Spectrophotometric Study of Mixed Uranium(IV) Chloro-Bromo Complexes in Nitromethane

CHR. KLIXBÜLL JØRGENSEN

Cyanamid European Research Institute, Cologny (Geneve), Switzerland

Crystalline $[P(C_6H_5)_3H]_2UBr_6$ and the similar salt of UCl_6^{2-} were prepared according to Venanzi and Day. The narrow absorption bands due to internal $5f^2$ transitions were used for detection of mixed complexes $UBr_xCl_{6-x}^{2-}$ in nitromethane solution (small amounts of alcohols destroy the octahedral symmetry of the uranium(IV)complex). The dimensionless consecutive formation constants for formation of $UBrCl_5^{2-}$ and $UBr_2Cl_4^{2-}$ by addition of $N(C_4H_9)_4Br$ to the hexachloro complex were found to be $K_1 = 0.3$ and $K_2 = 0.05$. The typical A character of U(IV) is clearly shown by chloride being bound at least 20 times stronger than bromide. The nephelauxetic ratio β is some 0.03 smaller in UBr_6^{2-} than in UCl_6^{2-}.

The octahedral species UCl_6^{2-} has been characterized in salt melts [1] and in ion-exchange resins [2] and the absorption spectrum of Cs_2UCl_6 and $[N(CH_3)_4]_2UCl_6$ has been thoroughly studied at low temperature [3,4]. The species UBr_6^{2-} is much more difficult to prepare, and the tetra(alkyl)ammonium salts are highly hygroscopic [5].

Recently, Mr. Philip Day and Dr. Luigi Venanzi, Oxford, pointed out that the triphenylphosphonium salts are comparatively easy to prepare and are resistant to air oxidation and deliquescence. The pale green $[P(C_6H_5)_3H]_2UCl_6$ and yellow-green $[P(C_6H_5)_3H]_2UBr_6$ can be recrystallized from nitromethane.

The absorption spectra of the two species are very similar, the main difference being that the wavenumbers of UBr_6^{2-} are in average 2 to 3 % smaller than of UCl_6^{2-}. This can be ascribed to the nephelauxetic effect [6-8] being more pronounced in the bromide than in the chloride. This is a remarkably great difference suggesting that the unknown term distances in gaseous U^{4+} are some 15 % larger than in UCl_6^{2-}. However, the theoretical interpretation of the absorption spectrum will be described elsewhere, partly by the authors cited above.

The reflection spectra of the solid compounds are closely analogous to the absorption spectra of solutions in CH_3NO_2, which does not seem to dissociate the hexahalides *.

Also the spectra in a mixture of half acetone and half nitromethane are nearly identical. Since it is evident from the data given below that UBr_6^{2-} would be more sensitive to possible solvolysis reactions than UCl_6^{2-}, 0.02 M UBr_6^{2-} was measured in 0.1 M $N(C_4H_9)_4^+Br^-$ in nitromethane, and found to have the same spectrum as given in Fig. 1. On the other hand, addition of a little alcohol modifies the spectra strongly, and in nitromethane containing 10 % methanol or ethanol, UBr_6^{2-} forms bright bluish green species with broad bands, the most prominent of which at 626 mμ. The intensity of these bands are much higher than of the octahedral species, suggesting that the center of inversion has been destroyed. Broad bands at somewhat different wavenumbers are observed of the uranium(IV) aquo ion of which the co-ordination number is not known: presumably it is 8 or 9. The situation is exactly the contrary of that prevailing for cobalt(II) where the pale pink aquo ion
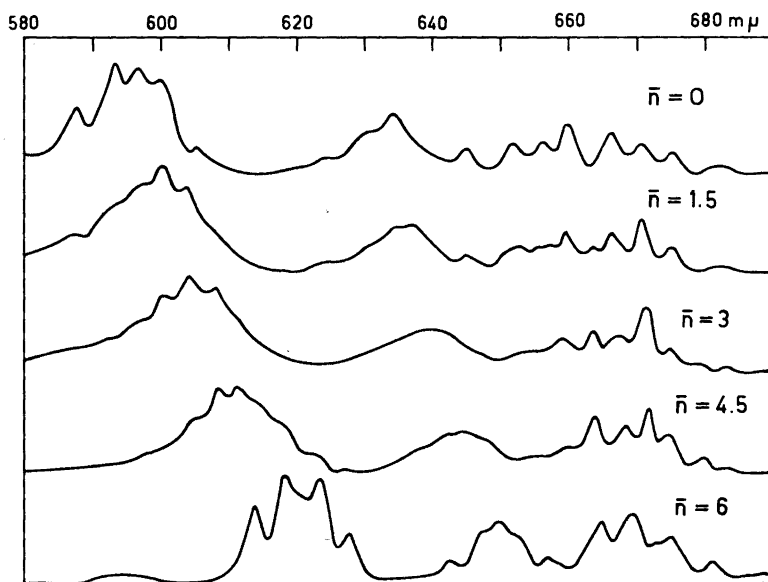

