

Synthesis, Characterization and Thermogravimetric Studies of Some Metal Complexes with N_2O_2 Schiff Base Ligand

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Abstract: The Schiff base ligand *N-N'*-Propylene-diylbis(3-(1-iminoethyl)-6-methyl 2H-pyran 2,4 (3H)-dione) (H_2L) and its complexes with Ti(III), Cr(III), Fe(III), Mn(III), VO(IV), Zr(IV) and $UO_2(VI)$ have been synthesized and characterized by elemental analysis, FTIR, solid state reflectance spectra, magnetic susceptibility measurements and thermal analysis. From analytical and spectral data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). IR spectral data suggest that the ligand behaves as a dibasic tetradentate molecule with *ONNO* donor sequence towards metal ions. The physico-chemical data suggest octahedral geometry for Ti(III), Cr(III), Fe(III) and $UO_2(VI)$ complexes and square pyramidal geometry for Mn(III) and VO(IV) complexes.

Key words: Synthesis • *N-N'*-Propylene-diylbis(3-(1-iminoethyl)-6-methyl 2H-pyran 2,4 (3H)-dione)
• TGA, Infrared spectra

INTRODUCTION

Studies on the metal chelates with Schiff base of dehydroacetic acid have been reported due to their excellent chelating capacity in modern coordination Chemistry [1]. They play a prominent role in biological applications. The compound dehydroacetic acid, is widely used as fungicide [2], herbicide and as a preservative that has powerful antimicrobial effect against bacteria yeast and particularly molds [3].

The synthesis and characterization of divalent metal chelates are quite common however, complexes of higher valent metal ions are limited in the literature. Keeping in view the importance we have undertaken the systematic study of the preparation and characterization of complexes of Ti(III), Cr(III), Fe(III), Mn(III), VO(IV) Zr(IV) and $UO_2(VI)$ with Schiff base ligand *N-N'*-Propylene-diylbis (3- (1-iminoethyl)-6-methyl 2H-pyran 2,4 (3H)-dione) (H_2L) derived from condensation of dehydroacetic acid with 1,3-diaminopropane.

Experimental

Material: All the chemicals and solvents used were of analytical grade. Chromium chloride, titanium trichloride, vanadyl sulphate pentahydrate and uranyl nitrate were of

S.D. fine chemicals. $Mn(OAc)_3 \cdot 2H_2O$ was prepared by the oxidation of $Mn(OAc)_2 \cdot 4H_2O$ using Christensen's method [4] and zirconium(IV) acetate was synthesized by the known method [5].

Instrumentation: The microanalysis of the carbon, hydrogen and nitrogen were performed on a Carlo Erba 1108 elemental analyzer. 1H -NMR spectrum was recorded on a JEOL-AMX 400 spectrophotometer in $CDCl_3 + DMSO-d_6$ solution and chemical shift are recorded in ppm with respect to tetramethylsilane. IR spectra were recorded on KBr pellets using Perkin-Elmer RXI spectrophotometer in the range $4000-400\text{ cm}^{-1}$. The reflectance spectra of the complexes were recorded on Cary-2390 spectrophotometer using MgO as reference. Magnetic susceptibility measurements were made on Gouy's balance at room temperature using $Hg[Co(NCS)_4]$ as a calibrant and experimental magnetic susceptibility were corrected for diamagnetism. Perkin-Elmer TG-2 thermobalance calibrated by crystalline $CuSO_4 \cdot 5H_2O$ was used for thermogravimetric analysis with a heating rate of $10^\circ\text{C min}^{-1}$. The metal contents of the complexes were analyzed gravimetrically after decomposing the complexes with a mixture of $HClO_4$, H_2SO_4 and HNO_3 and then igniting to metal oxide [6].

