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Schiff Base Complexes of Dioxouranium(VI), III. Commun.: Dioxouranium(VI) Complexes of Bibasic Tetradentate *Schiff* Bases

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With 1 Figure

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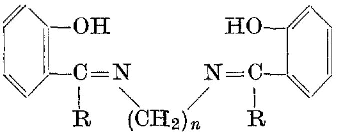
Bibasic tetradentate *Schiff* bases having the donor system OH—NX—NX—OH have been shown to form $UO_2(NO_3)_2(SBH_2)$ type of derivatives [SBH_2 is the molecule of the bibasic tetradentate *Schiff* bases such as $HOC_6H_4C(R):$ $:N(CH_2)_nN:C(R)C_6H_4OH$ (where R = H or CH_3 and $n = 2$ or 3) and $HOC(R'):CHC(CH_3):N(CH_2)_nN:C(CH_3)CH:$ $:C(R')OH$ (where $R' = CH_3$ or C_6H_5 and $n = 2$ or 3)]. The 1 : 1 stoichiometry of these complexes is shown by elemental analysis and conductometric titrations. The molar conductence values in nitrobenzene indicate the non-electrolytic behaviour and the magnetic susceptibility measurements by the Gouy method show these complexes to be diamagnetic.

Introduction

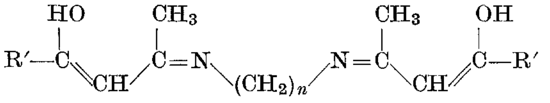
Dioxouranium(VI) complexes of bibasic tetradentate *Schiff* bases of the type $UO_2(SB)$ [where SB^{-2} is the dianion of the *Schiff* base, bis(salicylidene) ethylenediamine and bis(o-hydroxyacetophenone) ethylenediimine] were first reported by *Pfeiffer* et al.[1] in 1937, *Poddar* et al.[2] as well as Pasini et al.[3] described the synthesis of heptaco-ordinated adducts of the type $UO_2(SB)L$ (where L is the solvent molecule such as ethanol, pyridine, *DMF* etc.) and in these complexes the anions of the *Schiff* base molecules are coordinated to the central uranium atom.

In previous communications[4, 5] from these laboratories, dioxouranium(VI) complexes of monobasic bidentate and bibasic tridentate *Schiff* bases were reported. In this paper we report the synthesis and important properties of the *Schiff* base complexes of bibasic tetradentate *Schiff* bases (I and II):



I

(where R=H or CH_3 and n = 2 or 3)



II

(where R′ = CH_3 or C_6H_5 and n = 2 or 3)

It may be noted that in these complexes, the molecules and not the anions of the *Schiff* base are coordinated with the central metal ion as in many other dioxouranium complexes[1–3] reported earlier.

Experimental

Materials: Absolute ethanol, acetone (Merck), dimethylformamide (*DMF*), nitrobenzene were purified as reported earlier[4, 5]. Dioxouranium(VI) nitrate hexahydrate (B.D.H.) was used without further purification.

Preparation of Schiff Bases

The *Schiff* bases used in these reactions were prepared by the condensation of aldehyde with amine in the requisite amount as reported earlier[6–8]. These were crystallized before use in ethanol or water as indicated in table 1.

Synthesis of Dioxouranium(VI)—Schiff Base Complexes

These were synthesized by adding a calculated amount of the *Schiff* base in acetone and/or ethanol to the dioxouranium(VI) nitrate hexahydrate in the same solvent. The yellow orange solid, which separated out was collected by filtration, washed with acetone and/or ethanol and dried in vacuo. The details of synthesis and physical characteristics of the complexes are recorded in table 2.

Analyses and Physical Measurements

Uranium and nitrogen were estimated as described earlier[4, 5]. Carbon and hydrogen were estimated by Australian microanalytical services, Australia.

The magnetic susceptibility at the room temperature (30 ± 1 °C) in the solid state was measured by the *Gouy* method. Melting points were determined in sealed tubes (Table 2).

