Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 2235-2238

ASIAN JOURNAL OF CHEMISTRY

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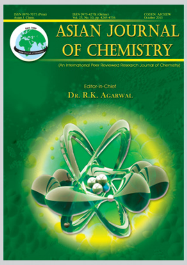

Synthesis, Characterization of Biological Active Bidentate Heterocyclic Schiff Base Metal Complexes

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(*Received*: 25 May 2011; *Accepted*: 20 December 2011) AJC-10870

The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with Schiff base ligands derived from heterocyclic compounds 3-acetyl-6-methyl-(2*H*)-pyran-2,4(3*H*)dione (dehydroacetic acid) and *o*-anisidine were synthesized and characterized by elemental analysis, conductance, magnetic, thermal, UV-VIS and ^{1}H NMR spectroscopy. The ligand field parameters have been evaluated for metal complexes which suggest an octahedral geometry for each of them. The magnetic moment and spectral data suggest the dimeric nature of Mn(II) complexes with octahedral geometry. The fungicidal activities of the ligands and their metal complexes have been screened *in vitro* against *Aspergillus niger* and the percentage inhibition of the metal complexes is found to be increased considerably than that of their corresponding ligands and the order is Cu > Ni > Fe > Mn > Co.

Key Words: Dehydroacetic acid, Schiff base, Transition metal complexes, Kinetic calculations, Fungicidal activity.

INTRODUCTION

Schiff bases are one of the most widely used as chelating ligands in coordination chemistry. Literature survey reveals that though some work has been done on the metal complexes of Schiff bases derived from dehydroacetic acid with aliphatic amines, hydrazides, thiosemicarbazides have been prepared and studied intensively[1]. However, much less attention has been focused on the metal complexes of Schiff bases derived from dehydroacetic acid and aromatic amines. In the view of the above fact, we report here the synthesis and characterization of the Schiff bases derived from biologically active dehydroacetic acid and *o*-anisidine (L^1). The complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal ions with this ligands were also prepared. The structure of the complexes has been established using analytical, magnetic, IR, electronic spectral data and thermal analysis.

EXPERIMENTAL

Dehydroacetic acid for synthesis is obtained from E-Merck, Gemaney. *o*-Anisidine AR grade is obtained from Lancaster are used for the synthesis of ligand. The AR grade metal chlorides from E-Merck and Qualigens were used for the synthesis of metal complexes. C, H and N analysis were determined on Perkin Elmer CHN Analyzer (2400). The metal contents were determined by atomic absorption spectra on Perkin Elmer atomic absorption spectrophotometer (2380). The molar conductance measurements were made using Systronics conductivity meter with a dip type cell (cell constant = 0.1) using approximately 10^{-4} M solutions of the complexes in DMSO. Magnetic measurements were carried out by using Gouy's balance at room temperature using $HgCo(CNS)_4$ as calibrant. The IR spectra of the ligands and their metal complexes were recorded as KBr pellets on a Perkin Elmer (1430) FTIR spectrophotometer in the range 4000-400 cm^{-1}. The electronic spectral measurements were made on Shimadzu UV-visible spectrophotometer UV-160. The TG and DT analysis were carried out in 25-650 ºC range using thermal analysis with a heating rate 100 min^{-1} using alumina as a standard. The NMR spectra of the ligands were recorded on Brucker FT 200 mhz NMR spectrophotometer in $CDCl_3$ solvent using TMS as a reference sample. The fungicidal activity tested from Department of Botany, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Synthesis of Schiff base: The asymmetric bidentate Schiff base ligand 3-1-(2-methoxyphenylimino)ethyl)-3*H*-pyran-2,4-dione, is synthesized in single step[2-4]. The equimolar solution of dehydroacetic acid and *o*-anisidine is refluxing in 50 mL ethanol on 1 RML Rotamantale for about 4-5 h. The Schiff base was cooled at room temperature and collected by filtration, followed by recrystallisation in ethanol. The purity of the ligands was checked by TLC technique and elemental analysis.

Synthesis of metal complexes: To a hot methanolic solution (25 mL) containing 2 mmol of the ligand, a methanolic solution (25 mL) of a metal chloride (1 mmol) was added drop wise with constant stirring. The pH of the reaction mixture was maintained around 7.5 by adding 10 % alcoholic ammonia solution and refluxed for about 2 h. The precipitated solid metal complex was filtered off under hot conditions and washed with hot methanol, petroleum ether (40-60 ºC) and dried over anhydrous $CaCl_2$ in vacuum desiccators.

