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The Direct Electrochemical Synthesis of Chelate Complexes of Uranium(IV) and Uranium(VI)

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Abstract

The electrochemical oxidation of uranium metal into acetone or acetonitrile solutions of the acids HL gave rise to the chelate complexes UL_4 (L = 2,4-pentanedionate (acac), 1,1,1-trifluoro-4-(1-thienyl)-2,4-butanedionate, tropolonate, or 8-hydroxyquinolate (oxine)). In an atmosphere of oxygen, the compounds $UO_2(acac)_2$ and $UO_2(oxine)_2\cdot$Hoxine were obtained, but the other ligands did not yield the analogous uranium(VI) species.

Introduction

The properties of the complexes formed by the actinide elements with chelating ligand such as β-diketonates have been investigated in some detail, in part because such species are important in the solvent extraction chemistry of the heavy elements [1]. The preparation of the solid complexes normally involves mixing the parent acid (HL) with an aqueous solution of a salt of the metal, followed by pH adjustment to bring about precipitation and recrystallisation. In many cases the products are adducts of the type $ML_n\cdot(HL)_m$. During work on the direct electrochemical synthesis of thorium(IV) compounds [2], we found that $Th(acac)_4$, $Th(tfha)_4$ and $Th(oxine)_4$ (acac = 2,4-pentanedionate; tfha = 1,1,1-trifluoro-2,4-heptanedionate; oxine = 8-hydroxyquinolinate) could be prepared in good yield by oxidising a thorium anode into an acetone solution of the parent β-diketone, following earlier studies of transition metal complexes [3]. We have now extended these experiments to the electrochemical synthesis of uranium(IV)/chelates, and find that in some cases *in situ* oxidation to the uranium(VI) complex can be achieved, in keeping with similar results recently reported for neutral and anionic halogeno complexes of this element [4].

Experimental

Materials

Uranium was supplied in the form of discs, approximately 1 cm diam. and 1 mm thick (Atomic Energy of Canada, Ltd.). The oxide surface layer was removed by treatment with conc. nitric acid, and the metal then washed with water and acetone. Acetone (Reagent Grade) was dried over anhydrous magnesium sulphate. Acetonitrile (Reagent Grade) was distilled before use and stored over phosphorus pentoxide. Acetylacetone was dried over potassium carbonate. Gases were dried by passing them over phosphorus pentoxide. All other substances were used as supplied.

Analysis and Spectroscopy

Uranium was determined as U_3O_8 after careful ignition at 600 °C for 2–3 h. Microanalysis was by Guelph Chemical Laboratories Ltd.

Infrared spectra were recorded on a Perkin-Elmer IR 180 spectrometer, using Nujol mulls, or pressed KBr or CsI discs as appropriate.

Electrochemical

The cell was essentially that used in previous work [2, 5], with the solution phases and electrochemical conditions delineated in Table I. The first series of experiments was carried out in an atmosphere of dry nitrogen, with a stream of the gas bubbling through the solution. Later experiments were in air, or dry oxygen.

Acetone proved to be a satisfactory solvent for the oxygen-free experiments leading to uranium(IV) species. Acetonitrile was used when uranium(VI) compounds were being prepared.

Isolation Procedures

In the case of $U(oxine)_4$ and $U(trop)_4$, the products precipitated *in situ*, and were collected and recrystallised from hot chloroform. The corresponding $U(acac)_4$ and $U(tta)_4$ species are soluble in the solution phases used, and in these cases the final solution was filtered to remove traces of solid thrown

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TABLE I. Experimental Conditions for the Electrochemical Synthesis of Chelate Complexes of Uranium.

Product[a]	Solvent[b]	Vol. (ml)	Wt./vol. HL (g/ml)	Atmosphere	Initial		Time of electrolysis (h)	Mass U dissolved (g)	% Yield of product[c]
					Voltage (V)	Current (mA)			
$\mathrm{U(acac)_4}$	acetone	40	4	N_2	30	30	4.3	0.39	60
$\mathrm{U(tta)_4}$	acetone	50	1.0	N_2	30	30	3	0.29	70
$\mathrm{U(trop)_4}$	CH_3CN	50	0.4	N_2	16	20	2	0.19	73
$\mathrm{U(oxine)_4}$	acetone	50	1.8	N_2	25	25	2.7	0.21	67
$\mathrm{UO_2(acac)_2}$	acetone	40	2	air	34	30	2	0.22	12
$\mathrm{UO_2(acac)_2}$	acetone	50	2	O_2	36	30	3.5	0.38	75
$\mathrm{UO_2(acac)_2}$	CH_3CN	50	2	O_2	26	30	3	0.37	78
U/tta	acetone	50	0.5	O_2	29	25	3.5	0.32	See text
U/tta	CH_3CN	50	0.6	O_2	21	25	2	0.21	
U/trop	CH_3CN	50	0.32	O_2	25	30	3.5	0.32	
$\mathrm{UO_2(oxine)_2}$·Hoxine	CH_3CN	50	1.0	O_2	25	30	2	0.23	70

[a] acac = 2,4-pentanedionate; tta = 1,1,1-trifluoro-4-(1-thienyl)-2,4-butanedionate; trop = tropolonate; oxine = 8-hydroxyquinolate. [b] Plus *ca.* 40 mg tetraethylammonium perchlorate. [c] Based on metal dissolved.

TABLE II. Analytical Results and Melting Points.

