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New Uranyl(VI) Complexes: Binding of Mono and Bidentate Ligands to UO_2(tridentate) Species

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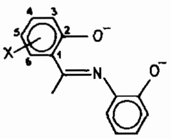
New species of the type $UO_2T{\cdot}D$, $UO_2T{\cdot}D{\cdot}H_2O$ and $UO_2T{\cdot}D{-}D$ are described (T = tridentate dianionic Schiff base ligand; D = monodentate donor e.g., H_2O, dmf, dmso, py etc.; D–D = bidentate donor e.g., 2,2'-bipyridyl). The infrared, pmr and thermal analyses data of the complexes are reported. The ν_3 frequency of the dioxouranium(VI) moiety is seen in the region 880–925 cm^{-1}. While this frequency is not very sensitive to the nature of D, on the average ν_3 with D = nitrogen donor is smaller than that with D = oxygen donor. Sufficient solubility for NMR work exists only in strongly donor solvents (py or dmso). In such solutions D is displaced by the solvent. On heating, complexes generally lose H_2O, D or D–D in one or more steps endothermically. The D–D complexes are particularly stable and loss of D–D occurs only at relatively high temperatures. It is proposed that the complexes are generally pentagonal bipyramidal. The five coordination positions on the equator are occupied by the combination of T and D, H_2O or D–D. In the case of UO_2TD a dimeric T-bridged structure is likely. The dramatic stereochemical difference between $UO_2T{\cdot}D$ and $MoO_2T{\cdot}D$ is noted.

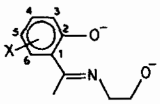
Introduction

Depending upon the chemical and stereochemical nature of the donor(s), the linear UO_2^{2+} ion commonly has coordination numbers 5 or 6 at the equator; the coordination number 4 is relatively uncommon [1–5]. In this work new UO_2^{2+} complexes derived from the dianionic tridentate salicylaldimine ligands **1** and **2** are reported. The moiety UO_2 (tridentate) abbreviated as UO_2T is coordinatively unsaturated and reacts with monodentate and bidentate donors giving rise to mixed species. The abbreviations of specific ligands are shown under **1** and **2**.



1

X = H, A
X = 5-CH_3, A'
X = 5-t-C_4H_9, A''



2

X = H, B
X = 5-CH_3, B'

General abbreviation, T

Experimental

Uranyl acetate, salicylaldehyde, *o*-aminophenol, γ-picoline, 2,2'-bipyridyl, triphenylphosphineoxide-(tppo), N,N-dimethylformamide(dmf), dimethylsulphoxide(dmso) and other starting compounds were of commercial (pure) grade. 5-methylsalicylaldehyde and 5-t-butylsalicylaldehyde were prepared from the corresponding phenols [6]. The tridentate ligands, TH_2, were obtained [7] by condensing salicylaldehydes with amines in ethanol. The orange-brown crystalline solids thus obtained were recrystallised from ethanol. In the case of 2-hydroxyethylamine, the ligand was obtained as an amber coloured oil.

Preparation of Complexes

$UO_2B{\cdot}4H_2O$

A solution of the ligand H_2B (1.65 g) in ethanol (50 ml) was added with stirring to uranyl acetate dihydrate (4.3 g) dissolved in ethanol (75 ml) and the mixture was heated on a hot plate. Heating and stirring was continued till the volume was reduced to half of the original volume. The orange-yellow product obtained on cooling was filtered, washed with ethanol and was then dried over $CaCl_2$.

The complexes $UO_2A{\cdot}4H_2O$; $UO_2A''{\cdot}4H_2O$ and $UO_2B'{\cdot}4H_2O$ were prepared following the same method.

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$UO_2A \cdot 2H_2O \cdot CH_3OH$

A solution of the ligand H_2A (2.1 g) in hot dry methanol (100 ml) was added with stirring to a solution of uranyl acetate dihydrate (4.3 g) in dry methanol (75 ml) and the mixture was heated to reflux for 45 min. It was then concentrated on a water bath to half the original volume. On cooling, a dark brown crystalline product deposited. This was filtered, washed with methanol and was then recrystallised from hot methanol to give shining reddish-brown crystals of $UO_2A \cdot 2H_2O \cdot CH_3OH$.

