Mixed Complexes of *N*,*N'*-Ethylenebis(salicylideneiminato)uranium(IV)

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Some mixed *N*,*N'*-ethylenebis(salicylideneiminato), salen, complexes of uranium(IV) of formula U(salen)X_2 (X = Cl, acetylacetonato, dipivaloylmethanato, *N*-methylsalicylideneiminato, dibenzoylmethanato) are reported. It is shown that U(salen)$_2$ and UCl_4 undergo a ligand redistribution reaction in tetrahydrofuran (THF) leading to U(salen)Cl_2,2THF. Chemical and mass spectrometric data are presented supporting the monomeric structure of the complexes of formula U(salen)(chelate)$_2$. Evidence is presented suggesting the transitory formation of the adduct U(salen)$_2$,UCl_4 in the course of the redistribution reaction leading to U(salen)Cl_2.

We know of only one example of *N*,*N'*-ethylenebis(salicylideneiminato) complex of uranium(IV), which is bis[*N*,*N'*-ethylenebis(salicylideneiminato)]uranium(IV), hereinafter abbreviated as U(salen)$_2$.[1]

Work has been carried out in the past on Schiff base metal complexes of 3*d* transition elements, especially with oxygen complexes[2] and organometallic compounds.[3,4] It was therefore of interest to extend our previous observations to uranium(IV) of f^2 configuration. In a preliminary note the preparation of U(salen)Cl_2 and U(salen)Cl_2,2THF (THF = tetrahydrofuran) has been reported.[5] We now describe further details of the redistribution reaction between U(salen)$_2$ and UCl_4 and some mixed complexes of general formula U(salen)X_2 (X = Cl, *N*-methylsalicylideneiminato, acetylacetonato, dibenzoylmethanato, dipivaloylmethanato).

RESULTS AND DISCUSSION

Treatment of UCl_4 with the Schiff base salenH_2 in tetrahydrofuran results in the formation of the adduct UCl_4,salenH_2,THF, compound (I). A similar adduct, with a lower content of tetrahydrofuran, was obtained with *N*-methylsalicylidineimine, compound (II). The salenH_2 adduct, by refluxing in chloroform with an excess of pyridine, followed by heating *in vacuo*, was converted into the dichloro-derivative (III), of formula U(salen)Cl_2. The latter is a microcrystalline solid sparingly soluble in the common organic solvents. Its magnetic moment at room temperature $\mu_{\text{eff}} = 2{\cdot}85$ B.M., which is in the range of values commonly encountered[6,7] for uranium(IV) complexes of f^2 configuration with a non-singlet ground state. The dichloro-derivative (III) can be recrystallised from tetrahydrofuran as the green U(salen)Cl_2,2THF (IVa).

The preliminary results of an *X*-ray investigation[8] have shown that (IVa) is a monomeric complex. Co-ordinated THF groups are also evidenced by two bands at 1030 and 870 cm^{-1}, attributed to the asymmetric and symmetric C–O stretching vibrations, respectively.

The possibility for *N*,*N'*-ethylenebis(salicylideneiminato)metal complexes acting as oxygen donors for *d* transition elements,[9-12] non-transition elements,[13,14] and

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alkali metal cations[15] is well documented in the literature. By treating dichloromethane solutions of $\mathrm{UCl_4}$ with $\mathrm{U(salen)_2}$ we found evidence of Lewis acid-base interaction but no well defined product could be isolated. On the other hand, $\mathrm{UCl_4}$ and $\mathrm{U(salen)_2}$, both initially *dissolved* in tetrahydrofuran, yielded a precipitate analysing for $\mathrm{U(salen)Cl_2,2THF}$ (IVb). The latter was found, by *X*-ray powder diagram, to be identical with (IVa). This observation shows that rearrangement of the ligands around the two uranium centres takes place in tetrahydrofuran, most probably *via* the preliminary formation of the 1 : 1 adduct, $\mathrm{U(salen)_2,UCl_4}$. The following equilibria are suggested to be operating in tetrahydrofuran solution:

$$\mathrm{U(salen)_2 + UCl_4 \rightleftharpoons U(salen)_2,UCl_4} \qquad (1)$$

$$\mathrm{U(salen)_2,UCl_4 \rightleftharpoons 2\,U(salen)Cl_2} \qquad (2)$$

Solvation by tetrahydrofuran is not shown in equations (1) and (2).

