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NOTES

Studies on Zr(IV) and Th(IV) Complexes of Mannich Bases

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Complexes of oxozirconium(IV) and Th(IV) with Mannich bases [3-(p-dimethyl amino anilino)-methyl salicylic acid hydrazide (DAMSAH) and β-(α-naphthyl amino)-2,3,4-trihydroxy propiophenone (NATPO)] with 1 : 2 (M : L) stoichiometry have been prepared. IR spectra of the ligands and complexes suggest the bidentate and tridentate nature of the ligands in Zr(IV) and Th(IV) complexes respectively.

The use of mannich bases as antibacterial[1], antiinflammatory[2] and analgesic[3] compounds are well known. But their complex forming tendency with metal ions has been studied only to a limited extent[4-7]. Here we report the preparation and characterisation of oxozirconium(IV) and thorium(IV) complexes with 3-(p-dimethyl amino anilino)-methyl salicylic acid hydrazide and β-(α-naphthyl amino)-2,3,4-trihydroxy propiophenone.

The ligands were obtained as reported earlier[8,9]. The ZrO(IV) salt/Th(IV) salt was dissolved in methanol and a dehydrating agent (2,2-dimethoxy propane) was added. The mixture was warmed over water bath with continuous stirring. A hot aqueous ethanolic solution (10 mmole) of the ligand was added gradually in a slight excess. The reaction mixture was stirred and refluxed over water bath at *ca.* 70°C for 2 hrs and the excess of solvent was removed by distillation. The complexes precipitated on cooling at room temperature after the addition of anhydrous diethyl ether, were filtered, washed with a little of alcohol, acetone and dry ether and dried in vacuo over anhydrous $CaCl_2$.

The analytical data of the complexes indicate the general composition ThL_2CL_2 and $ZrOL_2 \cdot H_2O$ ($L = C_{16}H_{19}N_4O_2$ or $C_{19}H_{16}NO_4$). All the complexes are fairly stable at room temperature and can be stored for a pretty long period. The complexes are non-hygroscopic and soluble in common organic solvents. The non-electrolytic behaviour of the complexes is confirmed by their molar conductivity measurement in acetonic solution (10^{-3} M).

The IR spectral data of zirconium and thorium(IV) chelates with DAMSAH indicated the absence of characteristic absorption band for —OH group, which appeared as a broad band at 3470 cm^{-1} in the ligand. This suggests that this group takes part in chelation and the proton is

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replaced from it by metal ion. But in case of NATPO complexes with Zr and Th, this band at *ca* 3400 cm^{-1} (in the ligand spectra) becomes slightly weak, indicating that only a single —OH group becomes deprotonated during chelation while the other two remain as such. In Th(IV) complexes, $\nu(C = O)$ gets shifted to lower frequency side (1620–1610 cm^{-1}), observed at *ca* 1650 cm^{-1} in the ligands. This suggests the participation of carbonyl group in complexation of Th(IV).

In the Zr(IV) and Th(IV) complexes with DAMSAH, the band observed at 3250 cm^{-1} (in the ligand spectra) gets shifted in the region 3210–3220 cm^{-1}, indicating the co-ordination of hydrazino nitrogen with the metal ions. $\nu(N—H)$ appearing at 3340 cm^{-1} as a weak band in the ligand (DAMSAH) remains unaltered in the complexes while $\nu(N—H)$, appearing at 3300 cm^{-1} in the spectra of NATPO, was found at *ca* 3265 cm^{-1} in the complexes. This is suggestive of non-participation of —N—H group in co-ordination in case of DAMSAH but participation in case of NATPO. Some new non-ligand bands were also observed in the spectra of the complexes in the region 465–480, 360–375 cm^{-1}, characteristic of $\nu(M—N)$ and $\nu(M—O)$ respectively. In the Th(IV) complexes $\nu(M—Cl)$ appears as *ca* 320 cm^{-1}. A weak band characteristic of $\nu(Zr{=}O)$ has been observed[1] at about 1030 cm^{-1} in the chelates of zirconium. $\nu(OH)$, $\delta(OH)$ and $\rho(H_2O)$, characteristic of co-ordinated water, were observed at *ca* 3475, 1600, 860 cm^{-1} in the spectra of Zr(IV) complexes and were found absent on removal of H_2O at 155°C.

All the complexes are stable upto 150°C. Above 150°C, oxozirconium complexes undergo decomposition endothermally and the mass loss corresponds to the removal of one molecule of water. Further decomposition in all the complexes starts between 280 and 350°C. At 350°C, the loss in mass corresponds to the elimination of one molecule of the ligand and finally a sharp exo-peak is observed at 520°C due to oxidation of metal.

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