Synthesis & Characterization of Pyrazinamide Complexes with Some Uranyl Salts

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Complexes of uranyl chloride, nitrate, sulphate and acetate with pyrazinamide have been prepared and characterized on the basis of analytical data, molar conductance, electronic and IR spectral measurements down to 200 cm⁻¹. It is shown that pyrazinamide, though a potentially tetradentate ligand, acts only as a monodentate ligand in the present complexes bonding through one of the pyrazine ring nitrogens. Tentative stereochemistries are assigned in each case.

Although uranyl complexes with pyrazine derivative like methylpyrazine, quinoxaline and 2,3-dimethylquinoxaline have been studied earlier, there is no report on the uranyl complexes with pyrazinamide, a potentially tetradentate ligand. The present note describes the preparation and characterization of the complexes formed by pyrazinamide with uranyl chloride, nitrate, sulphate and acetate.

Pyrazinamide was purchased from M/s Ega Chemie, West Germany and used as such. The uranyl chloride, nitrate and acetate complexes were prepared by mixing together ethanolic solutions of the respective uranyl salt and excess of pyrazinamide. The mixtures were concentrated on a water bath and then allowed to stand. The uranyl sulphate complex was prepared by adding the ligand solution in methanol to a hot solution of uranyl sulphate in the same solvent. The complexes, which crystallized out on standing, were suction-filtered, washed with ethanol (or methanol) and dried in an air oven at -80°C. Stoichiometries of the solid complexes were established by uranium and anion (except acetate) estimations gravimetrically. C, H and N contents of the acetate complex were determined by microanalysis.

Analytical data indicate that uranyl chloride, nitrate and sulphate complexes have 1:2 (metal:ligand) stoichiometries but uranyl acetate has 1:4 stoichiometry. Comparison of the IR spectra of these complexes with that of the uncoordinated ligand facilitated the assignment of bands due to the uranyl moiety and the coordinated anionic groups. Strong bands due to nitrato, sulphato and acetato groups in the range 1600-1000 cm⁻¹ superimposed and masked some of the bands due to the organic moiety. No absorption bands were observed which could be attributed to water or ethanol thus establishing these complexes to be anhydrous and free from coordinated or lattice water/ethanol. All the complexes are soluble in methanol and ethanol. The sulphate and acetate complexes behaved as non-electrolytes (1.6 and 2.9 Ω⁻¹ cm² mol⁻¹, respectively) while the chloride and nitrate complexes behaved as electrolytes (42 and 45 Ω⁻¹ cm² mol⁻¹, respectively).

Pyrazinamide possesses four potential donor sites—two tertiary nitrogen atoms in the ring at 1- and 4-positions, carbonyl oxygen and NH₂ group. Owing to the fixed orientation in space, the two nitrogens cannot coordinate simultaneously to the same metal ion. However, one cannot rule out the possibility of coordination of any two sites in the ligand molecule to different metal ions (bidentate bridging ligand) resulting in polymeric structures.

Significant IR absorption bands due to the amido group in pyrazinamide are: vNH (3420 and 3300 cm⁻¹), vCO (1665 cm⁻¹) and vCN (1090 cm⁻¹). In complexes with uranyl salts the carbonyl frequency (1665 cm⁻¹) of the uncoordinated pyrazinamide did not undergo any shift. Similarly, the vNH and vCN frequencies of the uncoordinated pyrazinamide remained unperturbed or underwent
slight positive shifts. This trend in the NH, CO and CN stretching modes indicates clearly that the amido group of pyrazinamide is inert towards coordination in these complexes. Although the pyrazine part of the pyrazinamide possesses two potential donor sites, their geometry precludes chelation but favours coordination of the two donor sites to different metal ions thus leading to the formation of polymeric chain structures. IR spectral studies have shown that in metal complexes where pyrazine is bonded through only one of its nitrogen atoms, medium intensity bands appear in the regions ~ 470, 1000 and 1250 cm$^{-1}$. Such bands are absent in uncoordinated pyrazine as well as in ligand-bridged polymers of long chain length. Weak bands, however, appear in metal complexes where the chain length is short. The intensity of these bands has been considered as a measure of chain length in metal complexes with this ligand$^{3-6}$.

IR spectra of the uranyl complexes with pyrazinamide showed additional medium intensity bands at ~ 470, 1000 and 1250 cm$^{-1}$ indicating clearly that pyrazinamide molecules were terminally bonded monodentate ligands$^{3-6}$. In addition to the ligand bands shifted/modified on account of coordination, IR spectra of the uranyl complexes showed strong bands at ~ 920 cm$^{-1}$ due to $v_2$ vibration of the uranyl group. The $v_1$ mode of the uranyl group is IR-forbidden in the free uranyl ion which has a linear OUO arrangement. Absence of a band assignable to this mode at ~ 850 cm$^{-1}$ implied that the linearity of the OUO group was maintained in all these complexes. The doubly degenerate OUO bending mode, $v_2$, was observed at ~ 260 cm$^{-1}$ in these complexes.