Fig. 1. Absorption spectra in the red of mixtures of $UCl_6{}^{2-}$ and $UBr_6{}^{2-}$ in nitromethane, having five different values of the average number $\bar{n}$ of bromide ligands per uranium atom.

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* Dr. Romano Pappalardo has here measured the absorption spectra of crystals of $[P(C_6H_5)_3H]_2UBr_6$ at 300° and 77°K. The former spectrum is closely analogous to that of the solution in nitromethane, except that two rather insignificant shoulders at 620 and 673 mμ are not observed in the crystals. At liquid nitrogen temperature, the bands become much more narrow and shift slightly. The bands at 623 and 627 mμ seem, at least in part, to be "hot" bands from vibrationally excited levels of the electronic groundstate. The widths of the groups 613.5 − 627.2 and 664.5 − 680.5 mμ are both 360 cm^{-1}, possibly twice the vibrational frequency corresponding to the odd stretching normal mode.[3],[4]

$Co(H_2O)_6^{2+}$ has a centre of inversion (at least to a good approximation) whereas the dark blue halides $CoCl_4^{2-}$ and $CoBr_2^{4-}$ lack a center of inversion. UCl_6^{2-} is somewhat more resistant to alcoholysis than UBr_6^{2-}; however, it only exists in insignificant amounts [1,2] in concentrated aqueous hydrochloric acid. Since the first chloride complex $UCl(H_2O)_x^{3+}$ has a relatively high [9] formation constant $K_1 \sim 2$, the reluctance to form UCl_6^{2-} may rather be explained by the tendency of U(IV) to have the coordination number N higher than 6 in aqueous solution. In organic solvents, N of many metal ions assumes easily lower values; thus, $NiCl_4^{2-}$ has recently been investigated in nonaqueous solvents [10–12]. This phenomenon may be related to the lower metal-halide internuclear distances which seem to prevail in organic solvents compared to water [13]. Actually, the lower N of a given central ion may have a considerably lower effective radius; thus, Sharp [14] points out that the ligand distances are 0.1 to 0.2 Å shorter in the compounds BF_3, SiF_4 and PF_5 compared to BF_4^-, SiF_6^{2-} and PF_6^- with higher N. The recent discussion by Katzin [15] of the factors determining N in a definite case emphasized the generality of octahedral-tetrahedral equilibria also outside the transition groups. In the present author's opinion, these factors are predominantly relative atomic size and a tendency of lower N when the electronegativity of the ligands is low, (as stressed by Pauling). Frequently, of course, these two trends co-operate in the same sense. The influence of organic solvents seems to be well represented by a decreased effective radius of the central atom.

DEMONSTRATION OF THE PRESENCE OF MIXED URANIUM(IV) HEXAHALIDES

Remarkably few well-authenticated cases of mixed halide complexes have been reported. They are sometimes available due to special reaction paths such as $trans$-$PtX_4Y_2^{2-}$ from the square-planar PtX_4^{2-} and Y_2. However, the attempts to make mixed osmium(IV) hexahalides give highly unexpected results [16]. Well-established cases in solution are mixed bismuth(III) chloro-bromo complexes [17] and mercury(II) halides [18]. Furlani and Morpurgo [11] studied the tetrahedral $NiBr_xCl_{4-x}^{2-}$ in organic solvents. The narrow and very characteristic bands of UCl_6^{2-} and UBr_6^{2-} should make the detection of mixed complexes by spectrophotometric methods particularly encouraging.

