MIXED URANYL COMPLEXES CONTAINING MULTIDENTATE SCHIFF BASES

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Abstract—A new class of mixed ligand complexes of uranium(VI) is reported. The complexes have the stoicheiometry $[UO_2L(A)]$, where L is a potentially tridentate or quadridentate Schiff base anion and A is an anion which may act as unidentate or bidentate ligand. The configurations of these complexes have been investigated by means of ¹H NMR, i.r. and u.v. spectroscopy. The complexes contain hepta-coordinated uranium with irregular pentagonal bipiramidal geometry. Conductivity measurements indicate that the complexes are non-electrolytes even in the presence of a large excess of triphenylphosphine oxide. Studies on the relative stabilities of the U–A bonds are reported. The influence of the anion on the stretching frequency of the N–H group of the Schiff base and on the antisymmetric stretching mode (ν_3) of the O–U–O group has been determined.

INTRODUCTION

THERE have been many reports on the relationship between physical properties (particularly i.r. and Raman spectra), structure and the nature of the metal-ligand bond in complexes [1-3]. Three distinct bonding modes of NO₃ and CH₃COO⁻ ligands are known to occur: unidentate, bidentate or bridging. While for the acetato complexes it is easy to distinguish among these configurations, in the nitrato complexes the D_{3h} symmetry of the free ion is lowered to C_{2v} in all types of coordination and so it is not possible to distinguish these three modes of coordination by means of the selection rules alone. It has been suggested, for the nitrato complexes, that the doubly degenerate asymmetric ν_3 stretching vibration (E' in the D_{3h} symmetry of the free nitrate ion [4]) should split upon coordination [5], since the symmetry of the nitrate would be reduced. The extent of splitting has been used as a guide to the coordination mode [6, 7]. Unfortunately, however, this criterion is highly unreliable[8]. The unidentate nitrato groups in Cs₂[U(NO₃)₆] gave almost the same splitting as the bidentate nitrato groups in Rb[UO₂(NO₃)₃][9]. In this case the metal-oxygen stretching bands in the far-i.r. may be more useful in distinguishing unidentate from bidentate coordina-

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tion [10]. Raman polarisation data also have been used to distinguish uni- and bi-dentate nitrato groups [5a, b].

In the present work these problems have been reinvestigated using uranyl complexes containing quadridentate Schiff base ligand of the type shown in Fig. 1. These are compared with analogous containing tridentate and bidentate Schiff base ligands.

The far-i.r. region has been studied in order to identify the uranium-halogen stretching frequencies and the δ (O-U-O) bending frequency. In addition, we report some observations on the stability of U-A bond toward attack by neutral unidentate ligands containing oxygen and nitrogen as donor atoms, and on the ability of C=O or C=S groups of salicylaldehydate, tropolonate, diethyldithiocarbamate to displace the N(CH₃)₂ group from its coordination site.

EXPERIMENTAL

Materials

The uranyl salts were C.Erba reagent grade chemicals. Absolute ethanol and commercial salicylaldehyde and amines were used without further purification. Unidentate ligands as Ph₃PO were prepared according to literature procedure[11].

The complexes $[UO_2(CH_3COO)_2(Ph_3PO)_2]$, $[UO_2((NO_3)_2 (Ph_3PO)_2]$, $[UO_2(trop)_2(MeOH)]$, $[UO_2(HL_c)_2A_2]$ $(HL_c = o HO-C_6H_4CH=NCH_2CH_3CH_3$, $A = CH_3COO^+$, NO_3^- , $CI^-)$ were prepared according to literature methods [12–15] and their purity was established by i.r. and NMR spectroscopy, melting points, and elemental analyses. TIOEt was obtained from



Fig. 1.

Schilling in reagent grade. The Tl¹ derivatives of salicylaldehyde were obtained as pale yellow crystals by mixing an equimolecular amount of salicylaldehyde and TlOEt in absolute ethanol. Elemental analyses were in good agreement with the formulation $C_7H_3O_2Tl$ (salTl).

