*Contribution from the Laboratorio di Chimica e Tecnologia dei Radioelementi del Consiglio Nazionale delle Riverche, Via Vigonovese, 52, 35100 Padova, and *Istituto di Chimica Generale ed Inorganica, Università di Padova, Via Loredan, 6, Italy.*

Uranyl Complexes with Potentially Tridentate Schiff Bases

M. Vidali,* P.A. Vigato, G. Bandoli, D.A. Clemente, and U. Casellato

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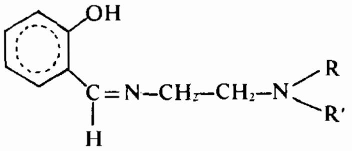
Reactions of dioxouranium(VI) salts with potentially tridentate Schiff bases have been investigated. The coordination in the solid state and in solution is discussed on the basis of physico-chemical data. Some reactions of these compounds with trans–[$Pd(phCN)_2Cl_2$] *are also reported.*

Introduction

While the interaction of certain potentially polydentate Schiff bases with various 3d metal ions is well known,[1,2] only a few papers have so far been published on dioxouranium(VI) complexes with the Schiff bases[1,2,3,4] In our laboratory we have previously developed methods of obtaining chelate complexes of UO_2^{2+} with ligands of this type, have described their properties[5] and have investigated the connection between properties of chelate ligands and the equatorial c.n.[6,7] Following these investigations, we have examined the reactions of tridentate ligands of the type:



R = H; R′ = C_6H_5 ($HsalenNHC_6H_5$)
R = H; R′ = C_2H_5 ($HsalenNHC_2H_5$)
R = R′ = CH_3 ($HsalenN(CH_3)_2$)

with various dioxouranium(VI) salts to study the coordination ability of the ligands under different condition of reaction.

In the present paper we report synthesis and characterisation of complexes having the general formula [$UO_2(salenNRR')_2$], discuss the type of coordination involved and, moreover, examine the reactivity of the amine group of the coordinated ligands towards transition metals compound as *trans*–[$Pd(phCN)_2Cl_2$] in polar (ethanol) and not-polar (benzene) media.

Experimental Section

Materials. The uranyl salts $UO_2Cl_2 . 3H_2O$ and $UO_2(NO_3)_2 6H_2O$ were reagent grade chemicals. TlOEt was reagent Schilling. Salicylaldehyde, amines, and solvents were used without purification, or drying; *trans*–[$Pd(phCN)_2Cl_2$] was prepared according to the method of Karash.[8]

The monodentate neutral ligands (ethanol, pyridine, acetone) were reagent grade chemicals. The tridentate bases ($HsalenNHC_6H_5$), ($HsalenNHC_2H_5$), and ($HsalenN(CH_3)_2$) were obtained and purified according to the general methods described in the literature.[1] The Tl^I derivatives of the ligands were obtained as pale yellow crystals on the bases of information from the literature.[9] $TlsalenNHC_2H_5$ only was instead obtained as an oil, which changed to a yellow crystalline solid, after a long cooling at 0°C. Elemental analyses are reported in Table I, together with some psysical properties.

Complexes of the Type [$UO_2(salenNRR')$]. Uranyl complexes of the type [$UO_2(salenNRR')_2$] were obtained on reacting 1 mmole of $UO_2Cl_2 . 3H_2O$ in 100 ml of absolute ethanol with the stoicheiometric amount of Tl^I derivatives of the Schiff bases (2 mmole) in 50 ml of EtOH.

After stirring the solution at 40°C for about 1 h, TlCl was filtered off. After about 8 hrs, orange crystals were obtained from the solution in quantitative yield. Elemental analyses and some physical properties are reported in Table I.

Complexes of the Type [$UO_2(H_2O)_2(salenNRR')_2PdCl_2$]. (1 mmole) of [$UO_2(salenNRR')_2$] was dissolved in 100 ml of benzene. A solution of *trans*–[$Pd(phCN)_2Cl_2$] (1 mmole in 50 ml of benzene) was added dropwise. The solution changed from orange to yellow and a precipitate was obtained.

