Synthesis, Characterization and Thermal Behaviour of VO(IV), MoO₂(VI) and UO₂(VI) Complexes of Hexadentate Tetraanionic Ligand

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Abstract

A new bis Schiff base ligand 2,4-dihydroxy-5-acetylacetophenone-2-aminothiophenol (H_2L) derived from the condensation of 2,4-dihydroxy-5-acetylacetophenone and 2-aminothiophenol in ethanol-DMF and its solid complexes with VO(IV), MoO_2(VI) and UO_2(VI) have been prepared .All the complexes were characterized on the basis of elemental analyses, magnetic moment, IR & electronic spectral data and thermogravimetric analysis (TGA). The IR spectral data reveal that the ligand behaves a tetraanionic hexadentate in nature. TGA and IR studies confirm the presence of coordinated water molecule in the complexes. The kinetic analysis of the TG data was performed by using the Coats–Redfern method and activation energy has been calculated. The complexes of MoO_2(VI) and UO_2(VI) are found to be octahedral while VO(IV) complex is square pyramidal geometry.

Introduction

The metal complexes of the ligands containing SNO donor atoms are known to possess pharmaceutical, biological, therapeutic activities and plant growth effect [1, 2]. The synthesis and properties of new transition metal complexes have been widely studied owing to their wide range of applications in a variety of fields. Bis ligands acts as a powerful chelating agent forming sTable coordination polymers, complexes with various transition and lanthanide metal ions. In recent years considerable attention have been paid to thermal analysis techniques in studying of the thermal behavior metal complexes [3]. In the physical and chemical properties and the structures studies of solid complexes of transition ions with organic ligands, it is customary to investigate the thermal decomposition of these complexes so as to obtain useful data on the metal-ligand bonds and stability trends. These results provide us to acquire information concerning the structure of coordination compounds, including their thermal behavior and modes of decompositions. In view of the importance associated with bis chelating type of compounds, we report here the synthesis, characterization and thermal study of VO(IV), MoO₂(VI) and UO₂(VI) complexes involving bis tridentate Schiff base ligand, derived from the condensation of 2,4-dihydroxy-5-acetylacetophenone with 2-aminothiophenol (Scheme 1.).

Experimental

All the chemicals used were of analytical grade and used without further purification. The solvents employed were purified by using standard procedures prior to use. Vanadyl sulphate

International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue – NCSC Jan-2015
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pentahydrate and uranyl nitrate hexahydrate were obtained from S.D. fine chemicals whereas [MoO$_2$(acac)$_2$] and 2,4-dihydroxy-5-acetylacetophenone were prepared by literature methods [4].

Synthesis of H$_2$L ligand

A hot ethanolic solution (25ml) of 2,4-dihydroxy-5-acetylacetophenone (3.88 gm, 0.02 mol) was added with a continuous stirring to an ethanol-DMF solution (60:40 v/v/, 25ml) of 2-aminothiophenol (2.18 gm, 0.02 mol). The resulting reaction mixture was refluxed on a sand bath for about 5-6 h. The mixture was kept overnight at room temperature. The golden brown colored product obtained was filtered, washed with ethanol, petroleum ether and dried over CaCl$_2$. Yield: 72%, mp = 242°C. Anal. Calc for C$_{22}$H$_{20}$N$_2$O$_2$S$_2$: C, 64.68; H, 4.93; N, 6.86 Found: C, 64.82; H, 4.93; N, 6.86%. ^{1}H-NMR (DMSO-*d6*, δ(ppm)): 2.8 (s, 6H, methyl); 3.90 (s, 2H, thiophenolic); 6.47-7.92 (m, 10H, phenyl); 12.15 (s, 2H, phenolic OH).
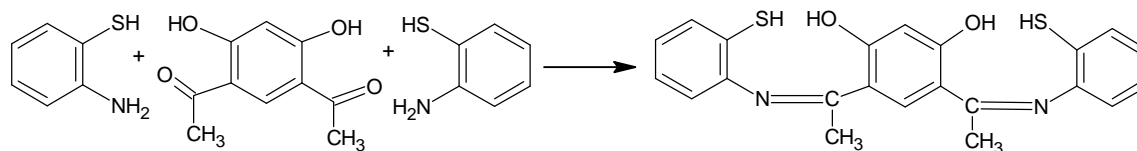
Scheme 1.