Preparation of [UO₂(sal)₂EtOH]

Thallium salicylaldehyde (0.650 g, 2 mmoles) in 75 ml of absolute ethanol was added to an ethanolic solution (100 ml) of uranyl chloride (0.395 g, 1 mmole). The white precipitate (TICI) was removed by filtration and the red solution, reduced to small volume, gave red crystals.

Preparation of $[UO_2L_aX]$ $L_a = \bar{o}O-C_6H_4CH=NC_2H_4NHC_2H_4N$ $(CH_3)_2$ and $X = NO_3^-$, CI^- , CH_3COO^- , F^- , Br^-)

To 0.244 g (2 mmoles) of salicyaldehyde dissolved in 50 ml of absolute ethanol, 0.190 g (2 mmoles) of N-dimethyldiethylenetriamine were added. To the yellow resulting solution 0.080 g (2 mmoles) of sodium hydroxide were added. The solution was stirred for 1 hr at room temperature and then pured into a stoicheiometric ethanolic solution (50 ml) of the appropriate uranyl salt (2 mmoles). The resulting red solution was stirred for 2 hr; the solvent was evaporated at reduced pressure and the residue extracted with CH₂Cl₂. The solution was then reduced to small volume and cooled to 0°C. The product, crystallized as yellow-orange or red crystals, was filtered, washed with cold CH₂Cl₂, and vacuum dried.

Preparation of $[UO_2L_aX]$ (X = Cl⁻, Br⁻, I⁻, SCN⁻, sal⁻, trop⁻, dtc⁻)

0.300 g (0.53 mmoles) of the complex $[UO_2L_aNO_3]$ were dissolved in 100 ml of absolute ethanol and a large excess (tenfold) of NaX ($X = Cl^-$, Br⁻, etc.) was added. The resulting red solution was stirred at 40–50°C for 3 hr. After the solvent was removed, the residue was extracted with CH₂Cl₂. The solution was reduced to small volume and cooled to 0°C. The product separated from the solution as yellow-orange or red crystals and was filtered, washed with cold CH₂Cl₂ and vacuum dried. (In the case of complexes with salicyclaldehydato (sal⁻), tropolonato (trop⁻) or diethyl-dithiocarbamato (dtc⁻) a stoicheiometric ratio was used.)

Preparation of $[UO_2L_b(X)]$ $L_b = \overline{o}O-C_0H_4-CH=NC_2H_4N(CH_3)_2$ and $X = NO_3^-$, CH_3COO^- , $trop^-$)

The complexes were prepared by methods described above. $[UO_2L_b(trop)]$ gave red-orange crystals in good yield, but some difficulty was encountered in the preparation of the nitrate and acetate complexes. Probably more than one product was formed.

Physico-chemical measurements

I.R. spectra were recorded from KBr pellets or Nujol mulls with a Perkin-Elmer 621 Spectrophotometer operating in the range 4000-200 cm⁻¹, and with a Beckmann i.r. 11 in the range 400-70 cm⁻¹; Nujol mulls were supported between polyethylene plates.

¹H NMR spectra were obtained with a 90 MHz Bruker Spectrospin from piridine- d_5 or dimethylsulphoxide- d_6 solutions (TMS as internal standard). Conductance measurements were carried out at 25°C with a Type 3216-B LKB conductivity bridge; u.v. spectra from sym-dichloroethane solutions or KBr pellets were recorded in the range 650-240 nm with a Perkin-Elmer 356 double beam spectrophotometer.