$UO_2A' \cdot 2H_2O \cdot CH_3OH$ was prepared following an identical method.

$UO_2B \cdot$dmso

$UO_2B \cdot 4H_2O$ (800 mg) in ethanol was added to a solution of 1 g dmso in 20 ml ethanol and the mixture was heated to reflux for 1 hr. The orange-brown crystals obtained on cooling were filtered and washed thoroughly with ethanol and were finally dried in air.

$UO_2A \cdot$dmf, $UO_2A \cdot$tppo, $UO_2B \cdot \gamma$-pic, $UO_2B' \cdot \gamma$-pic and $UO_2B' \cdot$py were prepared by similar methods.

$UO_2A'' \cdot \gamma$-pic$\cdot H_2O$

To a solution of $UO_2A'' \cdot 4H_2O$ (800 mg) in ethanol (25 ml) was added with stirring a solution of 1 ml γ-picoline in 10 ml ethanol. The mixture was then heated with stirring for 1 hr. Orange coloured crystalline product formed on cooling was collected by filtration and was washed with ethanol. The crystals were dried in air. Recrystallisation of $UO_2A'' \cdot 4H_2O$ from pure γ-picoline also yielded the same product.

$UO_2A'' \cdot$dmso$\cdot H_2O$, $UO_2A' \cdot$dmso$\cdot H_2O$, $UO_2A' \cdot$py$\cdot H_2O$, $UO_2A \cdot$py$\cdot H_2O$, $UO_2A \cdot \gamma$-pic$\cdot H_2O$, $UO_2A \cdot C_6H_5NH_2 \cdot H_2O$, $UO_2A \cdot$glycol$\cdot 2H_2O$, $UO_2A \cdot$phen and $UO_2A \cdot$bipy were prepared similarly. In the preparations of adducts with bidentate amines only a slight excess of the amine over the stoichiometric quantity was used.

$UO_2A \cdot 2NH_3 \cdot CH_3OH$

500 mg of $UO_2A \cdot 2H_2O \cdot CH_3OH$ was dissolved in methanol (75 ml) to give a reddish brown solution. Through this solution dry ammonia gas was passed for about 50 minutes. The shining orange-brown crystals formed were filtered and dried in air.

Physical Measurements

Infrared spectra were recorded on a Beckman IR Spectrophotometer (KBr disks); NMR spectra were obtained with either a Varian T-60 A or a Varian EM-390 spectrometer. Thermogravimetric measurements were made on a MOM derivatograph which records TG, DTG, DTA and temperature (T) simultaneously by photographic method.

Results and Discussion

Synthesis

The complexes prepared together with analytical data are set out in Table I. The case of ligand A will be considered first. The reaction of $UO_2(CH_3CO_2)_2 \cdot 2H_2O$ with H_2A in 1:1 ratio in hot methanol yields shining reddish brown crystals of composition $UO_2A \cdot 2H_2O \cdot CH_3OH$. If ethanol is used as the solvent instead of methanol an orange powder of composition $UO_2A \cdot 4H_2O$ results. The adducts of UO_2A with various Lewis bases were prepared by reacting either of the above two complexes with such bases. The adducts usually belong to one of the following type $UO_2A \cdot D$, $UO_2A \cdot D \cdot H_2O$, $UO_2A \cdot D{-}D$ (D = monodentate donor; D–D = bidentate donor). They are yellow to brown in colour, sparingly soluble in benzene and chloroform but soluble in pyridine and dmso. The chelate chemistry of ligands A′ and A″ are similar. The complexes of B and B′ are analogous to those of A and A′ but have even lower solubility.

