ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis, Spectral Characterization and Antimicrobial Studies of some Transition Metal Complexes with ONNO-donor tetradentate ligand

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ABSTRACT

The complexes of the type MLXn ,where M=VO(IV), Mn(II), Fe(III), Co(II),Ni(II), Zn(II) and Cd(II) ,X=H_2O/Cl and L is the schiff base ligand derived from 2,4- dihydroxy -5- acetylacetophenone and 1,4- diaminobutane have been synthesized. All the complexes isolated in solid state, are stable in air and characterized by the elemental analysis, metal content determination, magnetic measurements, thermogravimetric analysis (TGA), IR, and electronic spectral data. The physicochemical data suggest a square pyramidal structure to VO(IV), pseudo octahedral to Cu(II) and an octahedral for Mn(II), Fe(III), Co(II),Ni(II) and Cd(II) complexes. The ligand field parameters have been calculated and related to the electronic environment. The Schiff base and its complexes were screened for their antimicrobial activities against various bacteria and fungi.

Keywords: Schiff base, Metal complexes, Magnetic Study, TGA, Biological activity.

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INTRODUCTION

Schiff bases are most widely used as chelating ligands in coordination chemistry and investigated extensively for the last several decades leading to new synthetic routes of structure, biological and industrial applications [1-3]. They are also useful in catalysis and in medicine as antibiotics, antiallergic and antitumor agents [4-6]. Schiff base complexes with first transition series metal ions [7-10] have been well documented in the literature and have found to exhibit good physiological and pharmacological activities. However, metal complexes of Schiff base of 2,4-dihydroxy -5-acetylacetophenone and 1,4 diaminobutane have not been investigated so far. Hence, it was though of interest to carry out systematic investigation on VO(IV),Mn(II),Fe(III),Co(II),Ni(II),Cu(II),Zn(II) and Cd(II) complexes of Schiff base derived from 2,4-dihydroxy -5-acetylacetophenone and 1,4 diaminobutane.

EXPERIMENTAL

Physical measurements

Elemental analysis (Carbon, Hydrogen and Nitrogen) of all the samples was carried out at Central Drug Research Institute (CDRI), Lucknow, India. The metal contents were estimated after decomposition of the complexes with concentrated H_2SO_4 and HNO_3 as per literature procedures [11]. Magnetic susceptibility measurements were made on Gouy's balance at room temperature with $Hg[Co(SCN)_4]$ as a calibrant and the diamagnetic corrections were made using Pascal's constant. The diffuse reflectance spectra of the complexes were recorded on varian Cary-5E UV-visible spectrophotometer at SAIF, Indian Institute of Technology, Chennai. . ^{1}H NMR spectra of ligand ($CDCl_3$+*DMSO*) was recorded on a NMR-JEOL GSX-400 spectrophotometer and chemical shifts are indicated in ppm relative to tetramethylsilane. Infrared spectra of the ligands and their complexes were obtained in KBr pellets on a Perkin-Elmer spectrometer at SAIF, Chandigarh, India. Thermogravimetric analyses (TGA) of complexes were performed on a TGS-2 Perkin-Elmer thermal analyzer in an ambient air with a heating rate of 10 °C min^{-1}. The ligands and their metal complexes were screened for *in vitro* antimicrobial activity against the *E.Coli, S.Typhi, P. aeruginosa and S.aureus* by cup plate method.

Materials

All the chemicals and solvents used were of analytical grade. Vanadyl (IV)sulphate petahydrate, Manganese(II) acetate tetrahydrate, anhydrous ferric chloride (III) , cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate, zinc(II) acetate dihydrate, cadmium(II) chloride monohydrate were obtained from S.D's. fine Ltd , India

Synthesis of Schiff base ligand (DHADAB): -

The Schiff base was synthesize in two steps, the first step involved the preparation of 2,4-dihydroxy -5-acetylacetophenone and while in second step condensation of the acetophenone with 1-4 diaminobutane have been made.

Step I: Preparation of 2,4- dihydroxy - 5-acetyl acetophenone (DHA)

The acetophenone were prepared by refluxing (5 gm 0.05 mol) of resorcinol and (9ml, 0.05mol) acetic anhydride was taken in a 100 ml of round bottom flask for 45 minutes in presence of fused zinc chloride (7gm) the mix was allowed to cool at room temperature and them prepared on crushed ice with vigorous shaking. A radish brown precipitate separated out. It was filtered and boiled in water for 15 minutes. The boiling solution was filtered in hot condition the precipitate so obtained was washed with hot water, recrystallized from distilled ethanol and dried in vacuo.