RESULTS AND DISCUSSION

Using the quadridentate Schiff base L_a , complexes of the type $[UO_2L_aA]$ were obtained. These were soluble in most organic solvents, and stable in the solid state and in solution. Conductivity measurements have been made on some complexes ($A = NO_3^-$, CH_3COO^- , CI^- , Br^-) in CH_2Cl_2 solution. The results indicate that these complexes are non-electrolytes, suggesting that the bond between uranium and anions is essentially covalent in nature. The conductivities were not significantly affected by large excess of Ph₃PO, although some slight dissociation may be noted in the complexes containing CI^- or Br^- :

Table 1. Analytical data and physical properties of UO22+ complexes

	(——————— Н	ر ا	N	Halo	ogen	M.p.	
Complex	calcd	found	calcd	found	calcd	found	calcd	found	(°Ĉ)	Colour
$[\mathrm{UO}_2 L_a(\mathrm{NO}_3)]$	27.56	27.56	3.53	3.32	9.89	9.47			252 dec	Orange–red crystals
$[\mathrm{UO}_2 L_a(\mathrm{CH}_3\mathrm{COO})]$	31.97	31.44	4.08	4 ∙07	7.46	7.16			254-6 dec	Orange-yellow crystals
$[UO_2L_n(trop)]$	38.40	38.92	4.00	3.90	6.72	6.73			152-4	Orange powder
$[UO_2L_a(dtc)]$	33.02	33.45	4.89	4.71	8.56	8.18			15860	Orange powder
$[UO_2L_a(sal)]$	38.40	38.31	4.00	4.31	6.72	7.04			135-40 dec	Orange powder
$[UO_2L_a]$	29.82	30.33	3.82	3.79	8.03	7.84	3.63	3.87	292-4	Yellow powder
$[UO_2L_nC]$	28.91	29.32	3.70	3.71	7.78	7.54	6.58	6.58	270 dec	Yellow powder
$[\mathrm{UO}_2 L_a \mathrm{Br}]$	26.71	26.40	3.42	3.47	7.19	7.15	13.69	14.06	26466 dec	Orange-yellow powder
$[\mathrm{UO}_2 L_a \mathrm{I}]$	24.72	24.25	3.17	3.57	6.65	6.32	20.12	19-91	194°-5°	Orange-red powder
$[UO_2L_a(SCN)]$	29-89	30.35	3.56	3.84	9.96	9.76			251-3	Orange-red powder
$[UO_{1}L, (NO_{2})]$	25.23	25.68	2.87	3.15	8.03	7.94			150-152	Yellow powder
$[UO_{L}(CH_{C}OO)]$	30.00	29.75	3.46	3.35	5.38	5.29			153-5	Yellow powder
$[UO_2L_b(trop)]$	37.11	37.16	3.43	3.76	4.81	4.53			158-60 dec	Orange-red crystals
$[IIO_{1}(HL_{1})_{2}(NO_{2})_{2}]$	33.42	33.32	3.34	3.76	7.80	7.76			205-207	Yellow powder
$[UO_2(HL_c)_2C]_1$	36.09	35.78	3.61	3.93	4.21	3.97	10.67	10.34	255-227	Yellow powder
$[UO_2(HL_c)_2(CH_3COO)_2]$	40.44	40.12	4.21	4.33	3.93	4.24			146-148	Yellow powder





the uranium-anion bond is probably less covalent in the case of these complexes as already reported [16].

Two configurations may be written for the complexes containing the anions NO_3^- and CH_3COO^- both satisfying the requirement of penta-coordination [17–19].

The ¹H NMR spectra indicate that the Schiff base acts as quadridentate ligand. The spectra are similar to those obtained for the complexes containing unidentate anions as Cl⁻ or Br⁻ where the Schiff base certainly is quadridentate; the N(CH₃)₂ gives a peak at 3.28δ (in py) while the uncoordinated N(CH₃)₂ group has been found at 2.15δ in the complexes [UO₂(salenN(CH₃)₂]₂] (20) (see Table 2). These spectra bear distinct similarities to those of the complexes [UO₂(L_b)A] (see Table 2) where the geometry in the equatorial plane is reported in Fig. 3.



