# Plenary and Session Lectures

## A1

## New Stoichiometric and Catalytic Organometallic Chemistry with Actidines. C–H Activation and Phosphine/Phosphite Coordination Chemistry

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## A2

## Some Stereochemical Aspects of Actinide Coordination Chemistry

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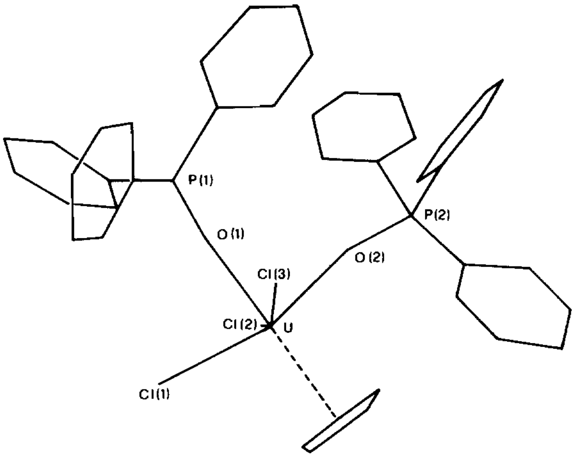
It has been recognised for many years that ligand field interactions are at best minimal in 5f transition element chemistry, and that such interactions will contribute very little to the kinetic stability of the complexes formed by these elements. Consequently such complexes can be regarded as kinetically labile, and there will be a considerable degree of flexibility in the coordination geometries adopted by the complexes formed with these elements. In addition, ligand exchange reactions occur quite readily, simply because there is little or no gain (or loss) of ligand field stabilisation energy involved in an intra- or intermolecular rearrangement. In such systems the steric crowding about the central metal atom becomes the most important factor in determining the coordination number and geometry adopted in both lanthanide and actinide complexes, which has led to many publications in recent years aimed at investigating the effects of bulky ligands on the stoichiometries of the complexes formed by these elements [*e.g.* 1–3]. Until recently, no attempts have been made to quantify the effects of steric crowding in actinide complex systems. The first systematic approach to this type of problem was made by Tolman [4], who used a 'cone-angle approach' to describe the size of phosphorus ligands, and this idea was extended by others [5, 6] who also introduced the idea of ligand profile. However, these approaches to the problem were more two-dimensional in character than three-dimensional, and in order to achieve some understanding of general steric effects which are neither restricted to a special type of ligand, nor restricted to systems in which one part of the coordination environment is left unchanged while the other parts are varied, one needs to go beyond the Tolman approach in order to obtain a unique description of steric crowding. Dr. Li Xing-fu in my group has done this by looking at the problem in terms of the actual solid angles subtended by the ligands in a given complex to the centre of the metal atom concerned [7, 8].

In order to apply this treatment one must distinguish between the first order steric crowding due to the atoms or groups of atoms directly bonded to the metal atom and the second order crowding which arises from the other atoms or groups of atoms bonded to the donor or other atom involved in bonding to the metal. To make this clear, consider the structure of the complex $[(\eta^5\text{-}C_5H_5)UCl_3(PPh_3O)_2]$ [9] shown below.

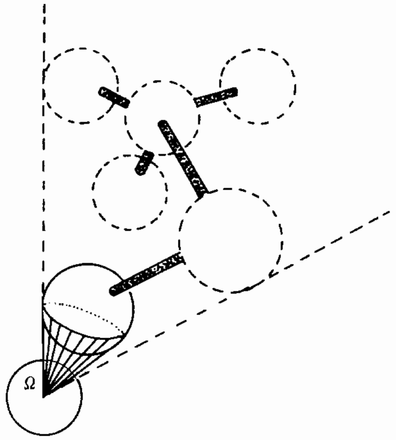


In this structure, two $PPh_3O$ molecules occupy *cis* positions in a pseudooctahedral geometry. The first order crowding is caused by the $C_5H_5$ group, two oxygen atoms from the $PPh_3O$ molecules and three chlorine atoms, while the second order crowding arises from the six $C_6H_5$ groups of the two $PPh_3O$ molecules. The distances between the chlorine atoms and hydrogen atoms of the $PPh_3O$ ligands are much greater than the sum of the Van der Waals' radii, so their interactions are negligible, and by meshing the $C_6H_5$ rings into the gaps between adjacent molecules of the $Ph_3PO$ ligands, repulsions between the $C_6H_5$ groups from the two $Ph_3PO$ molecules can be avoided. If these rings do not mesh in this way, repulsion between the two bulky ligands could shift them from the *cis* sites to *trans* sites. This would reduce the thermodynamic stability of such a complex, for one would then have an electron-withdrawing chlorine atom *trans* to the $\pi$ bonded $C_5H_5$ group which would weaken the metal–$C_5H_5$ bond.

