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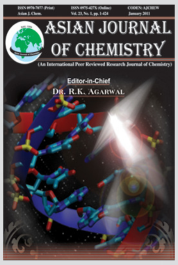

Synthesis and Structural Characterization of Manganese(II), Iron(III), Cobalt(II) and Copper(II) Complexes of 3-[1-(3,4-Dihydro-6-methyl-2,4-dioxo-2*H*-pyran-3-yl)ethylideneamino]-benzoic Acid

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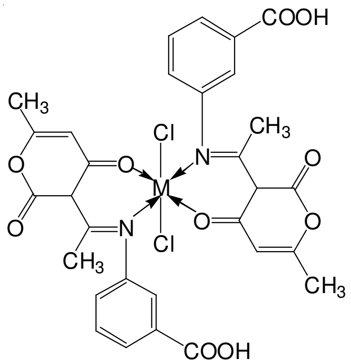
The solid complexes of Mn(II), Fe(III), Co(II) and Cu(II) with Schiff base derived from 3-acetyl-6-methyl-(2*H*)-pyran-2,4(3*H*)dione (dehydroacetic acid) and *m*-aminobenzoic acid have been synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic, IR, UV-vis and NMR spectral studies. From the analytical and thermal data, the stoichiometry of the complexes has been found to be 1:2 (metal:ligand). The low conductance values suggest that the complexes are non-electrolyte. IR spectral data suggest that the ligand behaves as a dibasic bidentate ligand with N:O donor sequence towards metal ions. The physico-chemical data suggests that all the complexes possess octahedral geometry. They are also screened for antimicrobial activity.

Key Words: Schiff bases, Dehydroacetic acid, *m*-Aminobenzoic acid, Metal complexes.

INTRODUCTION

Schiff bases possess strong ability to form metal complexes. The heterocyclic compounds played an important role in biological activity[1]. Synthesis and charactrisation study of amino acid as ligand are of recent intrest[2]. Dehydroacetic acid a heterocyclic compounds is an important biologically active compound, it has antibiotic, fungicidal[3], antiseptic[4] effects and used to enhance vitamin-C stability and protect vegetables during food processing[5]. It is well known from the literature that dehydroacetic acid moiety have a strong ability to form metal complexes. The numbers of Schiff bases of dehydroacetic acid with primary aliphatic, aryl amines are reported in literature. Schiff bases play a prominent role in biological applications due to excellent chelating capacity in modern coordination chemistry[6]. The extensive works in solid coordination complexes have been made possible with the help of various experimental techniques and has led to a number of interesting conclusions[7]. Though some work has been done on metal complexes derived from O, N donor ligands, formed from condensation of dehydroacetic acid with amines[8-11], there is no any work on *meta* substituted aromatic amines. In view of the above fact we report here the preparation and characterizations of complexes of Mn(II), Fe(III), Co(II) and Cu(II) metal ions with ligand, 3-[1-(3,4-dihydro-6-methyl-2,4-dioxo-2*H*-pyran-3-yl)-ethylideneamino]-benzoic acid, derived from condensation of dehydroacetic acid and 3-amino benzoic acid.



where, M = Cu(II), Co(II), Mn(II)

Expected structure of metal complexes

EXPERIMENTAL

All the chemicals and solvents used in all preparative and analytical works were of A.R. grade. Dehydroacetic acid used for the preparation of ligand is of Merck. The micro analytical data for carbon, hydrogen, nitrogen content in each sample were recorded on elemental analyzer 'Perkinelmer' model No. 2400; IR spectra (nujol) in the range of 4000-450 cm^{-1} were recorded on Perkin Elmer 1b model No. C75430, ^{1}H NMR spectra of the ligand were measured in $CDCl_3$. The AAS, TGA-DTA and XRD were recorded on Perkin Elmer PE-analyst 300, Ta/SDT-2960 and Philips 3701/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 done using a Gouy's balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductivity was measured on a conductivity meter EQ-660 with a dip-type cell using 10^{-4} M solution of complexes in DMF.

Synthesis of ligand: The ligands are synthesized by mixing equimolar solution of dehydroacetic acid and 3-chloro aniline (L1) and 3-amino phenol (L2) in double distilled dry ethanol and reflux the mixture on 1RML rotamental for 6 h. The content was cooled to room temperature. The solid obtained was separated washed and recrystalised from ethanol. The purity of the ligand were checked by TLC, melting point, elemental analysis and characterized by IR and PMR.

Synthesis of metal complexes: To a hot solution of the ligand (2 mmol) in (30 mL) methanol, the metal chloride (1 mmol) in (20 mL) methanol was added drop wise with stirring. The pH of the reaction mixture was maintained by adding 10 % methanolic solution of ammonia. The complexes of different metals were precipitated at different pH. It was then refluxed for 2-4 h. The resulting metal complex was filtered in hot condition and washed with chloroform, methanol, pet-ether (40-60 ºC) and dried over calcium chloride in vaccum desicators.