Compound	Colour	M.Pt. (°C)		U(%)	
		expt.	lit.	found	calcd.
$\mathrm{U(acac)_4}$	green-brown	176	176[a]	36.9	37.5
$\mathrm{U(tta)_4}$	red-brown	233	250 ± 10[b]	20.4	21.2[c]
$\mathrm{U(trop)_4}$	orange-brown	>300	–	32.0	32.7
$\mathrm{U(oxine)_4}$	orange	>300	–	29.0	29.2
$\mathrm{UO_2(acac)_2}$	yellow	260	230–235(dec.)[d]	46.2	50.4[e]
$\mathrm{UO_2(oxine)_2}$·Hoxine	brick red	colour change to green at 225	colour change to green at 210–215[f]	34.2	33.8

[a] Ref. 6. [b] Ref. 7. [c] Found C 34.5, H 1.62%; calcd. C 34.2, H 1.44%. [d] Ref. 8. [e] Found C 25.5, H 3.32%; calcd. C 25.5, H 3.40%. [f] Refs. 9, 10.

down during the electrolysis. Solvent was removed *in vacuo* until precipitation took place, and the resultant solids were recrystallised from benzene/petroleum ether solution. For $\mathrm{UO_2(acac)_2}$, the procedure was similar, with recrystallisation from hot benzene. The oxinate adduct $\mathrm{UO_2(oxine)_2}$·Hoxine precipitated during the electrolysis, and this product was washed several times with diethyl ether and dried *in vacuo*. Analytical results and melting points are given in Table II.

Attempts to prepare $\mathrm{UO_2(tta)_2}$ and $\mathrm{UO_2(trop)_2}$ by electrolysis of uranium in oxygenated solutions were unsuccessful. In the former case, $\mathrm{U(tta)_4}$ was recovered from the final solution, together with tarry or oily products which were not investigated. With tropolone in acetonitrile, a red precipitate began to form at the anode as soon as electrolysis started. This material partly redissolved as the experiment proceeded, and a yellow solution phase was finally obtained. At the end of the experiment (see Table I), we recovered 0.36 g of the insoluble material, identified as $\mathrm{U(trop)_4}$. The solution was evaporated to dryness, and the resultant solid treated with diethyl ether (20 ml); evaporation of this extract solution gave an orange solid (U 39.4%), which was not $\mathrm{UO_2(trop)_2}$ on the basis of the analytical and spectroscopic evidence. These experiments were not carried further.

Results and Discussion

Preparation

The products listed in Table II were identified by metal analysis, (and in some cases carbon and hydrogen analysis), by melting point and by colour. In each case, these latter properties were essentially those reported in the literature. The infrared spectra of the products were also identical to those published by previous authors [7, 11–14].

As in previous synthetic studies, the electrochemical method provides a simple, one-step route at room temperature to a number of chelate complexes of uranium(IV), and there seems every reason to conclude that the method could be equally well applied to other similar chelating ligands. As noted in the Introduction, conventional methods involve a series of operations, and in some cases a prior chemical [13] or photochemical [7] reduction of uranium(VI) is also required because of the redox instability of uranium(IV) in aqueous solution. Two further advantages of the electrochemical method are the high yields, and the absence of additional molecules of neutral HL in the final anhydrous product.

In order to produce uranium(VI) compounds, we found it necessary to bubble dry oxygen through the cell during electrolysis; opening the cell to the atmosphere, or bubbling air through the solution, did not yield satisfactory products. Even so, the results are not encouraging since in two cases (tropolone and tta) the experiment yielded the corresponding uranium(IV) compound as the only identifiable metal derivatives, possibly because of the easy cathodic reduction of any uranium(VI) species formed in electrochemical oxidation. With 8-hydroxy quinoline, the product is the known adduct $UO_2(oxine)_2$•Hoxine, which has been the subject of a number of previous investigations [10, and refs. therein]. We conclude that electrochemical oxidation of uranium metal is a less useful and general route to uranium(VI) chelate complexes than is the case for corresponding halides [4].

Electrochemical Efficiency

As in previous work, we have determined the electrochemical efficiency of the reaction, defined as moles of uranium dissolved per Faraday of electricity. For all the systems studied, irrespective of the oxidation state in the product, we find $E_F = 0.50 \pm 0.03$ mol F^{-1}. This is a surprising result, given that in all previous studies of similar systems [3], the overall stoichiometry established by E_F values is

$$\text{cathode: } n\text{HL} + ne \longrightarrow n\text{L}^- + \tfrac{1}{2}n\text{H}_2(\text{g})$$

$$\text{anode: } n\text{L}^- + \text{M} \longrightarrow \text{ML}_n + ne$$

Of special relevance is the E_F value of 0.25 mol F^{-1} found in experiments leading to synthesis of $Th(acac)_4$ and $Th(oxine)_4$. The formation of hydrogen at the cathode was observed in the present work. One interpretation of the E_F results is that the primary product of the anode is ML_2, which may react by either

$$ML_2 + 2HL \longrightarrow ML_4 + H_2$$

or

$$ML_2 + O_2 \longrightarrow MO_2L_2$$

While such reactions may indeed explain the observed formation of ML_4 and MOL_2 species, the proposed ML_2 intermediate appears to have no precedent in the solution chemistry of uranium, although a number of solid chalcogenides of the type US have been prepared [15]. Further work on this point is planned.

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