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Mass Spectral Studies of 1-(2'-Pyridylazo)-2-phenanthrol & of Its Chelates with Cu(II), Co(II), Co(III) & V(V)

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Mass spectra of 1-(2'-pyridylazo)-2-phenanthrol (PAPL) and its metal chelates with V(V), Co(III) and Cu(II) have been reported. The novel feature associated with the spectrum of V(V) complex is the existence of the species $V(PAPL)_2^+$ due to the reduction of V(V) to V(II). Peaks corresponding to the different isotopes of the metal have also been observed in the fragmentation pattern.

TRIDENTATE complexing agents containing an azo group, a heterocyclic nitrogen atom and a hydroxyl group ortho to the azo group have been extensively used as spectrophotometric¹ and complexing agents in the micro-determination of various metal ions. 1-(2'-Pyridylazo)-2-phenanthrol (PAPL) is a newly synthesized member of this series² and has recently been used as a spectrophotometric reagent for Co(II)³, UO₂(II)⁴, Pt(IV)⁵ and Os(VIII)⁶, as visual indicator in EDTA titrations and its metal chelates have found use as acid-base indicators⁸. The chelates of PAPL with 3d-transition metal

ions⁹⁻¹² have been prepared recently by the author and characterized by magnetic susceptibility measurements from room temperature to liquid nitrogen temperature, EPR and IR spectral studies. We describe here the results of our investigations on the mass spectral studies on V(V), Co(II), Co(III) and Cu(II) chelates of PAPL.

The fragmentation pattern of PAPL is shown in Chart 1. The fragmentation pattern supports the enol form of the molecule as confirmed by NMR spectrum taken in CDCl₃ which shows a signal at 15-28 ppm in the off field due to the phenolic -OH group and not the keto form.

The mass spectrum of PAPL shows the molecular ion as a strong peak at m/e 299, which fragments by the loss of nitrogen to give rise to ion (b) at m/e 271 which further loses hydrogen to give the ion (c) at 270.

The ion (a) may give the neutral molecule (d) and the ion (e) (m/e 152) in which the two benzene rings are linked by a four-membered ring. The ion (c) loses CO molecule to give ion (f) (m/e 242) which undergoes fragmentation by two different pathways to give rise to pyridine (m/e 78) and the ion (g) (m/e 165). A peak at m/e 51 confirms the loss of HCN from pyridine ion.

Vanadium-PAPL complex—Vanadium has two naturally occurring isotopes with the following masses and abundance: 51 (99.76) and 50 (0.24). As reported by us earlier⁸, we obtained the complex of V(V) of the composition VO₂(PAPL).H₂O. The mass spectrum of the complex exhibits peaks at m/e 399 and 398 corresponding to the molecular ions containing ⁵⁰V and ⁵¹V. The presence of these peaks also confirms the coordination of water molecule to vanadium. The spectrum shows two peaks at m/e 647 and 646 which may possibly be due to the ion $V(PAPL)_2^+$ where vanadium is in the +2 oxidation state, resulting from the reduction of V(V) to V(II) but it does not seem to undergo further fragmentation. Similarly, ions VO(PAPL).H₂O]⁺

