

## Synthesis, Characterization, Thermal and Electrical studies of Poly Schiff Base Chelates of VO (IV), MoO<sub>2</sub> (VI) and UO<sub>2</sub>(VI)

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**Abstract:** Polychelates of VO (IV), MoO<sub>2</sub> (VI) and UO<sub>2</sub>(VI) with Schiff base ligand 2,4 dihydroxy-5-acetyl acetophenone-1,4-diaminobutane (DHADAB) have been synthesized and characterized by elemental analysis, IR and electronic spectra, <sup>1</sup>H-NMR spectra, magnetic susceptibility, electrical conductivity measurements and thermogravimetric analysis. An octahedral geometry has been assigned to MoO<sub>2</sub>(VI) and UO<sub>2</sub>(VI) complexes while square pyramidal geometry for VO(IV) complexes. The thermal behaviour of the chelates was studied and kinetic parameters were determined by Coats-Redfern method and suggest more ordered activated state in complex formation. The solid state electrical conductivity of the ligand and its polychelates have been studied and it increases with increasing the temperature indicates their semiconducting behaviour.

**Key words:** Schiff base • Polychelates • Thermal analysis • d.c. electrical conductivity

### INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and have got a variety of applications in biological, clinical and analytical chemistry<sup>1,2</sup>. Polynuclear complexes derived from multidentate ligands have documented interesting structural features. The use of Schiff base complexes as catalysts for several organic reactions has received much attention during recent years<sup>3,4</sup>. Though there has been some work on Schiff base complexes of first transition series metal ions, indeed, to the best of our knowledge no work seems to have been carried out on higher valent metal ion complexes of 2,4-dihydroxy-5-acetyl acetophenone-1,4-diaminobutane (DHADAB). In this communication we report, the synthesis, characterization and thermal studies of new polychelates of VO (IV), MoO<sub>2</sub> (VI) and UO<sub>2</sub> (VI). Solid-state conductivity study has also been reported in temperature range 313-413K [1].

**Experimental:** All the chemicals used were of analytical grade. The solvent were dried and distilled before use according to the standard procedure<sup>5</sup>, vanadyl sulphate pentahydrate, uranyl nitrate hexahydrate were of analytical grade. [MoO<sub>2</sub> (acac)<sub>2</sub>] and 5-acetyl-2,4-dihydroxyacetophenone was prepared by the known methods with slight modification<sup>6-8</sup> [2].

**Synthesis of Ligand DHADAB (L):** The Schiff base ligand was synthesized in two steps. The first step involved the preparation of substituted hydroxyacetophenone (DHA) and while in second step the condensation of the acetophenone with 1, 4-diaminobutane has been made. The Schiff base used was prepared by the usual method of condensation of 5-acetyl-2, 4-dihydroxyacetophenone with 1, 4-diaminobutane as follows: An ethanolic solution (40mL) of 1, 4-diaminobutane (1mmol) was added to an ethanolic solution (30mL) of 5-acetyl-2,4-dihydroxyacetophenone (1mmol). The resulting mixture was then heated at reflux on a water bath for 4-5 h and kept overnight at room temperature. The resulting yellowish brown colored product obtained was filtered, crystallized from DMF-ethanol mixture (1:1 v/v) and dried in vacuum desiccator over anhydrous CaCl<sub>2</sub>.

**Synthesis of VO (IV), MoO<sub>2</sub> (VI) and UO<sub>2</sub> (VI) Complexes:** All complexes were prepared by following general procedure. An ethanolic solution (25 ml) of the desired metal salt (1.0 mmol) was added to a hot DMF solution (25 ml) of the ligand (1.0 mmol) with continuous stirring. The resulting mixture was refluxed on a sand bath for 3-5 h during which a coloured complex was precipitated out in each case. On cooling to room temperature the precipitated solid was filtered, washed

with ethanol, DMF, petroleum ether and followed by acetone to remove any unreacted reactants and dried in vacuo over anhydrous  $\text{CaCl}_2$ . Yield-60 to 70%.

