

Spectral and Thermal Studies of Dioxouranium(VI) Sulphato Complexes of some Schiff Bases of 4-Aminoantipyrine

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Frankuchen¹ in his structural study of sodium uranyl acetate concluded that the dioxouranium(vi) ion has collinear shape O—U—O ($D_{\infty h}$ symmetry). The UO_2^{II} group can coordinate 2 to 6 other atoms, ions or molecules in the equatorial plane with a strong tendency² to make these ligating atoms coplanar. Equatorial pentacoordination has been shown³ to be as prevalent as plane-square or plane-hexagon. The complexing ability of divalent dioxouranium(vi) is demonstrated with a wide variety of organic and inorganic ligands⁴. In recent years the coordinating behaviour of Schiff bases derived from 4-aminoantipyrine toward dioxouranium(vi) salts has been investigated by many workers⁵⁻⁸. But there is no formal report on dioxouranium(vi) complexes of these Schiff bases in presence of sulphato ion. For this purpose the following ten Schiff bases of 4-aminoantipyrine have been prepared using various aromatic aldehydes: 4-[*N*-(benzalidene)amino]antipyrine (BAAP), 4-[*N*-(salicylidene)amino]antipyrine (SAAP), 4-[*N*-(*o*-nitrobenzalidene)amino]antipyrine (*o*-NBAAP), 4-[*N*-(*m*-nitrobenzalidene)amino]antipyrine (*m*-NBAAP), 4-[*N*-(*p*-dimethylaminobenzalidene)amino]antipyrine (DABAAP), 4-[*N*-(*m*-methoxybenzalidene)amino]antipyrine (MBAAP), 4-[*N*-(4-hydroxy-3-methoxybenzalidene)amino]antipyrine (HMBAAP), 4-[*N*-(cinnamaldehyde)amino]antipyrine (CAAP), 4-[*N*-(2-hydroxy-1-naphthalidene)amino]antipyrine (HNAAP) and 4-[*N*-(furfural)amino]antipyrine (FFAAP).

Results and Discussion

The interaction of uranyl(vi) sulphate with

various Schiff bases resulted in the formation of the complexes with the composition $UO_2L_2SO_4$. The elemental analyses gave the satisfactory results. All the complexes are either yellow or orange-yellow coloured solids. The complexes are generally soluble in common organic solvents. The molar conductance values ($3.7-4.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of the complexes in nitrobenzene indicate their non-electrolytic nature. Thus it is concluded that sulphato ion is present inside the coordination sphere. Molecular weights of the complexes were determined in freezing $PhNO_2$. The complexes are either diamagnetic or weakly paramagnetic depending upon the diamagnetism of the other ions and the surrounding ligand field⁹.

Infrared spectra and the nature of coordination: Infrared absorptions of all the Schiff bases of 4-aminoantipyrine have been assigned by a comparison of their spectra with those of the five-membered pyrazole ring system¹⁰, antipyrine and 4-aminoantipyrine¹¹ and substituted 4-aminoantipyrine^{5-8,12}. The infrared spectra of all the complexes show a considerable negative shift in carbonyl (pyrazolone) absorption $\Delta\nu(C=O)$ by $45-50 \text{ cm}^{-1}$, indicating a decrease in the stretching force constant of $C=O$ as a consequence of coordination through the oxygen atom of the free base. It is known¹³ that as a result of coordination through the carbonyl oxygen the double bond character between the carbon and the oxygen is reduced. The $C=O$ stretching frequencies occurring at $1660-1640 \text{ cm}^{-1}$ in the free ligands

have been observed in the region 1610–1600 cm^{-1} in all the complexes. Another important band at 1590–1585 cm^{-1} is attributed to $\nu_{\text{C}=\text{N}}$ mode⁵⁻⁸. In spectra of all the complexes this band is shifted to lower wavenumber and appears at 1570–1550 cm^{-1} , indicating the involvement of N-atom of the azomethine group in coordination⁵⁻⁸. In the spectra of SAAP, HMBAAP and HNAAP the stretching frequency at 3400–3200 cm^{-1} is attributed to ν_{OH} mode. In all the three complexes, the hydroxyl frequency appearing at the same region as in the ligand, clearly indicates that the OH group is not taking part in the coordination. This observation agrees with the previous observations^{5,7}.

