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Uranyl Complexes Containing Polydentate Schiff Bases

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A number of uranyl complexes containing polydentate Schiff bases and neutral ligands have been synthesised in three different ways and characterized by physico-chemical measurements. The geometry of coordination of UO_2^{2+} and the relative tendencies of the ligands to bond to uranyl are discussed.

Introduction

Uranyl complexes containing polydentate Schiff bases (L) have been described previously.[1,2,3] To our knowledge the first report on this subject concerns the synthesis of complexes between UO_2^{2+} and Schiff bases.[4] In a study dealing with the coordination properties of the UO_2^{2+} ion, we have the problem of the characterization of these compounds and particulary of the coordination number of the central metal ion. In this paper, we report various ways of synthesising and characterising some complexes having the general formula $[UO_2(L)A]$ (L = polydentate Schiff base, and A = monodentate neutral ligand), and we discuss the template effect of UO_2^{2+} on the formation of the organic polydentate ligand. In addition we refer to recent structural information,[5,6] obtained in a parallel investigation.

Experimental

Materials. The uranyl salts $UO_2Cl_2 \cdot 3H_2O$ and $UO_2(NO_3)_2 \cdot 6H_2O$ were reagent grade chemicals.

Ligands. The polydentate Schiff bases $HO—C_6H_4—CH=N—C_6H_4N=CH—C_6H_4OH(L_1)$, $HOC_6H_4CH=N—C_2H_4N=CHC_6H_4OH(L_2)$, $HOC_6H_4CH=N—C_3H_6—N=CH—C_6H_4OH(L_3)$, $HOC_6H_4—CH=N—C_2H_4—NH—C_2H_4N=CH—C_6H_4OH(L_4)$, were obtained and purified according to the methods described in the literature.[4] In particular, as far as the compound L_3 (derived from 1,3-diaminopropane), is concerned, we found it to be a pale yellow crystalline solid and not an oil as previously reported.[4] Elemental analyses are reported in Table I, together with some physical properties.

The monodentate neutral ligands ethanol, py, aniline, dimethyl- sulphoxide, were reagent grade chemicals or (in the case of Ph_3PO) prepared according to the method reported in the literature.[7]

Complexes. The complexes with uranyl salicylaldehyde was prepared on the basis of information from the literature.[8] 1.185 grams (3 mmole) of $UO_2Cl_2 \cdot 3H_2O$ were dissolved in 30 ml of salicylaldehyde and the red solution heated at 120-150°C for 5 h. On reducing the volume by evaporation in vacuum a solid was obtained which crystallized from anhydrous benzene and gave a red crystalline solid. This compound was not very stable and decomposed slowly.

However, on treating it in $CHCl_3$ with excess Ph_3PO, the stable compound $[UO_2(sal)_2Ph_3PO]$ was obtained. Therefore, we assume according to the known coordinating properties of UO_2^{2+} that the original complex was $[UO_2(sal_2)H_2O]$.

The complexes of uranyl with polydentate amines, which are reported as intermediates in the following text, were not isolated in the solid state, but prepared in solution according to methods in the literature.[9] The only exception is the complex of UO_2Cl_2 with *o*-phenylene-diamine (OFD) which has been described previously. The complex $[UO_2(OFD)Cl_2]$ was isolated as a dark yellow precipitate on reacting $[UO_2Cl_2 \cdot (CH_3CN)]$ (obtained by the method of Bagnall *et al.*[10]), with the ligand in anhydrous ethanol.

The uranyl complexes $[UO_2(L)C_2H_5OH]$ were synthesised in three different ways.

