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Synthesis, Characterization and Antimicrobial Activity of 3-Acetyl-4-hydroxy-6-methyl-(2*H*)pyran-2-one Schiff Base with 2,2'-(Ethylenedioxy)diethylamine and its Co(II), Ni(II) and Cu(II) Complexes

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A Schiff base was synthesized by the interaction of 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one with 2,2'-(ethylenedioxy)diethyl-amine in ethanolic medium. The ligand was characterized on the basis of elemental analysis, infrared, ^{1}H and ^{13}C NMR spectra. Cobalt(II), Ni(II) and Cu(II) complexes of the type $ML(H_2O)_2$ were prepared by interaction of the metal(II) halides with hot ethanolic solution of the Schiff base. The complexes were characterized by elemental analysis, molar conductance, magnetic measurements, infrared and electronic spectral studies. Results show that the ligand behaved as dibasic tetradentate molecule, coordinating *via* imino nitrogens and the enolic oxygens, to form six-coordinate octahedral metal complexes. The compounds were screened for *in vitro* antimicrobial activity against some bacteria and yeasts. Results showed that some of the compounds are active against few microbes.

Keywords: Pyran-2-one, 2,2'-(Ethylenedioxy)diethylamine, Complexes, Antimicrobial.

INTRODUCTION

3-Acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one, commonly referred to as dehydroacetic acid, has continued to receive considerable attention due to the ease with which it reacts with amino compounds and hydrazines to form derivatives with interesting coordination chemistry, pharmaceutical importance and high biologically activity[1-5]. Dehydroacetic acid itself is well known for its fungicidal[6], herbicidal and antimicrobial activities[4]. It is also widely used in food technology, as vitamin C stabilizer and as a preservative in food products like fish sausages[7]. A number of Schiff base derivatives of 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one and their metal complexes have been reported[8-15]. The interest in Schiff bases is due to the fact they are superior reagents in biological, inorganic and analytical applications[16-20]. It has also been documented that upon coordination the antimicrobial properties of Schiff bases could be enhanced[21-25] or diminished[26]. Literature search revealed that no work has been done on 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one Schiff base with 2,2'-(ethylenedioxy)diethyl-amine and its metal complexes. In continuation of our series[27-29] on Schiff bases and their metal complexes, we report the coordination chemistry and antimicrobial study of Schiff base derived from 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one and 2,2'-(ethylenedioxy)-diethyl-amine with its Co(II), Ni(II), Zn(II) and Cu(II) complexes.

EXPERIMENTAL

All the solvents are of analytical grade and were used without further purification. 3-Acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one and 2,2'-(ethylenedioxy)diethylamine were used as supplied by Fluka. Elemental analyses of C, H and N were performed by using Carlo Erba Elemental analyzer EA 1108. Melting point were taken in open capillaries on a melting point apparatus Electrothermal 9100. Magnetic moments were done on a magnetic susceptibility balance–Sherwood Scientific Cambridge, Model No. MK-I. The molar conductance of the complexes was measured using Innolab conductivity meter Level 1. The percentage of metal in the complexes were determined using an Agilent ICP-MS7500Ce. IR spectra were recorded on a Perkin Elmer Spectrum 100. ^{1}H and ^{13}C NMR spectra were obtained from a Bruker AV 500 MH_Z for ^{1}H and 125 MH_Z for ^{13}C using a 5 mm Quadra Nuclei Probe (QNP).

Synthesis of 3-acetyl-4-hydroxy-6-methyl-(2*H*)pyran-2-one Schiff base ligand [DeAEddA]: A solution of 3-acetyl-4-hydroxy-6-methyl-(2*H*)pyran-2-one (3.36 g, 0.02 mol) in 20 mL ethanol was mixed with a solution of 2,2[1]-(ethylendioxy)diethylamine in ethanol 20 mL. The mixture was refluxed for 3 h and resulting solution was chilled to -10 °C, to obtained whitish product which was filtered, dried and recrystallized in water (Fig. 1).