Some literature results will now be briefly reviewed. The species $UO_2A \cdot 4H_2O$, $UO_2A \cdot H_2O \cdot C_2H_5OH$, $UO_2A \cdot 0.5H_2O$ and $UO_2A \cdot ROH$ (R = n-C_4H_9, i-C_5H_{11}) are reported [8]. $UO_2A \cdot 4H_2O$ is said to be obtained from aqueous methanol. We get $UO_2A \cdot 2H_2O \cdot CH_3OH$ in dry methanol. On the other hand, $UO_2A \cdot H_2O \cdot C_2H_5OH$ is reported to be isolated from ethanol solution [8]. We get only $UO_2A \cdot 4H_2O$ under these conditions. The reaction of UO_2Cl_2 with H_2A in 1:2 ratio in boiling acetone yields $UO_2(HA)_2$ in which HA is claimed to be tridentate [9]. Other dioxouranium(VI) complexes of potentially tridentate Schiff bases are either bis complexes of the type UO_2T_2 or are $UO_2(TH)_2Y_2$ (Y = Cl, I, NCS) [10–11].

Vibration Spectra

The neutral free ligands (H_2A, H_2B *etc*) show the presence of one or more broad bands near 2800 cm^{-1} due to stretch(es) of hydrogen bonded OH. Such bands are absent in $UO_2A \cdot$dmf, $UO_2B' \cdot$py *etc.* showing the loss of acidic ligand protons on complex formation.

All complexes exhibit a strong absorption in the range 880–925 cm^{-1} corresponding to ν_3 vibration of the UO_2 moiety (Table II). While the frequency of this vibration is not much influenced by the compound type and the donor present, on the average the frequencies of complexes with nitrogen donors are slightly lower than those with oxygen donors. In $UO_2A \cdot$dmf, the $\nu_{C=O}$ of dmf is considerably lower than that in free dmf. In the various dmso complexes, the ν_{SO} is again considerably lower than that in free dmso (~1055 cm^{-1}). Thus dmf and dmso bind through oxygen to the uranium atom. A similar lowering of the PO stretching frequency is observed in the Ph_3PO complex.

TABLE I. Analytical Data.[a]

Compound	%C		%H		%N		%U	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$UO_2T\cdot D$								
$UO_2A\cdot$dmf	34.63	34.81	2.90	3.00	5.05	4.95	42.94	42.82
$UO_2A\cdot$tppo	49.02	49.15	3.18	3.21	1.84	1.92	31.34	31.26
$UO_2B\cdot$dmso	25.83	25.72	2.95	2.97	2.74	2.68	46.55	46.46
$UO_2B\cdot\gamma$-pic	34.22	34.16	3.06	3.10	5.32	5.38	45.22	45.12
$UO_2B'\cdot\gamma$-pic	35.56	35.38	3.36	3.28	5.18	5.26	44.05	44.12
$UO_2B'\cdot$py	34.22	34.17	3.06	2.98	5.32	5.45	45.22	45.25
$UO_2T\cdot D\cdot H_2O$								
$UO_2A'\cdot$dmso$\cdot H_2O$	32.49	32.48	3.23	3.28	2.36	2.41	40.25	40.36
$UO_2A''\cdot$dmso$\cdot H_2O$	36.02	36.15	3.97	3.79	2.21	2.31	37.57	37.62
$UO_2A\cdot C_6H_5NH_2\cdot H_2O$	38.52	38.63	3.06	2.93	4.73	4.76	40.18	40.18
$UO_2A\cdot\gamma$-pic$\cdot H_2O$	38.52	38.62	3.06	3.21	4.73	4.91	40.18	40.14
$UO_2A\cdot$py$\cdot H_2O$	37.37	37.71	2.78	2.81	4.84	4.71	41.15	41.13
$UO_2A'\cdot$py$\cdot H_2O$	38.52	38.45	3.06	2.95	4.73	4.68	40.18	40.14
$UO_2A''\cdot\gamma$-pic$\cdot H_2O$	42.59	42.58	4.04	4.16	4.32	4.38	36.71	36.82
$UO_2T\cdot(D{-}D)$								
$UO_2A\cdot$phen	45.39	45.30	2.59	2.58	6.35	6.27	35.99	35.95
$UO_2A\cdot$bipy	43.33	43.01	2.69	2.59	6.59	6.53	37.34	37.21
Miscellaneous								
$UO_2A\cdot 2H_2O\cdot CH_3OH$	30.60	29.93	3.12	3.08	2.55	2.51	43.33	43.21
$UO_2A\cdot 4H_2O$	28.21	28.31	3.09	3.12	2.53	2.49	43.02	42.89
$UO_2A\cdot 2NH_3\cdot CH_3OH$	30.71	30.51	3.50	3.31	7.68	7.72	43.49	43.71
$UO_2A\cdot$glycol$\cdot 2H_2O$	31.09	31.21	3.30	3.21	2.42	2.53	41.09	41.21
$UO_2A'\cdot 2H_2O\cdot CH_3OH$	31.98	31.85	3.40	3.28	2.48	2.51	42.25	42.36
$UO_2A''\cdot 4H_2O$	33.50	33.51	4.13	4.23	2.30	2.32	39.06	38.92
$UO_2B\cdot 4H_2O$	21.39	21.41	3.39	3.28	2.77	2.71	47.11	47.01
$UO_2B'\cdot 4H_2O$	23.12	23.26	3.68	3.78	2.69	2.61	45.84	45.72

