Spectroscopic Studies of some Uranyl Complexes of Tetradentate Schiff Bases

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Summary: The dioxouranium complex of eight tetradentate ligands bis(isopropanoylacetone) dl-stilbenediimine(dl-H_2PA_2S), bis(isopropanoylacetone)meso-stilbenediimine(meso-H_2PA_2S), bis(acetylacetone) dl-H_2HAP_2S), bis(*o*-hydroxyacetophenone phenylethylenediiminedl-stilbenediimine (dl-H_2AA_2S), bis(*o*-hydroxyacetophenone) meso-stilbenediimine(meso-H_2HAP_2S), bis-(*o*-hydroxyacetophenone)dl-stilbeneiimine (dl-H_2HAP_2Pen), bis(salicylaldehyde) tetramethylethylenediimine (H_2SA_2Ten) and bis(salicylal dehyde) phenylpropylenediimine (H_2SA_2PP) have been prepared. The uranyl complexes of H_2SA_2Ten and H_2SA_2PP are precipitated as neutral complexes, but remaining are obtained as dinitro derivatives. The complexes are characterised by IR, ^{1}H-NMR and spectrophotometric techniques.

Introduction

Tetradentate Schiff bases have received a considerable attention as gas and liquid chromatographic reagents for the determination of copper(II), nickel(II), palladium(II), platinum(II) and vanadium(IV) [1-4]. The Schiff bases also react with uranium(VI) as tetradentate ligands to form neutral complexes [5] [$UO_2(L)$] or as bidentate ligands [$UO_2(L)(NO_3)_2$ where L=ligand molecule [6-8]. Some of the uranyl complexes of Schiff bases corresponding to $UO_2(L)(NO_3)_2$ have already been reported from this laboratory [8], but in the present work a few more complexes corresponding to $UO_2(L)$ and $UO_2(L)(NO_3)_2$ have been reported and their structure have been determined by recording their ^{1}H-NMR.

Results and Discussion

The results of elemental micro-analysis (Table 1) agreed reasonably to the expected values.

Table 1: Results of elemental micro-analysis

	Compound	Mol.formula	M.P.	% Expected			% Found		
				C	H	N	C	H	N
1.	Meso-$H_2PA_2SUO_2(NO_3)_2$	$C_{28}H_{36}N_4O_{10}U$	303(Dec)	40.68	4.39	6.77	41.19	4.35	6.75
2.	dl-$H_2PA_2SUO_2(NO_3)_2$	$C_{28}H_{36}N_4O_{10}U$	265(Dec)	40.68	4.39	6.78	40.90	4.24	6.77
3.	SA_2PPUO_2	$C_{23}H_{20}N_2O_4U$	338	44.09	3.22	4.47	43.88	3.74	4.18
4.	$H_2HAP_2PenUO_2(NO_3)_2$	$C_{24}H_{22}N_4O_{10}U$	>250	37.70	2.90	7.33	37.65	3.01	7.06
5.	SA_2TenUO_2	$C_{20}H_{22}N_2O_4U$	>250	40.54	3.74	4.7	40.70	4.25	4.55
6.	dl-$H_2AA_2SUO_2(NO_3)_2$	$C_{24}H_{26}N_4O_{10}U$	235(Dec)	37.50	3.41	7.29	37.40	3.22	7.04
7.	dl-$H_2HAP_2SUO_2(NO_3)_2$	$C_{30}H_{28}N_4O_{10}U$	225(Dec)	42.76	3.35	6.65	42.86	3.31	6.24
8.	meso-$H_2HAP_2SUO_2(NO_3)_2$	$C_{30}H_{28}N_4O_{10}U$	297(Dec)	42.76	3.35	6.65	42.17	2.73	6.48

