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Preparation and Characterization of Uranyl(VI) Complexes with Ethylene-1,2-Dioxydiacetic Acid

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Abstract

Different complexes have been prepared from the reaction of the uranyl(VI) ion and an open–chain polyether containing two carboxylic groups: ethylene-1,2-dioxydiacetic acid (edoda) or its disodium salt.

Polymeric complexes $[UO_2(edoda)]_n$ and non-polymeric complex $[UO_2(Hedoda)\cdot H_2O]NO_3$ have been prepared and characterized by infrared spectroscopy, conductivity and thermal decomposition.

Introduction

In recent years there has been increasing interest in cyclic polyether ligands, where the oxygen atoms, but also S and N substituted groups, are able to form a cavity to provide a coordination site for cations.

For this purpose the open–chain polyether ligands are of interest as they have less rigidity and can create a pseudo cavity with greater conformational flexibility.

In particular the open–chain polyether ligands which have carboxylic groups at the end of a chain, can help to hold the ligand in a pseudo cyclic conformation round the actinide ions, which have, as is known, a great affinity towards charged oxygen donors.

In order to examine the interaction effects of such ligands with uranyl(VI) and thorium(IV) ions, we have undertaken a research program dealing with the formation of complexes between some actinide ions and simple acyclic dicarboxylic ethers.

Attention was first directed to the ligand ethylene-1,2-dioxydiacetic acid (H_2edoda) which has two carboxylic groups and two ether oxygen atoms in the open–chain with the possibility of forming three five membered chelate rings with the central metal ion.

Experimental

The reagents were commercial products purified by standard methods.

Preparation and characterization of ethylene-1,2-dioxydiacetic acid (H_2edoda)

We have checked some methods of preparation and characterization reported in the literature [1–4] and then selected the method used in ref. [1] for the oxidation of triethylene glycol with nitric acid.

Using this procedure we obtained a blue–green viscous liquid that we recognized to be impure edoda by oxalic and oxydiacetic acid (Fig. 1a).

It was very difficult to purify this product; several different methods were tried and, finally, the product was extracted several times with chloroform.

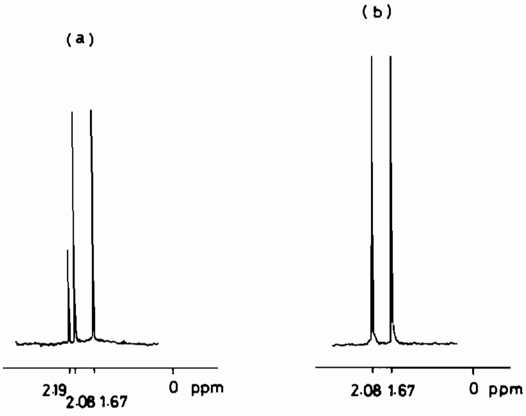

Fig. 1. NMR spectra of the free ligand H_2edoda a) before and b) after purification (proton shifts in ppm from acetone).

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The solvent was removed under reduced pressure and the resulting white solid was washed three times with diethyl ether.

The purity of H_2edoda was checked by ^{1}H NMR (Fig. 1b), alkalimetric determination of the formula weight (found for some samples: 177.6–178.4; calcd., 178.1) and elemental analyses, (Found, C, 40.48; H, 5.73; calcd., C, 40.45; H, 5.62).

Preparation of the Complex [UO_2(Hedoda)·H_2O]-NO_3 (I)

An ethanolic solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1 mmol) was added to an equimolar amount of H_2edoda in the same solvent (40 ml). The resulting solution was stirred for 3 h, reduced to 5 ml and added to a large quantity of diethyl ether. The yellow precipitate formed was washed with diethyl ether and dried *in vacuo*. Yield 60%. (*Found,* C, 13.67; H, 1.89; N, 2.86; calcd., C, 13.66; H, 2.09; N, 2.66).

An aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ (1 mmol) was added to an equimolar amount (1 mmol) of H_2edoda in the same solvent. The solution was stirred for 3 h and then the water was removed under reduced pressure. The residue was washed several times with diethyl ether and dried *in vacuo*. Yield 70%. (Found, C, 13.87; H, 1.78; N, 2.49; calcd., C, 13.66; H, 2.09; N, 2.66).

