

The Nature and Composition of the Complexes of Uranium(VI), Vanadium(IV) and Iron (III) with Gallacetophenone

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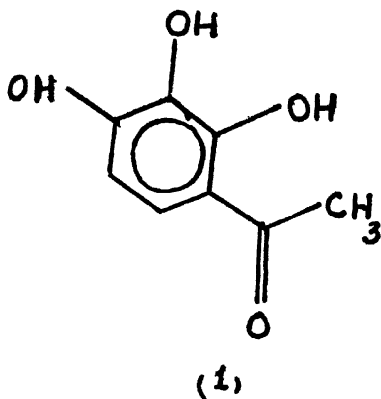
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Gallacetophenone (2, 3, 4-trihydroxyacetophenone) combines with metal ions to form chelates. The molar ratios of the chelates with U(VI), V(IV) and Fe(III) in ethanol are found to be 1 : 1, 1 : 2 and 1 : 3. The solid complexes isolated from methanolic solutions have been found to conform to the formulae $[UO_2L(CH_3OH)_4][NO_3]$, $[VOL_2]$ and $[FeL_3]$ where L is $C_8H_7O_4^-$. Tentative structures have been proposed for these complexes.

2-HYDROXYACETOPHENONES are chelating ligands and they form metal chelates very effectively and easily. The chelating power is enhanced if there is present an additional catechol unit which can itself give a metal complex. Thus gallacetophenone (1) can be a good complexing agent for metals.



It has earlier been shown by us¹ to give highly coloured spots with twenty-seven metal ions on a paper chromatogram. It was, therefore, considered interesting and useful to study some of these coloured complexes. In the present investigation, complexes of gallacetophenone with Uranium(VI), Vanadium(IV) and Iron(III) have been studied in solution (ethanol) and solid state. From the elemental analysis and infra-red spectra, an attempt has been made to assign structures to these chelates.

Experimental

Gallacetophenone was prepared by the method given by Leonte et al². It was repeatedly crystallized from benzene and petroleum ether when colourless crystals of gallacetophenone were formed (m.p. 173°, lit² 173°).

AnalaR uranyl nitrate, ferric chloride and vanadium(IV) sulphate were used for preparing standard solutions of metal ions, solvent being ethanol (95%). The metals were estimated by usual analytical procedures.

Nitrobenzene was dried over anhydrous calcium chloride and fractionated. The fraction distilling at 209° was collected.

In the molar ratio studies, the effect of pH on the absorbance of the complexes was studied by taking a series of solutions containing a fixed amount of metal (1.0 ml of $1.0 \times 10^{-3} M$) and excess of ligand (1.0 ml of $2 \times 10^{-1} M$) solution prepared at different pH values. The pH of the solutions was adjusted by using dilute HCl and NaOH. The total vol. in each case was kept at 10.0 ml. Reagent blanks of appropriate concentrations were used as reference. The spectra showed absorption maxima at 390 nm and 520 nm for U(VI) complex; 390 nm and 550 nm for V(IV) complex and at 380 nm and 460 nm for the Fe(III) complex. Since the ligand itself absorbs strongly at 390 nm, therefore in all the three cases only one complex species is formed showing absorbances at 520 nm, 550 nm and 460 nm respectively. It was found that max. absorbance is obtained in the pH range 3.0-6.5. The absorbance measurements were made at 520 nm, pH 4.0 for

U(VI) complex ; 550 nm, pH 4.5 for V(IV) complex and 460 nm, pH 3.5 for Fe(III) complex at $30 \pm 0.2^\circ$. $1.0 \times 10^{-3} M$ and $2.0 \times 10^{-3} M$ solutions were used in the continuous variation method^{8,9} and $1.0 \times 10^{-3} M$ solutions in slope ratio method⁸.

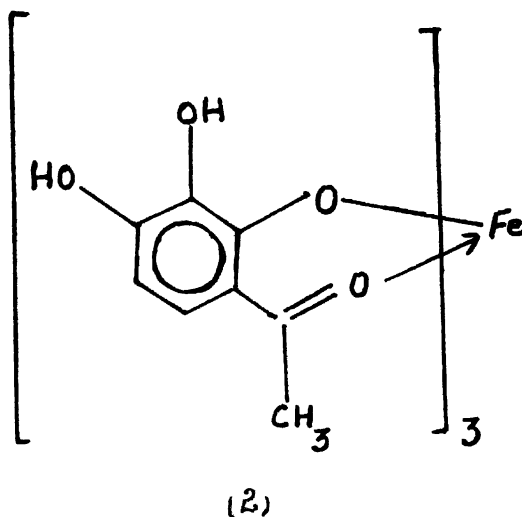
The solid complexes were isolated from methanolic solutions. Metal and ligand were mixed in stoichiometric proportions and their pH adjusted to 6.0, refluxed on a water bath and concentrated when the complexes separated out on the addition of an inert solvent. The complexes were recrystallized from methanol and dried over anhydrous calcium chloride in vacuum.

