Asian Journal of Chemistry Vol. 9, No. 2 (1997), 309–314

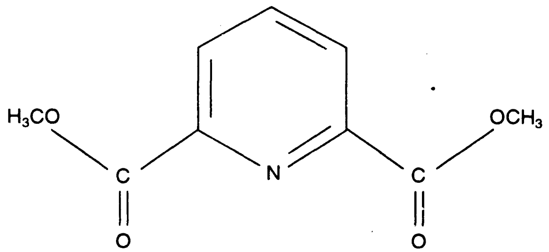
Synthetic and Structural Studies of Dioxouranium(VI) Complexes of Dimethyl Ester of Pyridine-2,6-Dicarboxylic Acid

KISHOR ARORA*, JITENDRA AMBWANI and M.C. PATHAK
Department of Chemistry
Government Post-Graduate College (Jiwaji University)
Morena-476 001, India

A series of dioxouranium(VI) complexes has been synthesised with an ester ligand, namely pyridine-2,6-dicarboxylic acid dimethyl ester (PDA). They are characterized by elemental analyses, conductivity measurements, molecular weight measurements and IR studies, to have the general composition $UO_2X_2\cdot(PDA)_2$ ($X = Br^-$, I^-, NCS^-, ClO_4^- and NO_3^-). The infrared spectral studies indicate that the ligand is coordinating to the metal ion through carbonyl oxygen atoms and Pyridine ring nitrogen atom. NMR spectral studies of the ligand and one of the representative complexes has also been studied.

INTRODUCTION

Actinide metal ions specially thorium(IV) and dioxouranium(VI) are of great interest for most of the workers because of their large size and high positive charge.[1] In the recent past studies on these metals with various oxygen donor ligands[2–5] and with N-donor ligands including Schiff bases[6–9] have been reported. In this present paper we wish to report the investigations on high co-ordination compounds with an ester ligand namely pyridine-2,6-dicarboxylic acid dimethyl ester (PDA) (I).



The ligand was found to act as neutral tridentate (O, N, O) ligand which leads to the formation of high co-ordination compounds having the general composition $UO_2X_2\,(PDA)_2$ ($X = Br^-$, I^-, NCS^-, ClO_4^- or NO_3^-). These complexes are generally soluble in common organic solvents and are quite stable and can be stored at room temperature except iodide complex which decomposes slowly at room temperature with evolution of iodine vapours.

EXPERIMENTAL

All the reagents were used as supplied by B.D.H. and Merck. Uranyl nitrate was obtained commercially and all other salts were prepared by respective reported methods.[10–13]

IR spectra were recorded on a Perkin-Elmer (4000–200 cm^{-1}) spectrophotometer using KBr/CsI pallets. NMR spectral studies were carried out on a 90 MHz Cw NMR spectrophotometer. Nitrogen was estimated in the laboratory by Kjeldahl's method. All other physico-chemical measurements were done according to the reported method[5] and metal was estimated as U_3O_8.[14]

Preparation of ligand

The ligand was prepared by condensing pyridine-2,6-dicarboxylic acid with dimethyl sulfide resulting in the crystallization of pyridine-2,6-dicarboxylic acid ester which was recrystallized in pure ethanol.[15] Pyridine-2,6-dicarboxylic acid was dissolved in absolute ethanol. 25 mL of the acid solution (1 mmol) was mixed with 10 mL solution of dimethyl sulfide (1 mmol) in the same solvent. The mixture was refluxed for about 6 h at *ca.* 30°C. Then, the contents were cooled in freezing mixture, resulting in the formation of crystals of the ester. The product was filtered, washed with ethanol followed by ether and dried *in vacuo* over anhydrous $CaCl_2$.

Synthesis of adducts

Bis (pyridine-2,6-dicarboxylic acide dimethyl ester) dioxouranium(VI) nitrate, $UO_2(NO_3)_2{\cdot}(PDA)_2$: This complex was prepared by treating isopropanolic solution (25 mL) of the metal salt (1 mmol) with the solution of ester ligand (2.1 mmol, *ca.* 0.41 g) in the same solvent (40 mL). The mixture was refluxed for 2 h at *ca.* 75°C. The complex was obtained after cooling the reaction mixture in ice. The product was then filtered and washed with ethanol first and then with ether and dried *in vacuo* over P_4O_{10}.

Bis (pyridine-2,6-dicarboxylic acid dimethyl ester) dioxouranium(VI) halides, $UO_2X_2{\cdot}(PDA)_2$ ($X = Br^-$, I^-, or NCS^-): The corresponding metal salt (1 mmol) was dissolved in absolute ethanol (30 mL) and was treated with the ester ligand (2.2 mmol, *ca.* 0.43 g) and on refluxing the resulting mixture for 1 h and on cooling, the desired products crystallized out. These were the filtered and washed with ethanol and dried *in vacuo* over P_4O_{10}.

