

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

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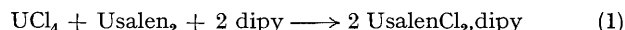
Summary A ligand redistribution reaction in tetrahydrofuran between Usalen_2 and UCl_4 led to the formation of $\text{UsalenCl}_2 \cdot 2\text{THF}$, which was also prepared by an independent method.

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 observations² 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

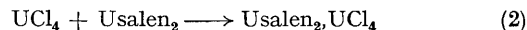
We have found that UCl_4 reacts with salenH_2 in tetrahydrofuran at room temperature to give a yellow-orange 1:1 adduct of formula $\text{UCl}_4\text{salenH}_2 \cdot \text{THF}$, (I). The latter by treatment with pyridine in chloroform, followed by heating *in vacuo* at 150° for two days, yielded the green UsalenCl_2 , (II), $\mu_{\text{eff}} = 2.85$ BM, 292 K, diamagnetic correction = 188×10^{-6} cgsu. The dichloro-derivative (II), by recrystallisation from THF, yielded the green THF adduct $\text{UsalenCl}_2 \cdot 2\text{THF}$, (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 investigation⁴ 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 $\text{UsalenCl}_2 \cdot 2\text{THF}$. 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 stoichiometry:



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.



The possibility of *NN'*-ethylenebis(salicylideneiminato)-metal complexes acting as oxygen donors with *d* transition elements⁵ and nontransition elements⁶ 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), $\mu_{\text{eff}} = 3.04 \text{ BM}$, 293 K, diamagnetic correction = $238 \times 10^{-6} \text{ cgsu}$.

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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