[a] All the complexes have melting points above 250 °C.

TABLE II. Infrared Data[a] of Dioxouranium(VI) Complexes (Frequencies are in cm^{-1}).

Compound	ν_3O=U=O	$\nu_{C=N}$	Selected Vibrations of D,D' and D–D
$UO_2A\cdot$dmf	910	1600	1640s (ν_{CO}), 670 s
$UO_2A\cdot$tppo	915	1609	1140s (ν_{PO}), 1120s
$UO_2B\cdot$dmso	890	1628	995s (ν_{SO})
$UO_2B'\cdot$py	900	1626	1442s, 1065m, 1005m, 750m
$UO_2B'\cdot\gamma$-pic	900	1625	1445s, 1020m, 760w
$UO_2A'\cdot$dmso$\cdot H_2O$	910	1612	3300 br,m, 1630m, 995s (ν_{SO})
$UO_2A''\cdot$dmso$\cdot H_2O$	901	1602	3320 br,m, 1635w, 995s (ν_{SO})

(continued overleaf)

TABLE II. *(continued)*

Compound	ν_3O=U=O	$\nu_{C=N}$	Selected Vibrations of D,D′ and D–D
$UO_2A\cdot C_6H_5NH_2\cdot H_2O$	870	1600	3450 br,m, 1455s, 750s, 670m
$UO_2A\cdot\gamma$-pic$\cdot H_2O$	889	1600	3200 br,m, 1632w–m, 750s
$UO_2A\cdot$py$\cdot H_2O$	883	1600	3310 br,m, 1460s
$UO_2A'\cdot$py$\cdot H_2O$	885	1612	3450 br,m, 1632m, 1468s, 788m, 680m–s
$UO_2A''\cdot\gamma$-pic$\cdot H_2O$	883	1605	3450 br,m, 1635m, 1462s–m, 1035w, 770m
$UO_2A\cdot$phen	890	1600	1420s, 1435s, 1150m, 830s
$UO_2A\cdot$bipy	900	1600	1400s, 1485s, 1015m, 750s
$UO_2A\cdot 2H_2O\cdot CH_3OH$	900	1600	3550 br,m, 1630m
$UO_2A\cdot 4H_2O$	925	1600	3400 br,m, 1630m
$UO_2A\cdot$glycol$\cdot 2H_2O$	900	1600	3570s (ν_{OH}), 3250 br,s, 1630m, 1070s, 1025s
$UO_2A\cdot 2NH_3\cdot CH_3OH$	882	1600	3450 br,m, 3150 br,m, 1300s, 970m, 750m
$UO_2A'\cdot 2H_2O\cdot CH_3OH$	916	1612	3200 br,m, 1630m, 1002s, 740s
$UO_2B\cdot 4H_2O$	885	1629	3300 br,m
$UO_2B'\cdot 4H_2O$	905	1623	3300 br,m
$UO_2A''\cdot 4H_2O$	900	1605	3300 br,m, 1625m, 730s

[a] Spectra were run in KBr pellets.

TABLE III. ^{1}H Chemical Shifts[a] (δ ppm) of some Selected Complexes.