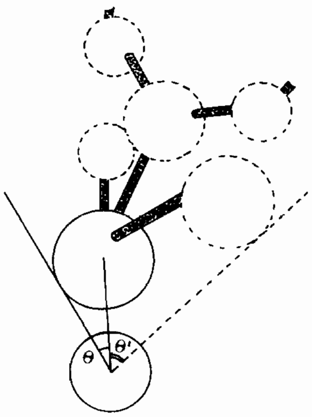
A single parameter is insufficient to describe steric crowding completely. Dr. Li Xing-fu therefore introduced two parameters, one termed the 'cone-angle factor' and the other the 'fan angle'. The cone-angle factor is defined as the solid angle of the cone comprising the metal atom at the apex and the primary coordinating atom or group (CAF) or the whole ligand (CAFS), which then includes the second order effect, divided by $4\pi$:

$$\mathrm{CAF} = \Omega/4\pi$$

This defines CAF as the fraction of the total sphere surface enclosing the metal atom which is occupied by the ligand, as shown below.

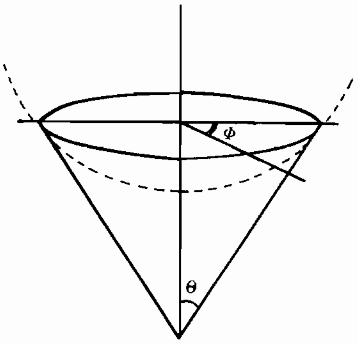


The 'fan angle' is defined in a similar manner as the angle subtended by the primary coordinating atom (FA) or the whole ligand (FAS) in the various symmetry planes. In this definition FAS has the same meaning as Tolman's [4] cone angle.



In order to describe the total steric crowding around the metal atom, it is necessary to sum all the values of CAF or CAFS for all the coordinating ligands. This sum, ΣCAF or ΣCAFS, then indicates the overall steric crowding, whereas the sum of FAS in each symmetry plane can be used to indicate the crowding in that plane.

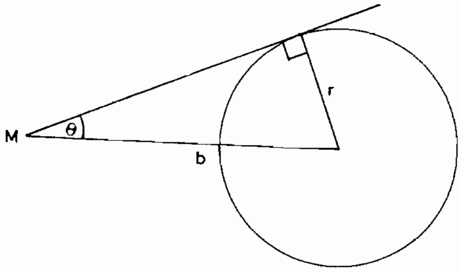
Mathematically, the solid angle subtended by a sphere placed in a cone (see below)



can be calculated from an equation of the form:

$$\Omega = \int_0^{\theta} \int_0^{2\pi} \frac{r^2 \sin\theta}{r^2} \, d\theta \, d\phi \cong 2\pi(1 - \cos\theta).$$

Then $\mathrm{CAF} = \frac{1}{2}(1 - \cos\theta)$ and $\mathrm{FA} = \theta$. Obviously ΣCAF can never reach unity (*i.e.* complete filling of the surface of the sphere about the metal atom) because there must be gaps between the ligands to allow for ligand–ligand repulsions in the molecule, and for simple, relatively small monodentate ligands one need only consider the atom that is directly coordinated to the metal.



From the above diagram, $\theta = \arcsin(r/b)$, where r is the Van der Waals' radius of the coordinating atom and b is the bond length between the metal atom and the coordinating atom. A somewhat similar approach can be used for the $\eta^5$-$C_5H_5$ groups and for more complicated ligands.