The suspension was stirred for 24 hrs and then filtered off. The yellow precipitate was washed with

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Table I. Analytical data and physico-chemical properties of the described complexes

Complex	C calc.	C found.	H calc.	H found.	N calc.	N found.	Cl calc.	Cl found.	M.P.	colour
$TlsalenNHC_6H_5$	40.60	40.40	3.41	2.98	6.31	5.90	—	—	152	yellow crystals
$TlsalenNHC_2H_5$	33.39	33.80	3.82	3.50	7.07	6.80	—	—	—	brown yellow oil
$TlsalenN(CH_3)_2$	33.39	32.95	3.82	3.53	7.07	6.95	—	—	33	yellow powder
$UO_2(salenNHC_6H_5)_2$	48.13	47.85	4.04	4.10	7.48	7.30	—	—	276 dec	pink crystals
$UO_2(salenNHC_2H_5)_2$	40.50	40.84	4.63	4,68	8.58	8.51	—	—	180	orange-red powder
$UO_2(salenN(CH_3)_2)_2$	40.50	40.84	4.63	4.68	8.58	8.67	—	—	192	orange-red powder
$UO_2(HsalenNHC_6H_5)_2(NO_3)_2$	41.20	41.50	3.69	3.68	9.60	9.20	—	—	211dec	yellow powder
$UO_2(HsalenNHC_2H_5)_2(NO_3)_2$	33.94	34.50	4.14	4.15	10.79	10.30	—	—	192-195dec	yellow powder
$UO_2(HsalenNHC_6H_5)_2Cl_2$	43.86	44.01	3.92	3.85	6.82	6.65	8.63	8.45	226-228	yellow powder
$UO_2(H_2O)_2(salenNHC_6H_5)_2PdCl_2$	37.46	37.64	3.56	3.34	5.82	5.52	7.37	7.21	244dec	yellow powder
$UO_2(H_2O)_2(salenNHC_2H_5)_2PdCl_2$	30.52	30.60	3.96	3.78	6.47	6.46	8.19	8.50	228-230dec	yellow powder
$UO_2(H_2O)_2(salenN(CH_3)_2)_2PdCl_2$	30.52	30.99	3.96	3.96	6.47	6.12	8.19	7.90	189dec	yellow powder
$Pd(salenNHC_6H_5)Cl$	47.27	47.24	3.97	4.01	7.35	7.29	9.30	9.43	279dec	orange crystals
$Pd(salenNHC_2H_5)Cl$	39.66	40.06	4.54	4.58	8.41	8.32	10.60	10.66	268dec	orange crystals

Table II. I.R. Data for Examined Complexes (cm^{-1}).

Compound	νNH	νC=N	$\nu O=U=O_{as}$	Other Bands			
$TlsalenNHC_6H_5$	3249	1619	—	1590(νC=C);		: 748(C–H) out of plane phenyl deformations	
$TlsalenNHC_2H_5$	3209	1630	—	1589(νC=C);		; 755 » »	
$TlsalenN(CH_3)_2$	—	1614	—	1583(νC=C);		; 751 » »	
$UO(salenNHC_6H_5)_2$	3237	1625	871	1600(νC=C);		; 760 » »	
$UO_2(salenNHC_2H_5)_2$	3234	1628	895	1595(νC=C);		; 755 » »	
$UO_2(salenN(CH_3)_2)_2$	—	1624	885	1596(νC=C);		; 760 » »	
$UO_2(HsalenNHC_6H_5)_2(NO_3)_2$	3414	1654	914	1603(νC=C);		; 755 » »	
$UO_2(HsalenNHC_2H_5)_2(NO_3)_2$	3260	1634	908	1593(νC=C);		; 760 » »	
$UO_2(H_2O)_2(salenNHC_6H_5)_2PdCl_2$	3103-3080	1629	900	1599(νC=C);	3362 (νOH):	760 » »	Pd–Cl (312)(?)
$UO_2(H_2O)_2(salenNHC_2H_5)_2PdCl_2$	3173	1626	894	1597(νC=C);	3400 broad(νOH);	755 » »	Pd–Cl (310) »
$UO_2(H_2O)_2(salenN(CH_3)_2)_2PdCl_2$	—	1627	904	1599(νC=C);	3450 broad(νOH);	756 » »	Pd–Cl (315) »
$Pd(salenNHC_6H_5)Cl$	3103-3081	1631	—	1599(νC=C);		756 » »	Pd–Cl (312) »
$Pd(salenNHC_2H_5)Cl$	3095 broad	1626	—	1599(νC=C);		758 » »	Pd–Cl (310) »

benzene and dried under vacuum. Elemental analyses are reported in Table I.

Complexes of the Type $[(UO_2(HsalenNRR')_2X)]$ *(X = NO_3^- or Cl^-).* $UO_2(NO_3)_2 \cdot 6H_2O$ or $UO_2Cl_2 \cdot 3H_2O$ (1 mmole) was disolved in 50 ml of absolute ethanol at room temperature. An ethanolic solution of salicylaldehyde (2 mmole) was added dropwise and then the stoicheiometric amount of the appropriate amine (2 mmoles), in EtOH (25 ml). After stirring for 5 hrs a product was obtained as a yellow precipitate. This compound was washed with anhydrous di-ethyl ether, and dried under vacuum.