**Physical Measurements:** Elemental analyses of ligand and complexes were performed on an Elemental vario Carlo-Erba 1108 C-H-N-analyzes at micro analytical unit SAIF, CDRI, Lucknow, India. IR spectra were recorded as KBr pellets on a Perkin-Elmer-1600 FT-IR spectrophotometer. The reflectance spectra of the complexes were recorded on a Carry-2390 spectrophotometer using  $\text{BaSO}_4$  as a dilutant and  $\text{MgO}$  as a reference in the range 300-1500 nm at SAIF, IIT Chennai.  $^1\text{H-NMR}$  spectra of the ligand have been recorded in a mixed solvent ( $\text{CDCl}_3 + \text{DMSO}$ ) on a bruker AC-200F, 300MHZ, NMR spectrometer using *TMS* as an internal standard at RSIC-Punjab university, Chandigarh, India. Magnetic measurements were carried out at room temperature using Gouy's method, employing  $\text{Hg}[\text{Co}(\text{SCN})_4]$  for calibration purposes and were corrected for diamagnetism by using Pascal's constant. Thermogravimetric analyses of the complexes were carried out using a TGS-2Perkin Elmer thermal analyzer in the temperature range 50-700°C at a heating rate of  $10^\circ\text{C min}^{-1}$ . Solid-state (d. c.) conductivity of the complexes was measured in their compressed pellet form over a range of 313-413 K temperature using Zentech electrometer [3].

## RESULTS AND DISCUSSIONS

The condensation of 5-acetyl-2, 4-dihydroxyacetophenon with *l*, 4-diaminobutane in a 1:1 molar ratio yields a Schiff base. The formulation of the Schiff base is supported by its elemental, IR and  $^1\text{H NMR}$  data. All the metal polychelates are coloured solids, air stable for long time, non-hygroscopic and insoluble in water and most common organic solvents but sparingly soluble in hot DMF and DMSO. The analytical data support the formation of complexes and the metal analyses confirm the presence of 1:1 metal: ligand ratio [4-6].

**Infrared Spectra:** The IR spectrum of ligand shows a medium intensity band at  $2935 \text{ cm}^{-1}$  due to the intramolecular hydrogen bonded hydroxyl group. Absences of this band in the metal complexes indicate the breaking of the hydrogen bond and coordination of oxygen atom to the metal after deprotonation [7]. In the spectra of the ligand a medium broad band This is supported by upward shift ( $15\text{-}33\text{cm}^{-1}$ ) in phenolic  $\nu(\text{C-O})$  stretching frequency. This shift towards

higher absorption also suggests the formation of the M-O bond<sup>9</sup>. The  $\nu(\text{C=N})$  (azomethine) stretch appears at  $1610 \text{ cm}^{-1}$  in the free ligand has been and this band is shifted to lower frequency by  $22\text{-}40 \text{ cm}^{-1}$  in the spectra of polychelates, indicating the coordination of the azomethine nitrogen atom<sup>10</sup>. It is further supported by the imino nitrogen and the phenolic oxygen involved in the complexation with the metal ion which is clearly evident from the appearance of new medium intensity bands in the region  $590\text{-}654 \text{ cm}^{-1}$  in DHADAB assignable to M-O,  $450\text{-}495 \text{ cm}^{-1}$  in DHADAB attributed to  $\nu(\text{M-N})$  vibrations respectively [8]. The infrared absorption band of the VO(IV) complex show a strong absorptions at  $968\text{-}970 \text{ cm}^{-1}$  in DHADAB, respectively due to  $\nu(\text{V=O})$  indicating the presence of a double bond in the  $\text{VO}^{2+}$  moiety arising from a combination of  $\sigma$  band  $\pi$  component due to electron flow  $\text{O}(\text{P}\pi > \text{Vd}\pi)$ . In DHADAB the observation of  $\nu(\text{V=O})$  stretch close to the normal range. The band observed at  $940 \text{ cm}^{-1}$  in  $\text{MoO}_2$  (VI) complex is due to  $\nu_{\text{asym}}(\text{O=M=O})$ <sup>11</sup>. This band in the as usual ranges assigned for the  $\text{MoO}_2$  (VI) complex<sup>12</sup>. The strong band is observed at  $905 \text{ cm}^{-1}$  due to the  $\nu_{\text{asy}}(\text{O=U=O})$  stretching which occurs in the reported range ( $870\text{-}950 \text{ cm}^{-1}$ ) observed for the majority of dioxouranium (VI) complex in DHADAB<sup>12</sup>. The VO(IV) complex exhibits medium intensity bands in the region  $3400\text{-}3500 \text{ cm}^{-1}$  and a weak band around  $830 \text{ cm}^{-1}$  due to  $\nu(\text{OH})$  of coordinated water [9].