The uranyl complexes of the ligands H_2SA_2Ten and H_2SA_2PP derived from salicylaldehyde only precipitated as neutral complexes, but the uranyl complexes of dl-H_2PA_2S, meso-H_2PA_2S, dl-H_2AA_2S, meso-H_2HAP_2S, dl-H_2HAP_2S and H_2HAP_2Pen separated as dinitro-derivatives (Fig. 1). ^{1}H-NMR of uranyl complexes of dl-H_2PA_2S, meso-H_2PA_2S, H_2SA_2PP and H_2SA_2Ten recorded in D^6 DMSO were compared with their corresponding reagents in $CDCl_3$ (Table 2). The uranyl complexes of dl-$H_2PA_2SUO_2(NO_3)$ and meso-$H_2PA_2SUO_2(NO_3)_2$ indicate doublets at δ 11.54 and 11.3 ppm respectively due to NH protons as observed in their reagents dl-H_2PA_2S and meso-H_2PA_2S at δ 11.79 and 11.64 ppm respectively. It supports that the ligands retain their NH protons during complexation. The uranyl complexes of dl-H_2PA_2S and meso-H_2PA_2S indicate doublets at δ 5.09 and 5.08 ppm respectively due to bridge -CH as compared to multiplets at δ 4.67 and 4.70 ppm in the ligands respectively. It is suggested that both of the oxygen atoms of the ligands are involved in the complexation, thus the possibility of fly over structure as suggested by Pasini *et al.* [9] cannot exist and bridge -CH signal (multiplet) in reagents changed into doublet in uranyl complexes due to the coupling with NH protons. In the case of ^{1}H-NMR the signal observed in the reagents H_2SA_2PP and H_2SA_2Ten at δ 11.56 and 14.62 ppm respectively disappeared in their uranyl complexes, thus support that dianion of the ligand is involved in the complexation.

The IR of uranyl complexes of dl-H_2PA_2S and meso-H_2PA_2S show a band around 3250-40 cm^{-1} at a comparable position observed in the spectra of reagent due to NH vibrations. A broad and strong band observed in the reagents dl-H_2PA_2S, meso-H_2PA_2S and dl-H_2AA_2S around 1600 cm^{-1} due to hydrogen bonded C=O group is not visible in their uranyl complexes, as for their

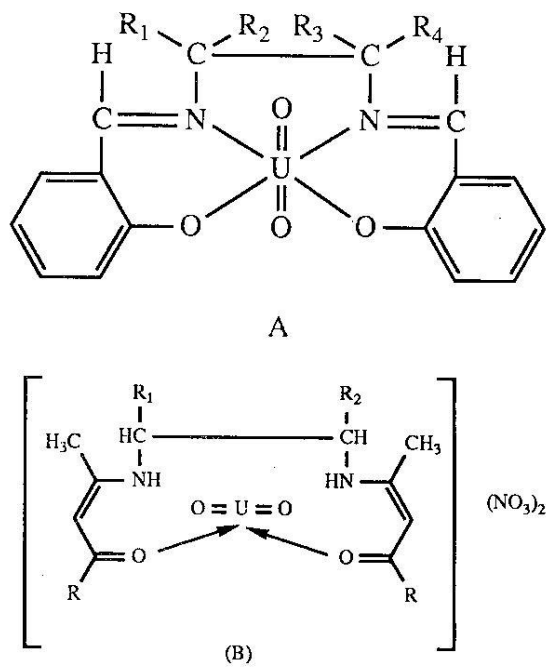

Fig. 1: Proposed structure of uranyl complexes. (A) (I) SA_2TenUO_2 = $R_1R_2,R_3,R_4=CH_3$. (II) SA_2PPUO_2= $R_1C_6H_5$, R_4= CH_3,R_2 and R_3=H (B) (I) dl-$H_2PA_2SUO_2(NO_3)_2$ = R = $(CH_3)_2$ CH, R_1 and R_2 = C_6H_5. (II) dl- $H_2AA_2SUO_2(NO_3)_2$ = R=CH_3, R_1 and R_2 = CH_3.

copper and nickel chelates [10]. Thus it supports that carbonyl group is involved in complexation. Two strong bands around 1545 and 1290 cm^{-1} and a band of weak intensity at 815 cm^{-1} have been reported in coordinated nitrate groups [6-8]. Our results agree with their results and a similar bands have been observed in uranyl complexes of dl-H_2PA_2S, meso-H_2PA_2S, dl-H_2AA_2S, dl-H_2HAP_2S, meso-H_2HAP_2S and H_2HAP_2Pen UO_2 vibration have been assigned to bands observed within 905-920 cm^{-1} and 565-545 cm^{-1}.