Although, as mentioned above, we were unable to isolate the 1 : 1 adduct of equation (1), we have verified that *N,N'*-ethylenebis(salicylideneiminato)nickel(II) forms a 1 : 1 adduct with $\mathrm{UCl_4}$ of formula $\mathrm{Ni(salen),UCl_4}$, compound (V). This adduct was obtained by reacting Ni(salen) with dichloromethane *solutions* of $\mathrm{UCl_4}$. The nickel : uranium ratio was one, independently of the stoicheiometric ratios employed between 1 and 0·5. The magnetic moment of the 1 : 1 adduct $\mu_{\mathrm{eff}} = 3{\cdot}04$ B.M., in good agreement with the value of $\mu_{\mathrm{eff}} = 2{\cdot}93$ B.M. found[16] for $\mathrm{UCl_4}$ itself thus showing no contribution to the magnetic susceptibility by nickel. Since Ni(salen) is a d^8 low-spin (diamagnetic) system, it is suggested that no important change of stereochemistry around the nickel atom has taken place upon formation of the 1 : 1 adduct.

We believe that the transitory formation of the $\mathrm{U(salen)_2,UCl_4}$ adduct is a necessary requirement for the redistribution reaction to take place. It may appear reasonable to suppose that similar redistribution reactions may occur with $\mathrm{UCl_4}$, provided the other reactant has some residual Lewis basicity. The scope of the redistribution reaction reported in this paper is now under investigation. It is also worth noting that redistribution reactions for uranium(IV) chelates have been little studied.[17] Siddall and Stewart have reported ^{1}H n.m.r. evidence of a slow intermolecular exchange between β-diketonato-complexes of uranium(IV).[18]

The reaction of $\mathrm{U(salen)_2}$ with $\mathrm{UCl_4}$ in tetrahydrofuran makes the dichloro-derivatives $\mathrm{U(salen)Cl_2}$ readily accessible. We have also verified that equimolar quantities of $\mathrm{U(salen)_2}$ and $\mathrm{UCl_4}$ react with 2,2'-bipyridyl (bipy) in the following manner:

$$\mathrm{U(salen)_2 + UCl_4 + 2\,bipy \xrightarrow{THF} 2U(salen)Cl_2(bipy)} \qquad (3)$$

(VI)

Compound (VI) was the only isolable product from reaction (3) and no detectable amounts of $\mathrm{U(salen)_2}$ or the nitrogen base[19,20] adduct $\mathrm{UCl_4,(bipy)_2}$ were observed.

Also the conjugate bases of acetylacetone (acacH), dipivaloylmethane (dpmH), and *N*-methylsalicylideneimine (mesalH) react with equimolar quantities of $\mathrm{U(salen)_2}$ and $\mathrm{UCl_4}$ yielding the mixed complexes:

$$\mathrm{U(salen)_2 + UCl_4 + 4\,acac^- \longrightarrow 2\,U(salen)(acac)_2 + 4\,Cl^-} \qquad (4)$$

$$\mathrm{U(salen)_2 + UCl_4 + 4\,dpm^- \longrightarrow 2\,U(salen)(dpm)_2 + 4\,Cl^-} \qquad (5)$$

$$\mathrm{U(salen)_2 + UCl_4 + 4\,mesal^- \longrightarrow 2\,U(salen)(mesal)_2 + 4\,Cl^-} \qquad (6)$$

Reactions (4)—(6) were carried out in tetrahydrofuran in the presence of anhydrous ammonia. The complexes resulting from the reactions were separated quite easily after elimination of the substantially insoluble ammonium chloride by filtration. The use of anhydrous ammonia for the preparation of uranium alkoxides from uranium halides and alcohols was reported by Gilman and his co-workers.[21]

It is important to realise that reactions (3)—(6) were carried out in two separate stages, the first one being that of reacting $\mathrm{U(salen)_2}$ with $\mathrm{UCl_4}$ over a time sufficient for equilibria (1)—(2) to be reached, in such a way that $\mathrm{U(salen)Cl_2}$ is the predominant reactive species. It has in fact been shown that $\mathrm{U(salen)_2}$ and $\mathrm{U(acac)_4}$ do not react appreciably under comparable conditions.