Infrared spectra were recorded in Nujol mulls and KBr optics with a Perkin-Elmer 337 grating infra red spectrophotometer in the 4,000 to 400 cm^{-1} region.

Molar conductance measurements were made in nitrobenzene and *DMF* at 30 ± 1 °C using a Tesla RLC.

Results and Discussion

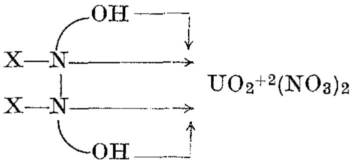
Schiff base dioxouranium(VI) complexes, which are isolated as yellow to orange solids, are mostly insoluble in organic solvents such as acetone, ethanol and benzene. These are stable against light and atmosphere and decompose at ≈ 200 °C. All these have been found to be diamagnetic and their magnetic susceptibility measurements are recorded in table 3.

Table 1. *Schiff Bases*

Schiff base*	Recryst.	Colour	M.P., °C
1. Bis-(salicylidene)ethylenediamine, $C_{16}H_{16}N_2O_2$	*Et*OH	yellow	138–140
2. Bis-(salicylidene)-1,3-propylenediamine, $C_{17}H_{18}N_2O_2$	*Et*OH	yellow	52–53
3. Bis-(o-hydroxyacetophenone)-ethylenediimine, $C_{18}H_{20}N_2O_2$	*Et*OH	yellow	182–190
4. Bis-(o-hydroxyacetophenone)-1,3-propylenediimine, $C_{19}H_{22}N_2O_2$	*Et*OH	yellow	128–130
5. Bis-(2,4-pentanedione)-ethylenediimine, $C_{12}H_{20}N_2O_2$	water	straw	116–118
6. Bis-(2,4-pentanedione)-1,3-propylenediimine, $C_{13}H_{22}N_2O_2$	water	straw	46–47
7. Bis-(benzoylacetone)-ethylenediimine, $C_{22}H_{24}N_2O_2$	*Et*OH	white	180–181
8. Bis-(benzoylacetone)-1,3-propylenediimine, $C_{23}H_{26}N_2O_2$	*Et*OH	white	108–110

* Formulas checked by CH and N determination.

Due to the presence of the donor system HO—NX—NX—OH, these *Schiff* bases offer four possible sites of coordination and the resulting 1 : 1 *Schiff* base complexes may be structurally represented as indicated below:



(where HO—NX—NX—OH represents the *Schiff* base molecule).

Table 2. *Reactions of Dioxouranium(VI) nitrate hexahydrate with the bibasic tetradentate Schiff base in 1 : 1 molar ratio*

	Reactants		Solvent medium	Solid product, yield (g) and colour	Decomposition Temperature, °C
	$UO_2(NO_3)_2 \cdot 6\ H_2O$ (g)	*Schiff* base (SBH_2) (g)			
1.	2.97	$C_{16}H_{16}N_2O_2$ 1.58	Acetone	$UO_2(NO_3)_2(C_{16}H_{16}N_2O_2)$ * 3.48 Yellow orange	208–212
2.	1.78	$C_{17}H_{18}N_2O_2$ 1.00	Acetone	$UO_2(NO_3)_2(C_{17}H_{18}N_2O_2)$ * 1.92 Orange	212–215
3.	1.58	$C_{18}H_{20}N_2O_2$ 0.93	Acetone	$UO_2(NO_3)_2(C_{18}H_{20}N_2O_2)$ * 2.05 Yellow orange	249–251
4.	1.44	$C_{19}H_{22}N_2O_2$ 0.89	Acetone	$UO_2(NO_3)_2(C_{19}H_{22}N_2O_2)$ * 2.02 Yellow orange	268–272
5.	3.34	$C_{12}H_{20}N_2O_2$ 1.49	Ethanol, Acetone	$UO_2(NO_3)_2(C_{12}H_{20}N_2O_2)$ * 4.04 Yellow	204–205
6.	1.90	$C_{13}H_{22}N_2O_2$ 0.90	Ethanol, Acetone	$UO_2(NO_3)_2(C_{13}H_{22}N_2O_2)$ * 2.12 Yellow	224–226
7.	0.87	$C_{22}H_{24}N_2O_2$ 0.61	Acetone	$UO_2(NO_3)_2(C_{22}H_{24}N_2O_2)$ * 1.14 Yellow orange	238–242
8.	3.17	$C_{23}H_{26}N_2O_2$ 2.28	Acetone	$UO_2(NO_3)_2(C_{23}H_{26}N_2O_2)$ * 4.25 Yellow orange	188–192