Physico-chemical Measurements. The I.R. spectra were recorded with a Perkin-Elmer 621 spectrophotometer from 4000 to 200 cm^{-1} in Nujol mulls or KBr pellets and the ^1H.n.m.r. spectra with a 90 MHz Bruker Spectrospin in $CDCl_3$ or pyridine-d_5 solution (TMS as internal standard).

Results and Discussion

Behaviour in the Solid State. In the reactions of tridentate Schiff bases with $UO_2(NO_3)_2 \cdot 6H_2O$ complexes of the type $[UO_2(HsalenNHR)_2(NO_3)_2]$ (R = C_2H_5 or C_6H_5) have been isolated. They are stable to light and the atmosphere in the solid state. The infrared spectra show no absorption band near 1380 cm^{-1}, where the free nitrate ion is known to absorb. It is concluded, therefore, that nitrate ions are bonded to UO_2^{2+}.

Since absorption peaks at about 1473 cm^{-1} and 1264 cm^{-1} are present, (assigned to the NO stretching and NO_2 asymmetric stretching frequencies respectively[10]), it is presumed that the nitrate ions are coordinated as unidentate ligands. Moreover, the NH stretching of these complexes occurs at the same frequencies as free ligands. This is in accordance with a formulation where the neutral molecules, and not the anions of the Schiff bases, are considered to be coordinated with the metal ion.[4] We suggest that the Schiff bases act as bidentate ligands forming six membered chelate rings. A similar case was previously reported in the complexes of uranyl ion with *o*-hydroxiquinoline, β-diektone and so on, in which the ligand molecules were considered to be bonded with the metal ion.[11]

On reacting Tl salenNRR′ with $UO_2Cl_2 \cdot 3H_2O$ the complexes $[UO_2(salenNRR')_2]$ were obtained under fairly mild conditions and in high yield. In these complexes the Schiff bases act as tridentate ligands. In fact when R = H and R′ = C_6H_5 or C_2H_5, the I.R. spectra in Nujol mulls show only one NH stretching at 3237 cm^{-1} and 3234 cm^{-1} respectively, while the free ligands present these bands at 3414 cm^{-1} and 3260^{-1}. Since the ν(NH) and ν(C=N) stretching frequencies observed for the complexes are single, it is also presumed that the compounds are in the *trans*

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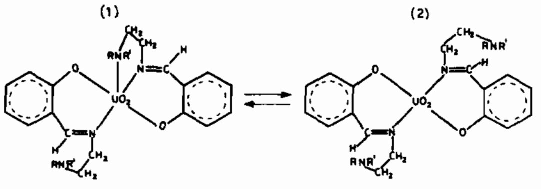
form. Some preliminary structural data confirm this configuration and suggest for complex [UO_2(salenN-$(CH_3)_2)_2$] an equatorial coordination number five; an analogue behaviour could be proposed for [UO_2(salenNHR$)_2$]. So the shift to lower frequency of the NH stretchings could be a result of an hydrogen bond.

Behaviour in Solution. The I.R. spectra in dry solvents, *e.g.* benzene or chloroform, show one absorption peak for ν(N–H), at 3414 cm^{-1} for [UO_2(salenNH$C_6H_5)_2$] and at 3260 cm^{-1} for [UO_2(salenNH$C_2H_5)_2$], in agreement with the assumption that the following equilibrium is present.



The ^{1}H.n.m.r. spectra give further information about these equilibria. The spectra of [UO_2(salenNH$C_2H_5)_2$] in $CDCl_3$ or pyridine-d_5 are identical, indicating according to the I.R. spectra, that only the form (2) is present, while (1) is in pratically negligible amount.

In fact, in addition to the peaks of the phenylic hydrogens centred at 7.10 δ and of hydrogens near the C=N at 9.20 δ, two triplets at 4.72 and at 3.43 δ (3.51 δ in py) are present. They are assigned to CH_2 near NH and CH_2 near N=C respectively. The quartet at 3.18 δ is assigned to CH_2 of the ethyl group and the triplet at 1.23 δ (1.18 δ in py) to CH_3 of the same group. The absence of other absorption peaks, could mean that form (1) is not present in solution. Configuration (1) and (2) are present for [UO_2(salenN-$(CH_3)_2)_2$].