The i.r. data give further useful information on the coordination of the potentially bidentate anions. For the acetate anion it is rather easy to distinguish between the configuration of the type A and B (Fig. 2). If coordination occurs symmetrically both the COO stretching bands (the antisymmetric, v_{as} , and the symmetric, v_{sym}) will be shifted to lower frequencies as compared with the free ion. If the acetate acts as monodentate the two bands are shifted to higher and lower frequencies, respectively. In the complex [UO₂L_a(CH₃COO)], v_{as} lies at 1639 cm⁻¹ and v_{sym} at 1356 cm⁻¹, while in the [UO₂L_b(CH₃COO)] v_{as} is at 1538 cm⁻¹ and v_{sym} is at 1415 cm⁻¹; the free ion has been found to absorb at 1582 and 1425 cm⁻¹. We conclude that the acetate group is unidentate in [UO₂L_a(CH₃COO)] and bidentate in [UO₂L_b(CH₃COO)].

The case of the nitrate ion is more complex because the split of the doubly degenerate ν_3 of the free ion into ν_4 and ν_1 is not reliable for distinguishing between unidentate and bidentate coordination. The stretching vibrations ν_4 and ν_1 are for $[UO_2L_a(NO_3)]$ at 1484 and 1278 cm⁻¹ and for $[UO_2L_b(NO_3)]$ at 1476 and 1298 cm⁻¹. It has been suggested [9, 10] that bidentate nitrato groups exhibit two

metal-oxygen frequencies whereas unidentate nitrato groups should only exhibit one. Two i.r. active metal-oxygen stretching frequencies have been observed in the i.r. region at 252 and 210 cm⁻¹ for $[UO_2L_b(NO_3)]$, and a single band at 261 cm⁻¹ for $[UO_2L_a(NO_3)]$. Some preliminary structural data[21] seem to confirm these considerations and suggest that in the complex $[UO_2L_a(NO_3)]$ the nitrate acts as unidentate ligand. Information on the mode of attachment of the NCS groups to the central atom in $[UO_2L_a(NCS)]$ can be obtained by comparing the vibrational spectra of these compounds with the spectra of dioxothiocyanatouranates(VI) in which the anionic complexes $[UO_2(NCS)_5]^{3-}$ have structures consisting of isolated units [22]. In the caesium salts the thiocyanate groups are not bridging groups and the vibrational frequency $\nu_{(CN)}$ is at 2080 cm⁻¹ [23]. When NCS acts as bridging group, $\nu_{(CN)}$ increases to 2160 cm⁻¹ [24, 25]. For $[UO_2L_2(NCS)]$ the frequency of the $\nu_{(CN)}$ lies at 2012 cm⁻¹ indicating that the NCS group is unidentate. The observed frequency of the $\nu_{\rm (CS)}$ is 797 cm⁻¹, indicating that the NCS group is coordinated to the uranyl ion through the nitrogen atom[26, 27].

Changes in the NH stretching frequency in the i.r. spectra of ammine complexes of transition metal ions have been reported frequently, and reviewed in detail [28]. This frequency is decreased when the amine molecule is bonded to a metal ion; the magnitude of the shift to lower frequency is enhanced by increase in the positive charge of the metal ion, covalency in the metal-nitrogen bond [29], and thermodynamic stability of the complex [30].

Hydrogen bonding between the anion present and the proton in the NH group also decreases the NH stretching frequency and the magnitude of the observed shift depends on the anion, decreasing in the order

$$I^- > Br^- > CI^- > F^- \ge NO_3^- > CH_3COO^-$$
.

This may tentatively be correlated with the ability of the anion to enter into the coordination sphere. A decreased covalency in the uranium-anion may be associated with an increase in the shift of NH stretching toward lower frequencies.

The far i.r. spectrum shows only one absorption band in the region of the U–Cl stretching vibrations at 228 cm^{-1} . This band is shifted, as expected, to 142 cm^{-1} when the chloride is replaced by bromide and to 412 cm^{-1} by