Fig. 1 gives the spectra between 580 and 690 mμ * of mixtures of 0.02 M $[P(C_6H_5)_3H]_2UCl_6$ and 0.02 M $[P(C_6H_5)_3H]_2UBr_6$ in nitromethane, having the average number $\bar{n}$ of bromide ligands per uranium atom equal to 0, 1.5, 3, 4.5, and 6. Actually, 26 spectra were recorded at large dispersion of solutions with $\bar{n} = 0, 0.25, 0.5, 0.75, 1, 1.25, \ldots, 5.75, 6$. By inspection of the curves, 19 different wavelengths were selected and the variation of the effective molar extinction coefficient ε as function of $\bar{n}$ was studied. Fig. 2 gives such curves

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* For our purpose, this is by far the most interesting region. The two characteristic strong peaks, of UCl_6^{2-} at 405 and 452 mμ and of UBr_6^{2-} at 420 and 463 mμ, curiously enough shift regularly in the intermediate complexes without showing conspicuous splitting effects. Satten, Schreiber and the present writer agree upon identifying the excited levels of these two peaks as the Γ_3 and Γ_5 components of $^3P_2$.
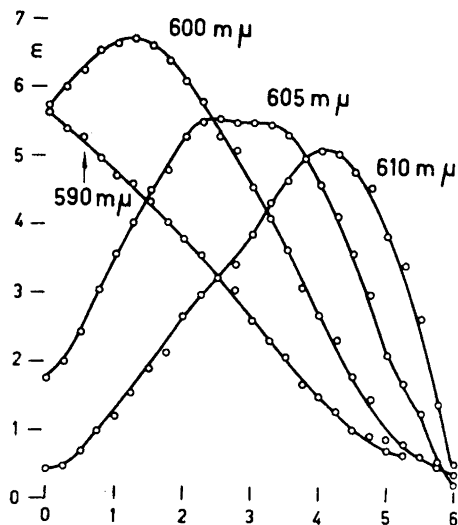
Fig. 2. Molar extinction coefficient ε at four wavelengths as function of $\bar{n}$, the average number of bromide ligands per uranium atom.

at 590, 600, 605, and 610 mμ. It is seen that mixed complexes are indeed formed; mixtures containing UCl_6^{2-} and UBr_6^{2-} alone would be represented by straight lines on the figure. When more than one complex is formed, Woldbye[19] emphasized that circonspection is needed for the application of Job's principle, the method of continuous variations. However, it is quite evident from Fig. 2 that some intermediate complexes *must* be formed; the curve for 600 mμ is particularly important establishing the presence of $UBrCl_5^{2-}$; and good evidence is also obtained for the intermediates $UBr_xCl_{6-x}^{2-}$ with $x = 2$, 3, and 4. It is worth remembering Wormser's warning [20] that frequently, the direct proof for the presence of all the intermediates is difficult to obtain in a way beyond experimental uncertainty. In the case of robust complexes, the isolation, *e.g.* by electrophoresis or chromatography, of the individual species is often a most useful support for the spectrophotometric work. In our case of labile complexes, where infra-red "finger-print" methods have not been applied, it is in a certain sense somewhat deceiving that the narrow peaks on Fig. 1 have not aided more in characterizing the individual intermediate complexes. From another point of view, however, there is hardly any doubt that the usual situation is as predicted by J. Bjerrum that all the intermediate species occur to some extent. As discussed by Kida [21], the exceptions from this rule are either caused by low-spin and high-spin extremes (say $Fe(H_2O)_6^{2+}$ and Fe dip_3^{2+}) or by interference with polymeric complexes (this is undoubtedly the reason why many intermediate cyanides are not known) though Kida [21] assumes some special effects to occur in platinum(II) cyanides and other complexes with strong π-bonding.
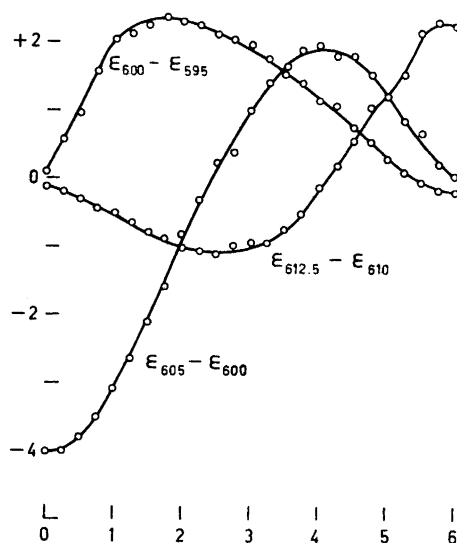
Fig. 3. Differences between ε at two adjacent wavelengths measured in three cases as function of $\bar{n}$.