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* Composition ascertained by analysis (U, N).

Conductance Measurements

The stoichiometry of these complexes is also confirmed by conductometric titrations of the *Schiff* base with dioxouranium(VI) nitrate hexahydrate in acetone and/or ethanol medium (Fig. 1). Only one sharp bend corresponding to the 1 : 1 molar ratio has been obtained and this suggests the formation of $UO_2(NO_3)_2(SBH_2)$ types of derivatives. Conductometric titrations of the *Schiff* bases derived from o-hydroxyacetophenone, and dioxouranium(VI) nitrate hexahydrate could not be successfully carried out due to the appearence of a solid phase during the titration and also due to the very little change in the conductivity before the equilibrium point. These reactions can be represented by the following equations:

Table 3. *Some Physico-chemical Properties of Schiff Base Complexes of Dioxouranium(VI)*

	Compound	Molar Conductance in (ohm^{-1} cm^2 mole^{-1})		Magnetic Susceptibility	
		Nitrobenzene	*DMF*	Specific susceptibility $-\chi_s \times 10^{-6}$ (c.g.s.)	Molar susceptibility $-\chi_m \times 10^{-6}$ (c.g.s.)
1.	$UO_2(NO_3)_2(C_{16}H_{16}N_2O_2)$	0.74	129.3	0.1203	79.7
2.	$UO_2(NO_3)_2(C_{17}H_{18}N_2O_2)$	2.33	121.0	0.1310	88.6
3.	$UO_2(NO_3)_2(C_{18}H_{20}N_2O_2)$	1.27	135.2	0.2058	142.1
4.	$UO_2(NO_3)_2(C_{19}H_{22}N_2O_2)$	2.52	142.3	0.2100	148.0
5.	$UO_2(NO_3)_2(C_{12}H_{20}N_2O_2)$	1.84	128.7	0.1328	82.1
6.	$UO_2(NO_3)_2(C_{13}H_{22}N_2O_2)$	4.30	135.3	0.1350	85.4
7.	$UO_2(NO_3)_2(C_{22}H_{24}N_2O_2)$	5.9	145.8	0.1790	132.9
8.	$UO_2(NO_3)_2(C_{23}H_{26}N_2O_2)$	4.64	140.6	0.1822	137.8

$$HOC_6H_4C(R)=N(CH_2)_nN=C(R)C_6H_4OH + UO_2(NO_3)_2 \cdot 6\,H_2O \xrightarrow[-6\,H_2O]{} [HOC_6H_4C(R)=N(CH_2)_nN=C(R)C_6H_4OH]UO_2^{+2}(NO_3)_2$$

(where $R = H$ or CH_3 and $n = 2$ or 3).

$$HOC(R')=CHC(CH_3)=N(CH_2)_nN=C(CH_3)CH=C(R')OH + UO_2(NO_3)_2 \cdot 6\,H_2O \xrightarrow[-6\,H_2O]{} [HOC(R')=CHC(CH_3)=N(CH_2)_nN=C(CH_3)CH=C(R')OH]UO_2^{+2} \cdot (NO_3)_2$$

(where $R' = CH_3$ or C_6H_5 and $n = 2$ or 3).