While this work was being done, A. J. Smith [10] reported a preliminary study based on the hypothesis that the coordination number of a complex is limited

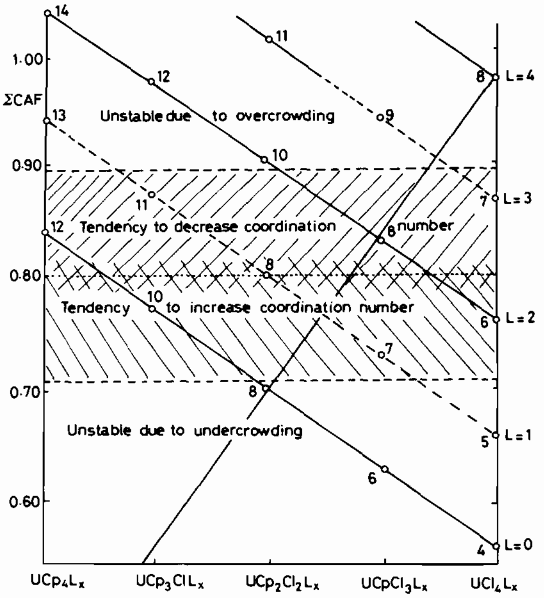


Fig. 1. Steric effects in cyclopentadienyl chloro-uranium(IV) complexes with oxygen-donor ligands. The numbers within the diagram refer to the co-ordination numbers of uranium atoms in the complexes.

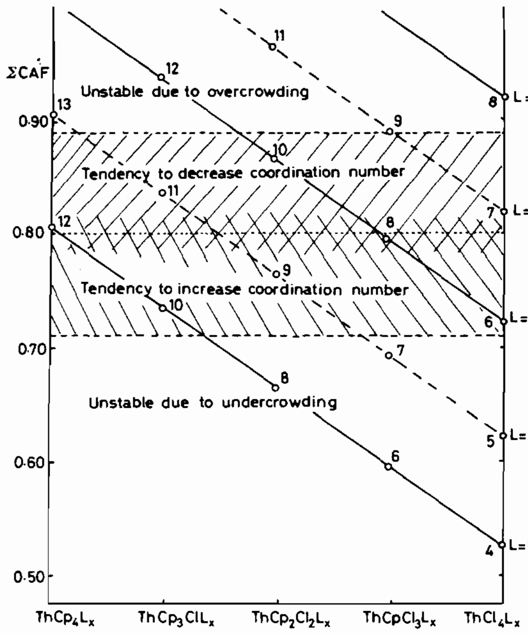


Fig. 2. Steric effects in cyclopentadienyl chloro-thorium(IV) complexes with oxygen donor ligands.

by the fact that the sum of the solid angles subtended at the metal centre by the Van der Waals' envelopes of the ligands cannot exceed $4\pi$ steradians, although for coordinative saturation the sum will approach this value as closely as possible. His calculations of the solid angles for thorium compounds of known structure were made in a different way from ours, and although there is some disagreement between his results and ours, there is also a measure of agreement.

From Dr. Li Xing-fu's approach, it has become apparent that the first order effects are of primary steric importance in most actinide complexes. For uranium(IV) compounds of known structure the observed values of ΣCAF average out at 0.80 ± 0.02 and for thorium(IV) compounds of known structure the values of ΣCAF are somewhat similar; this gives rise to what one may term a stable region for complexes as shown in Fig. 1.

The idea of a stable region has some predictive value. If we apply the idea to the known [11] complex $ThCl_4$·4dma (dma = $McCONMe_2$) the estimated value for ΣCAF would be 0.92 if the compound is a neutral complex, or 0.82 if it is ionic and of the form $[ThCl_3(dma)_4]^+Cl^-$. Repeated recrystallisation of $ThCl_4$·4dma from thf yielded $ThCl_4$·3dma (calculated CAF = 0.82) [12], although treatment of the tris dma complex with a solution of dma in acetone yielded $ThCl_4$·4dma. In both dma complexes the infrared spectra indicate that all dma molecules are coordinated to the metal.

It is interesting to note that the ΣCAF plot for thorium complexes of known structure, shown in Fig. 2, indicates that complexes of the form $ThCl_4 \cdot L_3$ are the most likely stable species for neutral complexes with ligands of reasonable size which do not involve second order crowding, and the results for the uranium(IV) systems suggest that both $UCl_4L_2$ and $UCl_4L_3$ are likely to be found for bulky and intermediate sized ligands.