Bis (pyridine-2,6-dicarboxylic acid dimethyl ester) dioxouranium(VI) perchlorate $UO_2(ClO_4)_2{\cdot}(PDA)_2$.: The perchlorate salt of the metal (1 mmol) in methanol (20 mL) was added to the ester ligand (1 mmol, *ca.* 0.41 g) in the same solvent (20 mL). The product was obtained after refluxing the reaction mixture for about 1.5 h at *ca.* 70°C followed by cooling in ice. The complex was washed with the solvent and dried *in vacuo* over P_4O_{10}.

RESULTS AND DISCUSSION

The reaction of dioxouranium(VI) metal salts with the ester ligand results in the formation of $UO_2X_2{\cdot}(PDA)_2$ ($X = NO_3^-$, Br^-, NCS^-, I^- or ClO_4^-) according to the following general equations:

$$UO_2(NO_3)_2 + 2PDA \xrightarrow[\text{reflux; 2 h}]{\text{Isopropanol}} UO_2(NO_3)_2(PDA)_2 \qquad \text{(i)}$$

$$\underset{(X = Br^-, I^-, \text{ or } NCS^-)}{UO_2X_2} + 2PDA \xrightarrow[\text{reflux; 1 h}]{\text{Isopropanol}} UO_2X_2(PDA)_2 \qquad \text{(ii)}$$

$$UO_2(ClO_4)_2 + 2PDA \xrightarrow[\text{reflux; 1.5 h}]{\text{MeOH}} UO_2(ClO_4)_2(PDA)_2 \qquad \text{(iii)}$$

The elemental analyses of these complexes are given in Table-1. These complexes are quite stable at room temperature (*ca.* 30°C) except the iodide one which decomposes to a sticky mass after a few weeks. All are sufficiently soluble in common organic solvents.

TABLE-1
ANALYTICAL, CNDUCTIVITY AND MOLECULAR WEIGHT DATA FOR UO_2^{2+}(VI) COMPLEXES OF PDA

Complexes (Empirical formula)	Dec. temp.	Yield (%)	Analysis, Found (Calcd.) %			Λ m ohm^{-1} cm^2 mol^{-1}	Average mol.wt. (Formula wt.)
			U	N	Anion		
$UO_2(NO_3)_2{\cdot}2PDA$ $(UC_{18}H_{18}O_{16}N_4)$	215	75	30.1 (30.3)	6.8 (7.1)	—	3.2	780 (784)
$UO_2Br_2{\cdot}2PDA$ $(UC_{18}H_{18}O_{10}N_2Br_2)$	219	73	28.7 (29.0)	3.1 (3.4)	19.8 (19.5)	2.8	816 (820)
$UO_2I_2{\cdot}2PDA$ $(UC_{18}H_{18}O_{10}N_2I_2)$	220	72	25.5 (26.0)	2.6 (3.0)	28.2 (27.8)	4.2	908 (914)
$UO_2(NCS)_2{\cdot}2PDA$ $(UC_{20}H_{18}O_{10}N_4S_2)$	208	71	30.2 (30.6)	6.8 (7.2)	15.1 (14.9)	3.8	772 (776)
$UO_2(ClO_4)_2{\cdot}2PDA$ $(UC_{18}H_{18}O_{18}N_2Cl_2)$	198	65	27.3 (27.7)	2.8 (3.2)	23.6 (23.1)	54.7	287 (859)

Electrical conductivities of the complexes were determined in nitrobenzene and the results are given in Table-1. The complexes $UO_2X_2{\cdot}(PDA)_2$ ($X = NO_3^-$, Br^-, I^- or NCS^-) are essentially non-electrolyte in $PhNO_2$ medium. The conductivity of the halo complexes is in general agreement with stability of U-halogen bond found earlier.[5] The conductance value for perchlorato complex $UO_2(ClO_4)_2{\cdot}(PDA)_2$ suggests the presence of ionic perchlorate groups. The ratio of the molecular weights of $UO_2X_2{\cdot}(PDA)_2$ ($X = Br^-$, I^-, NCS^- and NO_3^-) to be caculated is *ca.* 0.98 which shows that these complexes are monomeric in solution. In case of $UO_2(ClO_4)_2{\cdot}(PDA)_2$, this ratio is found to be 0.33 indicating the formation of 3 species in the solution of this complex.