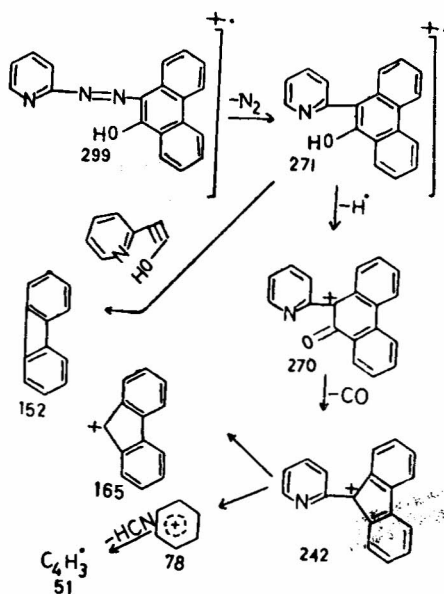


CHART 1

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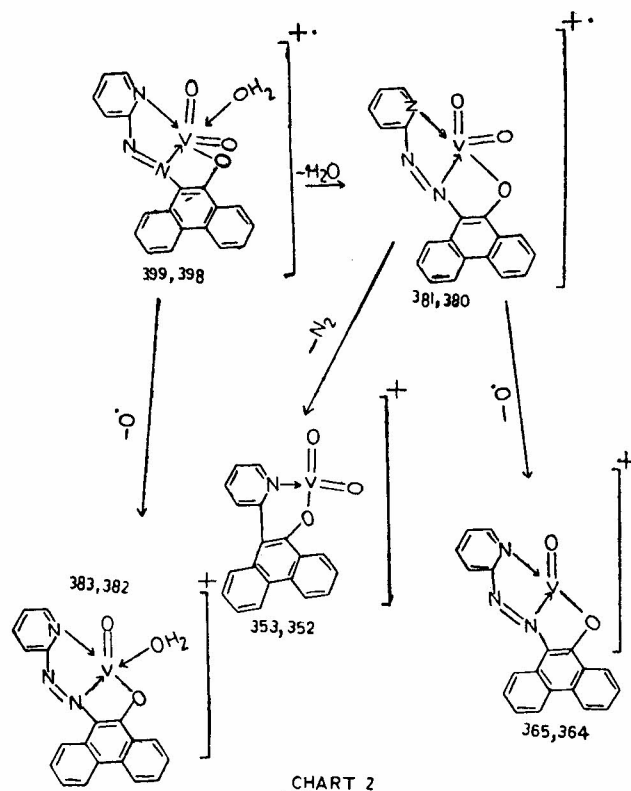
and VO(PAPL)]^+ also appear in the spectrum resulting from the molecular ion as a result of reduction of V(V) to V(IV). The isotopic abundance also made easy the identification of vanadium containing fragments in the spectrum. The major fragmentation pattern for the complex is shown in Chart 2.

Copper(II)-PAPL complex — The most abundant isotopes of copper are ^{65}Cu (60.09%) and ^{63}Cu (30.99%). The elemental analysis of the chelate¹⁰ corresponds to Cu(PAPL)Cl and correspondingly the spectrum shows the parent peaks at m/e 396 and 398; the existence of the doublet confirms the isotopic abundance of the two isotopes of copper and, moreover, it also demonstrates the stoichiometry in the chelate to be 1:1 (metal-ligand). The parent ion loses chlorine which also occurs in two abundant isotopes ^{35}Cl and ^{37}Cl . The loss of ^{35}Cl and ^{37}Cl from molecular ion at m/e 396 and 398 is expected to give rise to only one peak at m/e 361 and the same is confirmed by the appearance of a peak at m/e 361 which loses the ligand. The ligand then undergoes fragmentation in the same way as shown in Chart 1.

Cobalt(II) and cobalt(III) complexes — We have chosen both cobalt(II) and cobalt(III) chelates for the mass spectral studies. We have earlier reported the results of our investigations on the magnetic susceptibility measurements¹¹ from room temperature to liquid nitrogen on the two cobalt(II) complexes of PAPL (green and pink) prepared under inert atmosphere of nitrogen to prevent the oxidation of Co(II) to Co(III). The green complex of composition $\text{Co(PAPL)}_2 \cdot 4\text{C}_2\text{H}_5\text{OH}$ showed antiferromagnetic exchange interactions while the pink-coloured complex with composition $\text{Co(PAPL)}_2 \cdot 4\text{C}_2\text{H}_5\text{OH} \cdot \frac{1}{3}\text{CHCl}_3$ was found to have spin state equilibrium between $^4T_{2g}$ and 2E states characterizing the high-spin and low-spin states of cobalt(II). We now report the results of mass spectral investigations carried on these complexes, and the cobalt(III) chelates which have the chemical composition $[\text{Co(PAPL)}_2\text{Cl}]^+$ and $[\text{Co(PAPL)}_2\text{Br}]^+$.

Cobalt occurs only as one isotope, i.e. ^{59}Co (100%). Since the ethanol/chloroform molecules in green and pink complexes are present only as molecules of solvent of crystallization, at that temperature of recording the mass spectrum, these solvent molecules are expected to be lost and correspondingly Co(PAPL)_2 will give the molecular ion and in the mass spectrum of both the complexes, the molecular ion appears at m/e 655 which loses the ligand residue to give a peak at m/e 357 and the ligand residue undergoes fragmentation in the same way as shown in Chart 1.

Amongst the cobalt(III) complexes, we have chosen $\text{Co(PAPL)}_2\text{Cl}$ and $\text{Co(PAPL)}_2\text{Br}$ and from the conductance measurements, it has been established that both the complexes are 1:1 electrolytes and hence the Cl and Br are in the outer sphere of coordination. From the mass spectral studies point of view, both the complexes should give rise to molecular ions at m/e 655 corresponding to Co(PAPL)_2^+ and in fact in the mass spectrum of both the chelates, parent peaks have been obtained at m/e 655. In the spectrum of $\text{Co(PAPL)}_2\text{Cl}$, the



molecular ion loses one ligand molecule and finally the ligand undergoes fragmentation as discussed earlier. But in the spectrum of $\text{Co(PAPL)}_2\text{Br}$, the peak at m/e 436 is also observed and may possibly correspond to Co(PAPL)Br^+ and the oxidation state of cobalt seems to be +3 since Br has to be bonded to the cobalt in the inner coordination sphere. The further fragmentation pattern is the same as has been observed in other cases.

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