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Recent Advances in the Chemistry of UX_4 Complexes (X = Cl, Br and I)*

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Greatly improved methods have been developed [1, 2] for the preparation of UI_4 adducts which could act as starting materials for the study of iodo complexes of uranium(IV). A number of new iodo complexes, including some new types of coordination compounds, have subsequently been prepared and studied using a variety of neutral oxygen donor ligands. The properties of these compounds have been compared with those of their chloro and bromo analogues.

The room temperature reaction of uranium metal with two moles of iodine was studied in different non-aqueous solvent systems. Efforts were directed towards the isolation of a stable solid starting material, as well as a stable UI_4 solution, suitable for the preparation of UI_4 complexes. Red $UI_4(mecn)_4$ [1] (mecn = methyl cyanide) proved to be a very convenient and reliable solid starting material. It was prepared as described recently [2]. A UI_4 solution in methyl cyanide containing 6.5% ethyl acetate was found [2] to be even more stable and convenient than $UI_4(mecn)_4$ for the preparation of UI_4 complexes. Most of the UI_4L_x complexes could be prepared by [2] reacting this solution with the required number of moles of the ligand (L = neutral oxygen donor ligand and $x = 2$ to 8) and M_2UI_6 (M = very large cation, e.g., tetraphenylarsonium).

Results and Discussion

UI_4L_2 Complexes

Solid UI_4L_2 complexes have been isolated with a variety of bulky ligands, namely: amides [3], e.g., (tmu = *N,N,N′,N′*-tetramethylurea), pva = *N,N*-dimethylpivaloylamide, dmeu = *N,N′*-dimethylethyleneurea and bpmu = bis(pentamethylene)urea; a sulphoxide, e.g., dbso = dibenzyl sulphoxide; phosphine oxides, e.g., tppo = triphenylphosphine oxide, tpyrpo = tris(*N*-pyrrolidino)phosphine oxide and tdpo = tetra(dimethylamido)phosphine oxide, and an arsine oxide, e.g., tpao = triphenylarsine oxide.

Electronic spectra of complexes

The solid reflectance electronic spectra (400–2200 mμ) of all the UI_4L_2 complexes have spectra similar to their UX_4L_2 analogues (X = Cl and Br). All of the latter appear to have *trans*-octahedral structures except $UCl_4(tppo)_2$. A recent X-ray structural determination [3] of $UI_4(tmu)_2$ proved it to be *trans*-octahedral.

The electronic spectra of these iodo complexes exhibit significant shifts in the 900–1100 and 1800–2200 nm regions. These peaks shift to lower wave numbers for the stronger ligands. This phenomenon is best detectable for the major peak in the vicinity of 2000 nm. The positions for some UI_4L_2 species are: 2000 nm (pva), 1950 (tmu), 1950 (tppo), 1886 (tpyrpo) and 1840 (tpao). The corresponding peak for UI_6^{2-} is at 2165 nm. The dominance of the strong neutral donor ligands, as compared to Cl, Br and I, is also clearly illustrated when the peaks of $UX_4(pva)_2$ (a complex of a weak donor ligand) are compared to those of $UX_4(tpao)_2$ (a complex of a strong donor ligand) (X = Cl, Br and I), namely: for the chloride 1930 (1855); for the bromide 1970 (1840); and for the iodide 2000 (1840) nm (values for the tpao complexes are in brackets). Values for UX_6^{2-} are, 1980, 2050 and 2165 nm, for the chloro, bromo and iodo complexes, respectively. Whereas the influence of the halide can be noticed in the case of the pva complexes, those of the tpao complexes have peaks greatly different from the UX_6^{2-} species and are almost constant for all three halide complexes.

Earlier structural work for UCl_4L_2 and UBr_4L_2 species is in agreement with this, since U–O bond shortening occurs in going from chloride to bromide. Recent structural determinations of UX_4tmu_2 species indicate that the same effect is noticed in going from bromide to iodide [3, 4]. U–O bond distances for these species are 2.22, 2.21 and 2.19 Å, respectively, for the chloro, bromo and iodo complexes.

The reaction between UI_4 and tpao is uncommon, since two different forms of UI_4tpao_2 complexes are obtained. The red α-$UI_4(tpao)_2$ crystallizes from a CH_2Cl_2/ethyl acetate solvent mixture at room temperature. It appears to have a very exceptional auto-ionized structure, namely $[UI_2(tpao)_4][UI_6]$ [5]. It is non-hygroscopic and stable at room temperature. The solid reflectance spectra of the complex has both the typical UI_6^{2-} peak at 2165 nm and the $UI_2(tpao)_4^{2+}$ peak at 1750 nm. This peak is also present in $[UI_2(tpao)_4]^{2+}\cdot 2I^-$.