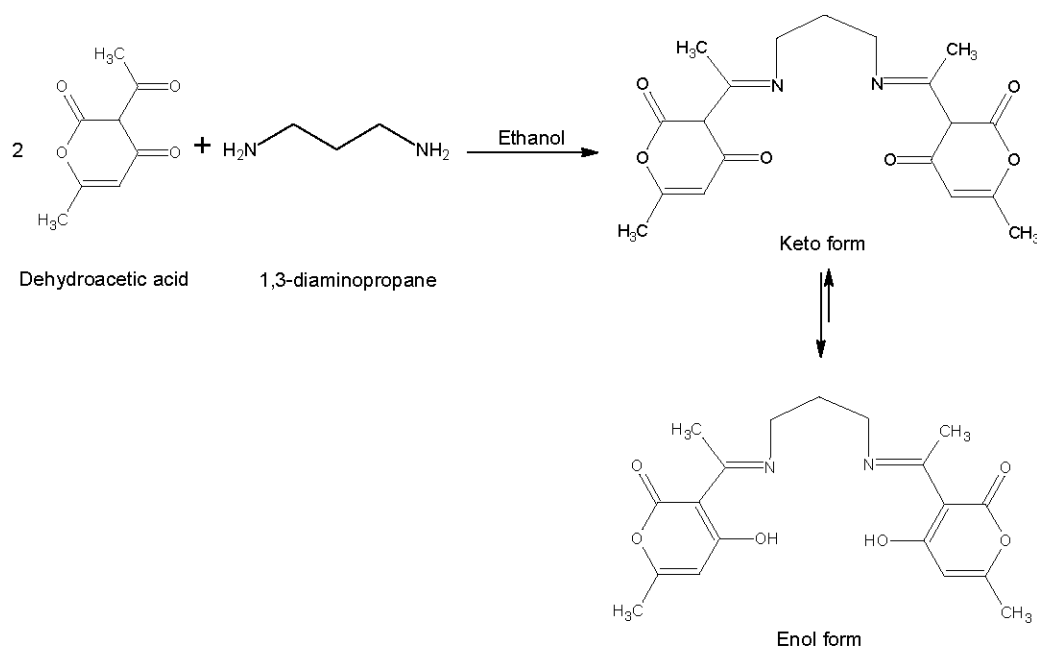


Fig. 1: Schematic representation of synthesis of H_2L ligand and its keto-enol tautomerism

Synthesis of H_2L Ligand: The Schiff base ligand H_2L was prepared by standard method in which dehydroacetic acid (DHA) dissolved in ethanol taken in a round bottom flask and then 1,3-diaminopropane was added drop wise with constant stirring. The reaction mixture was refluxed for 6-8 h and then it was cooled to room temperature. Solid obtained was separated and wash with ethanol and finally dried over calcium chloride. The purity of the synthesized ligand was checked by TLC and m.p. = 120°C. Yield: 74%.

1H -NMR (δ in ppm): 13.9 (br s, 2H, OH), 5.62 (s, 2H, ring-H), 3.60 (q, 4H, imine- CH_2), 2.54 (s, 6H, imine- CH_3), 1.99 (m, 8H, central- CH_2 and ring CH_3). The schematic representation of synthesis of H_2L ligand and its tautomeric form are shown in Figure 1.

Synthesis of Ti(III), Cr(III), Fe(III), Mn(III), VO(IV) and $UO_2(VI)$ Complexes: The ligand (0.01 mol) was dissolved in ethanol (10 ml) by heating at 80°C. To this hot solution, an ethanolic solution of appropriate metal salt solution (0.01 mol) [in case of VO(IV) DMF was used in place of ethanol] was added drop by drop with continuous stirring and the resulting reaction mixture was further refluxed for 4-6 h. The solid product obtained on cooling was filtered, wash thoroughly with ethanol and finally with petroleum ether. Finally, all these complexes were dried at room temperature over $CaCl_2$.

Synthesis of Zr(IV) Complex: Zirconyloxychloride octahydrate (0.02 mol, 0.64 g) was dissolved in methanol (10-15 ml) and to this solution methanolic solution of anhydrous sodium acetate (0.004 mol, 0.32 g, in 15 ml) was added and stirred for 5 min. The separated sodium chloride was filtered off. The H_2L ligand (0.002 mol) was dissolved in hot ethanol. To this solution, the solution containing oxozirconium(IV) diacetate was added and the mixture was refluxed for 6-8 h. The product obtained was filtered, washed 2-3 times with methanol followed by petroleum ether and dried at room temperature over $CaCl_2$.