Synthesis of VO$_2$(IV), MoO$_2$(VI) and UO$_2$(VI) complexes

A general method has been followed for the synthesis of complexes using reaction of appropriate metal salt and the Schiff base in molar ratio (M:L= 2:1). An ethanolic solution (25 ml) of the desired metal salt (2 mmol) was refluxed with a DMF solution (25 ml) of the ligand (1 mmol) on sand bath for 3-5 h ,during which a coloured complex was precipitated out in each case. After reducing the volume to *ca* 20ml, the flask was kept for overnight. The coloured sold was filtered, washed with ethanol, DMF and petroleum ether and then dried in a vacuum desiccators over CaCl$_2$. Yield: 63-70%. Anal. data for [(VO)$_2$L$^.$(H$_2$O)$_2$]$^.$H$_2$O: Calc: C, 44.60; H, 3.74; N, 4.73; V, 17.20, Found: C, 43.90; H, 3.03; N, 4.56; V, 17.95%. [(MoO$_2$)$_2$L$^.$(H$_2$O)$_2$]: Calc: C, 37.94; H, 2.89; N, 4.03; Mo, 27.55, Found: C, 38.16; H, 2.97; N, 4.61; Mo, 27.93%. [(UO$_2$)$_2$L$^.$(H$_2$O)$_2$]: Calc: C, 26.95; H, 2.06; N, 2.86; U, 48.55, Found: C, 27.13; H, 2.92; N, 2.74; U, 49.03%.

All the compounds were characterized by the similar physicochemical methods as described earlier [5].

Results and discussion

All the complexes are coloured, air sTable, non-hygroscopic in nature and insoluble in water and common organic solvents but fairly soluble in *DMSO* and *DMF*. Analytical data of the compounds,

International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue – NCSC Jan-2015
www.ijcps.org

together with their physical properties are consistent with their proposed molecular formula and complexes show 2:1 (metal: ligand) stoichiometry.

IR spectra

The IR spectrum ligand shows medium bands at 2910 and 2540 cm^{-1} due to intramolecular hydrogen bonded υ(OH) and υ(SH) vibrations respectively. Absence of both the bands in the spectra of complexes, indicate the deprotonation of the phenolic hydrogen and thiol group and coordinating to the metal on complexation [6]. This is further supported by the upward (10-24) shift of phenolic υ(C–O) mode and the appearance of band ~740 cm^{-1} due to υ(C–S) in the metal complexes. The IR spectrum of the free ligand revealed a very strong band at 1620 cm^{-1} due to υ(C=N) mode of ligand. This band is shifted to a lower energy by ~30 cm^{-1} in the complexes assigned that it has been affected upon complexation via metal ions [7]. The IR spectrum of the VO(IV) complex exhibits a strong band at 970 cm^{-1}, attributed to the asymmetric stretching vibration of the V=O bond. The [(MoO$_2$)$_2$L$\cdot$(H$_2$O)$_2$] exhibits a pair of sharp strong bands at 935 and 915 cm^{-1}, due to υ_{sym}(O=M=O) and υ_{asym}(O=M=O) stretches, respectively of the MoO$_2$(VI) moieties [8]. The data is indicative of the presence of cis-MoO$_2$ structure. The UO$_2$ complexes shows bands at 860 cm^{-1} and 781 cm^{-1} due to υ_{asy}(O=U=O) and υ_{sym}(O=U=O) modes, respectively. The presence of coordinated water molecules in the complexes are confirmed by a broad band around 3395-3420 cm^{-1} and two weak bands in the region 830-40 cm^{-1} due to δ(OH) rocking and wagging modes of vibrations, respectively. The new bands in the regions 524–578 cm^{-1}, 430–470 cm^{-1} and 418-427 cm^{-1} in all the metal complexes are assigned to stretching frequencies of υ(M–O), υ(M–N) and υ(M–S) bonds, respectively.

Electronic spectra and magnetic properties

The electronic spectrum of the VO(IV) complex shows three bands at 11123, 18691 and 27397 cm^{-1} due to $^2B_2 \rightarrow ^2E$, $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2A_1$, transitions, respectively, suggesting square pyramidal geometry around VO(IV) ion [9]. The magnetic moment of VO(IV) complex is found to be 1.71 B.M. which is close to the spin only values expected in S=1/2 system (1.73 B.M.) and may be indicative of five coordinated VO(IV) complex and consistent with the presence of single unpaired electron. The MoO$_2$(VI) and UO$_2$(VI) complexes are found to be diamagnetic as expected and may have a octahedral structure.

Thermogravimetric analysis

Thermal analysis of complexes was studied under dynamic air atmosphere. Dynamic TGA data with percent mass loss at different steps and their probable assignments are summarized in Table 1. The TG curve of [(MoO$_2$)$_2$L$\cdot$(H$_2$O)$_2$] complex is as shown in figure 1. The ligand shows two steps decomposition in the temperature range 40-600°C with the loss of C$_2$H$_{10}$O$_2$S$_2$ and C$_{20}$H$_{10}$N$_2$ in formal and

International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue – NCSC Jan-2015
www.ijcps.org

second steps, respectively. The thermogram of $[(MoO_2)_2L \cdot (H_2O)_2]$ indicates that the loss of ligand residue occurs in two different steps. First step starts at 140^oC and continues till 210^oC with an approximate mass loss of 4.86% (calcd. mass loss = 5.16%) corresponds to loss of two coordinated water molecules [10]. The second step starts immediately after the first one in the temperature range $210-700^oC$ with mass loss of 60.17% (calcd. mass loss = 61.81%) which is reasonably accounted for the loss of ligand (L) moiety from the complex. The observed percentage mass of the residue matches well with the theoretical value calculated for MoO_3. The complex $[(UO_2)_2L \cdot (H_2O)_2]$ seems to associated with two molecules of water as mass loss equivalent to two water molecules occurs in the temperature range $90-210^oC$ with estimated mass loss of 3.20% (calcd. mass loss = 3.67%). The next step is very similar to dioxomolybdenum. The observed mass loss is 43.95% (calcd. mass loss = 43.22%) due to the loss of ligand. The percentage residue obtained at the end of the thermal analysis is close to the theoretical value calculated for U_3O_3.

