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A Photochemical Synthesis of New Stable Uranium(IV) Carboxylate Complexes

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Up to now the main photoreaction of the uranyl ion in the presence of carboxylic ligands consisted in the direct oxidative decarboxylation of the organic ligands, with the concomitant reduction of U(VI) to U(IV) [1, 2].

These studies have been mainly confined to the identification and quantum yield determination of photodecomposed organic materials, while less attention was paid to the possibility of obtaining tetravalent uranium compounds in this manner.

As a part of our studies on the use of photochemical approach in the synthesis of U(IV) complexes, we have prepared some new stable compounds by photolysing aqueous solutions of uranyl nitrate in the presence of an excess of carboxylate ligands.

By this very easy and useful method, the following compounds were obtained in a good yield: $U(gly)_4 \cdot 2H_2O$ (I) (gly = CH_2OHCOO^-), $U(oda)_2 \cdot 2H_2O$ (II) (oda = $^-OOCH_2COCH_2COO^-$), $Na_2[U(oda)_3]2H_2oda \cdot H_2O$ (III), $U(MeOAc)_4 \cdot H_2O$ (IV) (MeOAc = $CH_3OCH_2COO^-$), and $UO(ida) \cdot 2H_2O$ (V) (ida = $^-OOCH_2CNHCH_2COO^-$).

When the carboxylate ligands are added to aqueous solutions of uranyl nitrate, there is a modification in the shape and intensity of the electronic spectrum of UO_2^{2+} ion [3–5].

The spectra in the 400–500 nm region are more intense and show much less vibrational structure than most other known uranyl complexes. Such a charge, as with inorganic ligands, may well result from a charge-transfer transition from the ligand to the metal ion (LMCT), within a preformed complex.

Absorbance data, to which the method of continuous variation [6] has been applied, indicate an acid/UO_2^{2+} ratio of 2:1 and 1:1 for monocarboxylic and dicarboxylic ligands, respectively. These results show that complex formation between the uranyl and carboxylate ligands takes place.

We find that the photolysis of uranyl carboxylate complexes in aqueous solution, with light absorbed by LMCT bands, using high pressure Hg lamp (interference filter, λ = 436 nm), for 10 hr, leads to oxidative decarboxylation of the ligand and, in the presence of a large excess of chelating carboxylic ions, the I–V tetravalent uranium compounds are formed.

Irradiation of UO_2^{2+}/Hgly and UO_2^{2+}/H_2ida systems in water gave dark green crystals of I and a pale-green powder of V respectively. Irradiation of the UO_2^{2+}/H_2oda system, under the same conditions, gave no precipitate but treatment of the irradiated solution with acetone led to precipitation of pale-green powder of II. Again, on treating the photolysate with NaOH and ethanol, the pale-green compound III could be obtained.

In the UO_2^{2+}/HMeOAc system, under the same conditions, the resulting dark green compound IV is obtained after pumping off the solvent and upon addition of ether.

Elemental analysis is in accordance with the proposed formulation. All the isolated complexes are very stable to oxidation in the solid state.

The I.R. spectra of all compounds have been monitored in the 4000–300 cm^{-1} region in KBr pellets. The spectra of I and IV are similar to those found for transition metal glycolate compounds [7]. The I.R. results are in agreement with a structure in which the polyfunctional ligands coordinate to an uranium atom both through the hydroxylic or methoxylic group and one of the oxygen atoms of the carboxylic group, thus forming a five-membered chelate ring. The I.R. spectra of II and III have features which agree with the previously suggested coordination way for analogous complexes of U(VI) [8] and Th(IV) [9]. Furthermore, the presence of

TABLE. Electronic Spectral Bands in the 5000–25000 cm^{-1} Region for $U(gly)_4 2H_2O$ and $U(oda)_2 2H_2O$ in KBr Pellets at 293 K.[a]

$U(gly)_4 2H_2O$	$U(oda)_2 2H_2O$
23 201	23 809
22 779 sh	22 935
20 746	21 505
20 040	20 325
18 181	20 000 sh
15 267	18 248
14 925 sh	16 447
11 904	15 197
10 869	12 500
9 615 sh	10 989
9 174	9 433
8 771 sh	8 928 sh
6 896	6 895
6 660	6 655

[a] sh = shoulder.

characteristic bands of H_2oda indicates, in complex III, the presence of acid molecules of crystallisation. The I.R. spectrum of V shows features consistent with a configuration that includes a U–N bond, differing from that found so far for known complex of the uranyl ion [10].

The electronic spectra from 5000–25000 cm^{-1} have been investigated in the following media: water (with 1*M* of the corresponding carboxylic acid) and KBr pellets at 293 K. Electronic data are given in the Table for I and II compounds. At least fourteen bands occur in each of the spectra that are common to all spectra (including the solid state spectrum), with relatively little deviation in band maxima. The general features of these spectra are similar to those found for 8-coordinate complexes of U(IV) [11].

As we surmise the structure of our complexes to be not far from square-anti-prismatic, the assignment of these bands to *f–f* transitions, within the f^2 U(IV) entity, is reasonable.

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