Synthesis of Dioxouranium Dialkylhydromates – Cluster Formation in Fast Atom Bombardment Mass Spectra (FAB-MS)

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Abstract

The synthesis of a series of dioxouranium(VI) dialkylhydromates, $UO_2(CH_3(CH_2)_nCONHO)_2$, n = 4, 5 and 6, is reported together with spectroscopic data. Surprisingly, the fast atom bombardment mass spectra of these complexes all show cluster formation of the form $(UO_2)_n^+$ (n = 1–6) very similar to those recently reported for $UO_2(acetate)_2$.

Introduction

The recent report of cluster formation in the fast atom bombardment (FAB) mass spectra of dioxouranium(VI) dinitrate and diacetate [1] prompts us to report very similar results in the FAB-MS of some dioxouranium(VI) dihydroxamates [$UO_2(CH_3(CH_2)_nCONHO)_2$], n = 4, 5 and 6, synthesized recently in our laboratories. Naturally occurring hydroxamic acids (siderophores) are involved in microbial transport of iron and in mammalian systems [2]. Recent interest has included the design of metal hydroxamates with biological activity [3] and the design of ligands for chelation therapy [4]. Hydroxamic acids have also been used as analytical reagents for a number of metal ions [5] including uranium(VI) where interest has centred on complexation with benzohydroxamic acid [6, 7]. In the present paper, we describe a number of dioxouranium(VI) complexes of alkylhydroxamic acids [$CH_3(CH_2)_nCONHOH$, n = 4, 5 and 6 of increasing chain length], with the aim of using spectroscopic methods including FAB-MS to investigate their structures; as seen below, the results obtained by this latter method were quite surprising. While this work was in progress, a publication appeared describing very similar results of a FAB-MS study of dioxouranium(VI) dinitrate and diacetate [1].

Experimental

All chemicals were Analar grade and used directly unless otherwise stated. Melting points were determined on a Gallenkamp melting point apparatus. Infrared spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier transform spectrometer (as 2% KBr discs). FAB-MS were run in a glycerol matrix on a VG7OE mass spectrometer with argon as bombardment gas at 8 kV.

Synthesis of Hydroxamic Acids

The ligands were prepared by acylation of hydroxylamine with the appropriate ester, and subsequent treatment with dry HCl gas liberated the free acid [8]. A typical preparation is as follows. Hydroxylamine hydrochloride (0.043 mol) in warm ethanol (50 ml) was treated with potassium hydroxide (0.086 mol) in hot ethanol (50 ml). On cooling in an ice-bath, KCl precipitated and was filtered. To the cold filtrate, ethyl hexanoate (0.043 mol) was added slowly. After standing the solution overnight at room temperature, dry HCl gas was passed through the solution until the pH reached 7. Again KCl was filtered, the volume reduced and filtered again. To the filtrate, 100 ml of hot ethyl acetate were added and any undissolved material filtered. After standing overnight at 0 °C, the hydroxamic acid was filtered and recrystallized from an ethanol/ethyl acetate mixture.

Synthesis of Uranyl Complexes

An aqueous solution of dioxouranium(VI) nitrate was treated with the appropriate hydroxamic acid (in aqueous ethanol) in a 1:2 molar ratio. After standing on a steam bath for 30 min, the resulting light brown complex was filtered, washed with water, ether and dried.

Results and Discussion

Dioxouranium(VI) dinitrate reacts with the alkylhydroxamic acids, $CH_3(CH_2)_nCONHOH$, n = 4, 5 and

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TABLE 1. Analytical and spectroscopic data for $UO_2[CH_3(CH_2)_nCONHO]_2$ and $CH_3(CH_2)_nCONHOH$, $n = 4, 5$ and 6