Compound	$\underset{H}{>}$C=N	$-CH_3$
$UO_2A\cdot\gamma$-pic$\cdot H_2O$[b]	9.36	2.10 (γ-pic)
$UO_2A\cdot 2H_2O\cdot CH_3OH$[b]	9.60	3.60 (MeOH)
$UO_2A''\cdot\gamma$-pic$\cdot H_2O$[c]	9.67	1.33 (*t*-Bu)
		2.30 (γ-pic)
$UO_2A''\cdot$dmso$\cdot H_2O$[c]	9.66	1.35 (*t*-Bu)
		2.53 (dmso)
$UO_2A\cdot$dmf[b]	9.66	2.63 (dmf)
		2.76 (dmf)

[a] Aromatic protons give signals on the region 6.60–8.50 ppm and are not tabulated. [b] In Pyridine-d_5. [c] In dmso-d_6.

In the complexes of 1, two medium to strong bands in the region 1600–1620 cm^{-1} and 1545–1560 cm^{-1} are assigned to $\nu_{C=N}$ and aromatic ν_{CO} respectively. In the complexes of 2, an additional band assigned to aliphatic ν_{CO} is seen near 1040 cm^{-1}. The binding of alkoxide oxygen to the dioxouranium(VI) is relatively uncommon. This makes the complexes of 2 particularly interesting.

^{1}H NMR Spectra

None of the complexes has sufficient solubility for NMR studies in $CDCl_3$. However, in a few cases spectra could be run in dmso-d_6 and pyridine-d_5. Such solutions display the signals for the tridentate ligand and for D and H_2O. The assigned compositions for the complexes $UO_2A\cdot 2H_2O\cdot CH_3OH$ and $UO_2A\cdot$dmf, were supported by the NMR data (Table III). However, it is significant that the signals for D ligands do not exhibit any shifts from the free ligand values

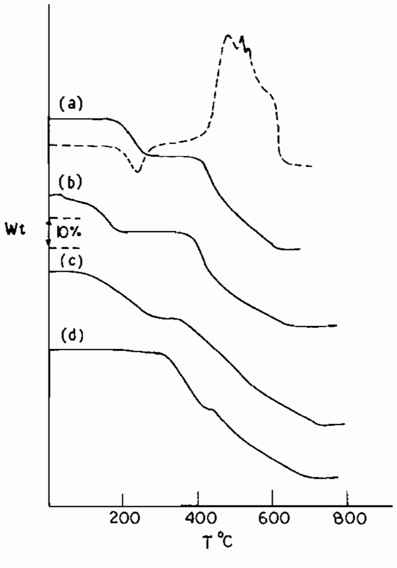


Fig. 1. Thermograms of a few selected systems. Solid curve shows percentage weight loss (wl) *versus* temperature (T °C): (a) $UO_2A\cdot$dmf; (b) $UO_2A\cdot 4H_2O$; (c) $UO_2A'\cdot$py$\cdot H_2O$; (d) $UO_2A\cdot$bipy. In one case DTA curve is also shown by dotted line (------).

TABLE IV. Thermogravimetric Data of some Selected Dioxouranium(VI) Complexes in Air Atmosphere.

Complex	Temperature[a] (°C) for Loss of D, H_2O and D–D		Weight loss (%)	
	T_i	T_f	Calc.	Found
$UO_2A\cdot$dmf	200	245	13.2	13.5
$UO_2A\cdot Ph_3PO$	380	440	36.6	35.5
$UO_2A\cdot$phen	450	480	27.2	27.8
$UO_2A\cdot$bipy	318	420	24.5	24.0
$UO_2A'\cdot$dmso$\cdot H_2O$	160	326	16.3	16.0
$UO_2A\cdot$glycol$\cdot 2H_2O$	120	195	16.9	16.7
$UO_2A\cdot\gamma$-pic$\cdot H_2O$	190	315	18.8	19.0
$UO_2A'\cdot$py$\cdot H_2O$	100	275	16.4	16.6
$UO_2A\cdot C_6H_5NH_2\cdot H_2O$	110	275	18.8	18.1
$UO_2A\cdot 2NH_3\cdot CH_3OH$	78	285	12.0	11.1
$UO_2A\cdot 2H_2O\cdot CH_3OH$	55	190	12.4	12.5
$UO_2A\cdot 4H_2O$	45	190	13.0	12.8
$UO_2A'\cdot 2H_2O\cdot CH_3OH$	50	182	12.1	12.0

[a] T_i = Initial temperature of loss; T_f = Final temperature of loss.