RESULTS AND DISCUSSION

All the complexes are coloured solids, stable to air and non-hygroscopic. They decompose at high temperature without melting. They are insoluble in water and sparingly soluble in common non-polar organic solvents. The molar conductance values 12.20-19.50 ohm^{-1} cm^2 mol^{-1} for 10^{-4} M solution of metal complexes in DMF indicates that the metal complexes are non-electrolyte in nature[12]. The elemental analysis revel mononuclear nature and 1:2 composition of M:L. The analytical results of complexes are presented in Table-1.

The ^{1}H NMR spectra of the ligand have been recorded in $CDCl_3$. The spectra shows sharp peaks at 2.17 (S, 3H, pyran C_6-CH_3), 5.77(S, 1H, pyrane C_5-H), 15.92 (S, 1H, Enolic OH for DHA moiety), 2.60 (S, 3H, CH_3-C=N) and 10.51(S, 1H of COOH). The phenyl moiety values 7.23-8.08 (m, 4H, for Ar-H).

The IR spectra of ligand shows bands at 3364, 1702, 1646, 1439 and 1622 cm^{-1} (Table-2) are assigned to ν(O-H) (hydrogen bonded), ν(C=O) (lactone), ν(C=N) (azomethine) ν(C-N) (aryl azomethine) and ν(C=O) (enolic) vibrations, respectively. The ligands in the present work are in tautomeric form. The carbonyl group may be in keto form or in enol form[13]. In the IR spectra of metal chelates no band is observed in the region 3364 cm^{-1} indicates the absence of enolic form of ligand in complexes. Coordinated site is supported by downward shift by 12-37 cm^{-1} in ν(C=N) azomethine[14] and 12-42 cm^{-1} in ν(C=O) enolic[15]. The new bands appeared in the region 632-562 and 535-490 which were absent in ligand may be due to formation of (M-N) and (M-O) bonds[16], respectively.

The above discussions indicate that the ligands behave as bidentate and coordinate to metal ions through enolic oxygen and azomethine nitrogen.

The magnetic moments of Cu(II) complexes are found to be well to 1.82 BM for which is expected for octahedral structure. The electronic absorption spectra of Cu(II) complexes show a broad band in the region 15385 and 28329 cm^{-1} assignable to $^2E_g \rightarrow ^2T_{2g}$ and due to charge transfer spectra, respectively, which is a characteristic of distorted octahedral stereo-chemistry[17].

The magnetic moments of Co(II) complex are found 4.69 B.M. suggests octahedral geometry. The electronic spectra of Co(II) complex showed three absorption bands around 10152, 18868 and 23169 cm^{-1} which are assigned to the transition $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$, respectively suggesting high spin octahedral geometry[18].

The electronic spectra of Mn(II) complexes shows the absorption bands around 14925, 24038 and 32154 cm^{-1}

TABLE-1
ANALYTICAL DATA OF LIGANDS AND ITS COMPLEXES

Compound/complex	Colour	Found (calcd.) (%)					m.w.	m.p. (ºC)/Decomposition	λ_{max} (mho cm^2 mol^{-1})
		C	H	N	Cl	M			
$C_{15}H_{13}NO_5$	White	62.18 (62.27)	4.45 (4.56)	4.51 (4.88)	–		287.27	238	–
$[C_{30}H_{30}Cl_2N_2O_8Cu]$	Dark green	50.78 (50.82)	3.55 (3.70)	3.45 (3.95)	9.65 (10.00)	8.78 (8.96)	708.99	220	16.2
$[C_{30}H_{30}Cl_2N_2O_8Co]$	Light pink	50.85 (51.15)	3.45 (3.72)	3.54 (3.98)	9.65 (10.07)	8.01 (8.37)	704.37	>270	14.6
$[C_{30}H_{30}Cl_2N_2O_8Mn]$	Light brown	51.06 (51.45)	3.25 (3.74)	3.78 (4.00)	9.85 (10.12)	7.47 (7.84)	700.38	>270	12.2
$[C_{30}H_{30}Cl_2N_2O_8Fe]Cl$	Brown	48.46 (48.91)	3.13 (3.56)	3.21 (3.80)	14.00 (14.44)	7.17 (7.58)	736.74	>270	19.5

TABLE-2
CHARACTERISTIC IR FREQUENCIES OF THE LIGAND AND ITS METAL COMPLEXES (cm^{-1})