Complex	A	Solvent	H _a	H _b ²	H _c	H _d	phenyl hydrogens ³
$H_{3}C^{a} CH_{3}$ $H_{3}C^{a} CH_{2}$ $H_{4}CH_{2}$ $H_{4}CH_{2}CH_{2}$	NO₃ [−] Cl [−] trop [−]	DMSO Py DMSO DMSO	3·36 3·28 3·33 3·21	3.74 3.91 3.60 3.58	4·58 4·43 4·52 4·06	9.58 9.28 9.55 9.44	6·91–7·96 6·79–7·59 7·66
$C=N CH_{2\ell} CH_{3}$	NO3 [−] trop [−] CH3COO [−]	DMSO Py DMSO Py Py	3.24 3.36 3.25 3.37 3.34	3.58 3.61 3.56 3.58 3.62	4.57 4.37 4.62 4.42 4.35	9.65 9.30 9.65 9.30 9.24	6·76–7·65 6·66–7·60
$(CH_{3})_{2}N$ CH_{2b} $(CH_{2b}$ H_{d} $(CH_{2b}$ $(CH_{2b}$ $(CH_{2b}$ $(CH_{3})_{2a}$ $(CH_{2b}$ $(CH_{3})_{2a}$ $(CH_{2b}$		CDCl₃ Py	3·38 2·25a' 3·40 2·15a'	4·34 2·90 <i>b'</i> 4·29 3·04 <i>b'</i>	5·06 5·20	9·13 9·22	6.75–7.13–7.53
H CH_2-CH_3 H CH_2c H_d H_d CH_2c H_d CH_2c H CH_3-CH_{2c} H	NO3	Ру			3.62	9.26	6.79-7.53

Table 2. ¹H NMR data for some complexes obtained (values in δ)¹

1. TMS as internal standard.

2. Values of He protons lie near Hb protons, only in the case of $[UO_2L_aNO_3]$ (py as solvent) a value of 3.60 δ for He protons is obtained.

3. For phenyl hydrogens, multiplets are obtained centered at the values given in the table.

4. From Ref. 17 where δ values of the protons in CH₂ groups have been erroneously transposed.

5. δ values of the protons in CH₃CH₂ groups are omitted; its integration is consistent with the formulation proposed above.

fluoride. We were not able to find the U-I stretching frequency which probably lies below 80 cm^{-1} .

There are conflicting reports on the deformation frequency of the uranyl ion. Earlier assignments at 140 cm⁻¹[31] and 212 cm⁻¹[32] are incorrect. Only one band has found in the range 268–249 cm⁻¹, implying that the ion is linear. The antisymmetric ν_3 (O–U–O) is easily observed in the characteristic region; it should be pointed out (see Table 3) that no correlation can be shown between the character of the U–A equatorial bond and the position of ν_3 in the i.r. spectra.

Solution measurements revealed only one absorption, assignable to ν_3 . The ν_3 in Nujol mull or KBr pellets was sometimes broad, but in a few cases it was resolved into a dublet or other multiplet. It has been suggested that Fermi resonance could account for these observations (33). However, the multiplets observed could be attributed to solid state unit cell coupling [34, 35]. X-ray analysis suggests [13] that when the complexes present a multiplet for ν_3 the unit cells contain more than one molecule.

Sometimes a weak band appears in the range 860-830 cm⁻¹. A similar band has been assigned to the symmetric stretch ν_1 [36, 37] which formally is i.r. forbidden but has been reported in the region 790-900 cm⁻¹ [38]. The hypothesis of a crystalline perturbation of the local symmetry of the UO₂²⁺ is more reasonable than a slight bending of this group.

Absorption spectra of $[UO_2L_aA]$ in sym-dichloroethane are shown in Fig. 4 where, for the sake of simplicity, spectra below 330 nm (ligand $\pi \to \pi^*$ region) are neglected: in this range a band or a shoulder is present at around 270 nm.