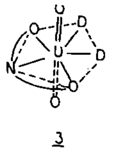
indicating, that such donors are likely to have been completely displaced from the metal ion by the strongly coordinating solvent molecules.

Thermal Analysis

The complexes were subjected to thermal analysis in air atmosphere under non-isothermal conditions. Representative thermogravimetric plots are displayed in Fig. 1 and additional results can be found in Table IV. The general behaviour consists of endothermic loss of H_2O, D or D–D in one or more steps followed by highly exothermic oxidative loss (>350 °C) of the tridentate ligand. The final solid product remaining is invariably U_3O_8. In systems of the type UO_2(tridentate)$\cdot$D and UO_2(tridentate)$\cdot$D–D the loss of D or D–D usually occurs over a relatively narrow range of temperatures. A typical example is $UO_2A\cdot$dmf in which the whole of dmf is lost within the temperature interval 200–240 °C. Complexes with bidentate donors, $UO_2A\cdot$bipy and $UO_2A\cdot$phen, are found to be extremely stable. The donors are lost in the range 320–400 °C. The species UO_2A produced in such reactions has not been investigated further. However, if heating is discontinued after UO_2A is formed and the mass is allowed to cool, it rapidly absorbs moisture possibly due to conversion to $UO_2A\cdot nH_2O$. In contrast to the above, species of the type UO_2(tridentate)$\cdot$D$\cdot H_2O$ loose D and H_2O in overlapping steps over a relatively wide range of temperature. A case in hand is $UO_2A\cdot$py$\cdot H_2O$ (Fig. 1).

Structure

The above results clearly demonstrate that D, H_2O and D–D occupy coordination positions. The planar tridentate T ligand can only span three meridional positions. We have prepared the complexes $UO_2A\cdot$2dmso and $UO_2A\cdot$dmso$\cdot H_2O$ and the structure of the former has been solved by three-dimensioned x-ray crystallography [12]. The gross structure is 3 in which T is indeed meridionally tridentate and the two molecules (oxygen-bonded dmso) completes the pentacoordinated equator. The structures 4 and 5 for complexes of type $UO_2T\cdot D\cdot H_2O$ and $UO_2T\cdot D–D$ are logical extensions of 3. In the complexes belonging to the miscellaneous categories of Table I it is very likely that all the potentially donor molecules are not bound to the metal ion directly and the coordination polyhedron may actually have a pentacoordinated equator.



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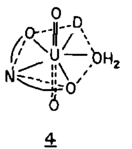

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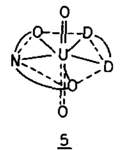

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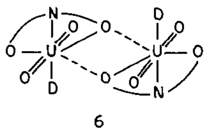

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This leaves us with the interesting $UO_2T\cdot D$ species. While the uncommon tetradentate equator is a possibility, it is quite likely* that pentacoordina-

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*We are thankful to a referee for the suggestion.

tion is actually achieved through dimerisation as in structure **6**. The bridging capabilities of phenoxide or alkoxide oxygen atoms of Schiff bases towards transition metal ions are well-documented [13]. An oxygen-bridged dimeric structure similar to **6** has been proposed for dioxobis(tropolonato)uranium(VI) [14]. The structure **6** can account for the thermogravimetric curves (only one endothermic peak for the loss of D) if the possible structural rearrangement due to the breaking of oxygen bridges are simultaneous with the release of ligands. Further studies on $UO_2T\cdot D$ species are on.

Recently we reported [15] a large number of monomolecular dioxomolybdenum(VI) complexes of type $MoO_2T\cdot D$. Here the MoO_2 moiety is angular (cis) and the labile D ligand is bound trans to a Mo=O bond nearly perpendicularly to the plane of T. The different electronic and stereochemical properties of the UO_2^{2+} and MoO_2^{2+} ions and their complexes are dramatically reflected in the two groups of complexes.

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