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Schiff Base Complexes of Dioxouranium(VI). VII. Dioxouranium(VI) Acetate Complexes With Monobasic Bidentate and Bibasic Tridentate *Schiff* Bases

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1:1 and 1:2 molar reactions of dioxouranium(VI) acetate dihydrate with the monobasic bidentate *Schiff* bases, o-$HOC_6H_4CH{=}NR$ or o-$HOC_{10}H_6CH{=}NR$ ($R = C_2H_5$, n-C_3H_7, n-C_4H_9 or C_6H_5) and bibasic tridentate *Schiff* bases, o-$HOC_6H_4CH{=}NR(OH)$ or o-$HOC_{10}H_6CH{=}NR(OH)$ ($R{=}$ —$CH_2CH(CH_3)$- or —$CH_2CH_2CH_2$—) have been studied and derivates of the type $UO_2(OAc)_2(SBH)$, $UO_2(OAc)_2(SBH)_2$, $UO_2(OAc)_2(SBH_2)$ and $UO_2(OAc)_2(SBH_2)_2$ (where SBH and SBH_2 represent monobasic bidentate and bibasic tridentate *Schiff* base molecules respectively) have been isolated. These have been characterized by elemental analysis, conductance measurements and IR spectral studies.

(Keywords: Dioxouranium(VI) acetate complexes; Infrared spectra; Schiff bases, complexes of)

UO_2^{2+}-*Komplexe von Schiff-Basen. VII. Uranylacetat-Komplexe mit monobasischen zweizähnigen und bibasischen dreizähnigen Schiff-Basen*

Es wurden in 1:1- und 1:2-molaren Reaktionen von $UO_2(OAc)_2 \cdot 2H_2O$ mit *Schiff*-Basen (L) Komplexe des Typs $UO_2(OAc)_2L$ bzw. $UO_2(OAc)_2L_2$ isoliert. Die Komplexe wurden mittels Elementaranalyse, Leitfähigkeitsmessungen und IR-Spektren untersucht.

Introduction

Neutral ligands containing an oxygen or nitrogen donor atom e. g. triphenylphosphine oxide, arsine oxide etc. can enter the coordination sphere of dioxouranium(VI) acetat with the formation of adduct derivatives[1]. However, in contrast to the wide variety of metal complexes of deprotonated *Schiff* bases, examples of coordination of neutral molecules of *Schiff* bases to the uranium atom are limited[2,3].

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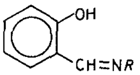
In earlier publications from these laboratories, a few adduct derivatives of dioxouranium(VI) nitrate and dioxouranium(VI) chloride with *Schiff* bases containing varied donor sites have been reported[4–8]. However, no attempts seem to have been made to prepare similar adducts of dioxouranium(VI) acetate.

Recently, *Tayim* and *A'ma*[3] have reported *Schiff* base adducts of the type $UO_2(OAc)_2L_2$ in which the molecule of the *Schiff* base is coordinated to the metal atom. During the course of the present investigations some more *Schiff* base complexes of dioxouranium(VI) acetate with monobasic bidentate (**1** and **2**) and bibasic tridentate (**3** and **4**) *Schiff* bases have been synthesized and the results discussed in the present paper.



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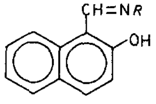
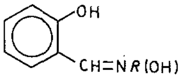


2

a: $R = C_2H_5$
b: $R = n\text{-}C_3H_7$
c: $R = n\text{-}C_4H_9$
d: $R = C_6H_5$



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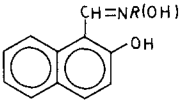

4

a: $R = \text{-}CH_2CH(CH_3)\text{-}$
b: $R = \text{-}CH_2CH_2CH_2\text{-}$

Experimental

Materials

Dioxouranium(VI) acetate dihydrate (BDH) was used without further purification. Absolute ethanol, dimethylformamide (*DMF*) and nitrobenzene were purified as reported earlier[4,5].

Preparation of Schiff Bases

2-[*N*-(Alkyl resp. Hydroxyalkyl)-iminomethyl]phenols **1 a**—**d** resp. **3 a, b**) were prepared by mixing equimolar amounts of salicyladehyde and desired amine or hydroxyamine in benzene and refluxing for several hours, followed by the removal of benzene-water azeotrope; 1-[*N*-(Alkyl resp. Hydroxyalkyl)-iminomethyl]-2-naphthols (**2 a**–**c** resp. **4 a, b**) were prepared by the condensation of equimolar amounts of aldehyde and amine or hydroxyamine in ethanolic medium; purification either by distillation or recrystallization.

