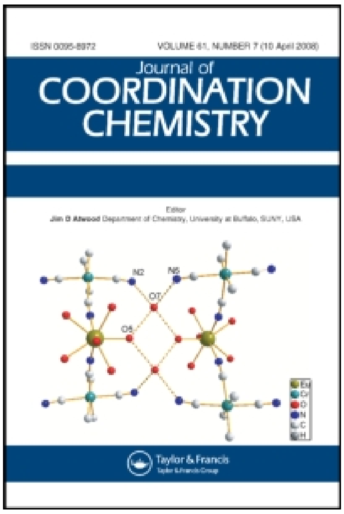

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SHORT COMMUNICATION
Infrared Spectral Evidence for Five-Coordinate Uranium(VI)

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The hexavalent state of uranium is most commonly exhibited by the uranyl ion, UO_2^{2+}. This cation is peculiar in that it behaves as a single entity as regards its coordination behaviour. In coordination compounds the linear OUO bonds of the uranyl group serve as an axis of symmetry while the other donor atoms form an equatorial polygon around it and the compounds, therefore, have the form of a bipyramid.[1] Although tetra-, penta- and hexa- gonal configurations are common for the uranium(VI) compounds,[1] a trigonal bipyramidal configuration with an overall coordination number five for uranium(VI) is rather unknown. We now report the isolation of a 1:1 uranyl sulphate complex with 2-methylbenzothiazole (possessing two potential donor sites – nitrogen and sulphur in the thiazole ring) which is shown from infrared spectral studies to have a five-coordinate arrangement around uranium(VI).

The 1:1 uranyl sulphate-2-methylbenzothiazole was obtained by adding an excess of the ligand to a methanol solution of uranyl sulphate. The compound which precipitated immediately was suction-filtered, washed with methanol and dried. Found: U, 46.4; SO_4, 18.3. Calc.: U, 46.2; SO_4, 18.6%. Infrared spectrum of this compound was recorded as nujol mull held between sodium chloride plates (rock salt region) and thin polythene sheets (15–50 μ) on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics.

I.r. spectrum of this complex is in agreement with those of other 2-methyl-benzothiazole complexes with metal salts indicating coordination of the thiazole ring through its nitrogen atom only.[2] In addition to the ligand bands i.r. spectrum of this complex shows strong absorption bands at 942 and 258 cm^{-1} due to ν_3 and ν_2 modes, respectively, of the uranyl group.[3] Absence of a band at ~850 cm^{-1} due to ν_1 mode of the uranyl group, i.r. forbidden in the free linear OUO ion, indicates that the linearity of the OUO group is maintained in this complex.

I.r. spectrum of the compound under investigation shows the presence of coordinated sulphate groups.[3] This is evident from the fact that the strong broad band at ~1120–1080 cm^{-1} due to triply degenerate SO stretching mode ν_3 in ionic sulphates splits up into its components at 1058, 1142 and 1240 cm^{-1} (masking the ligand bands in this region). The triply degenerate OSO bending mode ν_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 – 600, 616 and 641 cm^{-1}, in this complex. In addition to these, the ν_1 and ν_2, both i.r. forbidden in uncoordinated sulphates, appear at 1004 and 460 cm^{-1}, respectively, in this compound. The frequencies of absorption bands due to sulphate group in this complex are consistent with those normally associated with bidentate chelating sulphate groups.[3] In complexes of the uranyl ion the two oxygen atoms of the UO_2^{2+} group always lie in the apical plane while the other donor atoms lie approximately in the equatorial plane around the uranium. Thus from a consideration of (i) 1:1 metal:ligand ratio, (ii) bidentate chelating nature of the sulphate group, and (iii) coordination of 2-methylbenzothiazole through its nitrogen atom only, the 1:1 uranyl sulphate-2-methylbenzothiazole complex is tentatively assigned to have five-coordinated uranium(VI) with three atoms (one nitrogen from the organic ligand molecule and two oxygens of the bidentate chelating sulphate group) forming an equatorial ring perpendicular to the linear OUO group. The overall coordination number five is rather unknown for uranium(VI) and the present complex seems to be the first example. However, unambiguous characterization of this compound should be based on complete crystal structure determination.

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