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MIXED COMPLEXES OF URANIUM(IV) AND THORIUM(IV) WITH N,N'-ETHYLENEBIS(SALICYLIDENEIMINE) AND N,N'-PROPYLENEBIS(SALICYLIDENEIMINE).

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Recently, some uranium tetrachloride adducts with N-(hydroxyphenyl)salicylaldimine and N-(methoxyphenyl)salicylaldimine have been prepared in this laboratory (1); the study has been now extended to the complexes of Uranium(IV) and Thorium(IV) with N,N'-Ethylenebis(salicylideneimine), H_2salen, and N,N'-Propylenebis(salicylideneimine), H_2salpropen, with the aim to prepare fully substituted complexes, mixed complexes containing both chloride and Schiff base groups and adducts of tetrachlorides with free Schiff bases.

This paper reports the preparation and properties of the compounds $MCl_4(H_2salen)$, $MCl_4(H_2salpropen)$, M(salen)Cl_2 , M(salen)$_2$ and M(salpropen)$_2$, where M = U or Th.

These compounds are been characterized by elemental analyses and their IR spectra are reported and discussed.

Some of these compounds have been previously prepared by other methods, but their spectral data have not been extensively discussed: Selbin et al. (2) prepared U(salen)$_2$, Calderazzo et al. (3) prepared U(salen)Cl_2 and the UCl_4 adduct with H_2salen.

EXPERIMENTAL

The materials used were as follows: anhydrous uranium tetrachloride was prepared from uranium trioxyde and hexachloropropene (4); thorium tetrachloride (K & K Laboratories Inc.) was recrystallized from dimethoxyethane (DME): in this way the adduct $ThCl_4$.2DME was isolated and used in the preparation of the complexes.

The chemicals used for preparing the ligands were of reagent grade: salicylaldehyde was distilled before use; tetrahydrofuran and dimethoxyethane were firstly distilled from $LiAlH_4$, successive ly from Na/K alloy, using benzophenone as purity indicator; hexane was distilled from Na/K alloy.

H_2salen and H_2salpropen were prepared by refluxing salicylaldehyde and diamine in 2:1 proportions in ethanol; the separated Schiff bases were filtered and recrystallized from ethanol.

Thallium(I) Schiff base derivatives as Tl_2salen and Tl_2salpropen were obtained as follows: Tl_2salen was prepared by adding thallium(I) ethoxide to warm ethanolic solution of H_2salen (5); Tl_2salpropen was prepared by reacting thallium(I) salicylaldehyde with-1,3-diaminopropane in ethanol; thallium(I) salicylaldehyde was obtained from thallium(I) ethoxide and salicylaldehyde in ethanol.

All the operations for the preparation of the complexes described in this paper were carried out in a dry-box filled with prepurified nitrogen and dried with Na/K alloy.

Elemental analyses of C, H, N were performed as reported in ref (6), chlorides were titrated potentiometrically with $AgNO_3$.

IR spectra in nujol mulls were recorded on a Perkin-Elmer 621 Spectrophotometer (4000-400 cm^{-1}, CsI discs) and a Beckman IR 11 Spectrophotometer (400-100 cm^{-1}, polyethylene discs).

Preparation of adducts of MCl_4 with H_2salen and H_2salpropen.

A solution of UCl_4 or $ThCl_4$.2DME in tetrahydrofuran was treated with a slight excess of Schiff base(molar ratio 1:1) in tetrahydrofuran and the mixture was stirred at room temperature for about 10 hr; no evolution of HCl gas was observed. The precipitate formed was filtered, washed with THF and dried in vacuo at room temperature. The products were analysed correctly (see Table 1) for the formulas $UCl_4(H_2$salen)THF (compound I), $ThCl_4(H_2$salen)THF (compound II), $UCl_4(H_2$salpropen) (compound III) and $ThCl_4(H_2$salpropen)THF (compound IV).

Preparation of M(salen)$_2$ and M(salpropen)$_2$.