Molar conductance values of the resulting complexes in nitrobenzene ($10^{-3}M$) have been found to be below 6 ohm^{-1} cm^2 mole^{-1} and thus

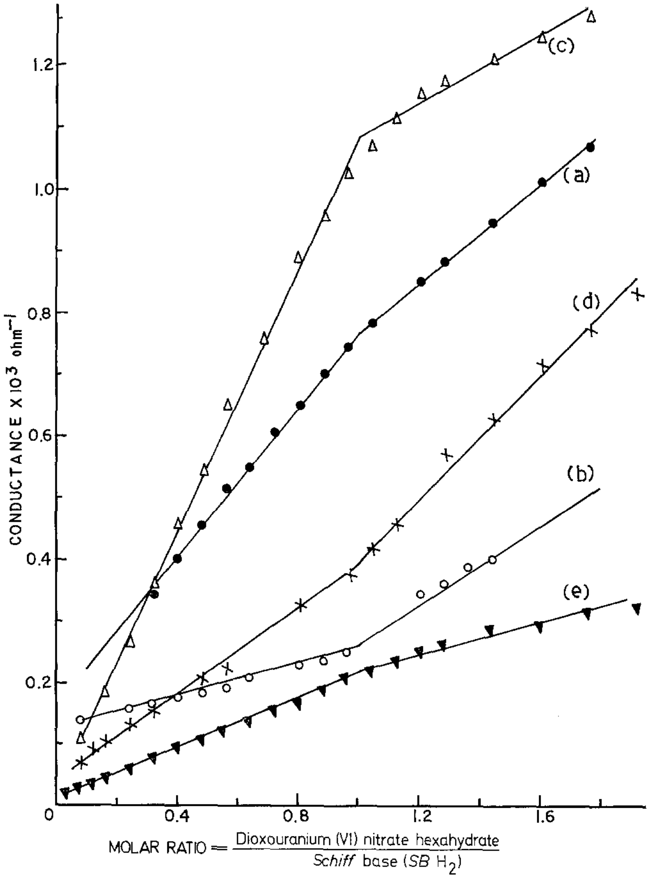

Fig. 1. Conductometric titrations of *Schiff* bases with dioxouranium(VI) nitrate hexahydrate. (*a*) Bis-(2,4-pentanedione) ethylene diimine (0.025*M*)-dioxouranium(VI) nitrate hexahydrate (0.5*M*) in ethanol. (*b*) Bis-(2,4-pentanedione)-1,3-propylene diimine (0.0125*M*)-dioxouranium(VI) nitrate hexahydrate (0.25*M*) in acetone. (*c*) Bis-(salicylidene) ethylene diamine (0.0125*M*)-dioxouranium(VI) nitrate hexahydrate (0.25*M*) in acetone. (*d*) Bis-(salicylidene)-1,3-propylene diamine (0.025*M*)-dioxouranium(VI) nitrate hexahydrate (0.5*M*) in acetone. (*e*) Bis-(benzoyl acetone)-1,3-propylene diimine (0.0125*M*)-dioxouranium(VI) nitrate hexahydrate (0.25*M*) in acetone

showing non-electrolytic behaviour. However, the conductance values of these complexes in *DMF* are in the range of 120 to 150 ohm^{-1} cm^2 mole^{-1}, which correspond nearly to 1 : 2 electrolyte. This shows that a co-ordinated solvent like *DMF* is able to displace the weakly co-ordinated nitrate group as reported earlier[4, 9] also.

Table 4. *Infrared Frequencies (in* cm^{-1}*) of Schiff Base and their Dioxouranium(VI) Complexes*

