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Synthesis and Characterization of Sodium Di-μ-hydroxo-bis[3,6-disulpho-1,2-naphthoquinone-1-oximato-*O*,*N*-dioxouranate(VI)]*

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The complexation of dioxouranium(VI) ion with disodium 1,2-naphthoquinone-1-monoxime-3,6-disulphonate (Na_2HL) in aqueous solution in the pH region 4–6 was recently studied in our laboratory [1]. The stoichiometry and formation constant for the main complex species $[(UO_2)_2(OH)_2L_2]^{4-}$ were resolved from potentiometric and spectrophotometric titration data by using MINIQUAD [2] and FA608 [3] programs, respectively. The complex and the ligand were also characterized in solution by ^1H and ^{13}C NMR spectroscopy [4].

A solid complex L/U of dioxouranium(VI) and Na_2HL has now been synthesized under the same conditions and characterized by TG, pyrolysis MS, IR and CPMAS ^{13}C NMR. The uranium content of the complex was determined by the DCP-AES technique.

Experimental

A solid complex L/U was synthesized by adding a dilute solution of sodium hydroxide (3 mmol) to a hot aqueous solution containing Na_2HL (1 mmol) and $UO_2(NO_3)_2 \cdot 6H_2O$ (2 mmol). The solution was concentrated and ethanol added. After cooling, the solid complex was separated, washed with cold water and dried in air. To ensure evaporation of the solvent, the complex was heated for 1 h at 150 °C.

The uranium content of the complex was determined with a Spectrametric SpectraSpan III single-channel plasma emission spectrometer. Determination was based on direct comparison of the signal of the sample solution to that of a standard (30 ppm). The intensities of emission were measured at 424.17 nm [5].

The instrumentation and techniques used in other experiments have been described elsewhere [1].

Results and Discussion

The uranium content determined for the solid complex L/U (Table I) was in good agreement with the stoichiometry (2 –2 2) of the main complex in solution [1].

TABLE I. The Determined and Calculated Uranium Content of the Complex L/U[a]

Sample (mg)	U Found		U Calc.	
	(mg)	(%)	(mg)	(%)
10.52	3.78	35.9	3.78	35.9
17.42	6.17	35.4	6.25	35.9

[a] The molecular weight used for L/U was 1326.

The CPMAS ^{13}C spectrum confirmed the observations made for the main complex in solution [4]: *i.e.*, the ketonic oxygen does not take part in the complexation and complexation occurs through the oxime nitrogen and oxygen. There was, in addition, a clear peak at 2.7 ppm in the ^1H spectrum, which may be taken as evidence for the existence of hydroxyl bridges [6].

Thermal decomposition of L/U (Fig. 1) proceeds with smooth steps, indicating that the different processes in the decomposition are partly simultaneous. This finding is in good agreement with MS analyses of evaporated gases and IR spectra of residuals at the same temperatures.

Analyses of the total ionic current (TIC) at temperatures 1–4 (Fig. 2) showed the first gaseous decomposition product to be CO, followed immediately by CO_2. These were replaced by SO_2 in increasing abundance at higher temperatures.

Also, the analyses of the solid residue made by IR spectrometry at selected temperatures were in good agreement with the above results. The ν(C=O) at

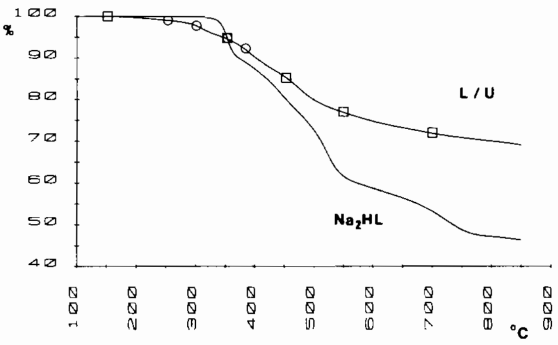

Fig. 1. The TG curve of the complex L/U. The inspection points in IR and MS are □ and ○, respectively. The corresponding TG curve of the ligand is presented for comparison.

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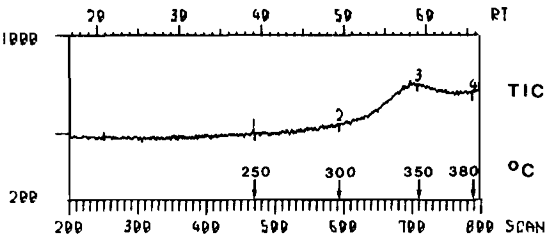


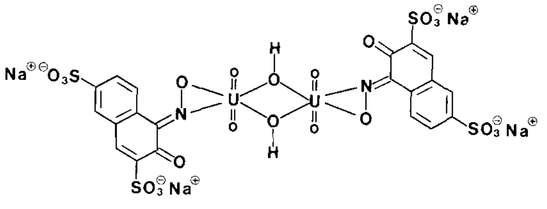
Fig. 2. The total ionic current (TIC) of the complex L/U (70 eV, EI) *vs.* temperature (scans).

1570 cm^{-1} decreased and disappeared, the ν(C=N) at 1670 cm^{-1} changed to ν(C≡N) at 2240 cm^{-1} and the stretching frequencies of two different sulphonic groups, ν(C–SO$_3$) at 600–700 cm^{-1} and $\nu_{as,s}$(S=O) at 1050–1300 cm^{-1}, gradually disappeared before 700 °C.

The clear stretching frequency ν(O–H) at about 3450 cm^{-1} disappeared between 550 and 700 °C; this may be taken as evidence of the existence of strong OH bridges between two uranium atoms.

The loss of weight between 150 and 600 °C was about 25%, corresponding almost quantitatively to the evaporation of all possible CO$_2$ and SO$_2$.

The results presented here for the complex L/U indicate it to be identical with the main complex in solution. Schematically it appears as follows:



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