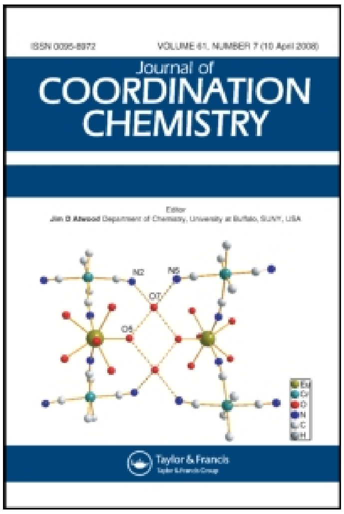

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STUDIES ON COMPLEX COMPOUNDS OF URANIUM(IV) WITH PYRIDINE AND QUINOLINE CARBOXYLIC ACID. PART II

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

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The reactions between bis(pyridine-2,6-dicarboxylato)-uranium(IV), U(dip)$_2$ and N-heterocyclic bases (L) in methanol (L = pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine) produce eight coordinate uranium(IV) complexes, U(dip)$_2$ (H$_2$O)L which have been characterised by elemental analysis, i.r. studies, thermal analysis and magnetic susceptibility measurement. The anionic complex (Ph$_4$As)$_2$ [U(dip)$_3$], 3H$_2$O has been isolated by reacting U(dip)$_2$ with pyridine-2,6-dicarboxylic acid in the presence of tetraphenyl arsonium chloride. Uranium(IV) complexes of the type U(quind)$_2$(acetate)$_2$, U(quin)(acetate)$_2$ (quindH = quinaldinic acid, quinH$_2$ = quinolinic acid, acetate = CH$_3$COO$^-$) have also been prepared by the interaction of the methanolic solution of uranium tetraacetate and the respective acids.

INTRODUCTION

In a previous report,[1] it has been stated that the reaction of uranium tetraacetate, U(acetate)$_4$ with pyridine-2,6-dicarboxylic acid gives the complex, bis(pyridine-2,6-dicarboxylato)uranium(IV), U(dip)$_2$. The present communication reports the isolation and characterisation of some mixed ligand complexes of uranium(IV) containing dip moieties with N-heterocyclic bases (pyridine, 2-methylpyridine, 3-methylpyridine and 4-methylpyridine). The reactivity of uranium tetraacetate with quinaldinic acid and quinolinic acid has also been studied.

EXPERIMENTAL

Uranyl acetate and quinaldinic acid were B.D.H. products. The complex U(dip)$_2$ was prepared as described earlier.[1] Uranium tetraacetate was prepared by the reduction of uranyl acetate with zinc amalgam.[2] Pyridine and methylpyridines were B.D.H. reagents and were distilled over potassium hydroxide prior to use.

Infrared spectra were recorded in Nujol mull in a Perkin Elmer model 421 infrared spectrophotometer. Magnetic susceptibility was measured by using the Gouy Balance. Analysis of the constituents was made as described earlier.[1]

PREPARATION OF THE COMPLEXES

U(dip)$_2$(H$_2$O)L

The N-heterocyclic base (0.5 ml) was added to a solution of U(dip)$_2$ (0.2 gm) in methanol (15 ml). The yellowish green solution was refluxed for 5 hours in a nitrogen atmosphere. The mixture was kept over sulphuric acid in a vacuum desiccator where methanol and the excess base were removed. The mass was digested with acetone, filtered and washed with acetone. It was then dried over potassium hydroxide in vacuum.

(Ph$_4$As)$_2$[U(dip)$_3$],3H$_2$O

0.2 gm of U(dip)$_2$ complex was added with stirring to a solution of a mixture of pyridine-2,6-dicarboxylic acid (0.1 gm) and tetraphenyl arsonium chloride (0.4 gm) in 20 ml water. Stirring was continued for a further 45 minutes. The yellowish green crystals then separated. These were filtered, washed with water, alcohol and finally dried in vacuum over potassium hydroxide.