Method I. The product was obtained on reacting either $UO_2Cl_2 \cdot 3H_2O$ or $UO_2(NO_3)_2 \cdot 6H_2O$ with the stoicheiometric amount of the appropriate Schiff base in absolute ethanol; *i.e.* according to reactions of the type:

$$UO_2Cl_2 \cdot 3H_2O + HOC_6H_4CH=N—C_6H_4—N=CH—C_6H_4—OH \xrightarrow{EtOH} [UO_2L_1(EtOH)] + 2HCl + 3H_2O$$

Method II. The product was obtained on reacting a freshly prepared solution of the complex $UO_2(sal)_2 \cdot H_2O$ with the stoicheiometric amount of polydentate

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Table I. Physico-chemic properties and elemental analysis

Compound	C% calc.	C% found	H% calc.	H% found	N% calc.	N% found	m.p.	Color
L$_1$	76.60	76.08	4.45	4.96	9.25	9.00	163	Orange crystals
L$_2$	71.80	72.41	5.85	5.86	10.58	10.40	127	Poor yellow crystals
L$_3$	76.51	76.31	6.78	6.79	10.60	10.57	56	Yellow crystals
L$_4$	69.23	68.95	6.81	6.73	10.28	10.12	—	Braun yellow oil
[UO$_2$(OFD)Cl$_1$]	16.07	15.78	1.78	1.98	5.74	6.20	> 270	Yellow crystals
[UO$_2$dien(OH)$_2$]	11.80	11.64	3.68	3.00	10.30	10.61	> 270	Yellow crystals
[UO$_2$L$_1$(EtOH)]	41.90	41.91	3.18	3.13	4.45	4.46	> 270	Red crystals
[UO$_2$L$_2$(EtOH)]	36.20	36.16	3.44	3.21	4.81	5.32	> 270	Red-yellow crystals
[UO$_2$L$_3$(EtOH)]	38.30	38.40	3.70	4.11	4.70	4.63	> 270	Red-yellow crystals
[UO$_2$L$_4$]	37.30	36.21	3.20	3.03	7.25	7.14	> 270	Yellow powder
[UO$_2$L$_1$(py)]	45.25	45.28	2.87	2.68	6.05	6.28	> 270	Red powder
[UO$_2$L$_2$(py)]	40.97	41.39	3.03	3.25	6.82	6.80	187	Red powder
[UO$_2$L$_3$(py)]	41.97	42.10	3.33	3.45	6.67	6.71	> 270	Red powder
[UO$_2$L$_4$(py)]	41.94	41.11	3.60	3.55	8.51	8.53	> 270	Red powder
[UO$_2$L$_1$(Ph$_3$PO)]	52.40	52.29	3.46	3.44	3.20	3.18	235	Yellow powder
[UO$_2$L$_2$(Ph$_3$PO)]	50.12	49.84	3.56	3.60	3.43	3.50	> 270	Yellow powder
[UO$_2$L$_3$(Ph$_3$PO)]	50.60	49.83	3.74	3.67	3.38	3.47	239	Yellow powder
[UO$_2$L$_1$(PhNH$_2$)]	46.50	46.22	2.81	3.06	6.22	6.27	> 270	Yellow powder
[UO$_2$L$_1$(DMSO)]	39.90	39.80	3.02	3.10	4.19	4.21	> 270	Bright yellow powder
[UO$_2$L$_2$(DMSO)]	35.10	35.20	3.26	3.37	4.55	4.61	> 270	Orange powder
[UO$_2$L$_3$(DMSO)]	36.30	36.55	3.50	3.60	4.46	4.46	> 270	Orange crystals

amine in absolute alcohol, *i.e.* according to reactions of the type:

$$[UO_2(sal)_2H_2O] + o\text{-phenylendiamine} \xrightarrow{EtOH} [UO_2L_1(EtOH)] + 3H_2O$$

Method III. The product was obtained on reacting the polidentate amine complexes of UO_2^{2+} with the stoicheiometric amount of salicylaldehyde, *i.e.* according to reactions of the type:

$$[UO_2(OFD)Cl_2] + 2sal + EtOH \rightarrow [UO_2(L_1)(EtOH)] + 2HCl + 2H_2O$$

The complexes [UO$_2$(L)(EtOH)] obtained by the three methods reported above were in all cases the same for a given L. They were recrystallized from absolute ethanol and appeared either as orange-yellow powders or as red-yellow crystalline solids. In the case of the complex containing the ligand L$_4$ the form [UO$_2$(L$_4$)] was obtained by dissolving the original precipitate in CH$_2$Cl$_2$ and precipitating with *n*-pentane.