Synthesis of Ni(II), Cu(II) and Co(II) metal complexes of DeAEddA: To an ethanolic solution (20 mL) of DeAEddA (0.45 g, 0.001 mol), ethanolic solution (10 mL) of the corresponding metal chlorides (0.001 mol) was added with constant stirring. The coloured mixture was then refluxed for 4 h. The resulting metal complex was filtered hot, washed with boiling mixture of 1:1 water/ethanol, dried under suction and kept in vacuum over $CaCl_2$.

Microorganisms and condition for cultivation: Condition for cultivation of microorganisms is similar to earlier report[29]. Ten bacterial strains and two yeast strains were obtained from the American Type Culture Collection (ATCC; Rockville, MD, USA). Other microorganism strains were obtained from Adnan Menderes University Faculty of Medicine. The Gram-negative (G-) were: *Escherichia coli* ATCC 25922, *Salmonella typhimurium* ATCC 14028, *Proteus sp*., *Serratia marcescens, Enterobacter sp*. and the Gram-positive (G+) were: *Micrococcus luteus* ATCC 9341, *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermidis* ATCC 12228, *Bacillus cereus* ATCC 11778, *Bacillus subtilis* ATCC 6633, *Bacillus thrungiensis*, *Enterococcus faecalis* ATCC 29212, *Enterococcus faecalis* ATCC 51299, *Streptococcus pneumoniae* ATCC 49617 and *Listeria monocytogenes*. Also, yeast strains as *Candida utilis, Candida albicans* ATCC 90028*, Candida glabrata*, *Candida trophicalis* and *Saccharomyces cerevisiae* ATCC 9763 were used. *Escherichia coli* ATCC 25922, *Staphylococcus aureus* ATCC 25923, *Staphylococcus epidermidis* ATCC 12228, *Salmonella typhimurium* ATCC 14028, *Listeria monocytogenes*, *Proteus sp*., *Serratia marcescens, Enterobacter sp*. were cultured in Nutrient Broth (NB) (Merck) at 37 °C, *Streptococcus pneumoniae* ATCC 49617, *Enterococcus faecalis* ATCC 29212 and *Enterococcus faecalis* ATCC 51299 were cultured in Brain Heart Infusion Broth (BHIB) (Merck) at 37 °C for 24 h.; *Micrococcus luteus* ATCC 9341, *Bacillus cereus* ATCC 11778, *Bacillus subtilis* ATCC 6633 and *Bacillus thrungiensis* were cultured in Nutrient Broth (NB) (Merck) at 30 °C, *Candida utilis, Candida albicans* ATCC 90028, *Candida glabrata*, *Candida trophicalis* and *Saccharomyces cerevisiae* ATCC 9763 were cultured in Malt Extract Broth (MEB) (Merck, USA) at 30 °C for 24 h.

Antimicrobial assay: The antimicrobial activities of all the synthesized compounds were studied by the disc diffusion method[30,31] and the minimum inhibitory concentration (MIC) was determined by broth dilution method[31].