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TABLE I
Analytical and magnetic moment data of the complexes

Compound	% found				% calculated				μeff (B.M.) at 300°K
	U	C	H	N	U	C	H	N	
$U(dip)_2(H_2O)(Py)$	35.65	34.19	1.88	6.28	35.79	34.29	1.96	6.31	2.73
$U(dip)_2(H_2O)(\alpha\text{-pic})$	34.91	35.26	2.17	6.21	35.02	35.35	2.21	6.18	2.68
$U(dip)_2(H_2O)(\beta\text{-pic})$	35.15	–	–	6.26	35.02	–	–	6.18	2.59
$U(dip)_2(H_2O)(\gamma\text{-pic})$	35.10	–	–	6.09	35.02	–	–	6.18	2.81
$(Ph_4As)_2[U(dip)_3].3H_2O$	15.28	53.02	3.41	2.64	15.32	55.31	3.54	2.70	–
$U(quind)_2(acetate)_2$	34.11	40.98	2.51	4.09	34.00	41.14	2.58	4.00	2.10
$U(quin)(acetate)_2$	45.71	25.28	1.63	2.68	45.68	25.33	1.72	2.69	2.05

α-pic = 2-methylpyridine, β-pic = 3-methylpyridine, γ-pic = 4-methylpyridine.

U(quind)$_2$(acetate)$_2$

0.2 gm of uranium tetraacetate was added to a solution of quinaldinic acid (0.3 gm) in 15 ml methanol. The mixture was refluxed for 2 hours in a nitrogen atmosphere. The solution was kept in a vacuum desiccator over potassium hydroxide and the volume of the solution was reduced to 5 ml. To the solution acetone (15 ml) was added with stirring. The greenish brown compound was filtered, washed with hot acetone and dried in vacuum over potassium hydroxide.

U(quin)(acetate)$_2$

This was obtained in the same way as the complex $U(quind)_2$ (acetate)$_2$ by the addition of a solution of quinolinic acid (0.16 gm) in 30 ml methanol to the solution of uranium tetraacetate (0.2 gm) in 10 ml methanol.

The analytical data of the compounds are given in Table I.

RESULTS AND DISCUSSIONS

When $U(dip)_2$ is treated with pyridine and methylpyridines, the complexes of the type $U(dip)_2(H_2O)L$ are isolated. It is noteworthy that the complexes with pyridine and methylpyridines contain only one molecule of the bases, even though the reactions were carried out in a large excess of base. The complexes are yellowish green crystalline substances and non-electrolyte in nitrobenzene. The compounds are insoluble in common organic solvents like benzene, chloroform, carbon tetrachloride, ethanol, acetone, etc., sparingly soluble in formamide, dimethylformamide and are readily and completely decomposed by boiling with water.

The complex $U(quind)_2$(acetate)$_2$ and U(quin)-(acetate)$_2$ are soluble in formamide and dimethylformamide and unaffected by water. $(Ph_4As)_2[U(dip)_3]$, $3H_2O$ was previously reported by Baracco.[3] This was obtained by reacting UCl_4 with tetraphenyl arsonium chloride and pyridine-2,6-dicarboxylic acid in water. Replacement of UCl_4 by $U(dip)_2$ has thus led to the formation of this complex. The colour, solubility and other properties of the two compounds are similar.

The TGA curve of the complex $U(dip)_2(H_2O)(Py)$ indicated that the substance began to lose weight from 190°C. The curve showed a horizontal from 280°C to 310°C which correspond to the loss of water and pyridine. The loss of water at such high temperature indicates that the water molecule is coordinated to the metal in the complex. On heating the substance to constant weight in an atmosphere of nitrogen at 275°–300°C, it lost 14.5% in weight and the loss in weight corresponds to the loss of a molecule of pyridine and a molecule of water. The analysis of the residue agrees with the formulation U(dip)$_2$.

The i.r. spectra of the complexes U(dip)$_2$(H$_2$O)L (Table II) were compared with the spectra of U(dip)$_2$. These are generally similar to the spectra of other complexes containing pyridine and pyridine-2,6-dicarboxylic acid. They all show the absorption bands characteristic of pyridine-2,6-dicarboxylato ion acting as a tridentate ligand having planar configuration.[1, 4, 5, 6] In each case the shift of carbonyl frequency from 1700 cm^{-1} in the free ligand to lower frequency (1645 cm^{-1}) in the complex proves the involvement of carbonyl group. The spectra of the complexes show strong υ(O–H) band at 3400–3500 cm^{-1}. This band is absent in the spectra of the complex U(dip)$_2$.

The infrared spectra of the complex (Ph$_4$As)$_2$-[U(dip)$_3$], 3H$_2$O is reported in Table II. The spectral features of this complex resemble those of the chelated complexes.[6,7] Therefore the environment of each metal ion is best represented as nonacoordinated with three nitrogens and six carboxylic oxygens belonging to three ligand molecules.