Compound	ν OH & ν NH	ν C=N	ν NO_2 asymmetric	ν NO_2 symmetric	ν NO_2 bending	ν UO_2^{+2} asymmetric	ν UO_2^{+2} symmetric
$C_{16}H_{16}N_2O_2$	3380 wb	1630 s, 1650 m	—	—	—	—	—
$UO_2(NO_3)_2(C_{16}H_{16}N_2O_2)$	3550–3400 sb	1640 s	1540 vs	1270 vs	805 m	910 vs	865 m
$C_{17}H_{18}N_2O_2$	3300 wb	1630 s	—	—	—	—	—
$UO_2(NO_3)_2(C_{17}H_{18}N_2O_2)$	3400 mb	1650 m	1540 sh	1280 vs	805 m	900 vs	860 sh
$C_{18}H_{20}N_2O_2$	2950–2850 sb	1607 vs	—	—	—	—	—
$UO_2(NO_3)_2(C_{18}H_{20}N_2O_2)$	3550–3400 sb	1605 vs	1530 sh	1280 vs	805 m	915 vs	850 s
$C_{19}H_{22}N_2O_2$	2950–2850 sb	1617 vs	—	—	—	—	—
$UO_2(NO_3)_2(C_{19}H_{22}N_2O_2)$	3550–3350 mb	1615 vs	1540 vs	1275 vs	810 m	920 s	850 vs
$C_{12}H_{20}N_2O_2$	3150 mb	1610 s	—	—	—	—	—
$UO_2(NO_3)_2(C_{12}H_{20}N_2O_2)$	3500–3400 mb	1610 s	1525 sh	1280 vs	810 m	915 vs	865 sh
$C_{13}H_{22}N_2O_2$	3100 mb	1601 s	—	—	—	—	—
$UO_2(NO_3)_2(C_{13}H_{22}N_2O_2)$	3500–3400 mb	1601 s	1540 vs	1270 vs	810 m	915 vs	865 sh
$C_{22}H_{24}N_2O_2$	3150 mb	1603 vs	—	—	—	—	—
$UO_2(NO_3)_2(C_{22}H_{24}N_2O_2)$	3500–3400 sb	1600 vs	1530 s	1275 vs	810 w	920 vs	850 sh
$C_{23}H_{26}N_2O_2$	3100 mb	1600 vs	—	—	—	—	—
$UO_2(NO_3)_2(C_{23}H_{26}N_2O_2)$	3550–3450 sb	1600 vs	1530 s	1275 vs	805 m	915 vs	870 m

Infra-Red Spectra

The IR spectra of the *Schiff* bases and their corresponding dioxouranium(VI) derivatives have been recorded (Tab. 4) and the important features may be summarized as below:

(i) In the case of bibasic tetradentate *Schiff* base, no absorption band appears beyond 3,150 cm^{-1}. On account of both types of hydrogen bonding intermolecular (O—H ... O) as well as intramolecular (O—H ... N), the frequency of the hydrogen bonded OH is probably lowered to a considerable extent and overlaps with the ν CH vibrations exhibiting a broad band in the region 3,150–2,950 cm^{-1}. *Freedmann*[10], has reported a similar absorption band in the region 2,800–2,600 cm^{-1} in the spectra of bis(salicylidene) ethylenediamine. However, in the resulting derivatives, a strong band is observed in the region 3,500–3,350 cm^{-1} and this may be assigned to the absorption band of the ν O—H or ν N—H groups. This further shows that the molecules of the *Schiff* bases are coordinated to the central uranium atom and not to their anions.

(ii) A strong band at $\approx$ 1,620 cm^{-1} is observed in the *Schiff* bases, which may be assigned to the azomethine (>C=N—) grouping. No appreciable shift in this band is observed on coordination to the uranium atom.

(iii) The infrared spectra of these complexes show two strong absorption peaks in 1,540–1,480 cm^{-1} and $\approx$ 1,280 cm^{-1} region and a medium intensity peak in the $\approx$ 800 cm^{-1} region and this may be assigned to the ν_4 (NO_2 asymmetric stretching), ν_1 (NO_2 symmetric stretching) and ν_6 (NO_2 deformation vibrations) of the coordinated nitrate group[11].

(iv) The dioxouranium(VI) ion exhibits three vibrational frequencies: the symmetric (ν_1) and asymmetric (ν_3) stretching and a bending (ν_2) frequency. In the present cases, only two bands in the region 950–900 cm^{-1} and 865–850 cm^{-1} are observed and these may be assigned to the ν_3 and ν_1 vibrations respectively. The band due to ν_2 vibration could not be noted as it appears in the lower region.

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