In agreement with the results reported above, we have also found that the mixed complex of uranium(IV) is obtained by reacting preformed $\mathrm{U(salen)Cl_2}$ (III) with dibenzoylmethane (dbmH) in the presence of anhydrous ammonia:

$$\mathrm{U(salen)Cl_2 + 2\,dbm^- \xrightarrow{THF} 2\,Cl^- + U(salen)(dbm)_2} \qquad (7)$$

It is interesting to note that in the case of the bis(acetylacetonato) mixed complex prepared according to reaction (4), no evidence was found of $\mathrm{U(salen)_2}$ and $\mathrm{U(acac)_4}$. As in the case of the 2,2'-bipyridyl adduct, it therefore appears that the mixed complex is thermodynamically favoured. However, in the case of the dipivaloylmethanato-complex resulting from reaction (5) we have found definite evidence of $\mathrm{U(salen)_2}$ and $\mathrm{U(dpm)_4}$ being present in the reaction mixture together

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with U(salen)(dpm)$_2$. The latter could be isolated in a pure form only by fractional crystallisation.

Definitive proof for the existence of the mixed complexes of uranium(IV) has been obtained by mass spectrometry of U(salen)(acac)$_2$ and U(salen)(dpm)$_2$, which appear to be the most volatile compounds among those prepared. The mass spectrometric results are reported in Tables 1 and 2. Both spectra show intense molecular ions at *m/e* 702 and 870, respectively, whereas the most abundant ions are those with *m/e* 603 and 687, corresponding to (M — acac) and (M — dpm), respectively. High resolution measurements performed with U(salen)(acac)$_2$ definitely confirm the assigned formulae.

TABLE 1

Mass spectrum of U(salen)(acac)$_2$

	Relative [a] intensities/		Mass	
m/e	%	Assigned formula	Measured	Calc.
702	50	[U(salen)(acac)$_2$]$^+$ (M^+)	n.d.	702·2442
603	100	[M — acac]$^+$	603·2000	603·1996
521	14	[UOH(salen)]$^+$	521·1515	521·1577
301·5	6	[M — acac]$^{2+}$	301·5992	301·5998

[a] The relative intensity of the ion [M — acac]$^+$ is set arbitrarily at 100. Isotopic ions, ions not containing uranium, and ions of relative intensities lower than 5% have been neglected.

TABLE 2

Mass spectrum of U(salen)(dpm)$_2$

m/e	Relative [a] intensities/%	Assigned formula
870	70	[U(salen)(dpm)$_2$]$^+$ (M^+)
687	100	[M — dpm]$^+$
520	42	[UO(salen)]$^+$
343·5	17	[M — dpm]$^+$

[a] The relative intensity of the ion [M — dpm]$^+$ is set arbitrarily at 100. Isotopic ions, ions not containing uranium, and ions of relative intensities lower than 5% have been neglected.