The spectrophotometric studies of the uranyl complexes in dimethylsulphoxide (DMSO) and

Table 2: ^{1}H-NMR of the reagents in $CDCl_3$ and uranyl complexes in D^6 DMSO

Compound	δ in ppm (possible assignment)
1. dl-H_2PA_2S	1.07(d), 1.38(d), 1.86(s) (-HC_3); 2.45(m), (-CH isopropyl); 4.67 (m) (-CH bridge), 4.995(s), (=CH), 11.79(d) (-NH); 6.49(m), 7.14(m) (C_6H_5)
2. dl-$H_2PA_2SUO_2(NO_3)_2$	0.9995(d), 0.931(d), 1.882(s) (-CH_3), 2.338(m) (-CH isopropyl), 5.0905(d) (-CH) bridge, 4.946(s) (=CH), 11.537(d) (-NH), 7.206(m) (C_6H_5).
3. meso-H_2PA_2S	1.078(d), 1.54(s), (-CH_3), 2.393(m) (-CH isopropyl), 4.695(m) (-CH brdige), 4.838 (=CH), 11.637(d) (- NH), 7.299(s) (-C_6H_5).
4. meso-$H_2PA_2SUO_2(NO_3)_2$	0.9335(d), 1.002(d), 1.781(s) (-CH_3) 2.328(m) (-CH isopropyl), 5.08(d) (-CH brdige), 4.941(s) (=CH), 11.3(d) (-NH), 7.196(m) (-C_6H_5).
5. H_2SA_2PP	1.2054(d) (-CH_3), 3.8321(m), 4.3976(d) (-CH bridge), 8.288(s), 8.321(s) (HC=N), 11.56(d) (OH), 6.808(m), 6.921(m), 7.1574(m), 7.249(m), 7.3139(m), 7.391(m) (-C_6H_5).
6. SA_2PPUO_2	1.489(d) (-CH_3); 5.1495(q), 5.6339(s), (-CH bridge), 9.2756(s), 9.4659(s) (HC=N), 6.6247(t), 6.136(t), 7.11(m), 7.4525(m), 7.507(m), 7.558(m) (-C_6H_5).
7. H_2SA_2Ten	1.4(s) (-CH_3), 6.873(m), 7.20(m) (-C_6H_5), 8.36(s) (HC=N), 14.62(s) (-OH).
8. SA_2TenUO_2	1.514(s) (-CH_3), 6.8(m), 7.6(m), (-C_6H_5) 9.329 (HC=N).

pyridine were carried out to examine the potentials of the reagents for spectrophotometric determination of uranium and to investigate the effect of solvent on different transitions.

The complexes dissolved easily in DMSO and pyridine to develop yellow colours. The uranyl complexes of dl-H_2PA_2S and meso-H_2PA_2S in DMSO indicate two bands in visible region within 428-29 nm and 441-43 nm, but in pyridine a single band is observed within 435-38 nm, with an improvement in the values of molar absorptvity (Table 3), may be due to better coordination of the solvent. Kim *et al.* [6] have assigned bands within 340-500 nm to triatomic UO_2 entity.

The uranyl complex SA_2PPUO_2 in visible region has a band at 379 nm along with a shoulder at 449 nm in DMSO as compared to pyridine in which it has three distinct bands at 353 nm, 387 nm and 456 nm. The values of molar absorptvity (Σ =740-3960 1.mole^{-1} cm^{-1}) are considerably higher than the uranyl complexes of dl-H_2PA_2S and meso-H_2PA_2S (Σ 16-80-1.mole-^{1}. cm^{-1}). Pasini *et al.* [5] have assigned absorption bands between 350-500 nm of uranyl complexes of bis(salicylaldehyde)-ethylenediimine and related compounds to charge transfer π-f involving orbitals of oxygen atoms of UO_2 and ligand to f orbitals of uranium. Thus increase in molar absorptvity of uranyl complexes of H_2SA_2PP and H_2SA_2Ten as compared to dl-H_2PA_2S and meso- H_2PA_2S may be attributed to π-f transitions involving also π orbitals of azomethine groups of Schiff bases H_2SA_2PP and H_2SA_2Ten, but in the case of uranyl complexes of dl-H_2PA_2S and meso-H_2PA_2S azomethine groups are not involved in complexation. Therefore a similar π-f transitions can not occur, resulting a decrease in molar absorptvity values.