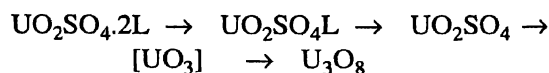
In far-infrared region, some new medium and weak bands are observed in the range 410–370 cm^{-1} in these complexes, where the ligands have no absorptions. These bands are tentatively assigned to $\nu_{\text{U}-\text{O}}$ and $\nu_{\text{U}-\text{N}}$ modes observed for several uranyl(VI) complexes^{7,8}.

Infrared spectra of these complexes show the presence of coordinated sulphato group¹⁴. The strong broad band at 1120–1080 cm^{-1} due to the triply degenerate SO stretching mode ν_3 in ionic sulphates splits up into its components at ~ 1240, 1120, 1050 cm^{-1} in the infrared spectra of these complexes. The triply degenerate OSO bending mode ν_4 which occurs as a sharp well defined band at ~ 610 cm^{-1} in sulphate with T_d symmetry, also splits up into its components in these complexes. In addition to these, ν_1 and ν_2 both infrared forbidden in uncoordinated sulphates, appear at ~ 1220 and 470 cm^{-1} respectively. The fundamental frequencies due to coordinated sulphato groups in all these complexes are consistent with those normally associated with bidentate sulphato groups¹⁴.

Complexation effect of uranyl ion spectra : In all the dioxouranium(VI) complexes, the ν_1 and ν_3 modes of $\text{O}=\text{U}=\text{O}$ are assigned at 835–825 and 930–925 cm^{-1} respectively¹⁵. Wilson's G-F matrix method¹⁶ was used to determine the stretching and interaction force constants from which the U–O bond distances were calculated following Badger's formula¹⁷. It is apparent from the cal-

culated data that the U–O bond length decreases with the increase in the value of symmetric stretching frequency (ν_1)¹⁸. A plot of ($\nu_1 + \nu_3$) versus force constants, gave a straight line. The U–O bond distances in dioxouranium salts generally range from 1.60 to 1.92 Å depending on the nature of the equatorial ligands¹⁹. The calculated values of the U–O bond distances in the parent complexes are close to 1.73–1.74 Å.

Thermal behaviour : The pyrolysis curves of representative complexes of BAAP, SAAP, DMBAAP and HNAAP have been studied and are similar in major details. The TG and DTA curves of these complexes do not show the presence of water molecule either in or out of the coordination sphere. All the complexes decompose endothermally. The exo peak at higher temperature is due to metal oxidation. The TG curves of these complexes indicate that in the first step, only one mole of ligand has been lost, while at ~ 430°, the remaining ligand mole has also been lost. Finally the oxide U_3O_8 is formed around 620° through the formation of UO_3 , following which there is no measurable change in weight²⁰. In brief these changes can be shown as :



(L = BAAP, SAAP, DMBAAP or HNAAP)

In conclusion, the present complexes involving eight-coordinated uranium(VI) with four oxygen atoms (two from pyrazolone ring and two from chelating sulphato groups) and two nitrogen atoms of azo methine group are in an equatorial plane around the linear OUO groups.

Experimental

Uranyl(VI) sulphate (AnalaR, 99.9% pure) was used as such. All the ten Schiff bases were prepared by the following general method. A mixture of an equimolar amount of 4-aminoantipyrine and the aromatic aldehyde in ethanol was refluxed for 2–3 h²¹. The yellow coloured crystals of the Schiff bases that separated on cooling were recrystallised from hot ethanol.

The uranyl(vi) sulphate complexes were prepared by adding the ligand solution (2 mmol in 20 ml ethanol) to a hot solution of uranyl sulphate (1 mmol in 10 ml methanol). The resulting complexes were washed with ethanol (or methanol) and dried in an air-oven at 80°, (yields ~ 80%).

All the analyses and physical measurements were performed as reported earlier^{7,8}. Thermal analysis was carried out on a Cahn RG electrobalance with a linear heating rate of 6° min⁻¹ in static air. The DTA was carried out in air using a DTA-02 Universal (DDR) analyser with a heating rate of 10° min⁻¹.

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