16)	14.45 (14.39)	96.4	3.25
Cu(L ¹)H ₂ O	52.41 (52.35)	4.15 (4.12)	16.91 (16.96)	15.32 (15.40)	82.3	1.84
Co(L ²)H ₂ O	51.10 (51.07)	4.08 (4.04)	14.95 (14.89)	12.61 (12.54)	98.3	4.83
Ni(L ²)H ₂ O	51.12 (51.09)	4.13 (4.05)	14.85 (14.90)	12.45 (12.50)	85.7	3.18
Cu(L ²)H ₂ O	50.65 (50.57)	4.06 (4.03)	14.82 (14.75)	13.45 (13.38)	95.3	1.86

*The values in the parenthesis were calculated one

III. RESULTS AND DISCUSSION

The analytical and physical data of the compounds are given in Table-1. The results of elemental analyses of the complexes correspond to stoichiometry for metal:ligand in 1:1 molar ratios. Molar conductance measurements of these complexes in DMF correspond to electrolytic in nature. The magnetic moment of the Co(L₁)H₂O, Co(L₁)H₂O and Co(L₁)H₂O are 4.85, 3.25 and 1.84 B.M respectively. The μ_{eff} values of Co(L₂)H₂O, Co(L₂)H₂O and Co(L₂)H₂O are 4.83, 3.18 and 1.86 B.M respectively are well within the range known for six coordinate octahedral geometry[12-13]. The electronic spectra of the complexes recorded in DMF display three bands at 11780-15625cm⁻¹(ν_1), 15605-19230cm⁻¹(ν_2) and 20835-22730cm⁻¹(ν_3). Six coordinate complexes with Oh symmetry show three spin allowed bands. These bands are due to ⁴T_{1g}(F)→⁴T_{2g}(F)(ν_1), ⁴T_{1g}(F)→⁴A_{2g}(F)(ν_2) and ⁴T_{1g}(F)→⁴T_{1g}(P)(ν_3) for cobalt complexes, ³A_{2g}→³T_{2g}(ν_1), ³A_{2g}→³T_{1g}(F)(ν_2) and ³A_{2g}→³T_{1g}(P)(ν_3) for nickel complexes and ²B_{1g}→²A_{1g}(ν_1), ²B_{1g}→²B_{1g}(ν_2) and ²B_{1g}→²E_g(ν_3) for copper complex[14-15]. IR spectra of ligand show a broad medium intensity band in the region 3450-3300cm⁻¹ due to phenolic-OH [16], in complexes these bands were not observed due to the complexation through O via deprotonation of phenolic-OH. The band in the region 1640-1590cm⁻¹ is assigned to HC=N group, indicates that the condensation between amino groups of 2,4-diamino-6-methyl-[1,3,5]-triazine and substituted salicylaldehyde. The band due to $\nu_{\text{C=N}}$ appears in the region of 1630-1590cm⁻¹ as a high intensity band in the complexes, indicating that the C=N group is involved in coordination of metal ions through nitrogen. In complexes the bands due to C=N group are shifted to lower frequency by 30-20cm⁻¹ as compared to ligands H₂L¹ and H₂L². In metal complexes bands appear in the region 3560-3530cm⁻¹ is due to involvement of water molecule and coordinated through oxygen of water molecule. The IR spectra of the triazine complexes showed new bands in the range 445-465 cm⁻¹ and 550-574 cm⁻¹, which refer to M-N and M-O bonds, respectively [17].

The ¹H NMR spectral data have been interpreted based on literature data [18-19]. In the NMR spectra of complexes we have observed a shift of electron density from the ligand to metal. The ligands fbmmot and afmmot show singlet at δ 8.7 and 2.2 ppm which is assigned to azomethine proton and methyl group protons attached to azomethine carbon, respectively. These signals deshielded in the spectra of metal complexes, suggests coordination of metal ion to azomethine nitrogen atom of the ligands. In addition to this, the signals at δ 12.1 and 12.6 ppm are ascribed to OH protons. Disappearance of these OH protons signals in the spectra of metal complexes supported the deprotonation of hydroxyl group. In the spectra of ligand multiplet signals around δ 7.1-8.4 and δ 6.3-7.6 ppm were assigned to aromatic protons. These multiplets show a slight shift upon coordination. In the spectra of 1:1 metal complexes singlet at δ 2.4 ppm is due to methyl group of 6-methyl[1,3,5]-triazine group of the ligands.