Step II: Condensation of the 2, 4-dihydroxy-5-acetylacetophenone with 1,4 –diaminobutane (DHADAB)

1,4 -diaminobutane (0.05 mol) was added dropwise to an ethanolic solution of 2,4-dihydroxy - 5-acetyl acetophenone (0.05 mol in 25 ml ethanol) in round bottom flask with continuous stirring. The reaction mixture was heated under reflux for about 3-4 h. After cooling to room temperature a colored product formed was filtered, washed with ethanol, dried at room temperature and finally crystallized from hot ethanol. yield 65% m.p. 170^{0}C.

^{1}HNMR of DHADAB

The ^{1}HNMR spectrum of ligand exhibits signal at δ 8.00 due to imine proton. The aromatic protons are observed in the range δ 7.35 - 7.65 (2H, s, phenyl), the phenolic OH appeared at δ 12.20 (2H, S, Phenolic OH), δ 3.10 (4H, t, N, CH_2), δ 1.90 (4H, m, CH_2), δ 2.6 (6H, s, methyl).

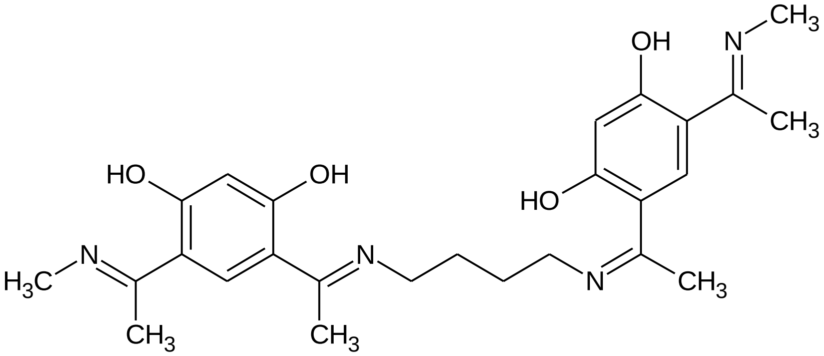

Fig. 1. Schiff base ligand DHADAB

Synthesis of the complexes

All the metal complexes were prepared by a following general method: Equimolar (1.00mmol) quantities of appropriate metal salts and ligand DHADAB were dissolved separately in minimum quantity (25-30 ml) of DMF. Both solutions were filtered and then mixed in hot condition with constant stirring. The reaction mixture was refluxed on a sand bath for a 3-4h. The resulting coloured product obtained was filtered, washed several times with DMF followed by acetone to remove unreacted ligand and metal salt. Finally, the complexes were dried in vacuuo over anhydrous $CaCl_2$. Yield: 60-70 %.

RESULTS AND DISCUSSION

Table 1. Analytical data of DHADAB and its Complexes

S.No	Compound	Formula Weight(gmol$^{-1)}$	Colour	Time of Reflux (h)	Elemental analyses % found (calcd.)			
					M	C	H	N
1	DHADAB	393.56	Yellow	3	--	66.93 (66.99)	6.35 (6.48)	12.01 (12.11)
2	[VO(DHADAB)] H_2O	439.35	Pharaoh	10	10.26 (10.32)	53.48 (53.55)	4.00 (4.09)	5.51 (5.68)
3	[Mn(DHADAB)2H_2O]	445.36	Cairo Bazaar	8	10.98 (11.00)	52.72 (52.90)	4.00 (4.04)	5.52 (5.61)
4	[Fe(DHADAB)H_2O Cl]	481.73	Pharaoh	7	10.50 (10.78)	51.01 (51.03)	3.61 (3.89)	5.30 (5.41)
5	[CO(DHADAB)2H_2O]	449.36	Grayish brown	8	11.59 (11.70)	52.46 (52.48)	3.95 (4.00)	5.41 (5.56)
6	[Ni(DHADAB)2H_2O]	449.12	Sapphire ice	9	11.50 (11.66)	52.48 (52.51)	4.00 (4.01)	5.45 (5.57)
7	[Cu(DHADAB)2H_2O]	453.88	Raven Song	10	12.48 (12.49)	52.00 (52.01)	3.86 (3.97)	5.42 (5.51)
8	[Zn(DHADAB)2H_2O]	455.81	Lemon Pie	12	12.70 (12.82)	51.72 (51.82)	3.80 (3.95)	5.38 (5.49)
9	[Cd(DHADAB)2H_2O]	502.8336	Day Break	8	20.13 (20.18)	47.28 (47.44)	3.56 (3.62)	5.00 (5.03)

All the complexes are coloured solids, air stable and insoluble in water and common organic solvents but found soluble in DMF and DMSO. The analytical data indicate 1:1 metal: ligand stoichiometry for all the complexes (Table 1).