Solid Tl_2salen or Tl_2salpropen was added slowly under agitation to a solution of UCl_4 or $ThCl_4$.2DME in tetrahydrofuran (molar ratio 2:1); the mixture was stirred at room temperature for about 6 hr, then TlCl was filtered out, the solvent from the resulting solution was partially evaporated under reduced pressure, hexane was added and the precipitate obtained was collected by filtration and dried in vacuo. The products were analysed correctly (see Table

I) for the formulas U(salen)$_2$ (compound V), Th(salen)$_2$ (compound VI), U(salpropen)$_2$ (compound VII) and Th(salpropen)$_2$ (compound VIII).

TABLE 1

Analytical data of Uranium(IV) and Thorium(IV) complexes (calculated values in parenthesis).

	Compound	colour	C %	H %	N %	Cl %
I	UCl$_4$(H$_2$salen)THF	yellow orange	33.30 (33.35)	3.58 (3.36)	3.78 (3.89)	19.70 (19.70)
II	ThCl$_4$(H$_2$salen)THF	pale yellow	33.40 (33.63)	3.62 (3.39)	3.71 (3.92)	19.63 (19.86)
III	UCl$_4$(H$_2$salpropen)	yellow	30.78 (30.83)	2.89 (2.74)	4.18 (4.23)	21.32 (21.41)
IV	ThCl$_4$(H$_2$salpropen)THF	yellow	34.48 (34.63)	3.49 (3.60)	3.71 (3.85)	19.38 (19.47)
V	U(salen)$_2$	brown	49.66 (49.87)	3.61 (3.66)	7.15 (7.27)	- -
VI	Th(salen)$_2$	pale yellow	50.64 (50.27)	3.84 (3.69)	7.29 (7.33)	- -
VII	U(salpropen)$_2$	red brown	50.80 (51.13)	4.02 (4.04)	6.87 (7.01)	- -
VIII	Th(salpropen)$_2$	yellow	51.53 (51.52)	4.08 (4.07)	7.02 (7.07)	- -
IX	U(salen)Cl$_2$.2THF	green	40.17 (40.07)	4.15 (4.20)	3.88 (3.89)	9.63 (9.86)
X	Th(salen)Cl$_2$.2THF	pale yellow	40.48 (40.40)	4.22 (4.24)	3.96 (3.93)	10.01 (9.93)

Preparation of M(salen)Cl_2.2THF.

These compounnds were prepared in THF as the ones previously described from UCl_4 or $ThCl_4$.2DME and Tl_2salen in molar ratio 1:1. The products were analysed correctly (see Table I) for the formulas U(salen)Cl_2.2THF (compound IX) and Th(salen)Cl_2.2THF (compound X).

Attempts to prepare U(salpropen)Cl_2 and Th(salpropen)Cl_2 complexes following a similar method, or by refluxing in chloroform H_2salpropen adducts with an excess of pyridine followed by heating in vacuo, or by reacting a THF solution of U(salpropen)$_2$ with UCl_4 and Th(salpropen)$_2$ with $ThCl_4$.2DME, failed. Similar redistribution reactions carried out in THF with U(salen)$_2$ and UCl_4 and Th(salen)$_2$ with $ThCl_4$, give the chloro-derivatives U(salen)Cl_2.2THF and Th(salen)Cl_2.2THF respectively.

Reaction of M(salen)Cl_2.2THF with Thallium(I) diethyldithiocarbamate, Tl(dtc).

Tl(dtc) was added slowly under agitation to a solution of U(salen)Cl_2.2THF (molar ratio 2:1) in tetrahydrofuran. The mixture was stirred at room temperature for about 6 hr, then TlCl was filtered out, hexane was added to the resulting solution and the precipitate obtained was collected by filtration and dried in vacuo. The brown product was analysed correctly for U(salen)(dtc)$_2$.

Anal.calcd. for $UC_{26}H_{34}N_4O_2S_4$: C, 38.99; H, 4.28; N, 6.97. Found: C, 39.02; H, 4.29; N, 6.82.

By reacting Th(salen)Cl_2.2THF with Tl(dtc), a white product which was analysed correctly for Th(salen)(dtc)$_2$, was obtained.

Anal.calcd. for $ThC_{26}H_{34}N_4O_2S_4$: C, 39.29; H, 4.31; N, 7.05. Found: C, 39.32; H, 4.28; N, 7.01.

