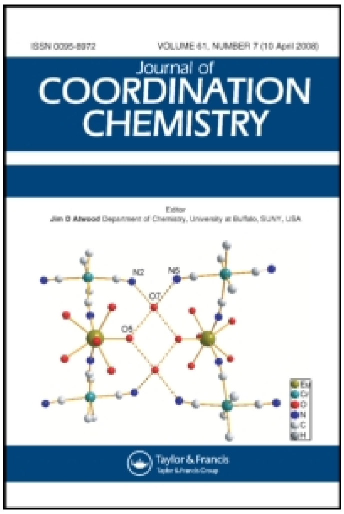

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STUDIES OF COMPLEX COMPOUNDS OF URANIUM(IV) AND URANIUM(VI) WITH PYRIDINE AND QUINOLINE CARBOXYLIC ACID. PART I

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Uranium tetraacetate reacts with the methanolic solution of pyridine dicarboxylic acid (pyridine-2,6-dicarboxylic acid, dipH$_2$) to give a complex U(dip)$_2$. Complexes U(pic)$_4$, U(picO)$_4$ (picH = picolinic acid, picOH = picolinic acid N-oxide) have also been reported. These have been characterised by elemental analysis and i.r. studies. The infrared spectra of the complexes show the asymmetric stretching frequency in the region 1650 cm^{-1} for the ketone (C=O) instead of unattached ketone frequency at about 1700 cm^{-1}, indicating the formation of metal–carboxyl oxygen bond. Uranium(VI) complexes of the type UO$_2$(quinH)$_2$, 2H$_2$O; UO$_2$(quin),H$_2$O; and UO$_2$(quind)$_2$, 2H$_2$O(quinH$_2$ = quinolinic acid, quindH = quinaldinic acid) have also been prepared by the interaction of the methanolic solution of uranyl acetate and the respective acids.

INTRODUCTION

Several uranium(VI) complexes with nitrogen–oxygen and oxygen–oxygen donor groups have been reported. These include the chelates with aminocarboxylic acids, aminophenols, 8-hydroxyquinols, and acetyl acetone. But the carboxylic acid derivatives of N-heterocycles and N-oxide heterocycles of uranium(IV) and uranium(VI) having nitrogen–oxygen and oxygen–oxygen coordination are scanty. A few uranium(VI) complexes of this type UO$_2$(pic)$_2$, UO$_2$(picO)$_2$,2H$_2$O,[1] UO$_2$(dip),2H$_2$O, UO$_2$(dip)(dipH$_2$),2H$_2$O[2] and UCl$_4$,2L[3] (L = picolinic acid N-oxide, nicotinic acid N-oxide, isonicotinic acid N-oxide) have been reported. No such studies have apparently been made with uranium(IV). We have undertaken a programme to make detailed studies on the formation, isolation, and characterisation of different pyridine and quinoline carboxylic acid complexes of both uranium(IV) and uranium(VI). The present communication deals with the stabilisation of uranium(IV) by complexation with picolinic acid, pyridine-2,6-dicarboxylic acid, and picolinic acid N-oxide and also uranium(VI) with quinolinic and quinaldinic acid.

EXPERIMENTAL

Picolinic acid, quinolinic acid and pyridine-2,6-dicarboxylic acid were prepared by oxidising α-picoline, quinoline and 2,6-lutidine respectively with potassium permanganate, with minor variations of methods cited in the literature.[4] Picolinic acid N-oxide was prepared from picolinic acid with the treatment of hydrogen peroxide. Uranium tetraacetate was prepared by the reduction of uranyl acetate with zinc amalgam.[5] Uranyl acetate and quinaldinic acid were B.D.H. products.

Uranium was estimated by igniting weighed amount of complexes in a platinum crucible to U$_3$O$_8$. Before ignition a few drops of concentrated nitric acid and sulphuric acid mixture were added.