Details on the synthesis and physical characteristics of the synthesized *Schiff* bases are reported in earlier publications[7,8].

Synthesis of Dioxouranium(VI) Acetate—Schiff Base Complexes

A weighed amount of dioxouranium(VI) acetate dihydrate (1-3 g) was dissolved in ethanol and requisite amount of the *Schiff* base was added. The solution immediately turned from orange yellow to red. The contents were then refluxed at a bath temperature of 110-120 °C for three h and from the resulting solution, the solvent was pumped off. The remaining solid was washed with ether and finally dried under reduced pressure. Elemental analysis and physical characteristics of the complexes are recorded in Table 1.

Analysis and Physical Measurements

Uranium and nitrogen were estimated as described earlier[6]. The liberated acetic acid by the hydrolysis of the acetoxy complexes was titrated against sodium hydroxide.

Infrared spectra were recorded in Nujol mulls using a Perkin-Elmer 337 grating IR spectrophotometer in the range 4,000-400 cm^{-1}. The IR spectra of a few *Schiff* bases and their complexes were recorded in the range of 650-200 cm^{-1} in Nujol mulls using Backman IR-12 infrared spectrophotometer.

Molar conductance measurements were made in dimethyl formamide (*DMF*) or nitrobenzene at 25 ± 1 °C using a Tesla RLC bridge with the cell having a cell constant 0.74 cm^{-1}.

Results and Discussion

The reactions of dioxouranium(VI) acetate dihydrate with monobasic bidentate (*SBH*) and bibasic tridentate (SBH_2) *Schiff* bases in 1:1 and 1:2 molar ratios yielded $\mathrm{UO_2(O}Ac)_2(SBH)$, $\mathrm{UO_2(O}Ac)_2(SBH)_2$, $\mathrm{UO_2(O}Ac)_2\,(SBH_2)$ and $\mathrm{UO_2(O}Ac)_2(SBH_2)_2$ types of derivatives in contrary to the reactions of dioxouranium(VI) nitrate and dioxouranium(VI) chloride which yielded only bis-type of products[4, 7].

Panattoni et al.[1] have also reported 1:1 and 1:2 derivatives of dioxouranium(VI) acetate with triphenylphosphine oxide, whereas with dioxouranium(VI) nitrate only 1:2 products could be isolated[9]. The difference of behaviour of dioxouranium(VI) nitrate with that of dioxouranium(VI) acetate can be explained by the fact that the *Schiff* base molecules as well as the anions of the salt compete for positions in the coordination sphere of the dioxouranium(VI) ion. Thus a decrease in the number of *Schiff* base molecules will correspond to an increase in the strength of the bond between the acid residue and the dioxouranium(VI) group[10]. However, the strength of the coordination bond formed with dioxouranium(VI) by the acido increases in the order. $Ac^- > \mathrm{Cl}^- > \mathrm{NO_3}^-$ and this coincides with the order of displacing powers of the anions in the dioxouranium(VI) complexes.

The newly synthesized *Schiff* base complexes are yellow to orange solids and stable against light and atmosphere. Their non-electrolytic nature is indicated by low conductance values as determined in

Table 1. *Elemental analysis and molar conductance of Dioxouranium(VI) acetate-Schiff base complexes*

