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LETTER

The new triaza macrocyclic complex of the dioxouranium(VI) ion

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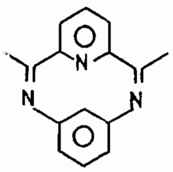
Coordination chemistry of the actinide elements has recently undergone considerable development but there have been relatively few reports of the ability of the actinide ions to act as templates for the synthesis of macrocyclic ligands and their complexes [1] when compared with the large numbers of papers involving d-electron elements and lanthanides. As a continuation of our investigation on the effectiveness of metal ions of varying radius and electron configuration in the synthesis of macrocyclic compounds [2] we have previously reported the first example of the template action of the yttrium and lanthanide ions in the synthesis of new triaza macrocyclic compounds [3]. We now report what we believe to be the first example of the effectiveness of the dioxouranium ion in the synthesis of a triaza macrocycle.

The UO_2^{2+} complex was prepared by adding *m*-phenylenediamine (0.1 mmol) in methanol (15 cm^3) to the mixture of $UO_2(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) in methanol (10 cm^3) and 2,6-diacetylpyridine (0.1 mmol) in methanol (10 cm^3). The reaction mixture was stirred for 24 h. Removal of the solvent left a yellow solid which, on washing with ether, gave a yellow powder. This was dried under vacuum.

Condensation of 2,6-diacetylpyridine with *m*-phenylenediamine with the use of hydrated dioxouranium nitrate as template agent gave the new ten-membered triaza macrocyclic complex of stoichiometry $[UO_2L((NO_3)(H_2O)](NO_3) \cdot H_2O$, where L is the Me_2bzopyo[10]tetraeneN_3 ligand. The formulation of the complex follows from spectral data (IR, UV–Vis, ^1H NMR and MS) and thermal analysis. Elemental analysis figures are consistent with the above formula. *Anal.* Calc. for $C_{15}H_{17}N_5O_{10}U$: C, 27.09; H, 2.57; N, 10.53. Found: C, 27.41; H, 2.48; N, 10.63%.



The IR spectrum of the complex in CsI pellets taken in the region 4000–200 cm^{-1} confirms the formation of the macrocyclic compound by the absence of uncondensed functional group (NH_2, C=O) stretching modes for the starting materials and the appearance of a strong absorption band at 1620 cm^{-1} attributable to the C=N stretching frequency indicative of Schiff base condensation. The strong absorption observed at 917 cm^{-1} is assigned to the asymmetric stretching vibration of the linear uranyl group. The U–O bond distance equal to 1.71 Å calculated [4] from this frequency is quite typical for uranyl complexes [5].

The IR spectrum of the complex shows the characteristic strong absorption at 1380 cm^{-1} and a weak band at 835 cm^{-1} typical for the ionic nitrate group. Two additional bands associated with the asymmetric stretch of coordinated nitrates occur at 1300 and 1500 cm^{-1}. The magnitude of the separation (200 cm^{-1}) along with the appearance of the band at 820 cm^{-1} are indicative of the interaction of the nitrate oxygen atom with the metal ion and provide evidence for the chelating behaviour of the nitrate group [6]. These features demonstrate the presence of both ionic and bidentate nitrates in the complex and parallel the findings for the UO_2 stretching vibration (917 cm^{-1}) characteristic of monocationic species [7].

The weak absorption bands around 530 and 450 cm^{-1} can be assigned to the metal–oxygen and metal–nitrogen stretching vibrations, respectively [8].

The broad diffuse band in the 3500–3200 cm^{-1} region and a weak absorption at 560 cm^{-1} suggest the presence of lattice and coordinated water. This is supported by the results of thermal analysis, which indicate a loss of one molecule of water at 40–60 °C and one water molecule at 140–180 °C.

The electronic spectrum of the complex for a solution in methanol exhibits an absorption band at 231 nm with a shoulder at 265 nm attributable to the $\pi \rightarrow \pi^*$ transitions of the coordinated macrocycle.

The ^1H NMR spectrum of the complex obtained in DMSO-d_6 solution shows pyridine protons at δ 7.6–8.3, benzene protons at δ 5.9–6.4 and methyl protons at δ 2.3 and 2.6 with integrated intensities in the ratio 3:4:6, respectively.

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The mass spectrum of the complex provides strong evidence for the presence of a macrocyclic compound showing the highest fragment at *m/z* 235 corresponding to the free macrocycle.

The data presented here lead to the conclusion that the dioxouranium(VI) ion may act as a template agent for the synthesis of a triaza macrocyclic compound.

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