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The yellow–green β-$UI_4(tpao)_2$ is expected to be *trans*-octahedral. It can be prepared by the reaction of UI_4 with tpao in a mecn/ethyl acetate solution at − 10 °C. A single sharp high wave number peak is obtained in the solid reflectance spectrum at 1840 nm. This compound is very hygroscopic. When suspended in a mecn/ethyl acetate solvent mixture it gradually dissolves, becoming dark red, and if the concentration in solution is high enough, small amounts of the red α-form precipitate.

Thermal stabilities

The thermal stability of the solid UI_4L_2 species vary greatly. $UI_4(tpyrpo)_2$ only starts to decompose at ~250 °C, whereas $UI_4(tppo)_2$ and $UI_4(tpao)_2$ complexes start to decompose at 130 and 110 °C, respectively. Both of these slowly decompose even at room temperature becoming more reddish in colour showing U–O bands of UO_2^{2+} in their IR spectra. The amide complexes, e.g., $UI_4(tmu)_2$, start to decompose at ~150 °C. The sulphoxide complexes can hardly be prepared at room temperature without some decomposition. Solid yellow–green $UI_4(dbso)_2$ fairly quickly turns red at room temperature.

IR spectra

The increasing Lewis acidity in the direction UCl_4, UBr_4 and UI_4 is also indicated by increasingly greater shifts in free ligand (C=O, P=O, As=O) stretch frequencies upon complexation in the same direction, e.g., C=O shifts in $UX_4(tmu)_2$ are 107, 113 and 117 cm^{-1}, respectively, and P=O shifts in $UX_4(tpyrpo)_2$ are 136, 163 and 198 cm^{-1}, respectively.

Non-aqueous conductivity

The conductivity of 0.002 M solutions of UI_4L_2 species in methyl cyanide are in the vicinity of 1:1 electrolytes, e.g., Λ_{500} values of $UI_4(tmu)_2$ and $UI_4(tpyrpo)_2$ are 109 and 121 S cm^2 mol^{-1}, respectively, whereas those of their chloro and bromo analogues are non-electrolytes (Λ_{500} values <20).

UI_4L_n Complexes ($n > 2$)

When UI_4L_2 species (L = amide) are reacted with more amide ligand in methyl cyanide solution, the electronic spectrum changes, indicating the formation of higher coordinated species than six. Solid complexes like $UI_4(tmu)_6$, $UI_4(dmeu)_5$ and $UI_4(bpmu)_4$ could be isolated. None of these solids has six-coordinated solid reflectance spectra. Bulky phosphine oxides and arsine oxide ligands, however, all form various six coordinated species when excess ligand is used, e.g., $UI_4(tpyrpo)_4$, $UI_4(tppo)_4$, $UI_4(tdpo)_5$ and $UI_4(tpao)_4$. The UI_4L_4 species all appear to be $[UI_2L_4]^{2+}\cdot 2I^-$ species if their solid reflectance electronic spectra is considered as well as the presence of only bound neutral ligand in their mull IR spectra.

When $UI_4(tpyrpo)_2$ is titrated with ligand in CH_2Cl_2 solution and the reaction followed spectrophotometrically, the O_h peak of $UI_4(tpyrpo)_2$ at 1905 nm increases four-fold in molar extinction and slightly shifts to ~1900 nm upon addition of one equivalent tpyrpo, suggesting the formation of $UI_4(tpyrpo)_3$ in solution. Upon addition of another equivalent of ligand the spectrum again rapidly changes to a lower molar extinction peak at 1835 nm, corresponding to the formation of $UI_4(tpyrpo)_4$. The solid $UI_4(tpyrpo)_4$ has a major peak at ~1800 nm. Further addition of ligand did not alter the spectrum. The ligand can not apparently replace more iodide in this system. No other solids of higher ligand to uranium ratios of 1:4 could be isolated for tpyrpo, even from methyl cyanide solution.

In the case of the very strong, bulky tpao as ligand a six-coordinated complex $UI_4(tpao)_6$ could be isolated. The solid reflectance spectrum has a major peak at 1712 nm. Its mull IR spectrum indicates only bound ligand. This suggests the presence of $U(tpao)_6^{4+}$ ions in the solid state.

References

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