The compounds are insoluble in non-polar organic solvents but are soluble in various solvents such as methanol, nitrobenzene and nitromethane.

Molecular weights were determined in nitrobenzene cryoscopically by Beckman methods (see Table 1 which also gives analytical data). Infra-red spectra of the ligand and the complexes were scanned over the middle frequency region (4000 to 700 cm^{-1}) in nujol on Perkin Elmer 137 spectrophotometer and over the far region (650 to 200 cm^{-1}) on Beckman IR-12 instrument using nujol mull on polyethylene discs.

Results and Discussion

The molar ratio studies give stoichiometries of 1 : 1, 1 : 2 and 1 : 3 (Metal : Ligand) for the U(VI) V(IV) and Fe(III) complexes. The formation of the complex species in ethanol in case of U(VI) may



V(IV) and Fe(III) complexes. The chelation sites are thus the carbonyl and hydroxyl groups at position 2'. In the uranyl complex the bands at 1035 – 1025 cm^{-1} , 940 cm^{-1} are characteristic of the uranyl ion^{8,9}. Similarly strong bands at 1040 cm^{-1} , 970 cm^{-1} are characteristic of $\text{V}=\text{O}^{10}$ and bands at 360 cm^{-1} , 330 cm^{-1} and 285 cm^{-1} show metal-oxygen bonding. The three small peaks 350 – 325 cm^{-1} indicate the metal oxygen stretching mode in the case of iron complex.

TABLE—1

| Complex | Colour | Mol Wt. Found | C% | | H(%) | | Metal (%) | |
|--|------------|------------------|-------|-------|-------|-------|-----------|-------|
| | | | Calc. | Found | Calc. | Found | Calc. | Found |
| $[\text{UO}_2(\text{C}_8\text{H}_7\text{O}_4)(\text{CH}_3\text{OH})_2]\text{NO}_3$ | Dark Red | 634 | 611 | 15.5 | 15.3 | 2.99 | 3.5 | 38.2 |
| $[\text{VO}(\text{C}_8\text{H}_7\text{O}_4)_2]$ | Dark Green | 432 | 401 | 47.5 | 47.8 | 3.8 | 3.7 | 10.2 |
| $[\text{Fe}(\text{C}_8\text{H}_7\text{O}_4)_3]$ | Blue Green | 583 | 557 | 51.3 | 51.7 | 3.5 | 3.7 | 10.2 |
| | | | | | | | | 10.0 |

therefore be visualized as :

$\text{UO}_2^{2+} + \text{C}_8\text{H}_7\text{O}_4 + 4\text{C}_2\text{H}_5\text{OH} \rightarrow [\text{UO}_2(\text{C}_8\text{H}_7\text{O}_4)(\text{C}_2\text{H}_5\text{OH})_4]^{2+} + 4\text{H}^+$. The complexes with V(IV) and Fe(III) can be formulated as : $[\text{VO}(\text{C}_8\text{H}_7\text{O}_4)_2]$ and $[\text{Fe}(\text{C}_8\text{H}_7\text{O}_4)_3]$.

The tentative structures are illustrated by that of the Fe(III) complex, (2).

A comparison of the IR spectra of the complexes with that of the ligand shows that the hydroxyl group frequency gets shifted from 3300 cm^{-1} in the ligand to 3400 cm^{-1} , 3400 cm^{-1} and 3450 cm^{-1} in the uranyl, vanadium(IV) and Fe(III) complexes^{8,9}. These shifts in frequency are indicative of chelation to the metal ions. Similarly the strong wave bands at 1600 cm^{-1} and 1500 cm^{-1} assigned to $\text{OH} \cdots \text{O}=\text{C}$ interaction and $\nu \text{C}=\text{O}$ stretching mode in the pure ligand get shifted to 1600 and 1550 cm^{-1} , 1600 and 1520 cm^{-1} and 1595 and 1540 cm^{-1} for the U(VI),

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