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Complexes of Dioxouranium(VI) with Zwitter-Ionic Forms of Bi- and Tetra-dentate *Schiff* Bases

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Potentially bi- and tetra-dentate *Schiff* bases derived from salicylaldehyde react with hydrated uranyl salts to give complexes: $UO_2H_2LX_2$, $UO_2H_2L'X_2$ and $UO_2(HL)_2X_2$ [H_2L = N,N'-propane-1,3-diylbis(salicylideneimine), H_2L' = N,N'-ethylenebis(salicylideneimine) and HL = N-phenylsalicylideneimine; X^- = Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, and NCS^-]. Because of marked spectral similarities with the structurally known $Ca(H_2L)(NO_3)_2$, the *Schiff* bases are coordinated through the negatively charged phenolic oxygen atoms and not the nitrogen atoms of the azomethine groups which carry the protons transferred from phenolic groups on coordination. Halide, nitrate, perchlorate and thiocyanate groups are covalently bonded to the uranyl ion, resulting a 6-coordinated uranium ion in the halo and thiocyanato complexes and 8-coordinated in nitrato and perchlorato complexes.

(Keywords: Complexes; Dioxouranium; Infra red; Schiff base complexes; Zwitter ion)

Komplexe von Dioxouranyl(VI) mit zwitterionischen Formen von zwei- und vierzähnigen Schiff-Basen

Von Salizylaldehyd abgeleitete zwei- und vierzähnige *Schiff*-Basen reagieren mit hydratisierten Uranylsalzen zu Komplexen folgenden Typs: $UO_2H_2LX_2$, $UO_2H_2L'X_2$ und $UO_2(HL)_2X_2$ [H_2L = N,N'-Propan-1,3-diyl-bis(salicylidenimin), H_2L' = N,N'-Ethylen-bis(salicylidenimin) und HL = N-Phenylsalicylidenimin; X^- = Cl^-, Br^-, I^-, NO_3^-, ClO_4^- und NCS^-]. Auf Grund eindeutiger spektraler Ähnlichkeiten mit dem bekannten $Ca(H_2L)(NO_3)_2$ wird auf Koordination über die negativ geladenen phenolischen Sauerstoffatome (und nicht über die Azomethin-Stickstoffe) geschlossen. Die Anionen X^- sind kovalent an das Uranyl-Ion gebunden; damit ergibt sich ein hexakoordiniertes Uranyl-Ion für die Halogen- und Thiocyanat-Komplexe und Oktakoordination für die Nitrat- und Perchlorat-Komplexe.

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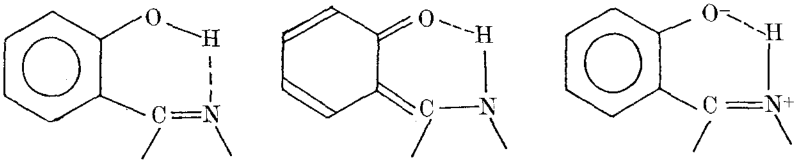
Introduction

There have been many reports[1–10] of U(IV) and U(VI) complexes with non-ionised *Schiff* bases mainly derived from salicylaldehyde, but the mode of coordination of the non-ionised base has been the subject of much controversy. *Doretti* et al.[2–4] suppose that the *Schiff* base is coordinated through the azomethine nitrogen atoms only; evidence for this came from infrared spectroscopy. Whereas others[5–10] interpreted essentially identical infrared results in terms of coordination through both nitrogen and phenolic oxygen atoms. Until recently no crystallographic work was reported to resolve the problem.