The ESR spectra of the copper complexes as polycrystalline sample have been recorded at room temperature, (ESR chart was calibrated with DPPH). The polycrystalline sample gives one broad isotropic signal centered approximately at 2.015 and 2.068 for the complex Cu(L¹)H₂O. The observed g values of the Cu(L¹)H₂O complex as follows g_{\parallel} = 2.035, g_{\perp} = 2.016, g_{av} = 2.028 and G = 2.19. While for Cu(L²)H₂O g_{\parallel} = 2.058 g_{\perp} = 2.022 g_{av} = 2.030 and G = 2.63. The isotropic g values have been calculated Kneubuhl's methods and methods reported earlier. $G = (g_{\parallel}-2)/(g_{\perp}-2)$ which measures the exchange interaction between copper centers in a polycrystalline solid has been calculated. According the Hathaway[20-21] if the G value is greater than 4,

the exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange in the solid complex.

On the basis of analytical data, electronic spectral, magnetic susceptibility and conductance measurements, IR, NMR and ESR spectral data the octahedral geometry has been assigned to all the metal complexes.

The prepared ligands [H₂L¹] and [H₂L²] and their Co(II), Ni(II) and Cu(II) metal complexes have been tested for antimicrobial activity [22]. The antimicrobial activity outcomes of the screened compounds are given in the Table 2. Antibacterial activity in opposition to *Escherichia coli* and *Staphylococcus aureus* and Antifungal activity in opposition to *Aspergillus niger* and *Cladosporium* were carried out. A normal drugs gentamycine and fluconazole were also tested for their antibacterial and antifungal activity at the same concentration under the circumstances analogous to that of the test compound [23].

The results suggest that the all metal complexes have exhibited good bacterial and fungal activities as compared to their ligands. Among the complexes, all copper complexes Cu(L¹)H₂O and Cu(L²)H₂O were found to be most active against all the microbes tested, as compared to their ligands, which due to the faster diffusion of the Cu(II) complexes. Whereas, Ni(II) and Co(II) complexes have shown moderate activity [24]. While, all metal complexes have improved antimicrobial activity than ligands [H₂L¹] and [H₂L²].

Table-2. The antimicrobial activity of ligand [H₂L¹] and [H₂L²] and their Co(II), Ni(II) and Cu(II) complexes evaluated in (mm).

Ligands/ complexes	Zone of inhibition in mm			
	Antibacterial activity		Antifungal activity	
	<i>Escherichia Coli</i>	<i>Staphylococcus Aureus</i>	<i>Aspergillus flavus</i>	<i>Cladosporium</i>
[HL ¹]	11	12	9	10
[HL ²]	13	14	8	11
Co(L ¹)H ₂ O	15	15	13	15
Ni(L ¹)H ₂ O	16	17	14	16
Cu(L ¹)H ₂ O	26	26	24	22
Co(L ²)H ₂ O	16	16	14	15
Ni(L ²)H ₂ O	15	17	16	13
Cu(L ²)H ₂ O	25	27	24	23
Gentamycine	28	30	--	--
Fluconazole	--	--	27	25

IV. CONCLUSION

In this paper reported that the microwave irradiative synthesis and characterization of a new pentadentate Schiff bases namely 2,4-di(2-hydroxy benzyldeneamino)-6-methyl[1,3,5]-triazine [H₂L¹] and 2,4-di(2-hydroxy-5-methoxybenzyldeneamino)-6-methyl[1,3,5]-triazine [H₂L²] and their Co(II), Ni(II) and Cu(II) complexes. All the complexes are coloured, stable in air and insoluble in water and common solvents but soluble in polar solvent like DMF and DMSO. The analytical data obtained suggested 1:1(M: L) stoichiometry for all complexes. The prepared complexes have electrolytic nature. Based on the above observations of IR, electronic spectral data, ¹H NMR spectra, ESR spectral, magnetic, conductance measurements, proposed the octahedral geometry for all the metal complexes. The ligands [H₂L¹] and [H₂L²] and their Co(II), Ni(II) and Cu(II) metal complexes have been tested for antimicrobial activity. It was found that all copper complexes (Cu(L¹)H₂O and Cu(L²)H₂O) were found to be most active against all the microbes tested, as compared to their ligands, which due to the faster diffusion of the Cu(II) complexes.

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