The spectra of U(quind)$_2$(acetate)$_2$ present the bands due to the carboxylate group at about the same frequencies as that of U(pic)$_4$,[1] indicating the formation of uranium-carboxyl oxygen bond. The bands at 1562 (υ_{asym}(COO)) and 1415 (υ_{sym}(COO)) in the complex U(quind)$_2$(acetate)$_2$ and the bands at 1520 (υ_{asym}(COO)) and 1405, 1350 (υ_{sym}(COO)) in the complex U(quin)(acetate)$_2$ indicate the presence of acetate group.[5, 8, 9]

The magnetic moments of the complexes are given

TABLE II
Infrared data (Nujol mull)

Compounds	Absorption maxima (cm^{-1})
U(dip)$_2$	384(m), 405(w), 550(w), 590(m), 685(m), 720(s,br), 760(s), 800(w), 880(w), 910(m), 1020(s), 1070(s), 1125(sh), 1170(s), 1260(m,br) 1310(w), 1350(s), 1425(sh), 1575(s), 1625(m), 1645(m)
U(dip)$_2$(H$_2$O)(Py)	382(m), 410(w), 552(w), 588(m), 648(m), 665(m), 715(s), 745(s), 795(w), 848(w), 900(w), 1003(m), 1054(m), 1125(w), 1156(m), 1252(m), 1350(br), 1410(m), 1490(w), 1525(w), 1540(sh), 1572(m), 1610(w), 1645(s), 2310(m), 3040(m), 3420(s,br)
U(dip)$_2$(H$_2$O)(α-pic)	390(m), 415(w), 552(w), 590(m), 645(w), 710(m), 740(s), 790(w), 846(m), 910(s), 1002(w), 1125(w), 1155(m), 1250(m), 1350(w), 1910(m), 1495(w), 1530(m), 1540(w), 1573(m), 1600(m), 1605(w), 1646(s), 3035(m), 3440(s,br), 3500(w)
U(dip)$_2$(H$_2$O)(β-pic)	718(m), 742(s), 800(w), 848(m), 903(w), 1002(m), 1120(m), 1152(m), 1243(m), 1360(w), 1408(m), 1535(w), 1580(m), 1600(m), 1615(m), 1645(s), 3090(m), 3460(s,br)
U(dip)$_2$(H$_2$O)(γ-pic)	670(m), 695(m), 735(s), 775(m), 800(m), 830(sh), 900(m), 920(s), 930(m), 1000(w), 1010(w), 1025(m), 1060(m), 1160(m), 1260(m), 1360(sh), 1370(s), 1420(m), 1425(sh), 1505(m), 1535(w), 1600(w), 1620(m), 1645(s), 3040(w,br), 3450(s,br)
(Ph$_4$As)$_2$[U(dip)$_3$], 3H$_2$O	665(w), 698(m), 740(s), 758(sh), 790(w), 882(w), 913(m), 1002(m), 1018(m), 1068(m), 1090(m), 1158(w), 1190(m), 1205(w), 1290(w), 1368(s), 1428(m), 1458(m), 1470(m), 1540(w), 1580(m), 1618(m), 1643(s), 2700(w), 3050(w), 3460(s,br)
U(quind)$_2$(acetate)$_2$	722(w), 765(sh), 782(m), 805(w), 860(w), 880(w), 922(m), 1020(w), 1122(w), 1160(w), 1168(w), 1223(m), 1262(w), 1390(s), 1415(m), 1472(s), 1562(m), 1580(w), 1600(w), 1625(m), 1650(s)
U(quin)(acetate)$_2$	684(w), 670(m), 708(m), 772(m), 835(m), 880(w), 935(m), 1020(w), 1055(w), 1100(s), 1150(w), 1230(w), 1270(w), 1350(m), 1390(w), 1405(m), 1440(sh), 1520(w), 1530(w), 1540(w), 1630(m), 1640(m)

s = strong, w = weak, m = medium, br = broad, sh = shoulder. α-pic = 2-methylpyridine, β-pic = 3-methylpyridine, γ-pic = 4-methylpyridine.

in Table I. The room temperature magnetic moments of the complexes $U(dip)_2(H_2O)L$ are comparable to those exhibited by other complexes of uranium(IV) which were assumed to possess octacoordination.[10] Low magnetic moments of the complexes $U(quind)_2$-(acetate)$_2$ and U(quin)(acetate)$_2$ may be attributed to strong metal–metal interaction through exchange involving oxygen bridging.

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