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URANIUM (IV) HALIDES

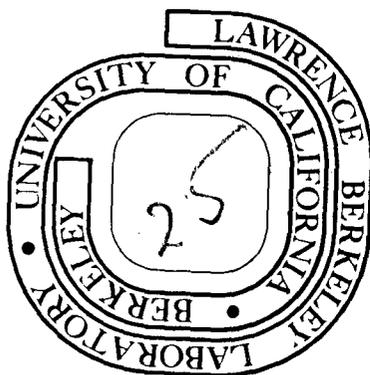
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REACTIONS OF DITHIOLATE LIGANDS WITH URANIUM (IV) HALIDES

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SUMMARY

The reactions of UCl_4 and UI_4 with 3,4 - toluenedithiol and bis-trifluoromethyl-1,2-dithietene are discussed. A compound with the empirical composition $U_2I_4(S_2C_7H_6)_2(H_2S_2C_7H_6)$ was isolated from the reaction of UI_4 and 3,4 - toluenedithiol. The chemical and spectroscopic evidence suggest a dimeric structure which has the $S_2C_6H_7$ ligands both bidentate and bridging and the $H_2S_2C_6H_7$ ligand as bridging. The reaction of UCl_4 and 3,4 - toluenedithiol did not produce an isolatable complex. Products with the empirical compositions $U_2Cl_4(S_2C_4F_6)$ and $U_3F_3I(S_2C_4F_6)_2$ were isolated from the reactions of UCl_4 and UI_4 with bis-trifluoromethyl-1,2-dithietene, respectively.

INTRODUCTION

During the past decade there has been considerable interest in d transition metal - 1, 2- dithiolene complexes, particularly because of their application to analytical, industrial, and bio-inorganic problems.¹ The unusual chemical properties of the dithiolene chelates have been thoroughly studied both theoretically and experimentally by several groups and the results have been summarized by McCleverty² and Hoyer and Dietzsch.³

In contrast to the d transition series, very little is known about actinide 1, 2 - dithiolene complexes. The anionic uranyl (VI) chelates, $(R_4N)_2UO_2(mnt)_2$, where R is C_2H_5 or n-propyl, $mnt =$ maleonitriledithiolate dianion, have been prepared.⁴ Contradictory results existed about a U(IV) dithiolene complex until Dietzsch and Hoyer⁵ synthesized $[As(C_6H_5)_4][U(mnt)_4]$ from the reaction of UCl_4 with Na_2-mnt . They also found that neither the reaction of UCl_4 in methanol with the disodium salt of 1,2 - dimercaptoethylene or with 4,5 - dimercapto-o-xylene led to stable compounds. Very recently the synthesis of $(C_5H_5)_2U(tdt)$, $tdt =$ toluenedithiol dianion, has been isolated from the reaction of $(C_5H_5)_2U(NEt)_2$ and H_2tdt .⁶ The proton NMR data indicate a monomer-dimer equilibrium below room temperature.

We present here the details of the reactions between UCl_4 and UI_4 and the ligands 3,4 - dithiotoluene (H_2tdt) and bis-trifluoromethyl-1,2 dithietene ($S_2C_4F_6$).

RESULTS AND DISCUSSION

Reactions with 3,4 - toluenedithiol

UI₄

Uranium tetraiodide reacts with 3,4 - toluenedithiol in refluxing hexane to give a red-brown compound which is insoluble in methylene chloride, benzene, or toluene. It is very soluble in THF or DMF giving a yellowish-red solution, but it cannot be recovered from these solvents. The compound immediately decomposes in air and dissolves completely in water giving a green solution. Total elemental analysis of the compound shows its composition to be U₂I₄(tdt)₂(H₂tdt). In agreement with this formulation the infra red spectrum shows a ν_{S-H} absorption at 2425 cm⁻¹ which, when compared with the free ligand (H₂tdt: ν_{S-H} = 2545 cm⁻¹), corresponds to a weaker S-H bond. Sublimation at 160°C and 10⁻⁵ torr gives a yellow-brown product which does not show any IR absorption bands characteristic of the H₂tdt ligand.

The proton nmr spectrum exhibits two different bands corresponding to two sets of ligands, as shown in Table I. The upfield resonances contain the H (CH₃) and H (CH_{ring}) bands of two tdt ligands. This large upfield shift relative to TMS shows these protons are strongly affected by the paramagnetic U(IV) ions which have the 5f² open shell configuration. The low field group (2.3 to 7.33 ppm downfield from TMS) exhibits two H (S-H) peaks in addition to the H (CH₃) and H (CH_{ring}) peaks. These resonances are at the same frequencies as in the spectrum of the free ligand. We suggest the U₂I₄(tdt)₂(H₂tdt) complex partially dissociates upon dissolving in THF due to a replacement of the H₂tdt ligand by two THF molecules. Note that in Table I the H(S-H) resonances of the free ligand in d₈-THF

and CDCl_3 are different while the $\text{H}(\text{CH}_3)$ and $\text{H}(\text{CH}_{\text{ring}})$ resonances are very similar. This fact may be due to hydrogen bonding of the protons in the S-H group by THF.