The crystal structure[11] of $Ca(H_2L)(NO_3)_2$, (H_2L = see abstract) has been determined recently, in which the *Schiff* base is best described by the tautometer **c**, namely, the charge separated (zwitter-ionic) form as well as two other possible tautomeric conversions, an enol-imine **a** to ketoenamine **b** which was reported[12]. Co-ordination takes place through the negatively charged phenolic oxygen atoms (and not the nitrogen atoms of the azomethine groups). The changes observed on comparing the infrared spectra of this compound and the free *Schiff* base in the C=N stretching region are the same for the present work and the other[1–10] complexes.



a **b** **c**

Experimental

Materials. Hydrated $UO_2(NO_3)_2$ and UO_2Cl_2 were (BDH) reagent grade and used as supplied. Ethanolic solution of UO_2Br_2, UO_2I_2, $UO_2(NCS)_2$ and $UO_2(ClO_4)_2$[13–15] were obtained by metathesis of $UO_2(NO_3)_2$ or UO_2Cl_2 with $BaBr_2$, BaI_2, KNCS and $AgClO_4$ respectively, and filtering off the insoluble metal nitrate or chloride and silver chloride. The ligands were prepared by routine method[16].

Synthesis of the Complexes. Most of the complexes were prepared by the addition of the stoicheiometric amount of the uranyl salt in hot tetrahydrofuran (*THF*) or ethanol to the solution of the ligand in the same solvent. A yellow precipitate formed almost immediately, this was filtered off and washed with *THF* several times and dried ($CaCl_2$). The ionised compounds were prepared by refluxing the stoichiometric amount of the hydrated uranyl acetate and the *Schiff* base in dimethylformamide (*DMF*) for two h. An orange precipitate was formed, this was filtered off and washed with ether and dried ($CaCl_2$). The compounds are not soluble in common organic solvents, only dissolve in *DMF* and dimethylsulphoxide (*DMSO*) and sparingly in hot alcohol.

Measurements. The infrared spectra in the region 4 000-200 cm^{-1} were recorded by using a Perkin-Elmer 598 as nujol and hexachlorobutadien mulls. Conductance measurements were carried out at room temperature (300 °K) in propanol and *DMF* solution (10^{-3} *M*) with a conductivity type CDM2e No. 207 421 produced by a radiometer company in Copenhagen.

Analysis. Uranium was determined complexicometrically[17]. Halides and thiocyanate as silver halide and silver thiocyanate. Nitrate and perchlorate analysed by precipitation with nitron[18]. The nitrogen was estimated by a standard method[17].

Results and Discussion

21 *Schiff* base complexes of dioxouranium(VI) described here are presented with analytical data and millimolar conductance in Table 1. The low molar conductivity in propanol solution indicating of the non-electrolytic[19] behaviour of the complexes in this solvent, whereas the high values observed in dimethylformamide solution show considerable dissociation due to some ligand exchange between the strong donor *DMF* and the weakly bonded anions in the coordination sphere of the uranyl ion in this solvent[20].

Infrared spectroscopy

(a) 4 000-2 500 cm^{-1}

The free *Schiff* base shows a strong intramolecular hydrogen bonding (OH...N) which gives rise to a broad absorption near 2 700 cm^{-1} (Ref.[21]). This band shifts to 3 000 cm^{-1} in the complexes as hydrogen bonding arrangements change ($O \ldots H^+N$)[11]. On comparing the infrared spectra of the complexes with the fully ionised *Schiff* base compounds, there is neither absorption near 2 700 cm^{-1} nor at 3 000 cm^{-1} only the aliphatic and the aromatic C—H vibrations observed; suggesting the coordination of the neutral ligands in these series of non-ionised *Schiff* base complexes.

(b) 1 700-600 cm^{-1}

The C=N stretching vibration for the free ligands and the complexes compared with $Ca(H_2L)(NO_3)_2$ in Table 2 and Fig. 1. The other compounds had very similar spectra in this region[1-11], the C=N stretching vibration of the free base increased in frequency (by 5-30 cm^{-1}) on complex formation. It has been shown[22] that $C=N^+$ groups have in general higher frequencies than the parent C=N groups,

Table 1. *Analytical data and millimolar conductance data of dioxouranium complexes*