Compound	Analysis	C	H	N	Melting point (°C)	Infrared bands (cm^{-1}) ν(NH)	ν(OH)	ν(CO)	ν(CN)	ν(O=U=O)
$C_5H_{11}CONHOH$	Calc. Found	54.9 55.1	9.9 10.5	10.6 10.6	62	3267	2763	1669 1629	1563	
$UO_2(C_5H_{11}CONHO)_2$	Calc. Found	27.2 27.2	4.5 4.6	5.3 4.1	179(d)	3304		1609	1535	921
$C_6H_{13}CONHOH$	Calc. Found	57.9 58.0	10.3 10.4	9.6 9.8	68	3260	2766	1664 1626	1565	
$UO_2(C_6H_{13}CONHO)_2$	Calc. Found	30.1 30.2	5.0 5.1	5.0 4.7	182(d)	3303		1611	1534	921
$C_7H_{15}CONHOH$	Calc. Found	60.4 60.0	10.7 10.7	8.8 8.7	79	3258	2762	1664 1625	1566	
$UO_2(C_7H_{15}CONHO)_2$	Calc. Found	32.8 32.7	5.5 5.4	4.8 4.4	185(d)	3305		1611	1534	920

6, to form the light brown coloured dioxouranium(VI) dihydroxamates, $[UO_2(CH_3(CH_2)_nCONHO)_2]$. Analytical and spectroscopic data are given in Table 1 together with data for the free ligands for comparison. The complexes are insoluble in most common solvents so only solid state (KBr) infrared spectra were obtained; however, solution occurred in dimethyl sulphoxide to give red solutions. The ^1H NMR spectra of solutions in DMSO-d_6 gave clear evidence for both coordinated and free ligand molecules indicating that partial solvolysis had occurred consistent with the change in colour on solution.

Infrared Spectra

The major infrared bands are shown in Table 1. The hydroxyl stretching frequency, ν(OH), occurring at about 2765 cm^{-1} in the free ligands is absent in the corresponding complexes and this fact, together with the marked shift on complexation of ν(CO) of the free ligand by about 50 cm^{-1}, is a clear indication that in these complexes the hydroxamate ligands coordinate in the normal manner through the carbonyl oxygen atom and the oxygen atom of the deprotonated hydroxamate group as observed previously in a range of first-row transition metal hydroxamates [9]. The band at 921 cm^{-1} is assigned to the asymmetric stretching mode (ν_3) of the linear UO_2 group in common with many uranyl complexes.

FAB-MS

Because of the insolubility of these complexes in a wide-range of solvents, it was not possible to carry out molecular weight determinations in solution. At the same time, we were not able to obtain suitable crystals for X-ray crystallography and so fast atom bombardment mass spectra were recorded in a glycerol matrix in an attempt to observe parent ion peaks.

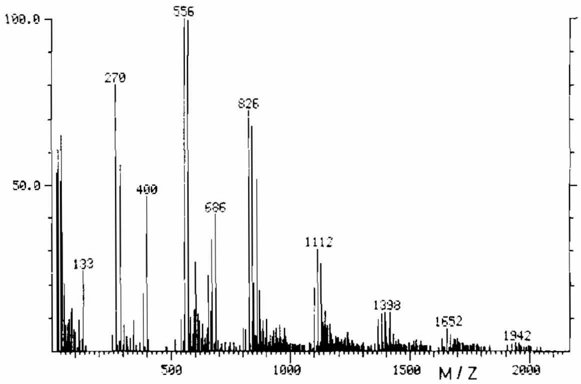

Fig. 1. The FAB-MS of $UO_2(C_5H_{11}CONHO)_2$.

However, parent ion peaks were not observed; instead the three complexes gave very similar spectra with dominant peaks resulting from oligomers $(UO_2)_n^+$ ($n = 1$–6), clusters of general formula $(UO_2)_nO_m^+$ and finally clusters containing a single coordinated ligand moiety, $[UO_2(CH_3(CH_2)_n\text{-}CONHO)]^+$. The FAB-MS of $UO_2(C_5H_{11}CONHO)_2$ is shown in Fig. 1 and assignments of the major cluster peaks given in Table 2. Similar results were obtained for heptano and octano complexes although in these cases satisfactory spectra could not be obtained above m/z values of 1000.