Carbon, hydrogen, and nitrogen were determined by the conventional combustion technique.

Infrared spectra were recorded in Nujol mull in a Perkin–Elmer model 421 infrared spectrophotometer.

PREPARATION OF THE COMPLEXES

Tetrakis(picolinato)uranium(IV), U(pic)$_4$. A solution of picolinic acid (0.17 g) in superdried methanol (40 ml) was added to the uranium tetraacetate (0.15 g). The mixture was refluxed for 2 hours in a nitrogen atmosphere. The green solution was kept in a vacuum desiccator where methanol was removed. The green mass was digested with acetone (dried over K$_2$CO$_3$), filtered and washed with warm acetone, benzene and small amount of methanol. It was then dried in a vacuum desiccator. Yield: 0.2 g (Found: U, 32.60; C, 39.45; H, 2.30, N, 7.85; Calc. for U(pic)$_4$: U, 32.78; C, 39.67; H, 2.20; N, 7.71%).

Tetrakis(N-oxide picolinato)uranium(IV), U(picO)$_4$. This was similarly prepared by treating the uranium tetraacetate (0.2 g) with picolinic acid N-oxide (0.25 g) in methanol. Yield: 0.25 g (Found: U, 30.00; C, 36.30; H, 2.20; N, 7.25; Calc. for U(picO)$_4$: U, 30.12; C, 36.46; H, 2.02; N, 7.09%).

Bis(pyridine-2,6-dicarboxylato)uranium(IV), U(dip)$_2$. The complex, U(dip)$_2$ was prepared in the same way as the complex, U(pic)$_4$ by the addition of a methanolic solution of pyridine 2,6-dicarboxylic acid (0.2 g) to the uranium tetraacetate (0.21 g). Yield: 0.2 g (Found: U, 41.30; C, 29.40; H, 1.20; N, 5.1; Calc. for U(dip)$_2$: U, 41.75; C, 29.47; H, 1.05; N, 4.92%).

Dioxobisaquobis(quinolinato)uranium(VI), UO$_2$(quinH)$_2$, 2H$_2$O. A solution of quinolinic acid (0.36 g) in 30 ml water was added to the solution of uranyl acetate (0.4 g) in 15 ml water with stirring. The yellow crystalline precipitates were filtered and washed first with water and then with ethanol. Yield: 0.3 g (Found: U, 37.42; C, 26.60; H, 1.43; N, 4.5; Calc. for UO$_2$(quinH)$_2$,2H$_2$O: U, 37.30; C, 26.33; H, 1.26; N, 4.39%).

Dioxo(quinolinato)aquouranium(VI), UO$_2$(quin), H$_2$O. This was obtained by the addition of a solution of uranyl acetate (0.4 g) in 30 ml methanol to the solution of quinolinic acid (0.15 g) in 40 ml methanol. Yield: 0.2g (Found: U, 52.29; C, 18.71; H, 1.3; N, 3.15; Calc. for UO$_2$(quin)H$_2$O; U, 52.42; C, 18.50; H, 1.10; N, 3.08%).

Dioxobis(quinaldinato)diaquouranium, UO$_2$(quinid)$_2$, 2H$_2$O. A solution of uranyl acetate (0.24 g) in methanol (25 ml) was added with stirring to the solution of quinaldinic acid (0.2 g) in 50 ml methanol. The yellow crystalline precipitates were filtered and washed with methanol. Yield: 0.2 g (Found: U, 36.49; C, 36.80; H, 1.98; N, 4.40; Calc. for UO$_2$(quind)$_2$, 2H$_2$O; U, 36.60; C, 36.92; H, 1.85; N, 4.31%).