TABLE 3

Analytical data (%) of uranium(IV) complexes

			Found					Calculated				
			C	H	Cl	N	U	C	H	Cl	N	U
(I) UCl$_4$(salenH$_2$)(THF)	$C_{20}H_{24}Cl_4N_2O_3U$	Yellow-orange	34·0	3·5	19·25	3·5	33·35	33·35	3·36	19·69	3·89	33·05
(II) UCl$_4$(mesalH)$_2$,0·25THF	$C_{17}H_{20}Cl_4N_2O_{2\cdot25}U$	Yellow-orange	30·2	3·15	21·3	3·7	35·1	30·56	3·02	21·22	4·19	35·62
(III) U(salen)Cl$_2$	$C_{16}H_{14}Cl_2N_2O_2U$	Green	32·6	2·45	12·85	5·3	41·2	33·41	2·45	12·33	4·87	41·38
(IVa) U(salen)Cl$_2$(THF)$_2$	$C_{24}H_{30}Cl_2N_2O_4U$	Green	40·6	4·3	9·9	4·45	n.d.	40·07	4·20	9·86	3·89	33·08
(IVb) U(salen)Cl$_2$(THF)$_2$			39·5	4·15	9·85	4·05	n.d.					
(V) Ni(salen),UCl$_4$	$C_{16}H_{14}Cl_4N_2NiO_2U$	Yellow-orange	27·5	2·6	19·5	4·2	33·55 [a]	27·26	2·00	20·12	3·97	33·77
(VI) U(salen)Cl$_2$(bipy)	$C_{26}H_{22}Cl_2N_4O_2U$	Light green	42·8	3·0	10·45	7·4	32·3	42·70	3·03	9·69	7·66	32·54
(VII) U(salen)(acac)$_2$	$C_{26}H_{28}N_2O_6U$	Green-yellow	44·1	4·0		3·55	33·9	44·45	4·02		3·99	33·88
(VIII) U(salen)(dpm)$_2$	$C_{38}H_{52}N_2O_6U$	Brown	51·95	5·95		2·6	n.d.	52·41	6·02		3·22	27·33
(IX) U(salen)(mesal)$_2$	$C_{32}H_{30}N_4O_4U$	Deep brown	49·55	3·95		7·1	30·5	49·74	3·91		7·25	30·81
(X) U(salen)(dbm)$_2$	$C_{46}H_{36}N_2O_6U$	Deep brown	57·9	4·0		2·9	24·75	58·11	3·82		2·95	25·03

[a] Nickel analysis: found, 8·15; calc., 8·33%.

In view of the reported[22,23] exchange occurring in the ion source of the mass spectrometer with some metal chelates, we have checked that the observed molecular ions were genuine. With a synthetic mixture of U(salen)$_2$ and U(acac)$_4$ under the same operative conditions, we have observed the spectra of both components[24a] and very small intensities of the mixed ions. Similar results were obtained with a mixture of U(salen)$_2$ and U(dpm)$_4$. On the other hand, the ions due to U(salen)$_2$ and the tetrakis-β-diketonato-complex observed in the mass spectra of the mixed complexes had low intensities (<5%).

The mixed complexes U(salen)(chelate)$_2$ are monomeric as shown by the observation of the molecular ions for U(salen)(acac)$_2$ and U(salen)(dpm)$_2$ and by the cryoscopic molecular weight determination carried out in nitrobenzene for U(salen)(dbm)$_2$. In agreement with these facts, and also with the structural data already obtained[8] for U(salen)Cl$_2$,2THF, we propose for the mixed complexes a monomeric structure in which the uranium atom attains its usual eight-co-ordination, and the salen donor atoms may have a substantially planar arrangement.

EXPERIMENTAL

All the operations described in this paper were carried out under an atmosphere of prepurified nitrogen. Solvents were carefully dried. Anhydrous uranium tetrachloride was prepared by a slight modification of the reported[24b] procedure, namely from UO$_3$ (or UO$_2$) and hexachloropropene, by pretreating the oxides at 240 °C in a slow stream of dry oxygen.

The i.r. spectra were measured as Nujol mulls with a Perkin-Elmer 337 grating instrument.

Low resolution (RP 1000) spectra were measured with a LKB 9000 mass spectrometer. High resolution (RP 10 000)

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spectra were measured with an A.E.I. MS 902 S mass spectrometer attached to an A.E.I. DS 10 data system. Both low and high resolution mass spectra were obtained by direct probe insertion at 70 eV and with a source temperature of 240—270 °C.

Adduct of UCl$_4$ *with* N,N′-*Ethylenebis*(*salicylideneiminato*), salenH$_2$, *Compound* (I).—To a suspension of UCl$_4$ (4·73 g; 12·45 mmol) in tetrahydrofuran (50 ml) a solution in the same solvent (150 ml) of the Schiff base (3·35 g; 12·49 mmol) was added in *ca.* 1 h. The yellow-orange precipitate formed was filtered off and dried *in vacuo* at room temperature (87% yield). The product analysed correctly (see Table 3) for the formula UCl$_4$,salenH$_2$,THF. The i.r. spectrum (Nujol mull) compared with that of the free ligand has typical bands at 3180s, *ca.* 2700w,br, 590s, and 555s cm^{-1}.

By using a similar procedure, the *N*-methylsalicylideneimine adduct with UCl$_4$, compound (II), was prepared.

