Synthesis & Characterization of a Ten-coordinated Uranium(VI) Complex

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A 1:2 complex of uranyl nitrate with bis-(2-pyridyl N-oxide)disulphide, a potentially tetradeutate ligand, has been prepared and characterized on the basis of elemental analysis, molecular conductance, electronic and IR spectral measurements down to 200 cm⁻¹. It is shown that the ligand acts only as bidentate chelating one bonding via N-oxide oxygen atoms leading to 9-membered ring formation. The nitrate groups also act as bidentate chelating ligands. The complex is tentatively assigned a chelating geometry as the two oxygens of the \[\text{V_O} \] group. So far, six is the maximum equatorial coordination number reported for the \[\text{UO}_2\]²⁺ ion with an overall coordination number eight around uranium(VI)¹⁻⁸. We now report the isolation of a 1:2 uranyl nitrate complex with bis-(2-pyridyl N-oxide)disulphide—a potentially tetradeutate ligand—which is shown to have an overall coordination number ten around uranium(VI) in the solid state.

The 1:2 uranyl nitrate complex with bis-(2-pyridyl N-oxide)disulphide (obtained from M/s Ega Chemie, West Germany and used as such) was prepared by mixing together hot ethanolic solutions of the two reactants in the 1:2 molar ratio. The complex which formed was suction-filtered, washed with ethanol and dried in an air oven at ~80°C. Stoichiometry of the isolated complex was established by uranium and nitrate estimations gravimetrically. C, H and N were determined by microanalysis [Found: U, 26.5; NO₃, 14.0; C, 27.0; H, 1.75; N, 9.31. \[\text{UO}_2\text{B}_2\left(\text{NO}_3\right)_2\] requires: U, 26.5; NO₃, 13.8; C, 26.7; H, 1.78; N, 9.35%]. The complex is soluble in DMF and behaves as a 1:2 electrolyte (\(\Lambda_M = 170 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}\)). Electronic spectrum of the complex was recorded in nujol in the range 200-600 nm on a Cary 14 recording spectrophotometer. IR spectra of the uncoordinated ligand and the complex were recorded in nujol on a Perkin-Elmer spectrophotometer Model 783 equipped with caesium iodide optics.

Bis-(2-pyridyl N-oxide)disulphide possesses four potential donor sites—(i) two sulphur atoms in between the two pyridyl rings, and (ii) two N-oxide oxygen atoms. Rock salt region IR spectrum of the uranyl nitrate complex indicates clearly that the ligand coordinates via the N-oxide oxygen atoms. Normal modes of bis-(2-pyridyl N-oxide)disulphide that are likely to be affected the most on N-oxide coordination are the \(v\text{NO}\) and \(\delta\text{NO}\). The \(v\text{NO}\), which appears as a doublet at 1248 and 1232 cm⁻¹ in the uncoordinated ligand, suffers a significant negative shift and occurs at 1210 and 1205 cm⁻¹ in this complex. This decrease in the frequency of \(v\text{NO}\) modes is attributed to a decrease in the \(\pi\)-bond character of the NO bond as a result of oxygen-to-metal coordination. The \(\delta\text{NO}\), appearing as a strong band at 836 cm⁻¹ in the uncoordinated ligand, is observed with almost similar intensity and frequency in the IR spectrum of this complex. These observations are consistent with those for N,N'-dioxide complexes with uranyl salts reported earlier¹⁰,¹¹. The two N-oxide oxygen atoms may coordinate either (i) to two different metal atoms (bidentate bridging) giving rise to polymeric structures, or (ii) to the same metal ion (bidentate chelating) resulting in the formation of 9-membered rings. The bridging form, being more symmetrical, gives rise to fewer absorptions in the IR while the unsymmetrical chelating form gives rise to a multiplicity of bands. IR spectrum of the 1:2 uranyl nitrate complex with bis-(2-pyridyl N-oxide)disulphide shows multiplicity of bands, thereby indicating that both the oxygen atoms of the organic ligand are bonded to a single uranilum atom resulting in the formation of 9-membered rings.

In addition to the ligand bands, IR spectrum of this complex shows absorption bands at 925 and 257 cm⁻¹ due to \(v_3\) and \(v_2\) modes, respectively, of the uranyl group. Absence of a band at ~850 cm⁻¹ due to \(v_1\) mode of the uranyl group, IR-forbidden in the free linear \[\text{UO}_2\]²⁺ ion, implies that the linearity of the OOU group is maintained in this complex.

The symmetrical stretching mode \(v_2\) at ~1360 cm⁻¹ in ionic nitrates (\(D_{3h}\) symmetry) splits up into its components which occur at 1520 cm⁻¹ (\(v_{1\downarrow}\)) and 1280 cm⁻¹ (\(v_3\)), masking the ligand bands in this region in the present compound. The doubly degenerate in-plane bending mode of the ionic nitrates at ~720 cm⁻¹ also splits up into its components at 746
cm\(^{-1}\) (\(v_3\)) and 704 cm\(^{-1}\) (\(v_4\)). In addition to these, the symmetric stretching mode \(v_1\) (IR-inactive in ionic nitrates) becomes IR-active because of lowered symmetry upon coordination (\(D_{3h}\) to \(C_2\)) and the frequency of \(v_2\) (~1045 cm\(^{-1}\) in ionic nitrates) is lowered (1032 cm\(^{-1}\)) in this compound. Moreover, two weak bands at 1775 and 1733 cm\(^{-1}\) are also observed in the nitrato combination mode region (1800-1700 cm\(^{-1}\)), which is more diagnostic of the mode of metal-nitrate coordination. The observed magnitude of separation (240 cm\(^{-1}\)) of \(v_1\) (1520 cm\(^{-1}\)) and \(v_2\) (1280 cm\(^{-1}\)) modes and of the nitrato combination modes indicates the exclusive presence of bidentate chelating nitrato ligands. Considering that (i) the nitrato groups act as bidentate chelating ligands for the uranyl group, and (ii) the organic ligand coordinates in a bidentate chelating manner (vide supra), the 1 : 2 uranyl nitrate complex with bis-(2-pyridyl N-oxide)disulphide is tentatively assigned a structure with ten-coordinated uranium(VI). Other possible structures involving the presence of both mono- and bi-dentate nitrato groups together are ruled out as these would require four bands (two sets corresponding to each type of coordination) in the 1800-1700 cm\(^{-1}\) region. Moreover, absence of a band in the region 1800-1790 cm\(^{-1}\) clearly eliminates the possibility of structures involving monodentate (12, 18) M-O(NO\(_2\))-M and/or bidentate (12, 19) M-ON(O)-O-M bridging nitrato groups.

The electronic spectrum of this complex exhibits three absorption bands at 485, 435, and 365 nm and is consistent with the vibronic structure of the triatomic entity of the uranyl group. The band at 485 nm corresponds to the transition from apical oxygen to \(f\) orbital of the uranyl group. The other two bands are the consequences of the transitions \(\pi \rightarrow f\) orbitals of the uranyl ion.

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References