RESULTS AND DISCUSSION

The reaction of dehydroacetic acid with 1,3-diaminopropane in ethanol yields the Schiff base. The reactions of Ti(III), Cr(III), Fe(III), Mn(III), VO(IV), Zr(IV) and $UO_2(VI)$ salts solution with H_2L have resulted in the formation of complexes. The resulting complexes are colored solids, which decomposed at high temperature. Physical and analytical data of the ligand and its complexes is presented in Table 1.

IR Spectra: On comparison of the infrared spectra of the complexes with that of parent ligand and literature value of absorption of similar type of compounds. The characteristic vibration frequencies have been identified and it is inferred that in the spectrum of free ligand

Table 1: Physical and analytical data of the ligand and its complexes

Compound	Molecular weight	Elemental analysis % found (calcd)			
		C	H	N	M
H ₂ L	374.38	60.16 (60.95)	6.34 (5.92)	7.96 (7.48)	—
[Ti(L)(Cl)H ₂ O].2H ₂ O	509.73	45.09 (44.77)	5.22 (5.14)	5.15 (5.50)	9.78 (9.39)
[Cr(L)(Cl)H ₂ O].H ₂ O	495.85	46.76 (46.02)	4.10 (4.88)	5.98 (5.65)	10.11 (10.49)
[Fe(L)(Cl)H ₂ O]	481.68	48.02 (47.38)	4.18 (4.60)	5.47 (5.82)	11.68 (11.59)
[Mn(L)(OAc)]	486.35	51.14 (51.86)	4.82 (4.77)	5.43 (5.76)	11.23 (11.30)
[VO(L)].2H ₂ O	475.34	48.74 (48.01)	5.27 (5.09)	5.81 (5.89)	10.99 (10.72)
[Zr(OH) ₂ (L)H ₂ O].2H ₂ O	551.65	41.64 (41.37)	4.98 (5.12)	5.36 (5.08)	16.86 (16.54)
[UO ₂ (L)]	642.40	35.06 (35.52)	3.22 (3.14)	4.49 (4.36)	37.82 (37.05)

exhibits a medium broad band at 3420 cm⁻¹ due to intramolecular hydrogen bonded OH group [7, 8]. In the spectra of all the complexes this band has been disappeared, indicating the coordination of (C=O) oxygen to the metal ion via deprotonation. The ligand spectrum however display a sharp $\nu(\text{C}=\text{O})$ absorption band at 1702 cm⁻¹ confirming that the condensation take place on the side chain carbonyl group of the acid; otherwise, two distinct bands would have been observed due to nonequivalent ring and side chain carbonyl group. The other bands at 1656 and 1575 cm⁻¹ are assignable to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ stretching vibrations respectively whereas the IR spectra of chelates shows the medium band in the range 519-540 cm⁻¹ and 577-627 cm⁻¹ which are assigned to M-N and M-O modes respectively.

The ligand exhibits strong band at 1656 cm⁻¹, due to C=N stretching on chelation this has been shifted to lower frequency 1638-1650 cm⁻¹ indicating the participation of azomethine nitrogen in bonding with the metal ions [9]. This lowering can be explained by the donation of electrons from nitrogen to empty d-orbital of the metal ion [10]. In case of Mn(III) complex two bands are observed at 1607 and 1405 cm⁻¹ which may be due to $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sy}}(\text{OCO})$ respectively. The difference of 198 cm⁻¹ between the two bands and their position indicates the monodentate nature of the acetate molecule [11]. Except Mn(III) and UO₂(VI) complexes, all other complexes show characteristic absorption bands for water. A broad band at 3233-3370 cm⁻¹ may be due to $\nu(\text{OH})$ of water [12, 13] and a sharp shoulder at 1525-1540 cm⁻¹ may be assigned to $\delta(\text{H}_2\text{O})$. Water molecules are coordinated, confirmed by occurrence off additional strong and sharp band at 815-865 cm⁻¹ arising due to OH rocking vibrations [14, 15]. In the spectra of VO(IV), Zr(IV) and UO₂(VI) complexes the additional bands observed at 972, 1138 and 912 cm⁻¹ assignable to $\nu(\text{V}=\text{O})$, $\delta(\text{Zr}-\text{OH})$ and $\nu_{\text{asy}}(\text{O}=\text{U}=\text{O})$ respectively [16, 17, 18].

