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The Coordination Chemistry of UCl_4 , UBr_4 , $ThCl_4$ and $CeCl_4$ in Acetone Solution and their Relationship to the Solid Complexes

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Concepts like ionization, molecule formation and auto-ionization are fundamental in the description of the solution behaviour of Lewis acids of the type MX_n (where M = metal ion, X = monoanionic ligand). An understanding of the relative significance of each of these in a particular system, e.g. MX_n (Lewis acid)/solvent/and neutral ligand, as well as the nature of the anion, the donor number and dielectric constant of the solvent and the donor number and stereochemistry of the neutral ligand, can cast considerable light on the coordination behaviour of the central metal ion. Specifically if it is possible to obtain some idea of the relative lattice energies of the possible solid species which can be formed and their relationship to the solution equilibria.

In order to study the above mentioned coordination chemistry, freshly prepared 0.001 M acetone solutions of each of UCl_4 , UBr_4 , $ThCl_4$, and $CeCl_4$ -ipa₂ [1] have been titrated with 0.1 M solutions of each of a number of ligands, e.g. tpao, tdpo, tmpo, tpoo, dmsO, dma, ipa, etc. and the reactions followed conductometrically [2], potentiometrically [3], spectrophotometrically [4] and enthalpimetrically [5], where possible.

Some of the more important equilibria involved in such systems are represented in Fig. 1.

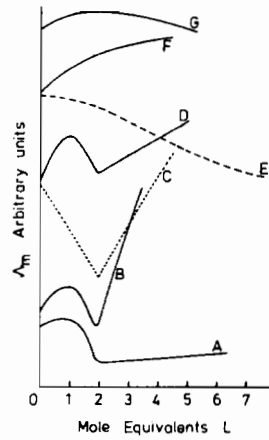


Fig. 2. Conductometric titrations.

These equilibria can be described in the light of the experimental data. The different types of interactions are best indicated by the results from conductometric titrations (see Fig. 2). The different important types of interactions are represented by curves A to E. Curve A is typical for the reaction of UCl_4 and moderately strong large approximately spherical (in overall shape) oxygen donor ligands, e.g. large P=O and S=O ligands, tdpo, tpoo and tbo. In the initial part of this titration the auto-ionization of UCl_4 is enhanced (*c*₁) and (*c*₂) species significant. The chloride ion concentration is at the same time only increased from 1×10^{-11} M in UCl_4 alone to 2×10^{-8} M after two mol equivalents tdpo have been added. After a mol ratio of 1 molecule formation of (*b*₃) (Fig. 1) becomes more important. A relatively sharp end point is obtained

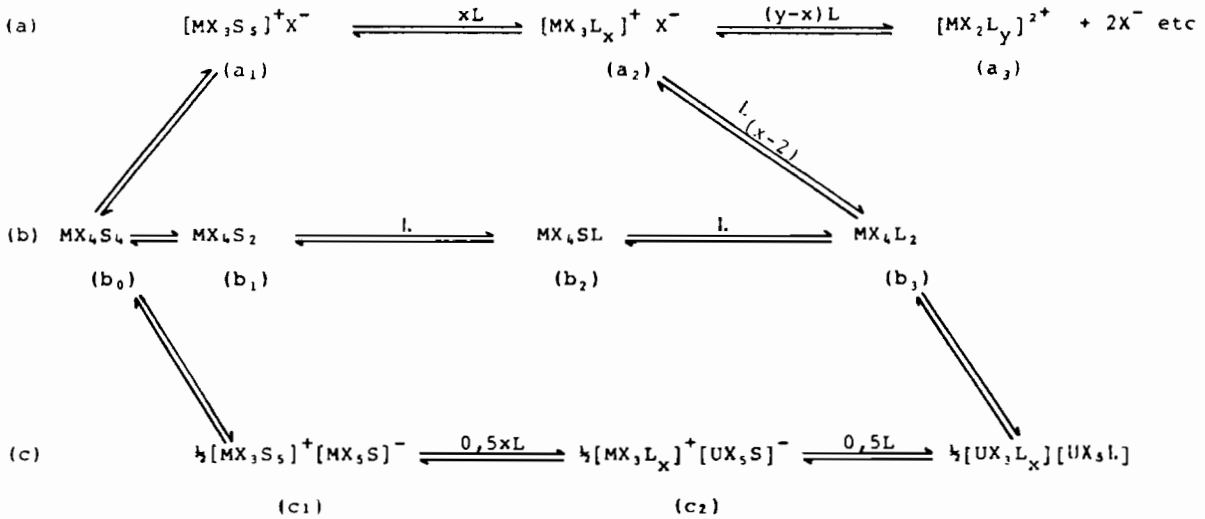


Fig. 1. a = ionization; b = molecule formation; c = auto-ionization.

at a mol ratio of 1:2 after which only slight additional ionization occurs [6]. Relatively strong end points are also obtained from these in enthalpimetric titrations and *trans* octahedral solids mostly precipitate readily.