Compound	O-H···N (H-bonded)	C=O Lactone carbonyl	C=N Azomethine group	C=O Enolic	C=C Aromatic ring	C-N Aryl azomethine	M-O	M-N
$C_{15}H_{13}NO_5$	3364	1702	1646	1622	1575	1439	–	–
$[C_{30}H_{30}Cl_2N_2O_8Cu]$	–	1681	1610	1600	1567	1463	565	533
$[C_{30}H_{30}Cl_2N_2O_8Co]$	–	1715	1638	1612	1577	1460	580	530
$[C_{30}H_{30}Cl_2N_2O_8Mn]$	–	1713	1578	1619	1546	1443	585	490
$[C_{30}H_{30}Cl_2N_2O_8Fe]Cl$	–	1695	1609	1585	1568	1459	632	535

assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}$ and ${}^6A_{1g} \rightarrow {}^6A_{lg}(G)$/charge transfer, respectively. The magnetic moment value for Mn(II) complexes is 5.70 BM. These facts indicate that the complexes has octahedral geometry[19-21].

The magnetic moment of Fe(III) complexes 5.38 BM suggest the octahedral geometry. The Fe(III) complex have expected four electronic absorption spectra due to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, ${}^6A_{1g} \rightarrow 4E_g$, ${}^4A_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}(D)$. But all these four transition are not generally observed. In present investigation three bands are observed around 15267, 22936 and 31153 cm^{-1}, which may be, assigned to high spin octahedral complexes, for transitions ${}^6A_{1g} \rightarrow {}^4T_1(D)$, ${}^6A_{1g} \rightarrow {}^4T_1$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$, respectively[22] corresponds to octahedral geometry. The last d-d band assigned to transition ${}^6A_{1g} \rightarrow {}^4T_{2g}$ in the present case may be associated with the charge transfer band traveling into visible region of spectrum[23].

Thermal study: The Mn(II) complex of ligand is chosen for thermal study. The thermogram of Mn complex shows no weight loss up to 325 ºC. The ligand starts to decompose at 325 ºC and shows about 10 % weight losses up to 375 ºC which may be due to loss of two coordinated chlorine (cal. 10.12 %). The first step decomposition takes place in the range 375-525 ºC as shown by DTA curve about 34 % weight loss takes place which may be due to non-coordinate part of ligand (cal. 34.37). The second step decomposition is in the range of 525-900 ºC which is due to coordinate part. After which a stable residue remains.

Thermogravimetric studies indicate that the metal complexes of Mn(II) do not contain coordinated water or lattice water and are thermally quit stable. The first step covering the reaction interval 325-525 ºC shows sharp exotherm at 347 ºC. The second step covering the reaction interval 525-900 ºC shows sharp exotherm at 734 ºC.

In order to calculate the kinetic parameters *viz*. n (order of reaction), E (energy of activation), Z (pre exponential factor), Δs (energy of activation) and G (free energy change). Three methods have been used namely Coats. Redfern[24], Mac Callum-Tanner[25] and Horowitz Metzger[26,27].

Coats-Redfern method:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\log\frac{ZR}{Eq}\left[1-\frac{2RT}{E}\right]-\frac{Ea}{2.304R}\frac{1}{T} \tag{1}$$

MacCallum-Tanner method:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right]=\log\frac{ZEa}{Rq}-0.485E^{0.435}-\frac{0.449+0.217Ea}{T}\times10^3 \tag{2}$$

Horowitz-Metzger method:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right]=\log\frac{ZRT_s^2}{Eaq}-\frac{Ea}{2.303RTs}+\frac{Ea\theta}{2.303RT_s^2} \tag{3}$$

The frequency factor (Z) was calculated by,

$$\text{Intercept}=\log\left(\frac{ZR}{qEA}\right)$$

and the equation used for calculating entropy change (ΔS) is

$$\Delta S = 2.303R\log\frac{Zh}{k}Ts$$

Using the computer Microsoft Excel programmers the linear plots of the left-hand side of eqns. 1 and 2 *versus* 1/T and against θ = (T - Ts) and for eqn. 3 were drawn by the method of least squares for different values of 'n' (order of reaction) ranging from 0-3 in increment of 0.01 and the corresponding correlation coefficient were evaluated. The highest value of correlation coefficient gave the correct value of 'n'. From the slope and intercept, Ea and Z values were calculated. Using Ea and Z values, the values of ΔS and ΔG were determined.

The values of n, E, Z, ΔS and G estimated by all the three methods are in good mutual agreement Table-3. The value of E is sufficiently high and is comparable with other observations[28,29].