Table 1: Thermal decomposition data of complexes

Complex	TG range /^oC	Mass loss/% obs/calcd.	Assignments
$[(VO)_2L \cdot (H_2O)_2] \cdot H_2O$	55-105	3.52/3.03	Loss of one mole of lattice water molecule
	105-190	6.97/6.26	Loss of two moles of coordinate water molecules
	190-700	74.90/75.77	Removal of ligand moiety
		85.39*/85.06	Leaving the metal oxide residue
$[(MoO_2)_2L \cdot (H_2O)_2]$	140-210	4.86/5.16	Loss of two moles of coordinate water molecules
	210-700	60.17/61.81	Removal of ligand moiety
		65.03*/66.97	Leaving the metal oxide residue
$[(UO_2)_2L \cdot (H_2O)_2]$	90-205	3.20/3.67	Loss of two moles of coordinate water molecules
	205-700	43.95/43.22	Removal of ligand moiety
		47.15*/46.89	Leaving the metal oxide residue

* Total mass loss

The $[(VO)_2L \cdot (H_2O)_2] \cdot H_2O$ complex shows elimination of one lattice water molecules up to 105^oC with an estimated mass loss of 3.52% (calcd. mass loss = 3.03%) [11]. In the temperature range $105-190^oC$ complex exhibits mass loss of 6.97% (calcd. mass loss = 6.26%), corresponding to two coordinated water molecules. In the $190-700^oC$ temperature range complex losses its mass 74.90% (calcd. mass loss = 75.77%) corresponds to the loss of the ligand moiety, leaving metal oxide as residue.

International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue – NCSC Jan-2015
www.ijcps.org

The thermodynamic activation parameters of decomposition processes of the complexes, such as activation energy (E*), frequency factor (Z) and Gibbs free energy (ΔG) are calculated from the TG curves using CR equations [12].

The data are summarized in Table 2.

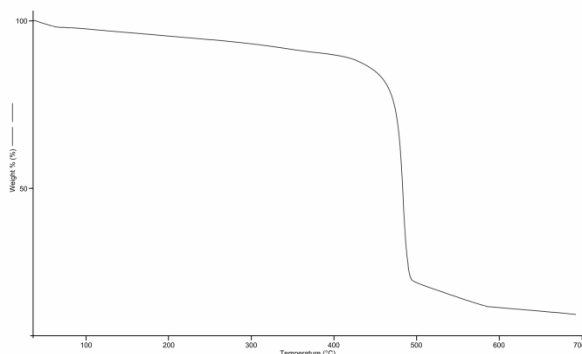$\log g(\alpha)/T^2 = \log[-\ln(1-\alpha)/T^2] = E/2.303RT$

Fig. 1: TG curve of $[(MoO_2)_2L^.(H_2O)_2]$ complex

The activation energy of decomposition was found to be in the range 58.37-75.36 kJ mol^{-1}. The high values of activation energies reflect the thermal stability of the complexes. Generally with decreasing value of E*, the value of Z increases. In complexes the high values of activation energy suggest the higher stability of such complexes due their covalent bond character [13]. Higher value of E and lower value of Z favours the reaction to proceed slower than normal.

Table 2: Thermal data of H_2L and its complexes

Compound	Half decomposition temperature (^{o}C)	Activation energy (E*) kJ mol^{-1}	Frequency factor (Z) S^{-1}	Free energy change (ΔG) kJ mol^{-1}
H_2L	330	39.50	3.76×10^{-7}	-11275
$[(VO)_2L^.(H_2O)_2].H_2O$	430	75.36	1.39×10^{-11}	-99245
$[(MoO_2)_2L^.(H_2O)]$	487	73.47	3.59×10^{-6}	-87921
$[(UO_2)_2L^.(H_2O)_2]$	480	58.37	3.58×10^{-9}	-13262

Conclusion

New complexes of $[(VO)_2L^.(H_2O)_2]^.H_2O$, $[(MoO_2)_2L^.(H_2O)_2]$ and $[(UO_2)_2L^.(H_2O)_2]$ were synthesized and characterized. IR spectra indicate that ligand acts as tetraanionic hexadentate in nature. An octahedral structure for $MoO_2(VI)$ and $UO_2(VI)$ complexes while square pyramidal to VO(IV)

International Journal of Chemical and Physical Sciences, ISSN:2319-6602
IJCPS Vol. 4 Special Issue – NCSC Jan-2015
www.ijcps.org

complex have been proposed. Thermal decomposition of complexes allowed establishing the number and nature of water molecule, the composition of complexes and also the intervals of thermal stability.

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