When metal species of moderately strong anions e.g. UCl_4 , $\text{U}(\text{NO}_3)_4$, ThCl_4 and $\text{Th}(\text{NO}_3)_4$ are titrated with very strong neutral donor ligands, e.g. tpao, tmao and tmpo type B curves are obtained in which enhanced auto-ionization (species (c_1)) are formed initially, followed by some degree of molecule formation in the ligand mol ratio region of 1 to 2. A very sharp break is obtained at a ratio of 1:2 since ionization occurs rapidly in this region. Relatively weak end points are obtained when these titrations are followed enthalpimetrically. (For UCl_4 and tmao the chloride ion concentrations are 9×10^{-6} and 4×10^{-4} , respectively, at mol ratios of 2 and 2.2). At the last mol ratio, solid $[\text{Utmao}_6]\text{Cl}_4$ starts to precipitate already at a stage where only a fraction of the first chloride ion is ionized. This 'solid state ionization' is driven by the high lattice energy and the strong donicity of tmao [7]. In these cases it is difficult to prepare pure complexes since a number of complexes of different U:L ratios are stable and the product is very dependent on the U:L ratio [8]. In the case of the slightly weaker donor tmpo $[\text{UCl}_2\text{tmpo}_6]\text{Cl}_3$ is precipitated [9].

When the stronger donor ion, chloride, is replaced by bromide, i.e. UBr_4 , and the same neutral ligands are used as above curves of type c are obtained. Molecule formation (b_3) is important in the coordinately unsaturated region at the expense of auto-ionized species (c_1) of UBr_4 where solvent is replaced by ligand (ratio up to 2). After a mol ratio of 2 ionization follows very rapidly and often precipitation of ionized species like $[\text{Utmao}_6]\text{Br}_4$ occurs long before a mol ratio of 1:6 is reached. Enthalpimetric endpoints of UBr_4 titrations are all weak in acetone solutions.

Type D curves are obtained when UCl_4 and UBr_4 are titrated with medium to weak and smaller oxygen donor ligands like dma, dmsO, etc. In such cases auto-ionization is the most important reaction type before and after a mol ratio of 2. The relative minimum at 2 is higher than that at a ratio of zero. The increase after 2 is bigger for the chloride than the bromide whereas the relative increase of halide ion concentration as a function of neutral ligand concentration is smaller, e.g. 1×10^{-11} M in chloride in UCl_4 and 6×10^{-11} M at a mol ratio of 1:2 dma. Species like c_1 and c_2 are thus important in solution. In solids $[\text{UCl}_3\text{depa}_4][\text{UCl}_5\text{depa}]$ [10] and $[\text{UCl}_2\text{dmsO}_6][\text{UCl}_6]$ [11] are known.

Curves E, F and G are obtained for very weak ligands as well as curves for ThCl_4 in which case auto-ionization is very unimportant (ThCl_6^{2-} is much less stable than UCl_6^{2-}). In the case of $\text{Th}(\text{NO}_3)_4$ auto-

ionized species are more important in combination with stronger neutral ligands like tmpo since the larger nitrate ion readily forms $\text{Th}(\text{NO}_3)_6^{2-}$ species where all nitrate groups are bidentate.

The behaviour of $\text{CeCl}_4\text{ipa}_2$ in acetone solution [1] is very similar to that of UCl_4ipa_2 . It appears as if the species in solution are also similar. The stoichiometry of the solid complexes of a variety of neutral ligands are also identical [1]. The crystal structures of $\text{MCl}_4\text{tdpo}_2$, where M = U and Ce, have been compared and found to be almost identical within experimental limits [12].

A comparison of the structural data of a number of UCl_4 complexes of the *trans* octahedral type clearly illustrate how the degree of the tetragonal distortion is a function of the donor strength of the neutral ligand [13].

By comparing the ESCA spectra of $\text{UCl}_4\text{tdpo}_2$ and $\text{ThCl}_4\text{tdpo}_2$ surprising results were obtained which indicated strong presence of 5f orbital-involvement in the ThCl_4 complex which is formally a d^0f^0 electronic system [14]. This behaviour is not present in ThO_2 or ThCl_4 [15].

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