**Electronic Spectra and Magnetic Properties:** The information about geometry of the coordination complexes is obtained from their electronic spectral data and magnetic moments. The diffuse reflectance spectrum of VO (IV) complex studied in the range 200-1000 nm and shows all the expected three bands at 910,530,396 nm which may be assigned to  $^2\text{B}_2\text{-}^2\text{E}(\text{dxy-dxz-dyz})$ ,  $^2\text{B}_2\text{-}^2\text{B}_1(\text{dxy-dx}^2\text{-y}^2)$ ,  $^2\text{B}_2\text{-}^2\text{A}_1(\text{dxy-dz}^2)$ , transitions, respectively. The magnetic moment of the VO (IV) complex is found to be 1.68B.M. at room temperature which is within the range of spin only value assigned square pyramidal geometry[10]. The solid state reflectance spectra of  $\text{UO}_2$  (VI) complex exhibit bands in the region 545-502 nm corresponding to  $^1\Sigma\text{g}^{+3} \pi\text{u}$ , transition typical for  $\text{O} = \text{U} = \text{O}$  symmetric stretching frequency. The  $\text{MoO}_2$  (VI) and  $\text{UO}_2$  (VI) complex are found to be diamagnetic as expected for  $d^0/f^0$  configurations [11].

**Thermogravimetric Analysis:** Thermogravimetric analyses for the complexes were performed from room temperature to  $700^\circ\text{C}$  at a heating rate  $10^\circ\text{C min}^{-1}$  under a dynamic air atmosphere. In order to know the presence of water molecules and decomposition pattern of ligand

Table 1: Thermal and electrical conductivity data of ligand and its metal chelates

S.N	Compound	Half decomposition Temperature (°C)	Activation Energy Ea (kJ mole <sup>-1</sup> )	Frequency factor Z (S <sup>-1</sup> )	Free energy change-ΔG (kJ mol <sup>-1</sup> )	Electrical conductivity (σ)(Ω <sup>-1</sup> cm <sup>-1</sup> -at 373K)	Activation energy(Ea) eV
1	DHADAB(L)	270	88.52	2.89x10 <sup>-11</sup>	85.62	--	--
2	[{VO H <sub>2</sub> O} L]. H <sub>2</sub> O	455	73.90	2.47x10 <sup>-9</sup>	10.87	1.67x10 <sup>-6</sup>	0.294
3	[MoO <sub>2</sub> (L)]	432	78.60	5.83x10 <sup>-10</sup>	64.75	4.12x10 <sup>-10</sup>	0.290
4	[UO <sub>2</sub> (L)]	410	58.42	4.77x10 <sup>-9</sup>	10.27	3.73x10 <sup>-9</sup>	0.560

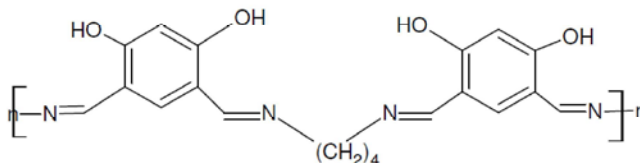


Fig. 1: Structure of ligand DHADAB

<sup>1</sup>H-NMR-δ 12.20 (2H, s, phenolic OH), δ 3.10 (4H, t, N, CH<sub>2</sub>), δ 1.90 (4H, m, CH<sub>2</sub>), δ 2.6 (6H, s, methyl), δ 7.35 and 7.65 ppm (2H, s, phenyl).