A possible structure for $\text{U}_2\text{I}_4(\text{tdt})_2(\text{H}_2\text{tdt})$ is given in Figure 1. In this structure each uranium ion is surrounded by four sulfurs and two iodines in a distorted octahedral configuration.

An appropriate reaction mechanism can be postulated which would lead to this structure. One molecule of H_2tdt reacts with UI_4 to give an intermediate UI_2tdt by replacement of two iodide ions as 2HI . The insufficient coordination about the U(IV) causes a dimerization with another molecule of UI_2tdt , with one sulfur of each ligand bridging between the two U ions. However, a third ligand is needed to give each uranium ion the favored six fold coordination, but this ligand cannot be reduced to a dianion without giving the uranium ions a formal oxidation state (+V). Therefore the third ligand is bonded as a solvated molecule (still containing the sulfur hydrogens) and is easily replaced. The lability of the neutral H_2tdt ligand is the main cause of the thermal instability, the reactivity towards air, and the reason the compound cannot be recrystallized from THF or DMF due to its reactions with these solvents.

The proposed structure is supported by the report of a monomer-dimer equilibrium for $\text{Cp}_2\text{U}(\text{tdt})^6$. The π -bonded cyclopentadienyl ion is a much better coordinating ligand than I^- so at room temperature the complex is monomeric. At lower temperatures the dimer becomes stabilized. By contrast, the iodo complex even at room temperature coordinates a neutral ligand in order to become coordinatively saturated.

UCl₄

Uranium tetrachloride reacts with H₂tdt in refluxing CCl₄ or ethylcyclohexane to give a brown compound. Total elemental analysis showed the main part was unreacted UCl₄ and decomposition products of the ligand. Part of the material dissolves in THF to give a green solution leaving a brown residue. A red complex is precipitated from the green solution after several days at -10°C but in insufficient quantity for characterization.

Reactions with bis-(trifluoromethyl) -1, 2 dithietene

UCl₄

Uranium tetrachloride was treated with bis(trifluoromethyl) -1,2 - dithietene in boiling ethylcyclohexane for several days to give a dark brown material of the empirical formula U₂Cl₄S₂C₄F₆ as determined by total elemental analysis. The mass spectrum only exhibited bands with very low intensity in the range between 840 and 860 mass units (molecular weight of U₂Cl₄S₂C₄F₆ = 844). The stretching frequency of the C = C bond (1607 cm⁻¹) showed only a small shift of -14 cm⁻¹ from the free ligand. This small shift is similar to that found in various dinuclear species containing a bridging dithiolene ligand, M-L-M, M = Fe, M = V, Cr, Mo and suggests the dithiolene ligand in this U complex may also be bridging. The material U₂Cl₄S₂C₄F₆ is very slightly soluble in THF and DMF but slowly decomposes in these solvents. Sublimation of this material yielded only UCl₄. We are presently unable to suggest a plausible structure for this material but it is possibly polymeric.

UI₄

Uranium tetraiodide was treated with S₂C₄F₆ in ethylcyclohexane at 130° for several days to give a brown material which was insoluble in common solvents. Total elemental analysis showed this material had an empirical formula U₃F₃I(S₂C₄F₆)₂. The excess of fluorine in this material indicates some of the ligand decomposed. The stretching frequency of the C = C bond (1618 cm⁻¹) is similar to that found for U₂Cl₄S₂C₄F₆. This material appears polymeric and no reasonable structure can be suggested for it.

Conclusion:

Uranium tetrachloride and uranium tetraiodide react with the ligands bis(trifluoromethyl) -1, 2 dithetene and 3,4 toluenedithiol in a very specific fashion which is dependent on the particular halide and ligand used. In the reactions studied no anionic species were found and no general formula can be given for the different reaction products. The only common feature of the reactions is that dinculear or polynuclear species were formed.

Experimental:

All work was carried out in Schlenk tubes or in an argon filled dry box because of the air and moisture sensitive nature of the uranium dithiolene complexes and the reagents used to produce them.

Analyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach, W. Germany.