The same complex was also obtained in ethanolic solution by mixing $UO_2(NO_3)_2 \cdot 6H_2O$ and H_2edoda in molar ratio 1:2.

Preparation of the Complex [UO_2 (edoda)]$_n$ (II)

This complex was prepared by the addition of a methanolic solution of $UO_2(CH_3COO)_2 \cdot 4H_2O$ (1 mmol, 10 ml of the solvent) to a stoichiometric amount (1 mmol) of H_2edoda in the same solvent (25 ml). The pale yellow precipitate formed was washed with ethanol and diethyl ether. Yield 75%. (Found, C, 16.62; H, 1.89; calcd., C, 16.29; H, 1.81).

The same complex was prepared by the addition of $UO_2(NO_3)_2 \cdot 6H_2O$ (1 mmol), dissolved in water (20 ml) to an equimolar amount of Na_2edoda in the same solvent. The solution was stirred at room temperature for 3 h and the pale yellow precipitate was formed by the addition to this solution of a large amount of ethanol. Yield 60% (Found, C, 16.48; H, 1.92; calcd., C, 16.29; H, 1.81).

In this case also it was possible to prepare the same complex using a different molar ratio.

Results and Discussion

The reaction of an aqueous or ethanolic solution of $UO_2(NO_3)_2 \cdot 6H_2O$ and H_2edoda in the molar ratio 1:1, (or 1:2) always yielded compounds of the same stoichiometric formula: [UO_2(Hedoda)·H_2O]-NO_3 (I).

By contrast, the reaction of an aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ and salified edoda (Na_2edoda) or the reaction of a methanolic solution of UO_2-$(CH_3COO)_2 \cdot 4H_2O$ and H_2edoda, in the molar ratio 1:1 (or 1:2), yielded compounds of the same stoichiometric formula [UO_2(edoda)]$_n$ (II), having however slightly different IR spectra.

We have compared the physico-chemical data of the free ligand (H_2edoda) with that of both uranyl-(VI)-complexes (I) and (II).

I.R. spectra

For both uranyl(VI)-complexes (I) and (II) the stretching frequencies of the ether group which lie in the region 1145–1050 cm^{-1} are slightly lower than in the free ligand (H_2edoda). These differences suggest that a coordination of both ether oxygen atoms to the uranium atom takes place, as usual.

This fact is confirmed by thermodynamic and ^{1}H nmr studies of the complexation of lanthanide ions by edoda (3,5), where it was concluded that the ether oxygens in edoda are bonded to the central metal ion in accordance with the tetracoordinate ability of the ligand.

The different coordination mode of the ligand in complexes (I) and (II) can be easily detected from the infrared absorptions in the carboxylic region; for the free ligand there are two stretching frequencies at 1755 and 1710 cm^{-1}. In both complexes (I) and (II) there is a very broad and intensive band at about 1585 cm^{-1} and two sharp bands in the region from 1480 to 1430 cm^{-1}.

In addition the I.R. spectra of complex (I) shows two bands at 1745 and 1680 cm^{-1} which are completely absent in complex (II). This is a clear indication that one carboxylic group is not involved in the coordination.

The geometry of complex (I) requires the presence of a NO_3 group which was detected by an intensive and sharp infrared band at 1385 cm^{-1} (NO_3 ionic) whereas no bands are present in the region where the coordination nitrates are known to absorb.

For complex (II) there were no bands above 1600 cm^{-1} and we have thus excluded the existence of monodentate carboxylic groups.

Conductivity data

We have studied both compounds (I) and (II) by conductivity measurement in comparison with that of $UO_2(NO_3)_2$. All the data were obtained in 10^{-3} aqueous solution at 20 °C using a Metrohm apparatus (E518 conductometer).

The values obtained (for $UO_2(NO_3)_2$, 0.27 mS cm^{-1}; [UO_2(Hedoda)·H_2O]NO_3, 0.13 mS cm^{-1}