Complexes	$M\%$	$X\%$	N%	Molar Conductance* (Ω^{-1} cm^2 mol^{-1}) in n-propanol	in DMF
$UO_2(H_2L')Cl_2$	38.85 (39.05)	11.52 (11.63)	4.45 (4.59)	10.50	34.22
$UO_2(H_2L')Br_2$	34.00 (34.12)	22.70 (22.91)	3.85 (4.01)	19.20	113.00
$UO_2(H_2L')I_2$	29.80 (30.03)	31.75 (32.02)	3.70 (3.53)	24.60	150.00
$UO_2(H_2L')(NO_3)_2$	35.75 (35.92)	18.50 (18.71)	—	16.30	137.00
$UO_2(H_2L')(ClO_4)_2$	32.10 (32.27)	26.72 (26.96)	3.55 (3.79)	11.30	110.00
$UO_2(H_2L')(NCS)_2$	36.20 (36.35)	17.50 (17.73)	8.45 (8.56)	16.10	75.60
UO_2L' DMF	38.90 (39.03)	—	6.75 (6.89)	1.30	1.22
$UO_2(H_2L)Cl_2$	37.90 (38.17)	11.40 (11.36)	4.35 (4.49)	8.60	24.50
$UO_2(H_2L)Br_2$	33.25 (33.40)	22.20 (22.42)	3.80 (3.93)	20.50	102.00
$UO_2(H_2L)I_2$	29.35 (29.51)	31.20 (31.46)	3.35 (3.47)	31.50	100.00
$UO_2(H_2L)(NO_3)_2$	34.95 (35.17)	18.10 (18.32)	—	25.40	128.00
$UO_2(H_2L)(ClO_4)_2$	31.45 (31.67)	26.30 (26.46)	3.60 (3.72)	22.30	99.70
$UO_2(H_2L)(NCS)_2$	35.30 (35.58)	17.10 (17.36)	8.15 (8.38)	19.40	67.30
UO_2L DMF	37.85 (38.16)	—	6.59 (6.73)	0.42	1.15
$UO_2(HL)_2Cl_2$	32.10 (23.36)	9.80 (9.64)	3.65 (3.80)	12.20	21.60
$UO_2(HL)_2Br_2$	28.65 (28.87)	19.50 (19.38)	3.20 (3.39)	24.10	87.50
$UO_2(HL)_2I_2$	25.70 (25.92)	27.45 (27.63)	2.90 (3.05)	37.20	107.00
$UO_2(HL)_2(NO_3)_2$	29.95 (30.18)	15.50 (15.72)	—	13.70	120.00
$UO_2(HL)_2(ClO_4)_2$	27.37 (27.56)	22.85 (23.03)	3.10 (3.24)	19.20	25.20
$UO_2(HL)_2(NCS)_2$	30.15 (30.49)	14.60 (14.87)	6.90 (7.17)	15.20	80.40
UO_2L_2	35.55 (35.82)	—	4.10 (4.22)	2.20	14.30

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* Millimolar conductance of the known compound $CaH_2L(NO_3)_2$ in n-propanol and DMF solutions were 8.5 and 110 (Ω^{-1} cm^2 mol^{-1}) respectively.

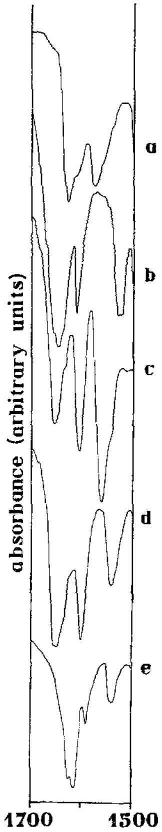

Fig. 1. Infra-red spectra for the ligand and the metal complexes in the region 1 700—1 500 cm^{-1} for *a* H_2L; *b* $CaH_2L(NO_3)_2$; *c* $UO_2H_2L(NO_3)_2$; *d* $UO_2H_2LI_2$; *e* UO_2L

thus the results are consistent with the presence of charge-separated forms, and therefore these and the other complexes[1–11] are likely to be structurally related in that the coordination takes place through the negatively charged phenolic oxygen atoms rather than the positively charged nitrogen atoms of the azomethine groups. A sharp absorption at 1 280 cm^{-1} assignable to C—O stretching vibration in the free ligands changes little on complex formation (Table 2). The C—O stretching vibration must include considerable contribution from the skeletal vibrations of the aromatic ring, and because the vibration changed little in the complexes it was suggested[11] that the bonding arrangements of the oxygen atoms were the same in the free ligands and the complexes.

