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Mono-, Bi- & Tri-nuclear Dioxouranium (VI) Complexes With Oximes & Polydentate Schiff Bases

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Dioxouranium (VI) salts (chloride, acetate and thiocyanate) react with furfuraldoxime (FDH), salicylaldoxime (H_2Salo) and a series of polydentate schiff bases obtained by the condensation of diacetyl monoxime with ethylenediamine (DMED), diethylenetriamine (DMDT), and triethylenetetramine (DMTT), respectively, to form a series of mono-, bi- and tri-nuclear complexes. These have been characterized by elemental analyses, conductivity and thermogravimetric measurements and IR spectral data. Bi- and tri-nuclear complexes appear to contain hydroxo bridges.

Previous reports from our laboratory[1,2] described the preparation and characterisation of mononuclear complexes of divalent dioxouranium (VI) with a series of multidentate schiff bases and also the binuclear complexes with bidentate schiff bases[3]. As an extension, we report here the synthesis and characterisation of uranyl complexes with bidentate furfuraldoxime (FDH), salicylaldoxime (H_2Salo), the tetradentate N, N'- ethylenediamine bis (isonitroso ethyl methyl ketone imine (DMED), the pentadentate N, N', N''-diethylenetriamine bis (isonitroso ethyl methyl ketone imine) (DMDT) and the hexadentate N, N', N'', N'''-triethylenetetramine bis (isonitroso ethyl methyl ketone imine) (DMTT).

Hydrated dioxouranium (VI) chloride and acetate (BDH) were used as supplied. Dioxouranium (VI) thiocyanate was obtained by metathesis of $UO_2(NO_3)_2$ by treatment with KCNS in EtOH[4]. Furfuraldoxime and salicylaldoxime were prepared by standard methods[5] and the ligands DMED and DMDT were synthesised in a manner similar to the procedure reported[6,7] for the preparation of the hexadentate ligand DMTT.

Electrical conductance measurements in DMF and/or DMSO and thermal measurements (T, TG, DTG and DTA) were performed as reported earlier[1-3]. IR spectra of all the complexes in the range 4000-400 cm^{-1} were recorded in KBr using a NICOLET 20 SXC FT-IR spectrophotometer fitted with a data station.

Complexes with oximes, viz. FDH and H_2Salo

Stoichiometric quantities of $UO_2(OAc)_2$ and FDH (1:2) reacted in EtOH to form mononuclear $[UO_2(FD)_2(H_2O)_2]$, whereas UO_2Cl_2 and FDH reacted to give the binuclear $[(UO_2)_2(\mu\text{-}OH)_2(FD)_2(H_2O)_2]$ when the *p*H was adjusted to 6 to 7 by the addition of 1% ethanolic KOH. UO_2Cl_2 and $UO_2(OAc)_2$ reacted with H_2Salo in 2:1 ratio in EtOH at *p*H 6 to 7 to provide the complexes $[(UO_2)_2(\mu\text{-}OH)_2Cl_2(H_2Salo)\ (H_2O)_2]$ and $[(UO_2)_2(\mu\text{-}OH)_2(Salo)\,H_2O)_2]$.

Complexes with schiff bases, viz. DMED, DMDT and DMTT

Treatment of UO_2X_2 (X = Cl, NCS) with DMDT or DMTT in 1:1 stoichiometry in EtOH afforded the binuclear (with DMED and DMDT) and trinuclear (with DMTT) complexes. Changing the stoichiometric ratio of ligand to metal did not affect the composition of the complexes isolated. The reactants were stirred vigorously at room temperature for 2 hr, the precipitated compounds were filtered and washed three or four times with EtOH (3 ml) and dried *in vacuo*. With DMED and DMDT binuclear complexes of the type $[(UO_2)_2(\mu\text{-}OH)_2(X)_2(L)]$ (L = DMED, DMDT; X = Cl, NCS) and with DMTT trinuclear complexes of the type $[(UO_2)_3(\mu\text{-}OH)_4(X)_2(DMTT)]$ (X = Cl, NCS) were formed.