No.	*Schiff* base	Compound formed	Analysis % U	Analysis % N	Analysis % O*Ac*	Molar conductance (Ω^{-1} cm^2 mol^{-1}) Nitrobenzene	Molar conductance (Ω^{-1} cm^2 mol^{-1}) *DMF*
1	**1a**	$UO_2(OAc)_2(C_9H_{11}NO)$ yellow solid	43.69 (44.30)	2.77 (2.61)	21.49 (21.98)	3.12	16.8
2	**1a**	$UO_2(OAc)_2(C_9H_{11}NO)_2$ orange red solid	34.91 (34.68)	3.97 (4.08)	17.73 (17.21)	3.39	21.7
3	**1b**	$UO_2(OAc)_2(C_{10}H_{13}NO)$ yellow solid	43.11 (43.17)	2.71 (2.54)	20.92 (21.42)	3.78	19.4
4	**1b**	$UO_2(OAc)_2(C_{10}H_{13}NO)_2$ orange red solid	33.09 (33.31)	3.92 (3.92)	16.46 (16.53)	4.03	20.9
5	**1c**	$UO_2(OAc)_2(C_{11}H_{15}NO)$ orange solid	41.30 (42.10)	2.66 (2.48)	20.27 (20.89)	4.01	17.6
6	**1c**	$UO_2(OAc)_2(C_{11}H_{15}NO)_2$ orange solid	32.49 (32.06)	3.84 (3.77)	16.47 (15.91)	4.51	22.4
7	**1d**	$UO_2(OAc)_2(C_{13}H_{11}NO)$ yellow solid	39.66 (40.65)	2.69 (2.39)	19.29 (20.17)	—	21.3
8	**1d**	$UO_2(OAc)_2(C_{13}H_{11}NO)_2$ yellow solid	30.63 (30.41)	3.69 (3.58)	15.23 (15.08)	—	23.3
9	**2a**	$UO_2(OAc)_2(C_{13}H_{13}NO)$ yellow solid	39.73 (40.52)	2.63 (2.38)	19.17 (20.10)	2.24	13.3
10	**2a**	$UO_2(OAc)_2(C_{13}H_{13}NO)_2$ yellow solid	29.93 (30.26)	3.73 (3.56)	14.38 (14.97)	2.63	17.5
11	**2b**	$UO_2(OAc)_2(C_{14}H_{15}NO)$ yellow solid	39.89 (39.57)	2.22 (2.33)	19.99 (19.63)	2.12	17.4
12	**2b**	$UO_2(OAc)_2(C_{14}H_{15}NO)_2$ yellow solid	29.78 (29.22)	3.42 (3.44)	14.96 (14.50)	2.48	24.4

13	**2c**	$UO_2(OAc)_2(C_{15}H_{17}NO)$ yellow solid	38.00 (38.67)	2.56 (2.27)	18.43 (19.15)	1.79	15.5
14	**2c**	$UO_2(OAc)_2(C_{15}H_{17}NO)_2$ yellow solid	28.50 (28.25)	3.31 (3.32)	14.80 (14.01)	2.94	21.6
15	**3a**	$UO_2(OAc)_2(C_{10}H_{13}NO_2)$ orange solid	40.96 (41.93)	2.55 (2.47)	20.03 (20.81)	2.14	7.7
16	**3a**	$UO_2(OAc)_2(C_{10}H_{13}NO_2)_2$ orange solid	32.75 (31.87)	3.82 (3.75)	15.17 (15.82)	3.01	6.7
17	**3b**	$UO_2(OAc)_2(C_{10}H_{13}NO_2)$ yellow solid	40.92 (41.93)	2.58 (2.47)	20.21 (20.81)	1.94	8.4
18	**3b**	$UO_2(OAc)_2(C_{10}H_{13}NO_2)_2$ yellow solid	31.23 (31.87)	3.78 (3.75)	15.63 (15.82)	3.20	11.4
19	**4a**	$UO_2(OAc)_2(C_{14}H_{15}NO_2)$ Red solid	37.17 (38.55)	2.42 (2.27)	18.43 (19.12)	1.87	8.2
20	**4a**	$UO_2(OAc)_2(C_{14}H_{15}NO_2)_2$ Red solid	27.99 (28.11)	3.40 (3.30)	13.67 (13.95)	1.59	10.8
21	**4b**	$UO_2(OAc)_2(C_{14}H_{15}NO_2$ Red solid	38.30 (38.55)	2.15 (2.27)	19.03 (19.12)	2.31	9.3
22	**4b**	$UO_2(OAc)_2(C_{14}H_{15}NO_2)_2$ Red solid	28.29 (28.11)	3.24 (3.30)	14.03 (13.95)	2.51	9.6

nitrobenzene and *DMF* at $10^{-3}M$ concentration and $25 \pm 1\,°C$. These are found to be below 5 and $25\,\Omega^{-1}\,cm^2\,mol^{-1}$ and these are too low to account for any appreciable dissociation of these complexes. Since the complexes are sparingly soluble in benzene their molekular weights could not be determined ebullioscopically.

In the resulting derivatives, the coordination of the metal through nitrogen of the azomethine group and oxygen of the OH group of the aldehyde residue of the ligand moiety is indicated by the IR spectra and thus the *Schiff* base molecules act as neutral bidentate ligands. The *Schiff* bases having the donor system HO—N—OH are potentially bibasic tridentate in nature. But in the present investigations, the possibility of coordination through the OH group at the amine residue of the ligand moiety is ruled out by the fact that no reaction has been found to take place between dioxouranium(VI) acetate dihydrate and *Schiff* bases of the type N-(hydroxyalkyl)-iminomethyl-benzene (see ref.[11]).