Preparation of U(salen)Cl$_2$ (III).—The adduct (6·70 g; 9·30 mmol) prepared as described above was treated in chloroform (100 ml) with pyridine (11 ml; 0·136 mol). The resulting suspension was refluxed overnight; the dark green solid was separated by filtration and dried *in vacuo* initially at room temperature and then at 150 °C for two days. The resulting green solid weighed 4·02 g, corresponding to a 75·1% yield. The thermal treatment was monitored by measuring the i.r. spectrum of the solid. The disappearance of a band at 700 cm^{-1} was found to be particularly advantageous to indicate a complete conversion into the final product.

The i.r. spectrum of (III) has main bands at 1630, 1600, 1550, 1300, 915, 815, 755, and 610 cm^{-1}.

The magnetic moment of (III) at 19 °C is μ_{eff} 2·85 B.M. ($\chi_{\text{M}}^{\text{corr}}$ 3470 × 10^{-6} c.g.s.u.; diamagnetic correction 188 × 10^{-6} c.g.s.u.).

Preparation of U(salen)Cl$_2$(THF)$_2$ (IVa).—Recrystallisation of (III) from tetrahydrofuran at about 100 °C in a stainless steel autoclave or at reflux temperature at ordinary pressure yielded the tetrahydrofuran derivative (IVa) as a green crystalline solid, whose analytical results are indicated in Table 3. The i.r. spectrum of (IVa) is quite similar to that of (III), except for two strong bands at 1030 and 870 cm^{-1} attributed to the asymmetric and symmetric C–O stretching vibrations of co-ordinated tetrahydrofuran. The similar bands in the iron(III) complex FeCl$_3$,THF, were observed [25] at 988 and 833 cm^{-1}.

Compound (IVb) shown by *X*-ray powder diagram to be identical with (IVa) was prepared by the following procedure.

A solution of U(salen)$_2$ (1·260 g; 1·63 mmol) in tetrahydrofuran (100 ml) was treated with anhydrous UCl$_4$ (0·620 g; 1·63 mmol) dissolved in tetrahydrofuran. The mixture was stirred for *ca.* 3 h and the resulting green precipitate was collected by filtration, washed with tetrahydrofuran, and dried *in vacuo* (0·90 g; 76·7% yield).

Preparation of Ni(salen),UCl$_4$ (V).—Uranium tetrachloride (0·58 g; 1·53 mmol) was dissolved in dichloromethane (40 ml) and stirred with *N,N′*-ethylenebis(salicylideneiminato)nickel(II), Ni(salen) (0·50 g; 1·54 mmol), for two days at room temperature. The resulting yellow-orange solid was filtered and dried *in vacuo*. The yield was substantially quantitative. The 1 : 1 adduct is sparingly soluble in dichloromethane and is decomposed by moisture. Similar results were obtained by using an excess of UCl$_4$ [1·50 mmol for 0·744 mmol of Ni(salen)].

The magnetic moment is μ_{eff} 3·04 B.M. at 293 K (diamagnetic correction 238 × 10^{-6} c.g.s.u.).

Preparation of U(salen)Cl$_2$(bipy) (VI).—A solution of U(salen)$_2$ (0·450 g; 0·58 mmol) in tetrahydrofuran (100 ml) was treated at room temperature with UCl$_4$ (0·255 g; 0·59 mmol). After 3 h, 2,2′-bipyridyl (0·364 g; 2·33 mmol) was added and the mixture was stirred over 20 h. The solvent from the resulting solution was partially evaporated under reduced pressure. The light green precipitate obtained was collected by filtration and dried *in vacuo* (0·40 g; 47·1% yield).

The main i.r. bands were observed at 1630, 1600, 1550, 1290, 1215, 1015, 860, 810, 770, 760, and 610 cm^{-1}.