These reagents are not sensitive enough for spectrophotometric determination of uranium, except H_2SA_2PP and H_2SA_2Ten, which show somewhat better sensitivity for the determination of uranium at mg levels.

Experimental

The ligands meso-H_2PA_2S dl-H_2PA_2S, dl-H_2HAP_2S, meso-H_2HAP_2S, dl-H_2AA_2S, H_2HAP_2Pen, H_2SA_2Ten and H_2SA_2PP were prepared as reported [10-12]. Elemental micro analysis were carried out from Elemental Micro-Analysis Ltd., Deven, U.K. Spectrophotometric studies were carried out on Hitachi 220 spectrophotometer. ^{1}H-NMR in D^6-DMSO were

Table 3: Spectrophotometric data of uranyl chelates in DMSO and pyridine

	Compound	Solvent	λmax nm (Σ -1. mole^{-1}cm^{-1})
1.	meso-$H_2PA_2SUO_2(NO_3)_2$	DMSO	428(20), 443(16)
		Pyridine	308(2787), 435(66)
2.	dl-$H_2PA_2SUO_2(NO_3)_2$	DMSO	278(2328), 336(2522) 429(42), 441(36).
		Pyridine	332(sh) (8045), 334(8595), 438(80).
3.	SA_2PPUO_2	DMSO	397(2209), 449(sh)(742),
		Pyridine	307(4897), 339(6474), 384(3430), 465(756).
4.	SA_2TenUO_2	DMSO	235(15392), 335(13200), 455(1420).
5.	dl-$H_2HAP_2SUO_2(NO_3)_2$	DMSO	350(1315), 390(725), 460(sh) (75).
		Pyridine	373(169), 462(345)
6.	meso-$H_2HAP_2SUO_2(NO_3)_2$	DMSO	350(796), 482(16)
		Pyridine	332(2980), 470(97)
7.	dl-$H_2AA_2SUO_2(NO_3)_2$	DMSO	303(2189), 416(15), 430(23), 446(15).
		Pyridine	351(1221), 439(226).

recorded at HEJ Research Institute of Chemistry, University of Karachi. The IR of the solid compounds in KBr were recorded on Perkin Elmer 1430 in the range of 4000-250 cm^{-1}.

A. Preparation of uranyl complexes [$UO_2(L)(NO_3)_2$]

Uranyl nitrate hexahydrate (0.50 g, .001M) dissolved in methanol was added to the hot equimolar solution of bis(isopropanoylacetone)meso-stilbenediimine(meso-H_2PA_2S), bis-(isopropanoylacetone) dl-stilbenediimine (dl-H_2PA_2S), bis(*o*-hydroxyacetophenone) dl-stilbenediimine (dl-H_2HAP_2S), bis(*o*-hydroxyacetophenone) meso-stilbene diimine(meso-H_2HAP_2S), bis-(acetylacetone)dl-stilbenediimine (dl-H_2AA_2S) or bis(*o*-hydroxy acetophenone) phenylethyl enediimine (H_2HAP_2Pen) in methanol (10 ml). The mix ture was refluxed for 15 min. The yellow precipi tate which separated instantly was filtered and washed with hot ethanol and dried.

B. Preparation of uranyl complexes [$UO_2(L)$]

Equimolar solution of uranyl nitrate hexahydrated (0.5 g, .001 M) dissolved in methanol (10 ml) was slowly added to the warm solution of bis(salicylaldehyde) tetramethylethylenediimine (H_2SA_2Ten) or bis(salicylaldehyde) phenylpropylenediimine (H_2SA_2PP) in methanol (10 ml). A yellow solid immediately precipitated. The solid was filtered off and washed with warm methanol and dried.

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