Complexes of the type [UO$_2$L(am)] (am = py or aniline). The complexes were obtained on dissolving [UO$_2$L(EtOH)] in the appropriate freshly distilled amine. After stirring the solution for about 30 minutes it was filtered and treated dropwise with excess pentane. The red precipitate obtained was reprecipitated with pentane.

Complexes [UO$_2$L(Me$_2$SO)]. The complexes containing dimethyl-sulphoxide as neutral monodentate ligand were obtained by a similar method, *i.e.* dissolving the appropriate [UO$_2$L(EtOH)] in the minimum amount of Me$_2$SO, stirring for 30 mins, and carrying out the precipitation with ether (see Table I).

Attempts to prepare the complexes with A = 3CN-py or CH$_3$CN, resulted in the first case in the absence of any reaction (even in the presence of a large excess of 3CN-py) and, in the second case in the formation of precipitates. These precipitates are presumably the complexes [UO$_2$L(CH$_3$CN)] (as was confirmed by the presence of characteristic ν(C≡N) absorptions in fast scanned IR spectra) but are very unstable and undergo rapid decomposition even in the absence of EtOH or moisture.

Physico-Chemical Measlurements. The I.R. spectra were recorded with a Perkin-Elmer 621 spectrophotometer and the ^{1}H n.m.r. spectra with a Perkin-Elmer R12 instrument.

Results and discussion

The characteristic features in the I.R. spectra for all the complexes [UO$_2$(L)(A)] are reported in Table II. The presence of ethanol in the coordination sphere in the case of the complexes [UO$_2$(L)(EtOH)] is not fully evident in the I.R. spectra, but was confirmed independently by ^{1}H n.m.r. measurements and by the X-ray diffraction study mentioned above.[5,6] As far as the infrared measurements are concerned, apart from the general agreement between I.R. data and proposed formulation, specific comment may be made on the data referring to the species [UO$_2$L(Me$_2$SO)]. The $\nu_{S=O}$ stretching frequencies (see Table II) are lower than stretch of pure Me$_2$SO (1100-1055 cm^{-1}) indicating that coordination occurs through the oxygen and not through the sulfur atom.[11] This is consistent with the general behaviour of the uranyl ion, which is known to be a tipical «hard» Lewis acid.[12,13] Also, for the complexes of the type [UO(L)(Ph$_3$PO)] where Ph$_3$PO is bonded to uranyl through the oxygen atom, a lowering of the ν(P=O) stretching frequencies is observed as compared to

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Table II. I.R. Spectra of complexes (data in cm^{-1})

Compounds	O=U=O	C=N	other characteristic	absorption bands
$[UO_2L_1(EtOH)]$	910	1602 1598	—	—
$[UO_2L_2(EtOH)]$	912	1638 1627	—	—
$[UO_2L_3(EtOH)]$	912	1640 1620	—	—
$[UO_2L_4]$	892	1622 1615	3225(NH)	
$[UO_2L_1(py)]$	895	1605 1598	—	—
$[UO_2L_2(py)]$	888	1630 1620	—	—
$[UO_2L_3(py)]$	897	1640 1625	—	—
$[UO_2L_4(py)]$	902	1625 1605	3225(NH)	
$[UO_2L_1(PhNH_2)]$	893	1620	3320-3270(NH_2)	
$[UO_2L_1(DMSO)]$	892	1605	992(S-O)	
$[UO_2L_2(DMSO)]$	879	1622	991(S-O)	
$[UO_2L_3(DMSO)]$	882	1622	995(S-O)	
$[UO_2L_1(Ph_3PO)]$	895	1604	1143(P-O)	440(P-O)
$[UO_2L_2(Ph_3PO)]$	883	1620	1150(P-O)	460(P-C)
$[UO_2L_3(Ph_3PO)]$	885	1622 1615	1160(P-O)	460(P-C)
Ph_3PO	—	—	1190(P-O)	446(P-C)