The complex compounds were found to be either diamagnetic or weakly paramagnetic depending upon the diamagnetism of the other ions and the surrounding ligand fields.[16, 17] Their magnetic susceptibilities are independent of field strength and temperature.[18] The ground states of these compounds contain no unpaired electrons. The compounds are, therefore, expected to be weakly diamagnetic as observed.[17, 19, 20]

Infrared spectra

The IR spectra were recorded in the range of 4000–200 cm^{-1} using KBr pellets. The IR spectra of the complexes, when compared with those of ligands show a considerable shift of the carbonyl absorption ν(C═O) to lower frequency indicating a decrease in the stretching force constant of C═O as a consequence of coordination through the oxygen atom of the C═O groups of ester. It is well known[21–24] that as a result of coordination through carbonyl oxygen, the double bond character between carbon and oxygen is reduced. The decrease in the bond order causes a bathochromic shift in the carbonyl stretching frequency. The C═O stretching frequency which occurs at around 1700 cm^{-1} in the free ligand has been observed in the region of 1680–1660 cm^{-1} in all the complexes. In the far infrared region one absorption at *ca.* 630 cm^{-1} has been assigned to in-plane bending of the carbonyl group in the free ligand.[25, 26] This shows a shift to higher frequency in the complexes. The pyridine ring deformation bands appear at 610 cm^{-1} (in-plane) and 430 cm^{-1} (out-of-plane) in the spectrum of the ester ligand (*i.e.* PDA).[27] In the uranyl complexes of PDA ester these bands show positive shift *ca.* 50–40 cm^{-1} which confirms the role of pyridinyl nitrogen in complexation.[27]

Some new medium and weak bands are observed in the range of 380–360 cm^{-1} and 470–450 cm^{-1} in the complexes where the ligand has no absorptions. These new bands are tentatively assigned to ν(M—O) stretching modes and ν(M—N) stretching modes and these are in agreement with ν(M—O) and ν(M—N) stretching modes observed for serveral other dioxouranium(VI) complexes.[28, 29]

The occurrence of two strong bands at *ca.* 1070 cm^{-1} and 615 cm^{-1} in the spectra of perchlorate complex attributed to ν_3 and ν_4 vibrations of the ionic perchlorate groups[30–32] suggesting the perchlorato groups are present outside the co-ordination sphere in complex.

NMR spectral studies

The NMR spectral study of one of the representative complexes was recorded and was compared with that of ligand. The NMR spectra of the ligand contain apparently NH and $COOCH_3$ signals and it is suggested that the compound is a pyridine derivative. The NMR spectra of a compound of ester *i.e.* $UO_2(NO_3)_2 \cdot (PDA)_2$ has been recorded either in $CDCl_3$, or in DMSO d_6. The important NMR signals of the ligand are 5.44839(s), 4.28700–4.20733(qt), 3.92169(s), 3.85788–3.82109(t), 3.66954(s) and 3.32448–3.30814(pt) and that of the complex $UO_2(NO_3)_2 \cdot 2PDA$ are 8.79150–8.77333(d), 8,62494–8.57219(t), 8.08198–8.03465(t), 7.30417(s), 4.73277(s), 3.38597–3.36620(d), 3.13081–3.99744(pt), 2.89780(s), 2.82140(s) and 1.32574–1.26737(pt).

TABLE-2
PARTIAL IR DATA (cm^{-1}) FOR UO_2^{2+}(VI) COMPLEXES OF PDA

Compound	ν(C=O) str.	ν(C=O) in-plane bending	Pyridine ring deformation bands		ν(M—O)	ν(M—N)
			In-plane	Out-of-plane		
PDA	1700 s	630 m	610 m	430 m	—	—
$UO_2(NO_3)_2$·2PDA	1660 s	640 m	650 sh	480 sh	360 m	450 m
UO_2Br_2·2PDA	1660 s	630 sh	660 w	480 sh	350 m	450 m
UO_2I_2·2PDA	1670 s	630 sh	650 sh	480 w	350 m	430 m
$UO_2(NCS)_2$·2PDA	1680 s	620 m	660 w	480 sh	360 m	440 m
$UO_2(ClO_4)_2$·2PDA	1660 s	620 sh	650 sh	480 w	360 m	450 m

Configuration of complexes

In halo and thiocyanato complexes both the anions are covalently bonded. In these cases, a ten coordinated uranium atom may be be considered. The infrared data of $UO_2(PDA)_2(NO_3)_2$ suggests that nitrato groups are monodentate in it as the separation of combination bands *i.e.* ν_1 and ν_4 appear to be 10 cm^{-1} and according to Lever *et al.*[33], if this separation is 5–26 cm^{-1} then nitrato group may be monodentate and if it is 20–66 cm^{-1}, it attributes to bidentate nitrato group. The spectral bands of the complex $[UO_2(PDA)_2{\cdot}(NO_3)_2]$ studied here are, 1020 (ν_2), 800 (ν_6), 750 (ν_3) and 705 cm^{-1} (ν_5) which suggests the monodentate nature of nitrate group. Thus it may be considered that this complex contains 10 coordinated uranium atom (4 oxygens and 2 nitrogens from two tridentate ester ligands and 2 oxygens from two mondentate nitrate groups). In perchlorato complex, conductance, molecular weight and infrared studies reveal that all the perchlorato groups are present outside the coordination sphere and hence suggesting the presence of 8 coordinated uranium in this complex.