Disc diffusion method: The standard method of antimicrobial disc susceptibility tests reported by the National Committee for Clinical Laboratory Standards[31] was used. Briefly, fresh stock solutions (1000 μg mL^{-1}) of all the synthesized compounds were prepared in DMSO. The inoculum suspensions of the tested bacteria and yeasts were prepared from the broth cultures (18-24 h) and the turbidity equivalent adjusted to 0.5 McFarland standard tube to give a concentration of 1×10^8 bacterial cells and 1×10^6 yeast cells/mL. To test the antimicrobial activity of all the synthesized compounds, a Mueller Hinton Agar (MHA) plate was inoculated with 0.1 mL broth culture of bacteria or yeast. Then a hole of 6 mm in diameter and depth was made on top with a sterile stick and filled with 50 μL of synthesized compounds. Plates inoculated with *E. coli* ATCC 25922, *S. typhimurium* ATCC 14028, *S. aureus* ATCC 25923, *S. epidermidis* ATCC 12228, *E. faecalis* ATCC 29212, *Enterococcus faecalis* ATCC 51299, *S. pneumoniae* ATCC 49617, *Listeria monocytogenes*, *Proteus sp*., *S. marcesecens*, *Enterbacter sp*. were incubated at 37 °C for 24 h, while those with *M. luteus* ATCC 9341, *Bacillus subtilis* ATCC 6633, *B. cereus* ATCC 11778, *B. thrungiensis, S. cerevisiae* ATCC 9763, *C. albicans* ATCC 90028, *C. glabrata*, *C. utilis* and *C. trophicalis* were incubated at 30 °C for 24 h. At the end of incubation time, the diameters of the inhibition zones formed on the MHA were evaluated in millimeters. Disc of chloramphenicol (C30), gentamycine (CN10), tetracycline (TE30), erytromycine (E15), ampicillin (AMP10) and nystatine (NS100) were used as positive controls. The measured inhibition zones of the study compounds were compared with those of the reference discs.

RESULTS AND DISCUSSION

Analytical and physical data: Analytical and physical data of all the study compounds are shown in Table-1. The elemental analysis show 1:1 (metal:ligand) stoichiometry for all the metal complexes. All the metal complexes are coloured and soluble in DMSO, DMF and anhydrous ethanol, however they are insoluble in hexane, pentane, chloroform and carbon tetrachloride. The low conductance of the metal complexes solution in DMSO supports their non-electrolyte nature[32-34].

FT-IR spectra: The relevant infrared spectral of both the ligand and metal complexes are listed in Table-2. The azomethine C=N stretching frequency in the spectrum of the ligand observed at 1665 cm^{-1} shifted to lower frequencies by about

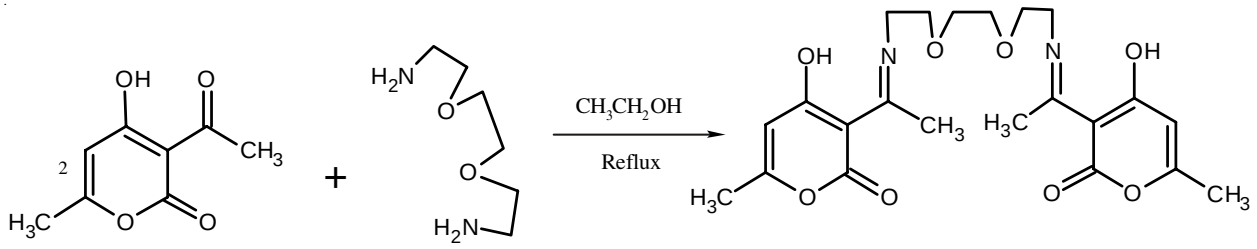

Fig. 1. Synthesis of DeAEddA

TABLE-1
ELEMENTAL ANALYSIS AND PHYSICAL DATA OF THE DeAEddA AND ITS METAL COMPLEXES

Compound	Colour	m.f.	Yield (%)	Elemental analysis (%): Found (calcd.)				Λ_M (ohm^{-1} cm^2 mol^{-1})	m.p. (°C)
				C	H	N	M		
DeAEddA	White	$C_{22}H_{28}N_2O_8$	85	58.32 (58.92)	5.98 (6.24)	6.44 (6.25)	–	–	155
CoDeAEddA	Brown	$C_{22}H_{30}N_2O_{10}Co$	64	49.30 (48.80)	5.12 (5.59)	4.75 (5.18)	11.22 (10.89)	9.12	285
NiDeAEddA	Pale blue	$C_{22}H_{30}N_2O_{10}Ni$	59	48.10 (48.83)	4.98 (5.59)	4.88 (5.21)	10.30 (10.85)	10.12	290
CuDeAEddA	Dirty green	$C_{22}H_{30}N_2O_{10}Cu$	55	47.87 (48.39)	6.20 (5.54)	4.55 (5.13)	11.20 (11.64)	8.10	280