RESULTS AND DISCUSSION

Table I shows the elemental analyses of the Uranium(IV) and Thorium(IV) complexes and in Table 2 the significative IR frequencies for the free Schiff bases and the relative complexes are given along with the appropriate assignements.

All the adducts (compounds I, II, III and IV) show a weak band in the 3200-3100 cm^{-1} region: this absorption could be assigned to the OH····N bond; in the free ligands the corresponding band falls at about 2700 cm^{-1} (broad and weak) owing to the intramolecular hydrogen bonded OH. Such a band has been found in the 3200-3000 cm^{-1} region in the adducts of Schiff bases with uranium tetrachloride (1), lanthanides (7), titanium (8), tungsten(VI) dioxodichloride (9) and in some Schiff base complexes of organotin where non coordinated OH are present (10).

TABLE 2

IR frequencies of the Schiff bases and Uranium(IV) and Thorium(IV) complexes.

	Compound	ν(OH)	ν(C=N)	ν(C=C)	ν(C-O)	ν(COC)	ν(COC)	ν(U-N)
	H$_2$salen	2730	1635	1590	1286			
	H$_2$salpropen	2735	1630	1590	1280			
I	UCl$_4$(H$_2$salen)THF	3148	1651	1605	1289	1021	867	576
II	ThCl$_4$(H$_2$salen)THF	3082	1651	1605	1279	1019	876	583
III	UCl$_4$(H$_2$salpropen)	3219	1658	1602	1268			596
IV	ThCl$_4$(H$_2$salpropen)THF	3105	1652	1602	1287	1028	870	583
V	U(salen)$_2$		1635	1596	1305			601
VI	Th(salen)$_2$		1632	1597	1311			598
VII	U(salpropen)$_2$		1626	1598	1303			591
VIII	Th(salpropen)$_2$		1623	1594	1306			589
IX	U(salen)Cl$_2$.2THF		1628	1597	1313	1030	870	591
X	Th(salen)Cl$_2$.2THF		1625	1597	1297	1026	860	586

In the other complexes no bands are present in this region,owing to the chelates formation through the oxygen atoms.

A strong band found for the free Schiff bases in 1635-1630 cm^{-1} region and assigned to C=N stretch, is observed at about 1650 cm^{-1} in the adducts. This shift towards higher frequency suggests coordination through the azomethine nitrogen. This results in an increase in the bond order of the carbon to nitrogen link.

This band due to the C=N stretch, in the complexes V-X does not show considerable shift or shows a shift towards lower frequency.

The bands at about 1600 cm^{-1} may be assigned to ν(C=C) vibrations.

The band due to the phenolic C-O stretch at about 1280 cm^{-1} in the free base, does not show appreciably shift in the adducts I-IV as also noticed in ref.(11, 12). The same band in the complexes V-X is shifted about 20 cm^{-1} towards higher frequency. An analogous behaviour has been observed for several complexes of Schiff bases (8, 11, 12-15) in which chelates are present.

In fact in the chelates formation the C=N stretching frequency shows a shift to lower frequencies, so indicating less double-bond character and the absorption frequencies of the phenolic C-O show a shift to higher frequencies in going from a hydrogen bonded structure to a covalent metal bonded structure.

The complexes I, II, IV, IX and X show two strong bands at about 1020 and 875 cm^{-1} attributed to the asymmetric and symmetric C-O-C stretching vibrations of coordinated tetrahydrofuran.

The IR data relative to the adducts I-IV indicate that the Schiff bases coordinate MCl_4 acting as bidentate ligands. The shift of the C=N bands in the adducts is of the same order as found for ligands which do not contain salicylaldehyde OH group (11, 12), so suggesting a coordination through the azomethine nitrogen and a consequent weakening of the OH····N bond, the oxygens of the salicylaldehyde rings being generally not involved in bonding formation, owing to the band at 3200 cm^{-1}.

The IR interpretation of V-X complexes, in which there are a lowering in the C=N stretch and an increase in the C-O stretch suggests that the coordination bond has been formed between metal ion and two azomethine groups of the ligands and oxygen-metal bonds have been set up.

We have assigned the definite strong band at about 590 cm^{-1} to the ν(M-N) vibration.

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