The characterisation data of the complexes synthesised are presented in Table 1. Evidences show that except for the $[UO_2(FD)_2(H_2O)_2]$, all other complexes have a bi- or tri-nuclear structure with one- or two- double hydroxo bridges between two adjacent U(VI) centres. The poor solubility of these complexes in organic solvents precluded their molecular weight determination and X-ray structural studies. The conductances of only a few complexes could be measured in dilute solutions (*ca.* 10^{-3} *M*) of DMF and DMSO. The conductance data show them to behave as non electrolytes[8]. Higher molar conductance values of the order of $50\Omega^{-1}$ mol^{-1} cm^2 in DMSO and $90\Omega^{-1}$ mol^{-1} cm^2 in DMF are obtained for the thiocyanato complexes, but the solid state IR spectra confirm the absence of ionic thiocyanate groups[9]. Since DMF and DMSO are coordinating solvents, it is likely that solvolysis or decomposition takes place in these solvents resulting in higher conductance values.

Table 1—Analytical and Other Characterisation Data of Dioxouranium (VI) Complexes[a]

Complex	Found (calc) %				
	U	C	H	N	Cl or S
(1)	(2)	(3)	(4)	(5)	(6)
$[UO_2(FD)_2(H_2O)_2]$ (**1**)	45.1 (45.2)	22.6 (22.8)	2.6 (2.3)	5.1 (5.3)	
$[(UO_2)_2(\mu\text{-}OH)_2(FD)_2(H_2O)_2]$ (**2**)	57.0 (57.2)	14.3 (14.5)	1.4 (1.7)	3.5 (3.4)	
$[(UO_2)_2(\mu\text{-}OH)_2Cl_2(H_2Salo)(H_2O)_2]$ (**3**)	57.9 (58.2)	10.6 (10.3)	1.6 (1.6)	1.7 (1.7)	8.9 (8.7)
$[(UO_2)_2(\mu\text{-}OH)_2(Salo)(H_2O)_2]$ (**4**)	63.3 (63.9)	11.5 (11.3)	1.6 (1.5)	1.9 (1.9)	
$[(UO_2)_2(\mu\text{-}OH)_2Cl_2(DMED)]$ (**5**)	54.2 (54.6)	13.2 (13.8)	2.6 (2.3)	6.7 (6.4)	8.5 (8.1)
$[(UO_2)_2(\mu\text{-}OH)_2(NCS)_2(DMED)]$ (**6**)	51.6 (52.0)	15.5 (15.7)	2.5 (2.2)	8.9 (9.2)	6.6 (7.0)
$[(UO_2)_2(\mu\text{-}OH)_2Cl_2(DMDT)]$ (**7**	51.7 (52.1)	15.5 (15.8)	2.9 (2.6)	7.7 (7.7)	7.8 (7.8)
$[(UO_2)_2(\mu\text{-}OH)_2(NCS)_2(DMDT)]$ (**8**)	49.3 (49.7)	17.6 (17.5)	2.3 (2.5)	10.2 (10.2)	6.5 (6.7)
$[(UO_2)_3(\mu\text{-}OH)_4Cl_2(DMTT)]$ (**9**)	56.2 (56.6)	13.0 (13.3)	2.6 (2.5)	6.7 (6.6)	5.3 (5.6)
$[(UO_2)_3(\mu\text{-}OH)_4(NCS)_2(DMTT)]$ (**10**)	54.3 (54.6)	15.1 (14.7)	2.6 (2.4)	8.3 (8.5)	5.3 (4.9)

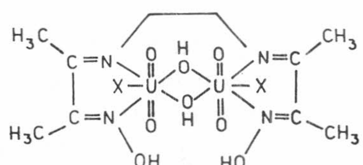
(a) Except for the complexes **3** and **4**, which are brick-red, all other complexes are yellow in colour; complexes do not melt or decompose upto 250°C

FDH = furfuraldoxime; H_2Salo = salicylaldoxime; DMED = N,N′-ethylenediamine bis(isonitroso ethyl methyl ketone imine); DMDT = N,N′,N″-diethylenetriamine bis(isonitroso ethyl methyl ketone imine); DMTT = N,N′, N″, N‴-triethylenetetramine bis (isonitroso ethyl methyl ketone imine)