TABLE-2
KEY IR ABSORPTION BANDS (cm^{-1}) OF THE DeAEddA AND ITS METAL COMPLEXES

Compound	ν(O-H)	ν(C=O) (lactone)	ν(C=N)	ν(C-O)	ν(C-O-C)	ν(M-O)	ν(M-N)
DeAEddA	3454	1703	1665	1324	1389	–	–
CuDeAEddA	3458	1707	1649	1270	1390	541	430
NiDeAEddA	3426	1703	1627	1295	1387	547	440
CoDeAEddA	3565	1705	1610	1246	1388	531	418

16-50 cm^{-1} in the spectra of the metal complexes. Furthermore the phenolic ν(C-O) absorption around 1324 cm^{-1} in the spectrum of the ligand shifted to lower frequencies by about 20-80 cm^{-1} in the spectral of the metal complexes. These shifts are of appreciable magnitude and suggest that there is coordination *via* the azomethine nitrogens[35,36] and deprotonated phenolic oxygens. The low frequencies bands that are characteristics of M-L vibrations were observed in the regions about 440-420 cm^{-1} ν(M-N) and 550-530 cm^{-1} in the spectra of metal complexes which further confirmed the coordination to C=N nitrogens and C-O oxygens[37-39]. Bands assignable to ν(O-C-O) and lactone carbonyl C=O were observed in the region about 1390 cm^{-1} and about 1700 cm^{-1} respectively[35,40], the feeble differences is an indication of the non-participation of these groups in ligation on forming the metal complexes. The band centered at 3454 cm^{-1} was assigned to ν(O-H) in the spectrum of the ligand. Broad band characteristic of ν(O-H) of coordination H_2O was observed in the region about 3560-3420 cm^{-1} in the spectra of the complexes[40]. This is further supported by rocking and wagging modes of water observed in the regions of 855-840 cm^{-1} and 750-735 cm^{-1} respectively[41,42]. These observations suggest that the ligand behaved as dibasic tetradentate molecule coordinatiing *via* imino nitrogens and the enolic oxygens.

^{1}H and ^{13}C NMR spectra: The ligand can exist in two tautomeric forms (enol and keto). The possible keto and enol forms are represented in Fig. 2.

The ^{1}H NMR spectrum of DeAEddA displayed six signals. The number of assignable signals suggest that the compound might be symmetrical. Each signal was assigned to a given pair of equivalent H's. The –CH_3 signals were assigned as follows: 2.11 δ (s,3H,-C=C-CH_3), 2.50 δ (s,3H, N=C-CH_3). The ring H's was observed at 5.62 δ (s, 1H, CH_3=C-H). Two supplementary signals were observed in the CH_2 region, in the form of a multiplet and a singlet corresponding to alkane chain protons and have been assigned as follows: 3.27 δ (s, 4H), 3.70 δ (m, 6H). The enolic hydrogen signal was observed at 13.80 δ (s, 1H, enolic OH), giving a strong indication that the ligand was isolated in the enol form. The enol form is further stabilized by conjugated double bond extending into the rings of the dehydroacetic acid moieties. The ^{13}C NMR spectrum of the ligand shows –CH_3 carbon signals at δ 18.27 and 19.58. The most deshielded carbons have been assigned relevant signals downfield. The equivalent carbons of lactone carbonyl O-C=O resonated at δ 183.66, the enolic C-OH carbons signal was observed at 176.03, the lactone ring H_3C-C-O carbons signal was observed at δ 162.47 while azomethine carbons signal was observed at δ 107.49. The signals at δ 95.92 and δ 70.36 have been assigned to the other two ring carbons. Signals assignable to -CH_2-O carbons was observed at δ 68.52 while CH_2-N carbon signal was observed at δ 44.12.