REFERENCES

1. P. Ramamurthy and C.C. Patel, *Canad. J. Chem.*, **44**, 856 (1964).
2. R.K. Agarwal, K. Arora and P. Dutt, *Polyhedron*, **13**, 957 (1994).
3. R.K. Agarwal and K. Arora, *Synth. & React. in Inorg. & Met-Org. Chem.*, **23**, 653 (1993).
4. ________, *Synth. and React. in Inorg. and Met-Org. Chem.*, **23**, 1671 (1993).
5. ________, *Polish J. Chem.*, **67**, 25 (1993).
6. R.K. Agarwal, K. Arora and P. Dutt, *Nat. Acad. Sci. Letters (India)*, **15**, 295 (1992).
7. R.K. Agarwal, K. Arora, Miss Priyanka and I. Chakravorti, *Polish J. Chem.*, **67**, 1913 (1993).
8. R.K. Agrwal, K. Arrora and P. Dutt, *Synth. & React. in Inorg. and Met-Org. Chem.*, **24**, 301 (1994).
9. K. Arora, *Asian J. Chem.*, **7**, 424 (1995).
10. S.S. Sandhu and S.S. Sandhu (Jr.), *Indian J. Chem.*, **IIA**, 369 (1973).
11. P. Ramamurthy and C.C. Patel, *J. Inorg. Nucl. Chem.*, **25**, 310 (1963).

12. N.V. Sidgewick, The Chemical Elements and Their Compounds, Oxford Univesity Press, Oxford (1952).
13. V.V. Savant and C.C. Patel, *J. Inorg. Nucl. Chem.*, **34**, 1462 (1972).
14. K.W. Bagnall and M.W. Wakerley, *J. Less Common Met.*, **35**, 267 (1974).
15. J. Major and I. Benedikoric, *Czech.*, **194**, 618 (1983).
16. M.P. Sahkari and A.J. Makhedhar, *J. Inorg. Nucl. Chem.*, **33**, 883 (1971).
17. E.D. Earthen, L. Breyer, L.A. Bromley, P.W. Gilles and N.L. Logferen, *J. Am. Chem. Soc.*, **72**, 4019 (1950).
18. J.P. Day and L.M. Venanzi, *J. Chem. Soc.*, 1363 (1966).
19. R.K. Connick and Z.H. Nugus Jr., *J. Am. Chem. Soc.*, **74**, 6012 (1952).
20. J.C. Eiscustein and M.H.L. Pryce, *Proc. Roy. Soc.*, **229A**, 20 (1955).
21. S.C. Jain and R. Rivest, *Canad. J. Chem.*, **45**, 139 (1967).
22. _______, *J. Inorg. Nucl. Chem.*, **29**, 2787 (1967).
23. R.C. Agarwal and P.P. Singh, *Z. Inorg. Allg. Chem.*, **332**, 103 (1964).
24. W. Girrard, M.F. Lappert, H. Pysozora and J.W. Wallis, *J. Chem. Soc.*, 2144 (1960).
25. V.V. Savant, P. Ramamurthy and C.C. Patel, *J. Less Common Metals*, **22**, 479 (1970).
26. R.K. Agarwal, A.K. Srivastava and T.N. Srivastava *Proc. Nat. Acad Sci. (India)*, **51A**, 79 (1981).
27. J. Ambwani and R.C. Sharma, *J. Indian Chem. Soc.*, **72**, 507 (1995).
28. P.A. Vigato, U. Casellato and M. Vidali, *Gazz. Chim. Italiana*, **107**, 61 (1977).
29. A.K. Srivastava, S. Sharma and R.K. Agarwal, *Inorg. Chim. Acta*, **61**, 235 (1982).
30. K. Nakamoto, Infrared Spectra of Inorganic and Co-ordination Compounds, Wiley, New York (1963).
31. S.S. Krishnamuthy and S. Soundarajan, *Canad. J. Chem.*, **47**, 995 (1969).
32. S.D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).
33. A.B.P. Lever, E. Mantiovani and B.S. Ramaswamy, *Canad. J. Chem.*, **49**, 1957 (1971).

(*Received:* 19 October 1996; *Accepted*: 2 December 1996) AJC-1200