RESULTS AND DISCUSSION

All the metal complexes are coloured solids, stable to air and non-hygroscopic. They are insoluble in water but soluble in DMF and DMSO. The physical characteristics, analytical and molar conductance data of the ligand and metal complexes are given in Table-1. The molar conductance values of all the metal complexes in DMSO at the concentration of 10^{-4} M are very low indicating their non electrolytic nature. The analytical data indicate 1:2 metal:ligand stoichiometry for the Cu(II), Ni(II), Co(II), Fe(III) and 1:1 stoichiometry for the Mn(II) complexes are given in (Figs. 1-3).

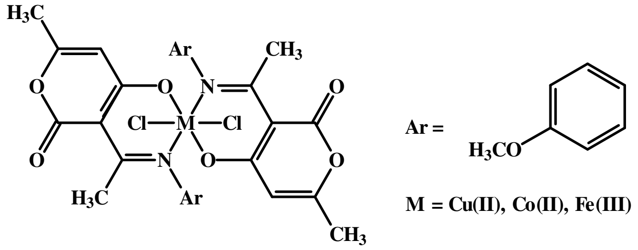

Fig. 1. Proposed geometry of complexes of ligand L[1]

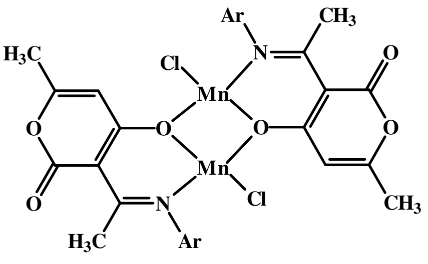

Fig. 2. Proposed geometry of Mn(II) complex of ligand L[1]

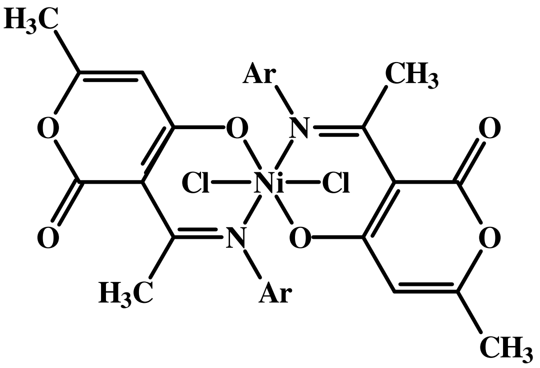

Fig. 3. Proposed geometry of Ni(II) complex of ligand L[1]

^{1}H NMR: The ^{1}H NMR spectra of the free ligands in $CDCl_3$ at room temperature showed the following signals at δ (ppm): for ligand L[1] 2.15 (3H, s, C_6-CH_3), 15.85 (1H, s, C_3-H), 5.72 (1H, s, C_5-H), for DHA moiety, 2.55 (3H, s, N=CH_3) methyl hydrogen bonded to carbon azomethine, 3.80 (3H, sC_2-CH_3), 7.0-7.4 (4H,m) for phenyl moiety.

IR: The characteristic IR frequencies of the ligand and their complexes are shown in Table-2. The IR spectrum of the free ligands show a broad weak band *ca.* 2600-2400 cm^{-1} attributed to intramolecular bonding ν(OH). The bands 1696 cm^{-1} are assigned to ν(C=O) (lactone carbonyl), ν(C=N) (azomethine), ν(C-N) (aryl azomethine) and ν(C-O) (enolic) streaching modes, respectively. The disappearance of IR band at 2600 cm^{-1} (intramolecular hydrogen bonding) in the spectra of all the complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion. It is further supported by an upward shift in ν(C-O) by 20-30 cm^{-1} in all complexes. A downward shift in ν(C=N) by 15-20 cm^{-1} indicates participation of azomethine nitrogen in complex formation. The IR spectra of the metal complexes showed new bands in the 652-540 and 580-450 cm^{-1} region, which can be assigned to ν(M-O) and ν(M-N) vibrations, respectively[5].