Table 2. *Selected infrared bands (cm^{-1}) of the ligands and dioxouranium(VI) complexes*

Complexes	C=N	C—O	ν_3UO_2	ν_2UO_2	U—O-ligand	other bands
H_2L	1 630 s	1 280 s	—	—	—	
$CaH_2L(NO_3)_2$	1 645 vs	1 280 m	—	—	—	
$UO_2H_2L(NO_3)_2$	1 655 vs	1 280 m	920 s	260 s	450 s	400 s U—O_2NO
$UO_2H_2LCl_2$	1 660 vs	1 290 s	920 vs	—	405 s	260 s U—Cl
$UO_2H_2LBr_2$	1 655 vs	1 285 s	900 s	255 s	400 s	
$UO_2H_2LI_2$	1 650 vs	1 280 s	895 s	260 s	400 s	
$UO_2H_2L(NCS)_2$	1 648 vs	1282 bb	900 s	260 s	410 s	
$UO_2H_2L(ClO_4)_2$	1 655 vs	1 285 s	900 vs	260 s	400 s	
$UO_2L\,DMF$	1 625 vs	1 300 vs	900 vs	240 m	370 vs	450 s U—N
H_2L'	1 630 s	1 280 s	—	—	—	
$UO_2H_2L'(NO_3)_2$	1 650 vs	1 280 m	920 vs	250 s	460 s	380 s U—O_2NO
$UO_2H_2L'Cl_2$	1 650 vs	1 290 s	920 vs	—	365 s	250 s U—Cl
$UO_2H_2L'Br_2$	1 660 vs	1 280 s	910 vs	250 s	390 s	
$UO_2H_2L'I_2$	1 640 vs	1 285 m	910 vs	240 m	370 s	
$UO_2H_2L'(NCS)_2$	1 635 vs	1 280 s	920 vs	250 m	380 s	
$UO_2H_2L'(ClO_4)_2$	1 640 vs	1 285 vs	890 vs	260 s	375 s	
$UO_2L'\,DMF$	1 620 vs	1 310 s	900 vs	260 s	380 s	460 s U—N
HL	1 620 s	1 280 s	—	—	—	
$UO_2(HL)_2(NO_3)_2$	1 650 vs	1 260 s	930 vs	255 s	450 s	300 s U—O_2NO
$UO_2(HL)_2Cl_2$	1 650 vs	1 290 vs	925 vs	—	350 s	240 s U—Cl
$UO_2(HL)_2Br_2$	1 640 vs	1 280 s	920 vs	250 s	330 s	
$UO_2(HL)_2I_2$	1 640 vs	1 275 s	920 vs	250 s	335 m	
$UO_2(HL)_2(NCS)_2$	1 630 vs	1 290 m	890 s	260 s	330 m	
$UO_2(HL)_2(ClO_4)_2$	1 640 vs	1 280 s	920 vs	250 s	340 m	

s, strong; b, broad; v, very; m, medium.

On examining the infrared spectra of these complexes and the fully ionised *Schiff* base compounds one can see that the $C=N$ stretching frequency of the ionised ligand has fallen on complex formation and the C—O stretching frequency increased to a higher frequency (Table 2 and Fig. 1). Therefore the results are consistent with those of the structurally known ionised compounds[23–24] where the coordination took place via oxygen atoms and the nitrogen atoms of the azomethine groups.