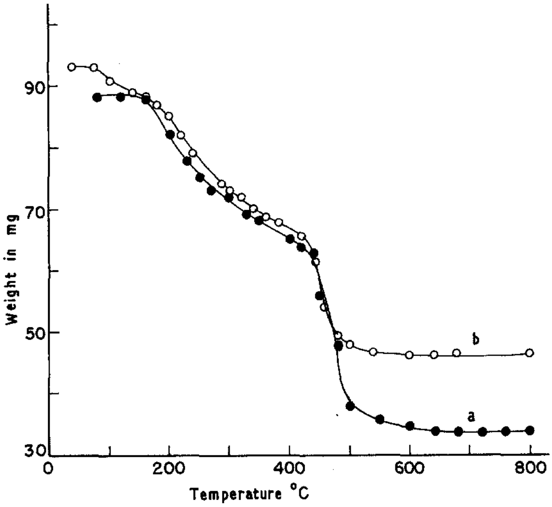

Fig. 1. Thermolysis curves: (*a*) $UO_2(OAc)_2(HOC_6H_4CH = NCH_2CHOHCH_3)_2$. Starting weight 88 mg; final weight 34 mg, Calcd. wt. for U_3O_8 33 mg, (*b*) $UO_2(OAc)_2(HOC_6H_4CH = NCH_2CHOHCH_3)$. Starting weight 93 mg final wt. 47 mg, Cald. wt. for U_3O_8 46 mg

Thermogravimetric analysis of $UO_2(OAc)_2(\mathbf{3a})_2$ (Fig. 1; curve a) shows that the complex is stable up to 160 °C. Then it looses both molecules of the ligand between 160-475 °C and finally it gets decomposed to the oxide (U_3O_8) at 600 °C. In the case of $UO_2(OAc)_2$(**3a**) (Fig. 1, curve b) a continuous thermogram without any intermediate step is obtained; the complex gets converted into the oxide (U_3O_8) at 550 °C.

Infra-Red Spectra

The infrared spectra of the *Schiff* bases and the corresponding dioxouranium(VI) derivatives were recorded and the following points appear to be significant for the nature of bonding.

(i) The *Schiff* bases show broad absorption peaks due to νOH in the 3,400-2,950 cm^{-1} region and this lowering may be due to the presence of both types of hydrogen bonding, intermolecular (O—H .... O) as well as intramolecular (O—H ..... N) invariably present in such compounds. However, in the dioxouranium(VI) complexes the absorption band of νOH is shifted towards the higher wave number side ($\sim$100 cm^{-1}) and this may be ascribed to the absorption of the coordinated OH group without deprotonation.

(ii) The bibasic tridentate *Schiff* base complexes of dioxouranium(VI) acetate also show an absorption band at $\sim$3,500 cm^{-1} and this may be assigned to the free OH group of the amine residue of the ligand moiety in the complexes; in the investigated complexes the *Schiff* bases coordinate therefore as neutral bidentate ligands.

(iii) In the spectra of the *Schiff* bases a sharp band of strong intensity is observed at $\sim$ 1,620 cm^{-1} which can be assigned to νC=N. However, it gets shifted to the higher wave number side ($\sim$ 10 cm^{-1}) in the resulting derivatives. A similar shift has been observed by *Vidali et al.*[12]

(iv) Three vibrational frequencies, symmetric (ν_1), asymmetric (ν_3) and bending (ν_2) appear in the case of dioxouranium(VI) ions. In the present case, only two bands in the regions 940-910 cm^{-1} and 860-845 cm^{-1} are observed and these may be attributed to ν_3 and ν_1 vibrations respectively. In a few cases another band in the far IR region (265-250 cm^{-1}) appears and this has been attributed to the bending vibration (ν_2) of the dioxouranium(VI) ion.

(v) Exact assignments in the resulting *Schiff* base complexes are rather difficult owing to the interference of νC=O modes with the νC=C and νC=N vibrations within the ligand. However, a new band is observed in the region 1,670-1,600 cm^{-1} in the dioxouranium(VI) acetate mono *Schiff* base complexes and this may be due to the ν asym absorption frequency of the bridging acetoxy group[13]. Further, in the dioxouranium(VI) acetate bis-*Schiff* base complexes, the acetoxy group seems to be most probably coordinated as unidentate ligand as this sort of arrangement will be preferred in providing coordination number eight to the central uranium atom.

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