Electronic spectra of all the uranyl complexes studied herein are almost identical with slight splitting and shifting of band positions. All the complexes exhibit three absorptions$^7$ in the regions ~ 525, 425 and 250 nm. Of the three absorptions, the first band (~ 525 nm) is attributed to the transition from apical oxygen to $f$ orbitals of the uranyl moiety. The other two bands at ~ 425 and 250 nm are the consequences of transitions from $\pi$-orbitals to $f$ orbitals of the uranyl ion. Electronic spectra of the complexes studied are consistent with the vibronic structure of the triatomic entity of the [UO$_2$]$^{2+}$ group in these complexes.

The far IR spectrum of the 1:2 uranyl chloride complex with pyrazinamide shows a strong band at 250 cm$^{-1}$ which is assigned as $v_{U-Cl}$ mode$^8,9$ in analogy with bands observed for monomeric 6-coordinated complexes of uranium(VI) containing terminally bonded chlorines. The 1:2 uranyl chloride complex with pyrazinamide is, therefore, tentatively assigned a monomeric, hexa-coordinated structure with four ligand atoms (two nitrogens from terminally ring nitrogen bonded pyrazinamide molecules and two terminally bonded chlorine atoms) forming an equatorial ring perpendicular to the linear uranyl group.

IR spectrum of the 1:2 uranyl nitrate complex with pyrazinamide shows the presence of coordinated nitrate groups$^{10-13}$. The doubly degenerate IR-active fundamentals of ionic nitrates, $v_3$ at ~ 1360 cm$^{-1}$ and $v_4$ at ~ 720 cm$^{-1}$, are split up into their components ($v_3$ to $v_1$ 1550 cm$^{-1}$ and $v_4$ 1280 cm$^{-1}$; and the $v_6$ to $v_3$ 755 cm$^{-1}$ and $v_6$ 713 cm$^{-1}$). Moreover, additional bands appear at 1035 cm$^{-1}$ and 809 cm$^{-1}$ which are assigned to $v_2$ and $v_6$ modes, respectively, of the coordinated nitrate groups. Further, IR spectrum of this complex shows bands in the combination tone region, 1785 and 1738 cm$^{-1}$ (separation 47 cm$^{-1}$) characteristic of bidentate chelating nitrate ligands$^{10-13}$. Considering that the nitrate groups act as bidentate chelating ligands and that the pyrazinamide molecules are terminally bonded monodentate ligands, it is suggested that the 1:2 uranyl nitrate-pyrazinamide complex is monomeric containing eight-coordinated uranium(VI). The six ligand atoms (two nitrogens of the two pyrazinamide molecules and four oxygen atoms of two bidentate chelating nitrate groups) form a hexagonal equatorial ring around the linear uranyl group.

IR spectrum of the 1:2 uranyl sulphate complex shows the presence of coordinated sulphato groups$^{14,15}$. The strong broad band expected at ~ 1120-1080 cm$^{-1}$ due to triply degenerate SO stretching mode, $v_3$, in ionic sulphates splits up into its components at 1050,1130 and 1230 cm$^{-1}$ in the IR spectrum of this complex, masking the ligand bands in this region. The triply degenerate OSO bending mode, $v_4$, which occurs as a sharp well-defined band at ~ 610 cm$^{-1}$ in sulphates with $T_d$ symmetry, also splits up into its components at 602, 625 and 650 cm$^{-1}$ in this complex. In addition to these, $v_1$ and $v_2$ modes, both IR-forbidden in uncoordinated sulphates, appear at 990 and 480 cm$^{-1}$, respectively. The frequencies due to coordinated sulphato groups are consistent with those normally associated with bidentate chelating sulphato groups$^{14,15}$ and the complex is considered to have monomeric hexa-coordinated uranium(VI) with four ligand atoms (two nitrogen atoms from the two terminally bonded monodentate pyrazinamide molecules and two oxygens of the bidentate chelating sulphato group) forming an equatorial ring around the linear OUO group.
IR spectrum of the 1:4 uranyl acetate-pyrazinamide complex shows absorption bands at 1587, 1470 and 685 cm\(^{-1}\) which are assigned to \(v_{as}OCO\), \(v_{s}OCO\) and \(\delta OCO\) modes, respectively, due to coordinated acetato groups. These fundamental frequencies are consistent with the exclusive presence of terminally bonded monodentate acetato ligands\(^{14}\). From considerations of both terminally bonded monodentate pyrazinamide molecules and acetato groups, the present complex is considered to have monomeric, eight-coordinated uranium(VI) with six ligand atoms (four nitrogen atoms of the four pyrazinamide molecules and two oxygen atoms of the two acetato ligands) forming an equatorial ring around the linear uranyl group.

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**References**