Magnetic measurements and electronic absorption spectra: The magnetic and electronic spectral data are given in Table-3. The data is of relevance for the proposed structure of the complexes. The electronic spectra of the Cu(II) complexes in DMSO shows the bands at 11976-16528 cm^{-1} for ligand HL[1] assignable to $^2Eg \rightarrow {}^2T_{2g}$ transition which is characteristic of distorted octahedral geometry. This is further supported by the magnetic moment values (1.80 μ_B) within the required range for d^9-system[6]. The electronic spectra of the Ni(II)-HL[1] complex shows three bands in range 10416(ν_1), 15151 (ν_2) and 23809 (ν_3) assigned to the transitions $^3A_{2g}$(F)

TABLE-1
PHYSICAL CHARACTERIZATION, ANALYTICAL AND MOLAR CONDUCTANCE DATA OF THE COMPOUNDS

Compound	f.w.	m.p. (ºC)	Colour	Found (calcd.) (%)				Λ_m (Scm^2mol^{-1})
				C	H	N	M	
HL[1] $C_{15}H_{15}NO_4$	273	138	Gray	65.21 (65.85)	5.46 (5.54)	5.27 (5.12)	–	–
$Cu(C_{30}H_{30}N_2O_8)Cl_2$	680	264	Green	52.88 (52.90)	4.37 (4.40)	4.10 (4.11)	9.34 (9.33)	19.4
$Ni(C_{30}H_{30}N_2O_8)Cl_2$	675	300	Brown	53.25 (53.28)	4.45 (4.44)	4.15 (4.14)	8.64 (8.68)	10.4
$Co(C_{30}H_{30}N_2O_8)Cl_2$	643	300	Green	55.90 (55.91)	4.64 (4.65)	4.32 (4.34)	9.14 (9.15)	10.9
$Mn_2(C_{30}H_{30}N_2O_8)Cl_2$	726	300	Black	49.55 (49.58)	4.12 (4.13)	3.80 (3.85)	15.12 (15.13)	11.1
$Fe(C_{30}H_{30}N_2O_8)Cl_2$	672	255	Brown	53.52 (53.53)	4.44 (4.45)	4.15 (4.16)	8.29 (8.30)	11.0

TABLE-2
CHARACTERISTIC IR FREQUENCIES (CM^{-1}) OF THE LIGANDS AND THEIR METAL COMPLEXES

Compound	ν(C=O)	ν(C=C)	ν(C=N)	ν(C-N)	ν(C-O)	ν(M-O)	ν(M-N)
$HL^1C_{15}H_{15}O_3N$	1696	1566	1660	1354	1233	–	–
$Cu(L^1)_2Cl_2$	1698	1567	1652	1380	1262	580	460
$Ni(L^1)_2Cl_2$	1696	1565	1645	1370	1254	564	450
$Co(L^1)_2Cl_2$	1696	1566	1649	1377	1255	652	580
$Mn_2(L^1)_2Cl_2$	1698	1576	1645	1375	1250	540	460
$Fe(L^1)_2Cl_2$	1698	1565	1646	1380	1252	540	485

TABLE-3
MAGNETIC AND ELECTRONIC ABSORPTION SPECTRAL DATA (IN DMSO) OF THE COMPLEXES

Complex	μ_{eff} (μ_B)	ν (cm^{-1})	Geometry
$Cu(C_{30}H_{30}O_8N_2)Cl_2$	1.80	11976, 16528, 28571	Octahedral (distorted)
$Ni(C_{30}H_{30}O_8N_2)Cl_2$	3.07	10416, 15151, 23809	Octahedral
$Co(C_{30}H_{30}O_8N_2)Cl_2$	5.12	10204, 18518, 25571	Octahedral
$Mn_2(C_{30}H_{30}O_8N_2)Cl_2$	5.04	16949, 23809	Tetrahedral
$Fe(C_{30}H_{30}O_8N_2)Cl_2$	5.40	16129, 23255, 29411	Octahedral