Fig. 3 expresses another variety of ε $(\bar{n})$ curves, the difference between ε at two adjacent wavelengths. This is as good qualitative evidence as Fig. 2 for the existence of intermediate complexes; if they did not exist, the curves on Fig. 3 would be differences between straight lines and hence straight lines themselves. The advantage of this method is that dust errors which are different in solutions with different $\bar{n}$ are corrected for.

Fig. 4 gives the extrapolated spectra of $UBrCl_5^{2-}$ and of UBr_5Cl^{2-} obtained from the solutions with $\bar{n} = 0.25, 0.5, 0.75$, and $5.25, 5.5$, and 5.75, respectively. If these solutions only contained the complexes mentioned and the pure hexahalides, the molar extinction coefficients ε_1 and ε_5 would be given by

$$\varepsilon_1 = \varepsilon_o + (\varepsilon(\bar{n}) - \varepsilon_o)/\bar{n} \tag{1}$$
$$\varepsilon_5 = \varepsilon_6 + (\varepsilon(\bar{n}) - \varepsilon_6)/(6 - \bar{n})$$

There is no doubt that eqn. (1) is only an approximation; if the consecutive formation constants were very different permitting nearly pure species at integral values of $\bar{n}$, sharp angles would be observed on Figs. 2 and 3. On the other hand, the material given in the next chapter seems to suggest that the extrapolation according to eqn. (1) is not very bad. Especially the three spectra obtained for $UBrCl_5^{2-}$ agree fairly well.

APPROXIMATE FORMATION CONSTANTS OF COMPLEXES FORMED FROM UCl_6^{2-} BY ADDITION OF BROMIDE

The set of spectra of solutions with known $\bar{n}$ values obtained above can be used for estimate of $\bar{n}$ in other solutions containing the same components by
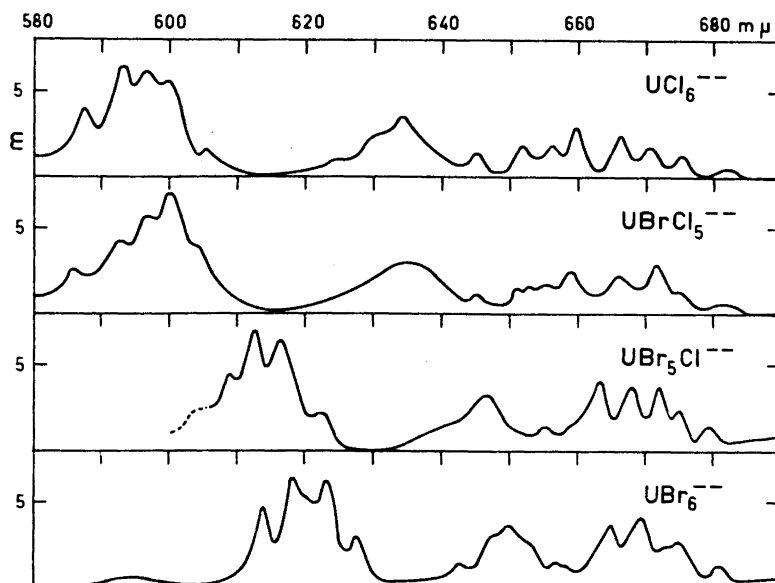
Fig. 4. Absorption spectra in the red of UCl_6^{2-}, $UBrCl_5^{2-}$, UBr_5Cl^{2-} und UBr_6^{2-}. The two intermediate species were treated by the extrapolation given in eqn. 1.

arguments related to J. Bjerrum's principle of corresponding solutions [22]. A solution of 1 molar tetra(butyl)ammonium bromide in nitromethane was mixed with 0.02 M UCl_6^{2-} in various proportions and the spectra compared with those of the low $\bar{n}$ values. Actually, rather than using Fig. 2, an even more sensitive method was to compare the ratios between the ε values of the three maxima at 594, 597, 600 mμ, of which the former represents the highest peak in UCl_6^{2-} whereas that at 600 mμ is much higher at $\bar{n} = 1$. It must be admitted that the $\bar{n}$ values of a given solution determined from various wavelengths show a scattering of about 0.1. Table 1 combines the average value of $\bar{n}$ and the characteristics of these solutions. From the data in Table 1,

Table 1. Total concentrations of uranium and bromide, and free concentration of non-ligated chloride and bromide in millimolar units.