These results are very similar to those of Jennings and coworkers [1] for dioxouranium(VI) diacetate and, as in that case, may arise by aggregation of mononuclear complexes under the conditions of the FAB-MS experiments. In our case, the proposed use of FAB-MS to determine the parent ion peak was clearly unsuccessful. It is now important to investigate cluster formation in FAB-MS more widely and determine if it is a general effect; for example,

TABLE 2. Cluster peaks in the positive ion FAB-MS of uranyl dihexanohydroxamate in glycerol solution

m/z (% internal reference)	Molecular formula and RMM species	Structure
254 (4.7)	UO^+ (254)	$(UO)^+$
270 (80.3)	UO_2^+ (270)	$(UO_2)^+$
287 (55.9)	UO_3^+ (286)	$(UO_2)O^+$
384 (17.4)	$UO_3C_6H_{12}N^+$(384)	$(UO)(C_5H_{11}CONHO)^+$
400 (46.7)	$UO_4C_6H_{12}N^+$ (400)	$(UO_2)(C_5H_{11}CONHO)^+$
540 (9.5)	$U_2O_4^+$ (540)	$(UO_2)_2^+$
556 (100)	$U_2O_5^+$ (556)	$(UO_2)_2O^+$
573 (99.5)	$U_2O_6^+$ (572)	$(UO_2)_2O_2^+$
654 (22.7)	$U_2O_5C_6H_{12}N$ (654)	$(UO_2)(UO)(C_5H_{11}CONHO)^+$
670 (33.2)	$U_2O_6C_6H_{12}N$ (670)	$(UO_2)_2(C_5H_{11}CONHO)^+$
686 (40.8)	$U_2O_7C_6H_{12}N$ (686)	$(UO_2)_2O(C_5H_{11}CONHO)^+$
826 (72.4)	$U_3O_7^+$ (826)	$(UO_2)_3O^+$
842 (67.5)	$U_3O_8^+$ (842)	$(UO_2)_3O_2^+$
859 (51.8)	$U_3O_9^+$ (858)	$(UO_2)_3O_3^+$
940 (6.8)	$U_3O_8C_6H_{12}N$ (940)	$(UO_2)_3(C_5H_{11}CONHO)^+$
956 (7.8)	$U_3O_9C_6H_{12}N$ (956)	$(UO_2)_3O(C_5H_{11}CONHO)^+$
972 (7.0)	$U_3O_{10}C_6H_{12}N$ (972)	$(UO_2)_3O_2(C_5H_{11}CONHO)^+$
1096 (18.8)	$U_4O_9^+$ (1096)	$(UO_2)_4O^+$
1112 (30.5)	$U_4O_{10}^+$ (1112)	$(UO_2)_4O_2^+$
1128 (26.5)	$U_4O_{11}^+$ (1128)	$(UO_2)_4O_3^+$
1145 (12.2)	$U_4O_{12}^+$ (1144)	$(UO_2)_4O_4^+$
1210 (3.3)	$U_4O_{10}C_6H_{12}N$ (1210)	$(UO_2)_4(C_5H_{11}CONHO)^+$
1226 (4.0)	$U_4O_{11}C_6H_{12}N$ (1226)	$(UO_2)_4O(C_5H_{11}CONHO)^+$
1366 (9.3)	$U_5O_{11}^+$ (1366)	$(UO_2)_5O^+$
1382 (11.0)	$U_5O_{12}^+$ (1382)	$(UO_2)_5O_2^+$
1398 (11.7)	$U_5O_{13}^+$ (1398)	$(UO_2)_5O_3^+$
1414 (11.6)	$U_5O_{14}^+$ (1414)	$(UO_2)_5O_4^+$
1635 (3.9)	$U_6O_{13}^+$ (1636)	$(UO_2)_6O^+$
1652 (7.0)	$U_6O_{14}^+$ (1652)	$(UO_2)_6O_2^+$
1667 (5.2)	$U_6O_{15}^+$ (1668)	$(UO_2)_6O_3^+$
1684 (3.7)	$U_6O_{16}^+$ (1684)	$(UO_2)_6O_4^+$
1700 (3.8)	$U_6O_{17}^+$ (1700)	$(UO_2)_6O_5^+$

whether it occurs with chelates of other oxymetal cations or only with those of the uranyl ion. Finally, monomeric complexes of known crystal structure should also be examined by FAB-MS to remove any uncertainties regarding the degree of aggregation of a given complex in the solid state. Further work is in progress in attempt to answer these questions.

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