The infrared spectrum of ligand exhibits a broad band at 2935 cm-^{1} due to presence of intramolecular hydrogen bonding between phenolic OH and azomethine nitrogen atoms [12]. This band is absent in spectra of complexes thereby suggesting the coordination of ligand to metal ion through the loss of phenolic proton on complexation. The ν C-O (phenolic) band in complexes is shifted to higher energy by ≤ 15-33 cm^{-1}, which indicates the coordination of the phenolic oxygen atom [13]. The ligand spectrum exhibits a strong band at 1610 cm-^{1} due to C=N stretching frequency which on coordination is shifted to lower frequency by 22-40cm-^{1} in the spectra of all complexes .The lowering may be due to a reduction in the electron density in the azomethine link[14] which indicate coordination to metal ion through azomethine nitrogen, it is further supported by the imino nitrogen and the phenolic oxygen are involved in the complexation with the metal ion which is clearly evident from the appearance of new medium intensity band in the region 590-654 cm^{-1} and 450-495 cm^{-1} assignable to M-O and M-N bands respectively [15].In the case of Fe(III) complex ν(M-Cl) band is observed at 380 cm^{-1} .The infrared absorption band of VO(IV) complex shows strong absorptions band at 968 cm^{-1} due to ν(V=O) due the presence of a double band in the VO^{2+} moiety arising from a combination of σ band π component due to electron flow $O(P\pi \rightarrow Vd\pi$. The observation of ν (V=O) stretches is close to the normal range [16]. The medium broad band and strong bands in the Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) in the region 3413-3440 cm^{-1} due ν(OH), and a strong sharp band 835 cm^{-1} due to the (H_2O) rocking and waging modes suggests these water molecules as coordinated one [13,14,17]. On the basis of above IR data (Table 2) thus it may be concluded that DHADAB ligand behave as a dibasic tetradentate ligand coordinating through deprotonated phenolic Oxygen and azomethine Nitrogen atom.

Table 2. IR Analysis (cm^{-1}) of the DHADAB and its Metal Complexes

S.N	Compounds	ν(O-H)	ν (C=N)	ν (C-O)	ν (M-O)	ν (M-N)	ν (H_2O)
1	DHADAB	2935	1610	1275	--	--	--
2	[VO(DHADAB)] H_2O	--	1586	1293	603	489	3425,835,1630
3	[Mn(DHADAB)2H_2O]	--	1585	1295	605	462	3413,843,1610
4	[Fe(DHADAB)H_2O Cl]	--	1578	1298	595	456	3415,827,1633
5	[CO(DHADAB)2H_2O]	--	1570	1305	540	451	3440,845,1638
6	[Ni(DHADAB)2H_2O]	--	1571	1298	650	491	3428,833,1643
7	[Cu(DHADAB)2H_2O]	--	1573	1308	654	495	3428,851,1640
8	[Zn(DHADAB)2H_2O]	--	1576	1297	633	490	3419,835,1631
9	[Cd(DHADAB)2H_2O]	--	1585	1291	593	450	3438,834,1628

The magnetic moment for VO(IV) complex found to be 1.68 B.M. at room temperature, which is within the range of spin only value for one unpaired electron [18]. The diffuse reflectance spectrum of VO(IV) complex displays three bands at 109890,188679 and 252525 cm^{-1} which may be assigned to the $^2B_2 \rightarrow {}^2E$ (dxy → dxz - dyz), $^2B_2 \rightarrow {}^2B_1$ (dxy → dx^2-y^2) and $^2B_2 \rightarrow {}^2A_1$ (dxy → dz^2), transitions, respectively for square pyramidal geometry around VO (IV) ion . The room temperature magnetic moment of Mn(II) complex is 5.98 B.M. suggesting octahedral geometry to the complex [17-19]. The Mn(II) complex shows three bands at 173010, 229885 and 259740 cm^{-1} . These spectral bands are assigned as to the 6A1g-$\rightarrow {}^4T_{1g}({}^4G){}^6A_{1g}$-$\rightarrow {}^4T_{1g}({}^4G)$ and $^6A_{1g}$-$\rightarrow {}^4T_{1g}({}^4Eg)$, transitions, respectively towards octahedral structure around Mn (II) ion. The magnetic moment for Fe(III) complex at room temperature is found to be 5.78 B.M. suggesting octahedral geometry to the complex. The reflectance spectrum of this complex exhibits three absorption bands in the region 13071-13422, 15432-15748 and 22222-22624 cm^{-1} Theses bands are assigned to $^6A_{1g}$ (S) → $^4T_{1g}$(G), $^6A_{1g}$ (S) → $^4T_{2g}$ (G) and $^6A_{1g}$ (S) → $^4A_{1g}$ (G) ,transition ,respectively in an octahedral environment. [20].The observed magnetic moment of Cu (II) complex is found to be 1.89 B.M. suggesting distorted octahedral geometry. The Cu (II) complex shows bands at 17006-17301, 19074-19455 and