Nitrato Complexes. The infrared spectra of three nitrato complexes showed no strong and broad absorption band near 1 380 cm^{-1} where the free nitrate ion is known to absorb[25]. However on comparing the spectra of the free ligands and the halide complexes with the nitrato complexes, the nitrate spectra were dominated by the strong absorption from ν_1 (1 480-1 500 cm^{-1}), ν_2 (1 020-1 030 cm^{-1}), ν_4 (1 280-1 300 cm^{-1}) and ν_6 (810-820 cm^{-1}) of the nitrato group in C_{2v} symmetry[25]. Since these spectra were essentially the same as that[11] of $Ca(H_2L)(NO_3)_2$ and the other[25–26] compounds, the nitrato groups are bidentate in these series of *Schiff* base complexes. The weak fundamentals ν_3 and ν_5 were masked by the strong ligand absorption (700-800 cm^{-1}).

Thiocyanato Complexes. The thiocyanato complexes exhibited very strong absorption band between 2 050-2 100 cm^{-1} corresponding to previous studies on the empirical ranges for the observed bands[27] for both S-bonding (thiocyanato-) or N-bonding (isothiocyanato-) indicated that all the complexes contain N-bonded thiocyanate groups. The same conclusion came from the consideration of the C—S stretching (800-830 cm^{-1}) and N—C—S deformation (460-480 cm^{-1}) and thus the class A character of the uranyl ion is emphasized.

Perchlorato Complexes. The two perchlorato complexes: $UO_2H_2L(ClO_4)_2$ and $UO_2H_2L'(ClO_4)$ showed strong absorption bands at 1 150, 1 100, 1 030, 965, 945, 620, 650, 470 cm^{-1} indicating that the perchlorato group must act as a bidentate ligand on C_{2v} symmetry[28] in these compounds. Since in $UO_2(HL)_2(ClO_4)_2$ the strong ligand absorption bands obscured the perchlorate absorption bands in the region interested it was not possible to draw any conclusion on the bonding mode of the perchlorate group, only the low molar conductivity of the said compound indicates the non-ionic character of the perchlorate group.

The infrared bands due to the UO_2^{+2} group are observed near 900 and 800 cm^{-1} as strong and weak bands corresponding to asymmetric stretching frequency ν_3 (UO_2) and the symmetric stretching frequency ν_1 (UO_2) respectively. The bending vibrations, ν_2 (OUO) are obtained at

250-270 cm^{-1} region and they are listed in Table 2. These observations indicate that the UO_2^{+2} moiety in the present compounds is virtually linear.

The two additional bands found near 1660 cm^{-1} and 650 cm^{-1} in the spectra of the ionised *Schiff* base compounds, UO_2LDMF and $UO_2L'DMF$ were assigned to the coordinated dimethylformamide[29] in these compounds.

(c) 600-200 cm^{-1}

Halide Complexes. The far i.r. spectra of the chloro complexes showed a strong absorption band in the region of the U—Cl[30-31] stretching vibration between 240-260 cm^{-1} (Table 2). We were not able to find the absorption bands due to the other metal-halide (U—Br and U—I) stretching frequencies which probably lie below 200 cm^{-1} (Ref.[31]).

The non-ligand bands occuring in 450-350 cm^{-1} and 300-400 cm^{-1} in the spectra of the non-ionised *Schiff* base complexes may be tentatively assigned to ν (U—O-ligand) and ν ($U—O_2NO$) modes respectively[31] while an additional band found at 400-500 cm^{-1} in the spectra of the ionised compounds could be attributed to the U—N stretching frequency (see Table 2).

Conclusion

On the basis of the properties of the complexes studied some features can be emphasised: (a) the non-ionised *Schiff* base coordinated through the negatively charged phenolic oxygen atoms only. (b) The halo and thiocyanato groups bonded unidentaly while the nitrato and perchlorato groups are bidentate, suggesting the 6-coordinated uranium in halo and iso-thiocyanato and 8-coordinated in nitrato and perchlorato complexes.

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