that of the free ligand. This can be associated with an increase in the P=O bond length, in agreement with analogous observations from the literature.[14]

The asymmetric ν_3 vibration, one of the peculiar normal vibrational modes of the uranyl group, lies in the range 883-912 cm^{-1} for all the complexes examined. These observations indicate that the vibration in the uranyl group is not strongly effected by the nature of the coordinated monodentate ligand. However, in this limited range, the higher frequencies relate to the complexes containing ethanol, which is the most labile of the ligands examined and the lower frequencies relate to the complexes with Ph_3PO the most inert of the ligands examined. Other vibrations of lower intensities, which could be assigned to the uranyl group, have been observed in the same range in few cases. This could be due in principle either to a different asymmetric transition or to the ν_1 symmetric vibrational mode, which only in a completely centrosymmetric structure would be inactive in the I.R..

All the examined compounds except $[UO_2L_4(A)]$, which requires separate comment are uranyl complexes containing five donor atoms in the equatorial plane. In addition to the elemental analyses and physico-chemical evidence support for this coordination comes from the recent X-ray diffraction studies on the complexes $[UO_2L_1(EtOH)]$[5] and $[UO_2L_2(MeOH)]$[6].

As far as the complexes with the ligand L_4 are concerned, these are the only cases of species containing a pentadentate Schiff base. The complex $[UO_2L_4]$ is easily obtained from $[UO_2L_4(EtOH)]$ and its basic structure is already reported in the literature.[15]

Therefore, if $[UO_2L_4]$ has can equatorial coordination number of five, the corresponding adducts, $[UO_2L_4(A)]$, might have an equatorial c.n. = 6. This finds correspondence in the chemical properties of the $[UO_2L_4(A)]$ complexes since the A ligands are very labile as compared to the corresponding labilities in the $[UO_2L(A)]$ species. In fact we were able to carry out a complete identification only of the ethanol and pyridine, adducts. The adducts with Me_2SO and aniline were obtained in the solid state, but they undergo a relatively fast decomposition, reverting to $[UO_2L_4]$.

The complexes of the type $[UO_2L(EtOH)]$ ($L = L_1, L_2, L_3$) undergo substitution reaction of the coordinated ethanol with various neutral monodentate ligands. Interchange reactions of the type:

$$[UO_2L(A)] + A' \rightarrow [UO_2L(A')] + A$$

indicate the following stability sequence depending on the nature of the neutral monodentate ligand:

$$Ph_3PO > Me_2SO > Py > \text{aniline} > EtOH$$

The same experiments carried out with the poor base 3CN-piridine shows that this ligand, even when present in excess in the reaction mixture, does not replace the coordination ethanol. All these reactions are reversible and equilibrium studies are now in progress to elucidate the dependence of the nature and basicity of the ligand in determining their relative tendencies to coordinate to uranyl.

An attempt has also been made to follow the kinetics of these processes, but they are too fast for conventional techniques.

Finally, a comment is required about the three methods that have been used for the syntheses of the $[UO_2L(EtOH)]$ complexes.

It seems quite clear that a sort of template effect is operating when the reactions are carried out by

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methods II and III. The fact that in all three methods the same compound is obtained in practically quantitative yield, means that methods II and III are preferable to method I only in that the product may be obtained in a single operation.

Further studies are in progress in order to define the role of the metal in the mechanism of condensation between carbonyl and amino groups.

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