and its complexes TG analysis have been carried out. The analysis of TG curves of ligand DHADAB and its metal complexes reveals three stage decomposition pattern for VO (IV) complex and two stage decomposition patterns for MoO<sub>2</sub>(VI) and UO<sub>2</sub>(VI) complexes. The complex of VO (IV) loss its weight in the temperature range 115-230°C corresponding to one lattice and one coordinated water molecules. A gradual weight-loss observed in the range of 135 °C indicates the elimination of one lattice water molecule of the ligand VO (IV) complex [% wt. loss, obs. / calcd. VO (IV): 5.69/5.70] and further loss their weights up to 230 °C corresponding to one coordinated water molecule [% wt. loss, obs. /calcd; VO (IV): 3.89/3.77]. The TG curves of MoO<sub>2</sub>(VI) and UO<sub>2</sub> (VI) complexes are almost stable up to 220°C as shown by TG plateau up to this temperature, indicating the absence of any lattice or coordinated water molecules in these complexes. The continuous and rapid weight-loss has been observed above 260°C corresponding to the elimination of the coordinated ligand. A gradual weight loss in all polychelates up to 670°C due to complete decomposition of coordinated ligand and horizontal curve are obtained in the temperature range 630-700 °C indicating the formation of stable metal oxide. Coats-Redfern<sup>13</sup> method has been used to calculate the kinetic parameters of the complexes. The fractional weight loss and the corresponding (1-α)<sup>n</sup> values have been calculated from the TG curves at different temperatures, where n depends upon the reaction model and α = (W<sub>o</sub>-W<sub>t</sub>)/(W<sub>o</sub>-W<sub>f</sub>). The weighted least square method (LSM) was used for obtaining the best-fit linear plots and kinetics

parameters were calculated. The decomposition of all the complexes has been observed to follow first order kinetics; as is evident from the linear plot of -log [-log (1-α)/T<sub>2</sub>] vs 1/T. The value of frequency factor (Z) and entropy of activation (S\*) was calculated from the following equations intercept =log ZR/âE and S\* = 2.303R log Zh/kT, where k is Boltzmann constant; h is the Planck's constant, T the peak temperature and â the heating rate. The thermoanalytical data of all the complexes is given in table1. In the present studies, the numerical values of Ea and frequency factor (z) indicate the smoothness of the feasibility of the reaction and reaction rate of the initial reactants and intermediate stage compounds. The negative value of S\* indicates that the activated complex has a highly ordered or more rigid structure than that of either the reactants or intermediate and that the reactions are slower than normal.

**Electrical Conductivity Measurements:** The solid state dc electrical conductivity of polychelates was measured in their compressed pellet from room temperature to 413 K. The electrical conductivity (σ) varies according to the relation σ = σ<sup>o</sup> exp (-Ea/kT) where σ<sup>o</sup> is a constant, Ea is the activation energy of electrical conduction, T is the absolute temperature and k is the Boltzmann constant. The solid state dc electrical conductivity increases with increases in the temperature and plots of log σ versus 1/T are linear over studied temperature ranged which indicates their semiconducting nature. The value of electrical conductivity lies in the range 1.67x10<sup>-6</sup> to 4.12 x10<sup>-10</sup> Ω<sup>-1</sup>cm<sup>-1</sup>at 373 K [12].

### CONCLUSION

The thermal behaviour of the chelates was studied and kinetic parameters were determined by Coats-Redfern method and suggest more ordered activated state in complex formation. The solid state electrical conductivity of the ligand and its polychelates have been studied.

### REFERENCES

1. Yong-Ming, C., W. Yan, J.C. Ying, X.J. Long, C. Wu and J. Coord., 2013. *Chem*, 66(13): 2325.
2. Mustapha, M., S. Thora, R. Sawant, G. Atram and R. Yamgar, 2011. *J. Chem. Pharm. Res.*, 3(4): 5.
3. Munde, A.S., A. Jagdale, S.M. Jadhav and T.K. Chondhekar, 2010. *J. Serb. Chem. Soc.*, 75(3): 349.
4. Savanini, L., L. Chiasserini, A. Gaeta and C. Pellerano, 2002. *Biorg. Med. Chem.*, 10(7): 2193.
5. Furniss, B.S., A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, 1989. *Vogel's Textbook of Practicle Organic Chemistry*, 5<sup>th</sup> Ed. Longmans's London.
6. Kaur, J., 1977. Ph. D. Thesis, Nagpur University.
7. Labadi, I., G. Kenessey and G. Lepta, 2005. *J. Therm. Ana. and Calori.*, 82: 55.
8. Taylor, L.T. and R.D. Patton, 1974. *Inorg. Chem. Acta*, 8: 191.
9. Li, B.W., Y.L. Zhou, Q. Chen and M.H. Zeng, 2010. *Polyhedron*, 29: 148.
10. Chang, C.J., J.A. Labinger and H.B. Gray, 1997. *Inorg. Chem.*, 36: 5927.
11. Kumar, D., A. Syamal and A.K. Singh, 2003. *Ind. J. Chem.*, 42A: 280.
12. Coats, A.W. and J.P. Redfern, 1964. *Nature*, 201: 68.