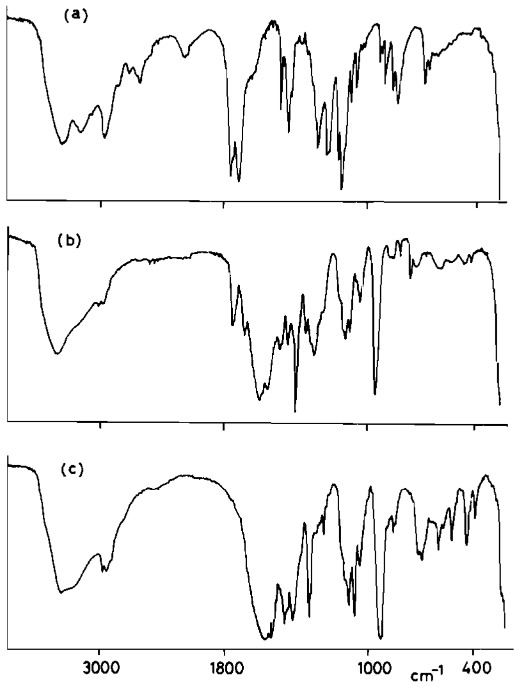

Fig. 2. IR adsorption spectra of a) free ligand H_2edoda; b) uranyl(VI)-complex(I); c) uranyl(VI)-complex(II).

and $UO_2[edoda]_n$ 0.01 mS cm^{-1}) suggest that compound (I) has an ionic nitrate and consequently one carboxylic group only involved in the coordination to metal ion; on the contrary for compound (II) the data suggest a non conductive structure.

Thermal Analysis

We report in Figs. 3a and 3b the simultaneous TG and DTA of the two uranyl(VI)-complexes; they were performed using a NETZSCH STA 429 thermoanalyzer in a dynamic atmosphere (200 ml/min) and a heating rate of 5 °C min^{-1}. The sample weight was about 90 mg and thermically inactive Al_2O_3 was used as reference material.

The samples were heated to 1300 °C and then the temperature was maintained until the weight was constant, corresponding to the UO_2 compound.

There was for both complexes absolute agreement for the found and calculated weight. For $[UO_2(Hedoda) \cdot H_2O]NO_3 \rightarrow UO_2$, found, 43.9 mg; calcd., 44.1 mg. For $[UO_2(edoda)]_n \rightarrow UO_2$, found, 37.9 mg; calcd., 36.9 mg.

For compound (I) it was possible to observe a step that can correspond to $[UO_2(Hedoda) \cdot H_2O]NO_3 \rightarrow [UO_2(edoda) \cdot H_2O]$.

The steps are in the range 150–200 °C forcompound (I) and 250–350 °C for compound (II).

The simultaneous DTA curves show a series of exothermic peaks for the first complex whereas the second complex shows an endothermic peak immediately followed by an exothermic one.

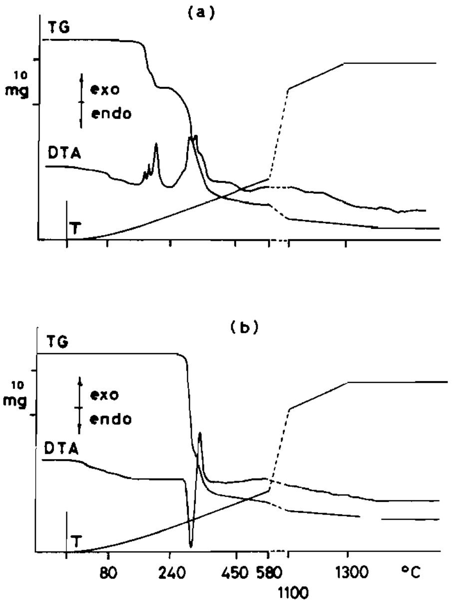

Fig. 3. Thermal behavior of a) uranyl(VI)-complex(I) (mg. 89.88); b) uranyl(VI)-complex(II) (mg. 90.43).

For complex (I) the elemental analysis, the evidence of the ionic NO_3 bond at 1385 cm^{-1}, clearly evident in the IR spectrum, the conductivity data and the thermal analysis data confirm the stoichiometry proposed, while one carboxylic group only is coordinated to the metal ion.

On the contrary, for complex (II) the values of elemental analyses, the small differences in the IR spectra, the insolubility in most common solvents, the absence of coordinate molecules of solvent, as shown by thermal analysis data, and the conductometric data, suggest that the compound possesses a polymeric structure.

It is known that the uranyl(VI) ion can reach a coordination number of five or six in the equatorial plane; for the various types of complex (II) we propose a polymeric complex, where edoda acts as quadridentate ligand toward one uranyl(VI) ion and as monodentate ligand (through the free C=O group), toward other different uranyl(VI) ions.

Acknowledgements

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