The IR active ν_{as} U-O modes in the complexes are observed in the 890-910 cm^{-1} region, as expected for the linear UO_2 moiety[10,11]. The IR spectrum of FDH exhibits bands at 3160 and 3040 cm^{-1} assignable to H-bonded νOH (ref. 12). These bands are absent in the complexes and new bands at 650-690 and 540 cm^{-1} appear which may be assigned to ν U-O (oxime) and ν U-O (furan ring) modes showing the bidentate coordination of the ligand FDH[12-14]. The ν C=N modes in these complexes appear at 1615 and 1632 cm^{-1} as compared to that of the free ligand at 1640 cm^{-1}. The ν C=N modes in the salicylaldoxime complexes appear at 1620 cm^{-1}, experiencing a shift of about 15 cm^{-1} from that of the free ligand (H_2Salo) at 1635 cm^{-1}. The fairly intense bands around 1200-1240 cm^{-1} are assigned to ν N−O modes[15] for the H_2Salo and FDH ligands and their complexes. An intense broad band in the region 3300-3500 cm^{-1} indicates the presence of coordinated water molecules[16] in the complexes of FDH and H_2Salo; the corresponding δ (OH) modes appear at 1620-1650 cm^{-1}. For these complexes as well as for those of the polydentate schiff bases DMED, DMDT and DMTT, a broad but strong band is seen at 1120-1170 cm^{-1} corresponding to the vibrations for the bridged hydroxo groups[3,16]. The IR spectra of the polydentate schiff base ligands show no characteristic absorption band assignable to either νC=O or νNH_2. The ν C=N modes in these ligands appear as medium intensity band in the region 1605-1625 cm^{-1} (see refs. 17, 18). In the complexes a fairly sharp band at 1600-1620 cm^{-1} suggests coordination of the ligands through the nitrogen of the azomethine group[19]. The νN−O mode shifts to higher frequency[20,21] on coordination of the oxime group through N. In these polydentate ligands and their complexes, the νN−O modes appear in the region 1150-1250 cm^{-1}. These tetra-, penta- and hexa-dentate ligands are coordinated to the metal center as neutral molecules and not as deprotonated ligands[1,22], and it appears that in all the cases only the four terminal nitrogen atoms are coordinated to U(VI) leaving one- or two- secondary amine N atoms free in the penta- and hexa-dentate ligands, respectively. The ligands DMDT and DMTT thus function essentially as tetradentate ligands. The thiocyanato complexes exhibited bands at 2025-2050 and

840 cm^{-1} corresponding to $\nu C \equiv N$ and $\nu C-S$ of the $-NCS$ group and suggest N-coordination of this ambidentate anion[23].

Di- or tri-meric complexes for uranium(VI) are rather rare[24,25]. The X-ray structure of uranyl hydroxide chloride, $[(UO_2)_2(\mu-OH)_2Cl_2(H_2O)_4]$, shows it to be a dimer where two uranium(VI) centers are joined by a double hydroxo bridge[26]. We had also reported earlier[3] similar double hydroxo-bridged bi-nuclear dioxouranium(VI) complexes with bidentate heterocyclic schiff bases. Based on these evidences, bi- and tri-nuclear complexes presently synthesised can have structures I-III. The U(VI) atoms at the sides have a coordination number of 7 with the central U(VI) having a coordination number 6 in the tri-nuclear uranyl complexes with DMTT.



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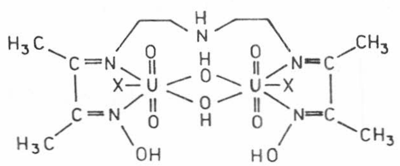
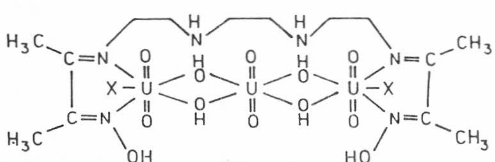


II



III

(X = Cl, NCS)

The complexes **1**−**4** (Table 1) lose coordinated water molecules when heated to about 120-150°C. Above 150°C, simultaneous deligation of the complex in steps and loss of one H_2O molecule from the double hydroxo bridge takes place giving rise to the oxo-bridged species UO_2-O-UO_2 as has been observed by us earlier[3]. Invariably U_3O_8 is obtained as the stable end-product in most cases at around 600°C. However, in some cases the stoichiometry of the end product could not be ascertained and it is probable that some sort of non-stoichiometric compounds are also formed.

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