Dichloro-derivatives of *NN*′-Ethylenebis(salicylideneiminato)uranium(IV) and a Redistribution Reaction for a Uranium(IV) Chelate

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Summary A ligand redistribution reaction in tetrahydrofuran between Usalen$_2$ and UCl$_4$ led to the formation of UsalenCl$_2$,2THF, which was also prepared by an independent method.

COMPARISON between *d* and *f* transition elements is a subject of current interest in view of the still debated problem of the *f* orbital contribution to bonding in actinide compounds.[1] We plan to extend our previous observations[2] on Schiff base complexes of *d* transition elements to uranium(IV) having an f^2 configuration. To the best of our knowledge, the only known example of an *NN*′-ethylenebis(salicylideneiminato) complex of uranium(IV) is Usalen$_2$.[3]

We have found that UCl$_4$ reacts with salenH$_2$ in tetrahydrofuran at room temperature to give a yellow-orange 1:1 adduct of formula UCl$_4$salenH$_2$,THF, (I). The latter by treatment with pyridine in chloroform, followed by heating *in vacuo* at 150° for two days, yielded the green UsalenCl$_2$, (II), $\mu_{\text{eff}} = 2{\cdot}85$ BM, 292 K, diamagnetic correction $= 188 \times 10^{-6}$ cgsu. The dichloro-derivative (II), by recrystallisation from THF, yielded the green THF adduct UsalenCl$_2$,2THF, (IIIa). Co-ordinated THF groups are evident from the two bands at 1030 and 870 cm^{-1} in the i.r. spectrum, attributed to the asymmetric and symmetric C–O stretching vibrations, respectively. Preliminary results of an *X*-ray investigation[4] show that (IIIa) is monomeric and the uranium atom is octaco-ordinate with the chloro-groups on opposite sides of the salen ligand.

Equimolar quantities of UCl$_4$ and Usalen$_2$ react in THF solution to give a precipitate, (IIIb), analysing as UsalenCl$_2$,2THF. Compounds (IIIa) and (IIIb) were found to be identical by *X*-ray powder diagrams. Equimolar quantities of UCl$_4$ and Usalen$_2$ also react with 2,2′-dipyridyl (dipy) according to the following stoicheiometry:

$$\text{UCl}_4 + \text{Usalen}_2 + 2\ \text{dipy} \longrightarrow 2\ \text{UsalenCl}_2\text{,dipy} \qquad (1)$$

These results can be rationalised in terms of the redistribution reaction (3), the latter being most probably preceded by the formation of the 1:1 adduct shown in equation (2). Solvation is not shown in equations (2) and (3) for simplicity.

$$\text{UCl}_4 + \text{Usalen}_2 \longrightarrow \text{Usalen}_2\text{,UCl}_4 \qquad (2)$$

$$\text{Usalen}_2\text{,UCl}_4 \longrightarrow 2\ \text{UsalenCl}_2 \qquad (3)$$

The possibility of *NN*′-ethylenebis(salicylideneiminato)-metal complexes acting as oxygen donors with *d* transition elements[5] and nontransition elements[6] is well documented.

We believe that the formation of the 1 : 1 adduct shown in equation (2) is a necessary requirement for the redistribution reaction to take place. We have verified that UCl_4 adds to Nisalen in dichloromethane giving the yellow-orange 1 : 1 adduct Nisalen,UCl_4, (V), $\mu_{eff} = 3{\cdot}04$ BM, 293 K, diamagnetic correction $= 238 \times 10^{-6}$ cgsu.

Satisfactory analytical results were obtained for all the compounds.

Redistribution reactions of uranium(IV) chelates have been little studied.[7] The scope of the redistribution reaction (3) and its preparative implications are now under investigation.

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