C_U	C_{Br}	C_{Br}/C_U	$\bar{n}$	$[Cl^-]$	$[Br^-]$	$[Br^-]/[Cl^-]$
19.6	19.6	1	0.3	5.9	13.7	2.3
18.9	56.7	3	0.6	11.3	45.4	4.0
18.2	91	5	0.75	13.6	77	5.6
16.7	167	10	1.0	16.7	150	9.0
14.3	286	20	1.35	19.3	267	13.8

plotted as a formation curve, values can be estimated of the two first consecutive formations constants

$$K_1 = \frac{[UBrCl_5^{2-}]\,[Cl^-]}{[UCl_6^{2-}]\,[Br^-]} = 0.3 \tag{2}$$

$$K_2 = \frac{[UBr_2Cl_4^{2-}]\,[Cl^-]}{[UBrCl_5^{2-}]\,[Br^-]} = 0.05$$

These values should not be taken too seriously, since it is obvious that the conditions for the validity of the mass action law in concentration units may be rather far from being fulfilled. However, they inform us about two interesting aspects. Firstly, it is clear that U(IV) behaves as an A element [23]. Since the statistical contribution to K_1 is a factor 6, chloride is bound at least twenty times better than bromide in these complexes. Secondly, the ratio K_1/K_2 is distinctly above the statistical value 2.4 (defined as the case where $K_n = (7-n)K_{av}/n$) showing that the intermediate complexes rather are favoured, as usually is the case [21].

There are not many other ligands which at the same time have sufficiently large radii and low electronegativity, and still would form octahedral uranium(IV) complexes at all. Thus, it seems [24] that the solid thiocyanates become eight-coordinated $M_4U(NCS)_8$. A solution of 0.02 M UBr_6^{2-} and 0.5 M $N(C_4H_9)_4^+ I^-$ in CH_3NO_2 turns orange-brown; however, the spectrum is essentially that of the original UBr_6^{2-} superposed a broad background possibly due to minute traces of uranyl iodide. (The electron transfer spectrum of these complexes are later to be discussed). The A character of U(IV) is hence once more borne out by the reluctance to form an iodide complex under circumstances where the hexabromide exists.

We conclude that J. Bjerrum's idea of formation of intermediate complexes essentially has been confirmed in this case of uranium(IV) hexahalides in nitromethane.

EXPERIMENTAL

The analogous triphenylphosphonium salts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ were studied by Allison and Mann [25]. The UBr_6^{2-} salt was made by hydrogenation of 24 g depleted (*i.e.* [238]U) uranium metal filings from A. D. Mackay, New York, to black UH_3 powder, and cautious reaction with bromine vapour, carried by argon, from 27 ml Br_2 in a heated flask, to anhydrous UBr_4. After cooling, 160 ml actone and 60 ml 60 % AnalaR aqueous hydrobromic acid was added, and then a solution of 50 g triphenylphosphine (filtered from a cloudy white ppt.) in 200 ml acetone. Standing at 0°C for some days induced crystallization of a grey powder. In some of the preparations, this contained large amounts of a black by-product which easily could be separated by extraction with 250 ml hot nitromethane, from which filtrate the salt desired appeared by cooling as brownish green crystals.

For the UCl_6^{2-} synthesis, 12 g uranium filings as above were dissolved in 200 ml 6 M aqueous hydrochloric acid. This reaction frequently gives a brownish black by-product which only is very slowly soluble in HCl. Whereas attempts to make more concentrated U(IV) solutions nearly invariably leads to excessive heating and formation of the polymeric hydroxide, there seems always to occur another reaction at the surface of the metal dissolving, giving the black ppt. The filtrate was added to a solution of 27 g triphenylphosphine (previously filtered) in 200 ml actone and pale green crystals appeared in good yield. They can be recrystallized in somewhat larger amounts of hot nitromethane than needed for the bromide. They may be recrystallized, but with a great loss, from absolute ethanol.

24 ml 0.02 M $[P(C_6H_5)_3H]_2UCl_6$ were used for a series of experiments, where appropriate amounts (until 24 ml) 0.02 M $[P(C_6H_5)_3H]_2UBr_6$ from a 10 ml burette, producing the values of $\bar{n}$ between 0 and 3 in steps of 0.25 [given by the formula $\bar{n}(4\ \text{ml})/(1-(\bar{n}/6))$]. The interval of $\bar{n}$ between 6 and 3 was covered in a similar series, adding UCl_6^{2-} to the UBr_6^{2-} solution. The tetra(butyl)ammonium bromide and iodide used were from Fluka.

The spectra were measured in 5 cm cells on a Cary 14 recording spectrophotometer with great dispersion (2.5 mμ per division of paper, 0.5 mμ per second).

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