Preparation of U(salen)(acac)$_2$, (VII).—U(salen)$_2$ (2·12 g; 2·75 mmol) was treated with UCl$_4$ (1·06 g; 2·79 mmol) in tetrahydrofuran (50 ml) over 40 h at room temperature. To the resulting reaction mixture acetylacetone (1·10 g; 10·99 mmol) was added and the reaction flask was then saturated with anhydrous ammonia. After 4 h the gas absorption had ceased. The reaction mixture was filtered and the solid was washed with tetrahydrofuran (125 ml). The filtered solution on cooling separated 0·17 g (4·4% yield) of crystalline product having the correct analysis for U(salen)(acac)$_2$. The mother liquor, by partial reduction of the volume and addition of heptane, separated 1·1 g (28·5% yield) of product having the correct analysis for U(salen)(acac)$_2$. Finally, the solid which had been left from the first filtration was rapidly washed with deaerated water to eliminate NH$_4$Cl and dried *in vacuo* (1·4 g; 36·2% yield): also this solid, according to the analytical results, was U(salen)(acac)$_2$. The total yield of analytically pure compound was therefore 69·1%.

The compound is slightly soluble in tetrahydrofuran, insoluble in and unaffected by water.

The main i.r. bands were observed at 1630, 1580br, 1530, 1300, 1280, 1210, 1155, 1130, 1050, 1020, 990, 920, 915, 865, 810, 780, 760, 650, 600, and 580 cm^{-1}.

The magnetic moment was μ_{eff} 2·78 B.M. at 22 °C ($\chi_{\text{M}}^{\text{corr}}$ 3270 × 10^{-6} c.g.s.u.; diamagnetic correction 277 × 10^{-6} c.g.s.u.).

Preparation of U(salen)(dpm)$_2$, (VIII).—U(salen)$_2$ (0·83 g; 1·08 mmol) was treated with UCl$_4$ (0·41 g; 1·08 mmol) in tetrahydrofuran (50 ml) over 3 h. To the resulting reaction mixture, dipivaloylmethane (0·79 g; 4·29 mmol) was added and anhydrous ammonia introduced. After 2 h ammonium chloride was separated by filtration. Fractional crystallisation from heptane gave 0·12 g (6·4% yield) of a brown microcrystalline solid which was shown to be U(salen)(dpm)$_2$ by elemental analysis (see Table 3) and mass spectrometry.

By a procedure essentially similar to those reported for U(salen)(acac)$_2$ and U(salen)(dpm)$_2$, compound (IX) of Table 3 was obtained in 70% yield.

Preparation of U(salen)(dbm)$_2$, (X).—A suspension of U(salen)Cl$_2$, (III) (1·046 g; 1·82 mmol), in tetrahydrofuran (100 ml) was treated with dibenzoylmethane (0·82 g; 3·66 mmol), saturated with gaseous ammonia at room temperature, and stirred for 3 h. The resulting solution was filtered to eliminate NH$_4$Cl and heptane was added to it: the deep brown precipitate so obtained was collected by filtration and dried *in vacuo* (1·25 g; 72·2% yield).

The molecular weight by cryoscopy in nitrobenzene was found to be 937 (calc. 950·8).

The main i.r. bands were observed at 1630, 1590, 1510,

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[25] L. S. Benner and C. A. Root, *Inorg. Chem.*, 1972, **11**, 652.

1300, 1220, 1150, 1070, 1020, 930, 905, 800, 745, 715, 680, and 600 cm^{-1}.

The magnetic moment was μ_{eff} 2·69 B.M. at 20 °C (χ_M^{corr} 3080 c.g.s.u.; diamagnetic correction 420 c.g.s.u.).

Compounds (VI), (VII), and (VIII) are soluble in common organic solvents, especially polar ones.

Attempted Reaction of U(salen)$_2$ *with* U(acac)$_4$.—Tetrakis(acetylacetonato)uranium(IV) (0·17 g; 0·27 mmol) was treated with U(salen)$_2$ (0·205 g; 0·27 mmol) in tetrahydrofuran (80 ml) over 3 h. After partial evaporation of the solvent under reduced pressure, a green solid (0·16 g) was obtained. The latter had a C,H analysis very close to that of U(salen)$_2$ and its i.r. spectrum was substantially identical to that of U(salen)$_2$ with some bands of low intensity due to U(acac)$_4$. From the filtered solution more solid was obtained which had an i.r. spectrum very similar to that of U(acac)$_4$.

We wish to thank Snam–Progetti for support, Dr. S. Frediani for measuring the magnetic susceptibilities, and Mr. Mancini for measuring the mass spectra.

[3/2261 *Received, 2nd November*, 1973]