These spectra are very similar as expected for electronic transitions mainly localized on the Schiff base

Compounds	ΗΝų	νC=N	0-U-0 ₆₄	<i>v</i> ₂0−U−0	Other characteris	stic bands		
[U0,L _a (N0,)]	3186	1617	206	255		1484 ν_4 , 1278 $\nu_1(NO_3)$	261	$\nu(\rm U-ONO_2)$
[NO,L, (NO.)]	1	1614	892	268		$1476 \nu_4, 1298 \nu_1(NO_3)$	252, 201	$\nu(\rm U-ONO_2)$
[UO,(HL,),(NO,),]	1	1657	920	248		$1480 \nu_4, 1280 \nu_1(NO_3)$	264	$\nu(\rm U-ONO_2)$
[U0 ₂ L _a (CH ₃ CO0)]	3191	1619	668	256	$1639(\nu_{\rm as}-COO)$	$1356(\nu_s-COO)$	275	v (U-0C0CH3)
[U0 ₂ L ₆ (CH ₃ COO)]	I	1613	902	254	$1538(\nu_{\rm as}-\rm COO)$	$1415 (\nu_{\rm s}-COO)$	270	<i>ν</i> (U-0C0CH ₃)
[UO ₂ (HL _c) ₂ (CH ₃ COO) ₂]	1	1651	904-896	255	$1660 (\nu_{\rm as} - COO)$	$1300 (\nu_{\rm s} - COO)$	269	v(U-0C0CH ₁)
$[UO_2L_a(trop)]$	Not	1622	882	1	1610 (vC=0 trop	(
I	resolved							
$[\mathrm{UO}_2 L_b(\mathrm{trop})]$		1624	896	ļ	$1592 (\nu C=0 \text{ trop})$			
$[UO_2L_a(sal)]$	3223	1622	885	ļ	$1658 (\nu C=0 \text{ sal})$			
$[UO_2L_a (dtc)]$	3232	1620	886	ļ				
[U0 ₂ La F]	3183(br)	1625	889	258			412br	$\nu(U-F)$
IUO ₂ L _a CII	3180	1617	907	254			228	<i>ν</i> (U-Cl)
[UO ₂ L _a Br]	3167	1617	908	249			142	$\nu(U-Br)$
	3112	1624	892	258				
$[UO_2L_a(NCS)]$	3204	1615	906	252	2012 (ν C=N)		797 vC=S	
$[UO_2(HL_c)_2C]_2$		1656	901	261			243	ル(U−Cl)
[UO ₂ (EtOH)(sal) ₂]	1	1	923	I	1618(vC=O sal)			

Table 3. Infrared data for uranyl complexes (cm^{-1})



moiety [39] and show three rather strong and easily detectable bands with maxima at around 500, 390 and 340 nm in the charge-transfer region (above 340-350 nm). We may suppose the apical oxygens $\rightarrow f$ transition of the uranyl moiety, centered at around 390-450 nm, has been disguised by the strong absorption corresponding to the charge-transfer transition from the equatorial ligands to the uranium atom. Probably a charge-transfer $\pi \rightarrow f$ transition from the Schiff base orbitals to the f orbitals of the uranium takes place.

A shift toward lower wavelengths of the bands at around 500 nm is observed for the compounds in the order $F^->Cl^->Br^-$. These results may be compared with those obtained in the i.r. spectra in the $\nu_{(NH)}$ region. However, the shift is small, and the correlation is, only tentativly, proposed.

Pyridine or dimethylsulphoxide do not displace the $N(CH_3)_2$ group from its coordination site; moreover, in the complexes ($UO_2L_a(sal)$] and [$UO_2L_a(trop)$] (for ¹H NMR see Table 2) the carbonyl group does not displace

the dimethylamino group, so the salicylaldehydato and tropolonato anions act as unidentate ligands. This may be explained by a chelate effect, which is large for transition metals [40] and increases the stability of the complexes with increasing dentate character of ligands [41, 42]. A similar coordination is proposed for $[UO_2L_a(dtc)]$, which is not very stable and decomposes in air.

A final comment may be made on the stability of the complex $[UO_2L_a(I)]$. This complex is stable for several days in the solid state, which is not the case for the known etherate adducts. This particular behaviour of the complex can be explained by a stabilization of the U-I bond by the Schiff base. However, this bond is weaker than other U-X bonds (X = Br, Cl, F) as is confirmed by the decomposition temperature being 50-60°C lower than the others.

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