X-Ray diffraction: The X-ray powder diffraction of Co(II) complex is studied as a representative system. The observed 2θ with relative intensity more than 10 % are indexed and have been used for evaluation. The 10 reflections of 2θ between 10.58-36.58 with maximum intensity at 2θ = 20.53 and d = 4.32 Å are observed. The X-ray diffraction pattern of the complex with respect to their prominent peaks has been indexed by using computer software[30]. The above index method also yielded miller indices (h, k, l) values (Table-4), unit cell parameters, volume of unit cell and space group. The unit cell parameters for the given diffractogram are a = 15.34769 Å, b = 4.52683 Å and c = 8.7738 Å, with α = γ = 90.000 and β = 107.810. The sample is found to be monoclinic in nature with space group P2/m. The experimental density value of the complex was determined by using specific gravity method[31], which is further used to calculate the volume of unit cell. The experimental density and theoretical density value 1.32141 and 1.4321 g cm^{-3}, respectively of complexes found to be in good agreement within the limits of experimental error. The other parameters such as porosity and particle size were calculated and are 7.728 % 147.32 Å, respectively. The number of molecules (n) per unit cell were calculated using equation ρ = nm/Nv and found 4 molecules per unit cell.

TABLE-3
KINETIC PARAMETERS DERIVED FROM THERMAL ANALYSIS

[$C_{30}H_{30}Cl_2N_2O_8Mn$]

	n	Ea (KJ/mol)	Z/S	ΔS (J/K/mol)	G (KJ/mol)
CR	1.5	58.33336	7740959	-119.135	67.20279
MT	1.2	58.84208	23405.55	-167.379	71.30316
HM	1.6	52.82553	75984.75	-157.587	64.55757

TABLE-4
XRD DATA OF Co(II) COMPLEX

$2\theta_{observed}$	$2\theta_{calculated}$	d-observed (Å)	d-calcu. (Å)	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	Miller indicies			Relative intensity
						h	k	l	
10.580	10.582	8.3547	8.3532	0.008501	0.008503	0	0	1	93.8
12.115	12.104	7.2996	7.306	0.011136	0.011116	2	0	0	26.6
13.411	13.430	6.5970	6.5875	0.013634	0.013672	-2	0	1	32.0
18.406	18.402	4.8164	4.8173	0.025578	0.025566	2	0	1	66.8
20.531	20.523	4.3225	4.324	0.031758	0.031735	1	1	0	100
23.985	23.996	3.7072	3.7055	0.043175	0.043211	1	1	1	86.6
26.865	26.866	3.3160	3.3158	0.053964	0.053966	3	1	0	26.6
28.886	28.882	3.0885	3.0887	0.062207	0.062191	-2	1	2	36.5
30.990	30.994	2.8833	2.8829	0.071372	0.071390	3	1	1	57.0
36.585	36.569	2.4542	2.4552	0.098513	0.098430	5	1	0	39.6

TABLE-5
YIELD OF MDW IN mg

Concentration (ppm)	MDW in mg (inhibition %) in ligand	MDW in mg (inhibition %) control	MDW in mg (inhibition %) in complexes of			
			Mn(II)	Fe(III)	Co(II)	Cu(II)
200	54 (38.63)	88	54 (38.63)	53 (39.77)	44 (50.00)	41 (53.40)
400	26 (70.45)	88	19 (78.40)	29 (67.04)	25 (71.59)	07 (92.04)

Fungicidal activity: The ligand and their corresponding metal chelates were screened by mycelial dry weight (MDW) method *in vitro* against *Aspergillus niger* for their fungicidal activity in glucose nitrate (GN) media. Medium prepared by adding 10 g of glucose, 2.5 g of KNO_3, 1 g of KH_2PO_4 and 0.5 g of $MgSO_4$ in 1 L of distilled water and the fungus was cultivated on GN media. The ligand and complexes under investigation were added to GN medium (200 and 400 ppm) preparing solutions/suspension. The conical flask containing medium with ligand and complexes, autoclaved at 15 lbs for 0.5 h, inoculated with *A. niger*, after 168 h the mycelium obtained was collected by filtration through Whattman filter paper. The yield of MDW was recorded. The ligand exhibited toxicity in the inhibition. Due to synergistic combination of the coordinated metal ions with the ligands, the inhibition has been increased in complexes by 80-100 %. The order of inhibition with respect to metal ion is Co > Fe > Mn > Cu. The results obtained are shown in Table-5. The results are similar to the observations made by other workers[10,11,32].

Conclusion

From the above discussion we proposed distorted octahedral geometry for the Cu(II), Co(II) and octahedral geometry for Mn(II) and Fe(III) complexes. The ligand behaves as O, N bidentate coordinating through azomethine nitrogen and oxygen of enolic carbonyl group. The complexes are biologically active since they exhibit enhanced antifungal activities compared to their parent ligands. The thermal study of Cu(II) complex indicates that complexes are thermally stable. The XRD study suggests monoclinic P2/m crystal system.

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