Electronic spectra and magnetic studies: The significant electronic absorption bands in the spectral of the study compounds recorded in DMSO solution and the magnetic measurement results are presented in Table-3. The study compounds show high frequency bands in the region 331-352 nm and 224-250 nm assignable to n→π* and π→π* respectively[43,44]. Generally, *d-d* transitions are electronically forbidden, however spectra of very low absorbance are often observed in metal complexes because of slight relaxation in the Laporte rule[45], which is often the case when the metal complexes are non-centrosymmetric. No bands could be ascribed to *d-d* transitions in the spectra of the metal complexes, probably because they were too weak to be observed. This may be attributed to the centrosymmetric

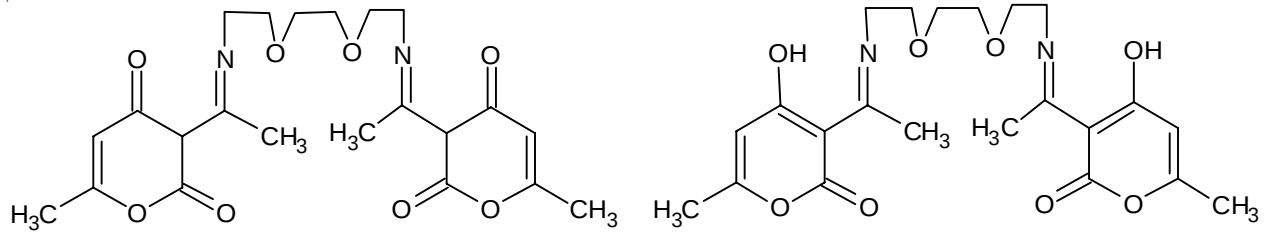

Fig. 2: Tautomeric forms of DeAEddA

TABLE-3
ELECTRONIC SPECTRAL DATA AND MAGNETIC MOMENT RESULTS OF THE STUDY COMPOUNDS

Compounds	λ_{max} (nm)	μ_{eff} (BM)
DeAEddA	224, 249, 331	–
CoDeAEddA	256, 318, 328	4.97
NiDeAEddA	250, 320, 345	2.85
CuDeAEddA	240, 330, 352	1.93

nature of the complexes and the possibility that the metal-ligand bonds vibrate with the ligand maintaining its centrosymmetric equilibrium position and thereby not encouraging vibronic coupling[46]. The magnetic moment results of the metal complexes is suggestive of octahedral geometry[47,48].

On the basis of microanalytical data, magnetic moments, conductivity measurements and spectral analysis, the following structures have been proposed for the metal complexes (Fig. 3).

Antimicrobial test results: The results of antimicrobial activities of DeAEddA and the metal complexes reported as inhibition zone diameter (mm) are showed in Table-4. The

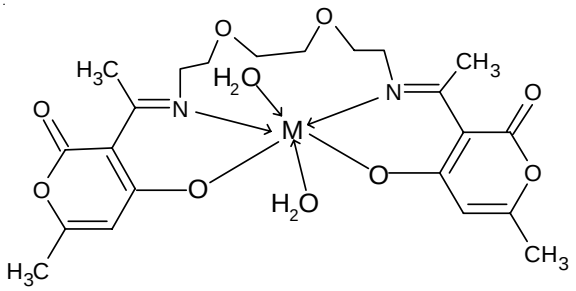

Fig. 3. Proposed structure of the metal complexes [M= Co, Ni and Cu]

inhibition zone diameter of the reference antibiotics used on the test microorganisims are presented in Table 5. The ligand show antimicrobial activity against only *Micrococcus luteus*, ATCC 9341, Co(II) complex showed appreciable activity against *Salmonella typhimirium* ATCC 14028, *Micrococcus luteus* ATCC 9341, *Bacillus subtilis* ATCC 6633, *Serratia marcescens* and *Candida albicans* ATCC 90028, while the Ni and Cu complexes showed no antimicrobial activity against