$\rightarrow {}^3T_{2g}$ and a charge transfer transition, respectively, suggesting square planar geometry of the complex. Also the diamagnetic nature supports to the structure[7]. The electronic absorption spectrum of Co(II) complexes had three bands in range 10309 (ν_1), 17543 (ν_2) and 25777 (ν_3) which may be attributed to three spin-allowed transitions ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, respectively, suggesting an octahedral geometry[8]. The effective magnetic moment values (4.451 μ_B) were found to be well within the range as expected for octahedral geometry. The electronic spectra of the Mn(II) complex showed two bands at 17543 cm^{-1} (ν_1) and 23222 cm^{-1} (ν_2) assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$, respectively, indicating tetrahedral geometry. The magnetic moment values (5.13 μ_B) which is slightly lower than the spin only value expected for tetrahedral Mn(II) complexes[9]. This may be due to the presence of magnetic exchange and small traces of Mn(II) spacies[10]. In addition to the metal analysis, this is an additional evidence for the dimeric nature of Mn(II) complexes. The subnormal magnetic moment values are indicative of metal-metal interactions supporting dimeric nature. The electronic spectra of the Fe(III) complexes showed three bands at 16129 (ν_1), 22727 (ν_2) and 29411 cm^{-1} (ν_3) assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(D)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}$ and ${}^6A_{1g} \rightarrow {}^4T_{2g}$, respectively and the magnetic moment values (5.59 μ_B) suggesting high spin octahedral geometry[11-13].

Thermal analysis: The simultaneous TG/DT analysis of the Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal complexes was studied from ambient temperature to 1000 ºC under a nitrogen atmosphere using alumina as the reference. The TG curve of the Cu(II) and Ni(II) metal complexes exhibited no mass loss upto 280 ºC indicating the absence of coordinated water[14]. Therefore, the complexes exhibits high thermal stability and the TG thermogram show single step exothermic peaks at 343.5 ºC which indicate the decomposition temperature of the complexes. The complexes starts decomposing partially giving metal oxide at 343.5 ºC, the organic part completely decompose in the temperature range 335-492 ºC as indicating by DT curve. The TG curve of Co(II) complexes shows two stage decomposition the weight loss encountered at 110.5 ºC supported by broad exothermic peak in TG curve which is characteristics of lattice water[15]. The second step was encountered at 240 ºC the organic constituent of the complex starts breaking and decomposes at 337 ºC shown in TG curve supported the two endothermic peaks at 312 ºC and 486 ºC in DTA curve. The constant weight corresponds to cobalt oxide, as a final product. The TG Thermogram of Mn(II) complex shows the decomposition temperature at 256.9 ºC indicated by sharp peak, the organic part completely decompose the range 231-289 ºC was supported by DTA curve. The TG curve of Fe(III) complex shows a exothermic peak at 87.9 ºC, however the temperature 274 ºC may be the decomposition temperature of organic matter and the exothermic peak at 328 ºC indicate decomposition temperature of the complex. The FeO is obtained the end product at 554 ºC showed in DT curve. All the complexes finally decomposed to their metal oxides[16].

Kinetic calculations: The kinetic and thermodynamic parameters *viz.*, energy of activation (Ea), free energy change (ΔF), entropy change (ΔS), the pre-exponential factor (Z) for non-isothermal decomposition of the metal complexes, were determined by the Horowitz-Metzer (HM) approximation method. The obtained data are given in Table-4.

The thermograms of the Cu(II) and Ni(II) complexes show one stage thermal decomposition with single DTG peak at 314.6 and 343.5 ºC, respectively. The thermograms of the Co(II), Mn(II) and Fe(III) complexes show more than one stage thermal decomposition. Theoretically, with decreasing the

TABLE-4
THERMAL KINETIC PARAMETERS OF THE METAL COMPLEXES CALCULATED BY HOROWITZ-METZGER (HM) METHOD

Complexes	Stage/temp. (0 K)	E_A (KJ mol^{-1})	ΔS (Jk^{-1} mol^{-1})	ΔF (KJ mol^{-1})	Z (S^{-1})
L^1-Cu(II)	I/587	96.59	197.00	110.10	623
L^1-Ni(II)	I/610	66.08	164.57	78.15	302
L^1-Co(II)	I/513.4, II/610.4, III/824	22.22, 15.70, 14.31	197.03, 199.74, 199.24	123.33, 137.54, 137.54	549, 470, 653
L^1-Mn(II)	I/529.9, II/722	63.6, 30.45	203.61, 204.31	174.43, 153.24	264, 167
L^1-Fe(II)	I/547, II/601	24.74, 38.93	205.49, 209.74	133.63, 190.41	204, 168