20408-20920 cm^{-1} due to $^{2}B_{1g} \rightarrow {}^{2}A_{1g}$, $^{2}B_{1g} \rightarrow {}^{2}B_{2g}$ and $^{2}B_{1g} \rightarrow {}^{2}E_{g}$,transitions ,respectively, towards Pseudo octahedral structure around Cu(II) ion[21].The Co(II) complex shows magnetic moment 4.75 B.M. suggest high spin octahedral geometry for Co(II) complex . The electronic spectrum Co(II) complex shows three bands in the regions 7704-7812, 10050-9881 and 16129-16722 cm^{-1} assignable to $^{4}T_{1g} \rightarrow 4T_{2g}$(F), $^{4}T_{1g} \rightarrow 4A_{2g}$ (F) and $^{4}T_{1g} \rightarrow 4A_{1g}$ (P),transitions, respectively, in an octahedral environment around the cobalt ion. Ligand field parameters for Co(II) complex have been calculated by using standard equation [22] and values are found. The reflectance spectral parameters for Co(II) are found to be Dq=1631.3cm^{-1}, B= 569cm^{-1}, β= 0.619and % covalency= 38.1. The magnetic moment of Ni(II) complex is 2.86 B.M. which lies in the normal range of octahedral Ni(II) complexes. The electronic spectrum of Ni(II) complex exhibits three bands at 10329-10559 , 16977-17543 and 24875-25188 cm^{-1}. These bands may be assigned to the transitions 3A2g $\rightarrow {}^{3}T_{2g}$, $^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{2g}$ and $^{3}A_{2g} \rightarrow {}^{3}T_{1g}$, (P), respectively in octahedral configuration [23, 24]. The Zn(II), Cd(II), MoO_2(VI) UO_2 (VI) complexes are found diamagnetic as expected from their electronic configurations .

Thermal analyses of the complexes were carried out upto 700^{o}C. All the complexes show a gradual mass loss indicating decomposition by fragmentation with increase in temperature and follow the similar pattern of their thermal decomposition. The complexes remains unaffected up to 60^{0}C after this a slight depression is observed up to 120^{0}C. The weight loss at this temperature range is corresponds to one water molecule for VO(IV) Fe(III), and two water molecules for Mn(II), Co(II),Ni(II), Zn(II) and Cd(II) complexes. After the loosed of coordinated water, anhydrous complexes remain stable for a while at 320^{o}C and thereafter again the complexes show rapid degradation presumably due to decomposition of organic constituent of the molecules as indicated by the steep fall in the percentage of weight loss and continued up to 620^{o}C . TG curves show continuous mass loss in a temperature range 320 – 650 ^{o}C and attain a horizontal level above 650^{O}C suggesting the formation of final decomposition product as stable metal oxides [25, 26].

Table 3. Antimicrobial activity ligand and its complexes (mm)

S.N	Compounds	*E. Coli*	*S. Typhi*	*P. aeruginosa*	*S.aureus*
1	DHADAB	16	15	12	17
2	[VO(DHADAB)] H_2O	11	R	12	15
3	[Mn(DHADAB)2H_2O]	17	R	12	18
4	[Fe(DHADAB)H_2O Cl] [Fe(DHADAB)H_2O Cl]Cl]Cl]	13	15	16	14
5	[Co(DHADAB)2H_2O]	14.5	13	11	16
6	[Ni(DHADAB)2H_2O]	16	15	11	17
7	[Cu(DHADAB)2H_2O]	12	13	R	14
8	[Zn(DHADAB)2H_2O]	13	R	12	18
9	[Cd(DHADAB)2H_2O]	10	9	11	12

Antimicrobial activity was carried out by the cup plate method [27, 28]. The ligand DHADAB and its VO(IV), Fe(III), Mn(II), Co(II),Ni(II), Zn(II) and Cd(II) Complexes have been screened for their antimicrobial activities at 100 μg/0.1cm^3 concentration. The inhibition effect of ligands and their metal complexes on growth of various bacteria is summarized in Table 3. The growth of E. *Coli* and S. *aureus* is more inhibited by almost all the compounds as compared to other bacterial species. The Cu(II),Mn(II),Cd(II)are highly active against S. *aureus* whereas VO(IV), Fe(III), Ni(II) and Zn(II)are found to show good activity against E.*Coli*. All the compounds are either resistant or weak to moderately active and low sensitive against P.*aeruginosa* and S. *typhi* [29].

ACKNOWLEDGEMENT

The author is thankful to SAIF, CDRI Lucknow, India, AICT Hydrabad, SAIF, IIT Chennai, SAIF Chandigarh, Sant Gadge Baba Amravati University, Amravati, India for the laboratory facility.

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