RESULT AND DISCUSSION

The uranium(IV) carboxylate complexes reported in this paper are stable under anhydrous conditions and can be kept for a long period in a vacuum desiccator. The dried uranium(VI) carboxylates are stable at room temperature for an indefinite period. They are insoluble in the common dry solvents such as benzene, carbontetrachloride, petroleum ether, cyclohexane, diethyl ether, chloroform and acetone. They are, however, soluble in formamide and dimethyl formamide. The uranium(IV) complexes are readily soluble in water with decomposition. Insolubility and solvolytic decomposition of these complexes in polar and nonpolar solvents precludes any investigation of their conductivity, molecular weight and spectral properties in solution.

The elemental analysis results indicate that the uranium(IV) complexes may be represented as U(pic)$_4$, U(picO)$_4$, U(dip)$_2$. The i.r. spectra (1800–1500 cm^{-1}) of these complexes in Table I show that all of them possess absorption band in the region 1640–1650 cm^{-1} which is expected to be due to the asymmetric stretching frequency for the ketone (C=O) instead of ketone stretching frequency at about 1700 cm^{-1}, indicating the formation of metal–carboxyl oxygen bond.[6] Again the nature of shifts of other bands (1800–1500 cm^{-1}) of these complexes are very nearly same as found in the corresponding complexes with other metals.[7–13] This indicates that nitrogen atom of the pyridine carboxylic acid acts as a donor. The absorption band at 1225 cm^{-1} in the complex U(picO)$_4$, considered to be due to the vibration of the amino oxide group, also support the same type of bonding.[9] Therefore, the environment of each metal ion is best represented as octacoordinated in the complexes U(pic)$_4$, U(picO)$_4$ and hexacoordinated in U(dip)$_2$.

TABLE I
Infrared data (Nujol mull)

Compound	Absorption maxima (cm^{-1})†
U(pic)$_4$	1650 vs^a, 1600 m, 1560 m
U(picO)$_4$	1650 vs^a, 1595 m, 1560 w
U(dip)$_2$	1645 m^a, 1625 m, 1575 s
UO$_2$(quin), H$_2$O	1630 m^a, 1610 m, 1590 m, 1555 s
UO$_2$(quinH)$_2$, 2H$_2$O	1680 s, 1640 m^a, 1625 m, 1600 m, 1560 s
UO$_2$(quind)$_2$, 2H$_2$O	1630 s^a, 1620 br, 1550 (w, br), 1500 w

† = Bands marked^a are assigned to ν_{asym}(COO).
s = strong, vs = very strong, m = medium, br = broad, w = weak.

The infrared spectra (1800–1500 cm^{-1}) of the complexes UO$_2$(quin),H$_2$O; UO$_2$(quinH)$_2$,2H$_2$O and UO$_2$(quind)$_2$,2H$_2$O are reported in the Table I. They give the asymmetric stretching frequency at 1630, 1640, 1630 cm^{-1} respectively for the C=O bands indicating the formation of metal–carboxyl oxygen bond. Again in the complex UO$_2$(quinH)$_2$,2H$_2$O besides the asymmetric stretching frequency, one additional band at 1680 cm^{-1} was found. This band corresponds probably to the presence of free carboxylic acid. Besides the bands due to carboxylato group the uranium(VI) complexes of quinolinic acid and quinaldinic acid give O—H stretching frequencies at 1610, 1625 and 1620 cm^{-1} respectively. The spectra of the above free acids do not give any bands in the region 890–950 cm^{-1}, so the bands at 900 cm^{-1} in $UO_2(quin), H_2O$; 910 cm^{-1} in $UO_2(quinH)_2, 2H_2O$; 930 cm^{-1} in $UO_2(quind)_2, 2H_2O$ correspond to the ν_3 frequency of O=U=O bands which resemble those of the complexes.[14] It is very difficult to detect the ν_1 frequency of O=U=O band in the spectra of the complexes, since both quinolinic acid and quinaldinic acid give bands in the region 800–890 cm^{-1}. However, comparing the sharpness of the bands between the free acids and complexes, it appears that the ν_1 frequency in these uranyl complexes are located at about 830, 835, 840 cm^{-1} respectively.

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