value of Ea, the value of Z increases and the higher value of activation energy suggest the higher stability. However some other inherent physical and chemical factors may cause a change or deviation in this trend. The higher values of Cu(II) and Ni(II) complexes show higher stability than Co(II), Mn(II) and Fe(III) complexes. Higher values of activation energy (Ea) (Table-5) and lower values of frequency factor (Z) favour the reaction to proceed slower than normal. In present studies, the numerical values of activation energy, frequency factor and entropy of activation altogether indicate about the smoothness of the feasibility and reaction rate of the initial reactants and intermolecular stage compounds. The negative values for entropy of activation indicates that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and the reactions are slower than normal which is further supported by low values. The order to thermal stability of compound comes to be 2 > 1 > 5 > 4 > 3 (on the basis of decomposition stage) and 4 > 3 > 5 (on the basis of second decomposition stage). The order of the stability of compounds on the basis of activation energy can be set as 1 > 2 > 4 > 5 > 3 (for first stage) and 5 > 4 > 3 (for second stage)[17]. The variation in the trend might be interpreted to be due to some intermolecular interactions (structural as well as electronic) occurring there in.

TABLE-5
ANTIFUNGAL ACTIVITIES OF LIGANDS AND THEIR METAL COMPLEXES BY MYCELIAL DRY WEIGHT (MDW) AT 250 AND 500 PPM

Compound	*Aspergillus niger*	
	250 ppm	500 ppm
L^1	45	40
Control	65	63
$Cu(L_2)Cl_2$	31	20
$Ni(L_2)Cl_2$	25	15
$Co(L_2)Cl_2$	34	18
$Mn_2(L_2)Cl_2$	43	31
$Fe(L_2)Cl_2$	46	35

Fungicidal activity: To evaluate antifungal activity of the ligand and the corresponding metal complexes, their effect on the growth of *Aspergillus niger* was studied. For fungicidal activity, compounds were *in vitro* against *Aspergillus niger* by mycelia dry weight method[18]. They are given in Table-5. The fungus was grown on standard glucose-nitrate (GN) medium prepared by adding 10 g glucose, 2.5 g KNO_3, 1 g of KH_2PO_4 and 0.5 g of $MgSO_4$ to 1 L of distilled water and fungus was cultivated on the GN media. The ligands and complexes under investigation were added to the GN medium of either 300 or 500 ppm to prepare solution/suspension. The medium either alone or with the ligand and complexes, was taken in conical flask, autoclaved at 15 lbs for 0.5 h, inoculated with *A. niger*, inoculated for 7 days and the mycelium obtained was collected by filtration through Whatmann filter paper. The yield of mycelial dry weight (MDW) Table-2 for each treatment was recorded which enhanced with that obtained on standard GN medium. The ligands show 60-70 % inhibitions. The complexes have greater antifungal activity than the corresponding ligands. The toxic effects of metal complexes were augmented and restricted the growth of *A. nigar* from 80-100 %. All the copper complexes arrested the total growth of the fungus. Growth inhibitions were not found only due to the metal ions but the cumulative effect of metal and ligand. Thus the metal complexes show synergistic combinations. It was also found that during incubation, there was a change in colour of the media. This could be because of degradation of the complexes brought about by *A. niger* by enzyme activity. The order of inhibition with respect to the metal ion was Cu(II) > Ni(II) > Fe(III) > Mn(II) > Co(II). The results obtained are in good agreement with earlier finding[19,20].

Conclusion

Based on the physicochemical and spectral data discussed above, distorted octahedral geometry for the Cu(II) complexes, octahedral geometry for the Ni(II), Co(II) and Fe(III) complexes and tetrahedral geometry for Mn(II) complexes are proposed. The ligands behave as bidentate, coordinating through carbonyl oxygen and the imino nitrogen of dehydroacetic acid moiety. The complexes are biologically active and exhibit enhanced antifungal activities compared to their parent ligands. The thermal study revealed that the all complexes are thermally stable.

ACKNOWLEDGEMENTS

The authors SMS and BSM express their sincere thanks to UGC (WRO) Pune, for the award of a TRF under UGC-XIth plan.The authors are also grateful to Dr. B. R. Arbad for valuable suggestions.

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