TABLE-4
ANTIMICROBIAL ACTIVITIES OF DeAEddA AND ITS METAL COMPLEXES

Test microorganisms	Inhibition zone diameter (mm)			
	DeAEddA	CoDeAEddA	CuDeAEddA	NiDeAEddA
Escherichia coli ATCC 25922	–	–	–	–
Salmonella typhimirium ATCC 14028	–	10	–	–
Micrococcus luteus, ATCC 9341	8	12	–	–
Stapylococcus aureus ATCC 25923	–	–	–	–
Stapylococcus epidermidis ATCC 12228	–	–	–	–
Bacilllus cereus ATCC 11778	–	–	–	–
Bacillus subtilis ATCC 6633	–	11	–	–
*Bacillus thrungiensis**	–	–	–	–
Entereococcus faecalis ATCC 29212	–	–	–	–
Entereococcus faecalis ATCC 51299	–	–	–	–
Streptococcus pneumoniae ATCC 49617	–	–	–	–
*Proteus sp.**	–	–	–	–
*Serratia marcescens**	–	15	–	–
*Enterobacter sp.**	–	–	–	–
*Listeria monocytogenes***	–	–	–	–
Candida albicans ATCC 90028	–	11	–	–
*Candida utilis**	–	–	–	–
*Candida trophicalis**	–	–	–	–
*Candida glabrata**	–	–	–	–
Saccharomyces cerevisiae ATCC 9763	–	–	–	–

(-): No zone of inhibition; *Special gift from Faculty of Medicine, Adnan Menderes University. **Food isolated

TABLE-5
INHIBITION ZONE DIAMETER OF THE REFERENCE ANTIBIOTICS TO TEST MICROORGANISMS

Test microorganisms	Inhibition zones (mm): Reference antibiotics					
	C30	CN10	TE30	E15	AMP10	NS100
Escherichia coli ATCC 25922	24	21	15	11	–	NT
Salmonella typhimirium ATCC 14028	17	16	15	8	8	NT
Micrococcus luteus ATCC 9341	25	15	26	30	28	NT
Stapylococcus aureus ATCC 25923	23	20	22	23	20	NT
Stapylococcus epidermidis ATCC 12228	22	17	19	11	17	NT
Bacilllus cereus ATCC 11778	23	24	25	26	–	NT
*Serratia marcescens**	23	19	10	–	15	NT
*Enterobacter sp.**	19	20	14	–	–	NT
*Listeria monocytogenes***	16	11	10	–	–	NT
Candida albicans ATCC 90028	NT	NT	NT	NT	NT	22

C30: Chloramphenicol (30 mg Oxoid), CN10: Gentamycin (10 mg Oxoid), TE 30:Tetracycline (30 mg Oxoid), E15: Erytromycin (15 mg Oxoid), AMP10: Ampicillin (10 mg Oxoid), NS: Nystatin (100 mg Oxoid); (-):No zone; NT: Not tested; *Special gift from Faculty of Medicine, Adnan Menderes University. **Food isolated

all the microbes studied. A number of reasons have been ascribed to the relative antimicrobial activities of ligands and their metal complexes, some based on accessibility of the compounds to cellular targets, depending on the nature of cell walls, and /or, lipophilicity of the metal complexes[49-51] and the possibility of hydrogen bonds with cellular targets[52]. It is not clear yet what role the relative concentrations of these compounds play in the extent of antimicrobial acti-vities. In the present study, 20 microorganisms were subjected to antimicrobial screening and only five were vulnerable to the studied compounds.

Conclusion

A 3-acetyl-4-hydroxy-6-methyl-(2H)pyran-2-one Schiff base with 2,2'-(ethylenedioxy)diethylamine and its Co(II), Ni(II)and Cu(II) metal complexes have been synthesized and characterized. Physico-chemical and spectral data show that the metal: ligand ratio is 1:1 in all the metal complexes. The ligand behaved as a dibasic tetradentate molecule coordinating *via* imino nitrogens and the phenenolic oxygens. The spectral data and magnetic moments are in favour of octahedral geometry for Ni(II), Cu(II) and Co(II) complexes. Only few microorganisms were affected appreciably by some of the study compounds.

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