Infrared spectra were taken in KBr pellets or nujol and halocarbon mulls and recorded on a Perkin-Elmer IR-9 machine. The proton magnetic resonance data were obtained on a JEOL PS-100 FT spectrometer and a Varian T-60 spectrometer.

Reagents:

All solvents were dried by standard methods and kept under argon. 3,4-toluenedithiol was obtained from Eastman Organic Chemicals and was degassed and kept under argon. Bis(trifluormethyl) dithietene was prepared by bubbling hexafluorobutyne-2 (Pierce Chemical, Rockford, USA) through boiling sulfur as described by Krespan⁹. UCl_4 ¹⁰ and UI_4 ¹¹ were prepared by published methods.

Reaction between UI_4 and H_2tdt

841 mg of UI_4 was suspended in 10 ml CCl_4 and a solution of 1.4g H_2tdt in 10 ml CCl_4 was added. The mixture was refluxed for 24 hours, cooled to room temperature and then filtered. The isolated brown product is very sensitive to oxygen and moisture.

Analysis for: $U_2I_4(S_2C_7H_6)(H_2S_2C_7H_6)$:

| | U | C | S | H | I |
|--------|-------|-------|-------|------|-------|
| calc. | 32.86 | 17.41 | 13.28 | 1.39 | 35.04 |
| found. | 32.70 | 16.83 | 13.41 | 1.88 | 35.40 |

The values found for C- and H were less accurate probably due to a partial decomposition of the compound.

Reaction between UCl_4 and H_2tdt :

942 mg UCl_4 was suspended in 10 ml CCl_4 and a solution of 2.94g H_2tdt in 10 ml CCl_4 was added. The mixture was refluxed for 3 days. The mixture was allowed to cool to room temperature and filtered, leaving a brown residue. This residue was washed with hexane and dried.

Reaction between UI_4 and $S_2C_4F_6$:

792 mg of sublimed UI_4 were refluxed together with 1.6 g $S_2C_4F_6$ in 7 ml ethylcyclohexane. A large amount of iodine was evolved. After the reaction was completed, the product was allowed to cool down; filtered and washed with hexane until the hexane remained colorless.

Analysis for $U_3F_3I(S_2C_4F_6)_2$:

| | U | C | S | I | F |
|--------|-------|------|------|------|-------|
| calc. | 52.88 | 7.11 | 9.48 | 9.40 | 21.11 |
| found. | 53.15 | 7.11 | 9.60 | 9.36 | 20.81 |

Reaction between UCl_4 and $S_2C_4F_6$:

A mixture of 625 mg UCl_4 , 10 ml ethylcyclohexane and 1.3 g $S_2C_4F_6$ was refluxed for seven days. A dark brown precipitate formed. After the mixture was allowed to cool to room temperature it was filtered and the residue washed with a large amount of hexane and then dried in high vacuum.

Analysis for $U_2Cl_4S_2C_4F_6$:

| | U | C | S | Cl | F |
|--------|-------|------|------|-------|-------|
| calc. | 56.39 | 5.69 | 7.59 | 16.80 | 13.51 |
| found. | 56.33 | 5.50 | 7.37 | 17.06 | 13.65 |

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References and Footnotes

- * Work done under the auspices of the U. S. Atomic Energy Commission
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Table I. H-NMR frequencies of 3,4-toluenedithiol and
 $U_2I_4(tdt)_2(H_2tdt)$.

| Assignments | 3,4-toluenedithiol | | $U_2I_4(tdt)_2(H_2tdt)$. |
|---------------------|--------------------|---------------|---------------------------|
| | In d_8 -THF* | In $CDCl_3$ * | In d_8 -THF* |
| CH ₃ | -2.16 | -2.30 | -2.30 |
| S ₁ H | -4.00 | -3.50 | -4.10 |
| S ₂ H | -4.40 | -3.66 | -4.20 |
| ring H ₁ | -6.60 | -6.66 | -6.76 |
| | -6.73 | -6.80 | -6.83 |
| ring H ₂ | -7.06 | -7.03 | -7.13 |
| | -7.16 | -7.18 | -7.33 |
| ring H ₃ | -7.03 | -7.06 | -7.10 |
| CH ₃ | | | 9.35 |
| ring H ₁ | | | 11.64 |
| | | | 11.72 |
| ring H ₂ | | | 56.69 |
| | | | 56.85 |
| ring H ₃ | | | 56.45 |

*Units are ppm referenced to TMS.

Figure 1 - Proposed structure for $U_2I_4(S_2C_7H_6)_2(H_2S_2C_7H_6)$. The curved line represents the $C_6H_3CH_3$ backbone of the 3,4-toluenedithiol ligand.

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