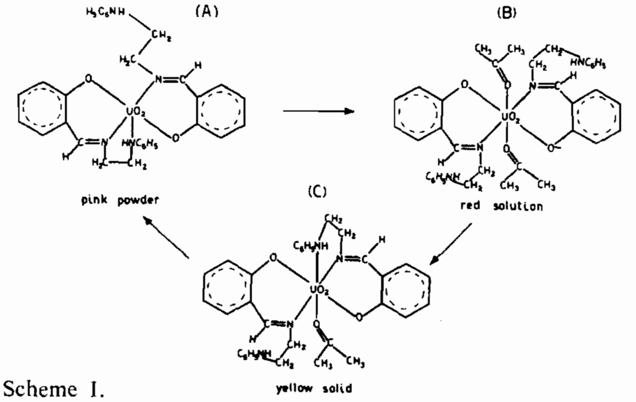
The ^{1}H.n.m.r. spectra show two absorption peaks at 5.06 and 4.34 δ in $CDCl_3$ (5.20 δ and 4.29 δ in py) for CH_2 near amine nitrogen and one peak at 2.90 δ (3.04 δ in py) for CH_2 near N=C; two peaks for CH_3 are present at 3.38 and 2.25 δ (3.40 and 2.15 δ in py).

In addition peaks centred at 7.13 δ(phenylic hydrogens) and one peak at 9.13 δ($\underset{\mathrm{H}}{\underset{|}{\mathrm{C}}}$=N) are present.

Reactivity: in a coordinating solvent such as acetone, only one peak occurs in the I.R. spectra, for the NH stretching frequency at 3414 cm^{-1} for [UO_2(salenNH$C_6H_5)_2$] and at 3260 cm^{-1} for [UO_2(salenNH$C_2H_5)_2$]. The uranly complexes undergo reactions according to the Scheme I.

The yellow solid obtained from solution shows two peaks at 3414 and 3237 cm^{-1} for NH, and ν(C=O) for acetone is also present at 1705 cm^{-1}.

The complexes change in the solid state from yellow to pink with a subsequent shift of the NH stretching at 3237 cm^{-1}. In addition, the ν(C=O) of coordinated acetone disappears. This is in accordance with the Sheme I proposed. In this complex the chelate effect is more important than the hardness of the neutral monodentate ligand and it may explian the imposibility of obtaining stable (B) or (C) in the solid state.



Scheme I.

The reaction of [UO_2(salenNRR'$)_2$] with *trans*-[Pd(phCN$)_2Cl_2$] shows the important role of the solvent.

In ethanol at 40-50°C the reactions are very complicated, and more than one species are present. We have isolated complexes of the type [Pd(salenNRR')-Cl] and [$UO_2(H_2O)$(salenNRR'$)_2PdCl_2$].

On the contrary using benzene at room temperature, the reaction mixture initially red, turned slowly yellow and a precipitate was obtained. The reaction is:

$$[UO_2(\mathrm{salenNRR'})_2] + [Pd(\mathrm{phCN})_2Cl_2] \rightarrow$$
$$[UO_2(H_2O)(\mathrm{salenNRR'})_2PdCl_2] + 2C_6H_5CN$$

The physico-chemical data and analyses are identical for the mixed complex obtained in benzene or ethanol.

The antisymmetric ν_3, one of the peculiar normal vibration modes of the UO_2^{2+} group ($D_{\infty h}$), lies in the range 895-871 cm^{-1} for the complexes [UO_2(salenNRR'$)_2$] while for the mixed complexes [$UO_2(H_2O)_2$(salenNRR'$)_2PdCl_2$] it occurs in the range 904-894 cm^{-1} (see Table II). This is in accordance with a change in the equatorial cordination of the UO_2^{2+} ion. The coordinated H_2O, is confirmed by the presence of the ν(OH) broad stretching (3400-3362 cm^{-1}).

The coordination of the amine group to palladium, when R=H and R' = C_6H_5 or C_2H_5, is suggest by the shifts (c.a. 100 cm^{-1}) of the ν(NH) stretch, in accordance with those of the analogous square planar Pd-amine complexes.[12]

The Pd–Cl stretching frequencies in these mixed complexes, are not well resolved and appear in the range (315-310 cm^{-1}), as in the case of [Pd(salenNHR)Cl].

Cis or *trans* configurations around Pd and UO_2^{2+} are possible for the mixed complexes; a *cis* configuration, involving a very complicated mechanism, may be an unfavorable one. On the other hand, *cis* complexes of palladium(II) are common only for chelate ligands.

A polymeric structure may be also assumed for all these mixed compounds even if molecular weight determinations were unsuccessful owing to their low solubility.

Acknowledgment. We thank F. Benetollo and M. Faggin for their experimental assistance.

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