Electronic Spectra and Magnetic Moment: The electronic spectrum of Cr(III) complex exhibits three bands at 18600, 25644 and 38573 cm⁻¹ which may be assigned to ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}(\text{F})$, $\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ and $\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{P})$, transitions, respectively for an octahedral stereochemistry. The interelectronic repulsion parameter *B* is found to be 561 cm⁻¹ which is lower than the free ion value (920 cm⁻¹), suggesting delocalization of electron on metal into molecular orbital which cover both the metal and ligand [19]. The values of \hat{a} and ν_2/ν_1 are found to be 0.61 and 1.37 respectively. The electronic spectrum of Mn(III) complex exhibits an intense band at 27228 cm⁻¹ which may be due ligand to metal charge transfer transition. In the second region three d-d bands are observed at 13710, 16987, 20203 cm⁻¹ which may be due to ${}^5\text{B}_1 \rightarrow {}^5\text{B}_2$, ${}^5\text{B}_1 \rightarrow {}^5\text{A}_1$ and ${}^5\text{B}_1 \rightarrow {}^5\text{E}$, transitions, respectively suggesting square pyramidal geometry around Mn(III) ion. Three bands are observed in case of Fe(III) complex at 15125, 24032 and 23255 cm⁻¹ belongs to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ transitions, respectively, indicating octahedral geometry of Fe(III) complex [20, 21]. The electronic spectrum of Ti(III) complex show broad band in the region ~18189 cm⁻¹ due to ${}^2\text{T}_{2g} \rightarrow \text{E}_g$ transition, which indicates an octahedral geometry around the metal ion [22]. The VO(IV) complex shows weak d-d bands in its spectrum at 13888, 16949 and 22222 cm⁻¹ which are assigned to ${}^2\text{B}_2 \rightarrow {}^2\text{E}$, ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ and ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$ transitions, respectively. The fourth band appears at 29411 cm⁻¹ may be due to charge transfer transition (between d_{z^2} orbital of vanadium and $2p_x$ or $2p_y$ orbital of oxygen atom) which is consistent with square pyramidal geometry around VO(IV) ion. The magnetic moment of 3.99 B.M. for Cr(III) complex is consistent with octahedral geometry around metal centre. The Mn(III) complex shows magnetic moment of 4.85 B.M. expected for four unpaired electrons. The value of 5.85 B.M. would suggest high spin six coordination for Fe(III) complex. For

Ti(III) and VO(IV) complexes, magnetic moment is found to be 1.83 and 1.62 B.M. respectively, indicate presence of one unpaired electron.

Thermogravimetric Analyses: Thermal decomposition behavior of the compounds has been studied under dynamic air atmosphere at a heating rate of 10 min⁻¹. The thermogram of H₂L and its complexes indicate that the complexes of Ti(III), Cr(III) and Zr(IV) decompose in three steps while complexes of Fe(III) and VO(IV) decompose in two steps. The Mn(III) and UO₂(VI) complexes are stable up to 210°C, suggesting the absence of any water molecule i.e. lattice and coordinated water. The Ti(III), VO(IV) and Zr(IV) complexes losses their weight up to ~140°C corresponding to two lattice water molecules, while one water molecule for Cr(III) complex [% wt. loss obs/calcd: Ti(III): 7.42/7.06; Cr(III): 3.92/3.76; VO(IV): 7.09/7.57; Zr(IV): 6.98/6.52]. Further complexes show weight loss up to ~220°C corresponding to one coordinated water molecules for Ti(III), Cr(III), Fe(III) and Zr(IV) complexes [% wt. loss obs/calcd: Ti(III): 4.02/3.79; Cr(III): 3.12/3.76; Fe(III): 3.02/3.73; Zr(IV): 3.18/3.48]. In all the complexes rapid weight loss was observed around 300°C, indicative of decomposition of coordinated ligand. Finally, the horizontal nature of the thermogram above 550°C observed, suggests the formation of final decomposition products corresponding to the metal oxide. It was observed that the TG curve of ligand is broader while the curves of its metal complexes are steeper suggesting that the decomposition rate of the metal complexes is faster than that of the ligand and this may be due to catalytic action of metal ion present in them.

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