These investigations have been followed a little further by looking at the corresponding thorium(IV) and uranium(IV) thiocyanate systems. In the uranium case we had already found that complexes of the form $[(\eta^5\text{-}C_5H_5)U(NCS)_3L_2]$ could not be obtained with thf or pyridine or with the smaller amides, such as dma, but such complexes were obtained quite easily with second order bulkier ligands, such as $Me_3CCONMe_2$, $(Me_2N)_3PO$ or $Ph_3PO$ [8]. With the non-organometallic species, both 7- and 8-coordination appears to be possible, depending on the bulkiness of the ligand, and a number of tris amide complexes have been obtained. The structure of one of these, $[U(NCS)_4(dmiba)_3]$ (dmiba = $Me_2CHCONMe_2$) is a pentagonal bipyramid with a rather bent SCN–U–NCS axis [13].

Pentagonal bipyramidal coordination geometry is rather unusual for actinide(IV) complexes, although it is very common in dioxouranium(VI) compounds, in which the linear O=U=O group provides a rigid axis. Following this we have also found that the cation in the complex $UCl_4$·2.5depa (= $[UCl_3$-

$(depa)_4]^+$ $[UCl_5(depa)]^-$; depa = $EtCONEt_2$) also adopts pentagonal bipyramidal geometry with a Cl–U–Cl axis [14]. Subsequent work in my laboratory has provided evidence of a number of other complexes of the type $MCl_4L_3$ and it seems probable that 7-coordination will be found to be quite common in this area of the Periodic Table.

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## A3

# Acyclic and Macrocyclic Schiff Base Complexes of Lanthanides and Actinides

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The work reviewed here is the result of a collaborative project designed to explore the interaction of lanthanides and actinides with acyclic and macrocyclic Schiff base ligands. The ligands are penta- and hexa-dentate in character and have present arrays of donors drawn from oxygen, nitrogen and sulphur atoms. The acyclic ligands are capable of allowing binuclear incorporation to occur; this feature was included in the study as, in the area of selective metal extraction, a single ligand capable of removing two cations simultaneously would have cost benefit advantage over a ligand capable only of removing a single cation.

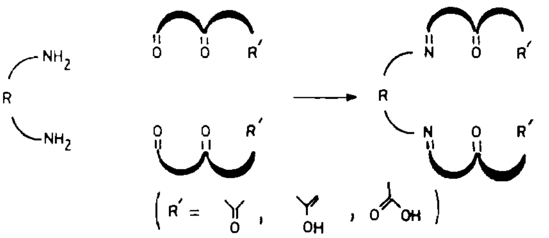
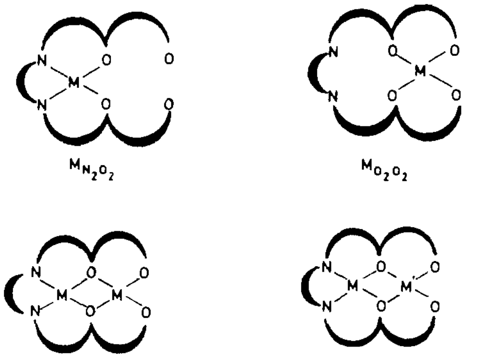


Fig. 1. Synthesis of compartmental ligands.



Homodinuclear complex Heterodinuclear complex

Fig. 2. Mononuclear positional isomers.

## A. Complexes Derived from Acyclic Ligands

During the last few years we have developed a series of ligands capable of incorporating one, or two, metal cations derived from the reaction of α,ω-alkanediamines with β-triketones or β-ketophenols. These ligands have been collectively termed Compartmental Ligands [1] (Fig. 1). They provide adjacent, dissimilar donor sets capable of forming mononuclear positional isomers, homobinuclear and heterobinuclear complexes (Fig. 2). These ligands have been exploited in the formation of a wide range of transition metal complexes and we here describe the complexation properties of ligands, derived from β-ketophenols and α,ω-alkanediamines, towards dioxouranium(VI). The corresponding complexation of lanthanide cations will be presented in the poster session.

### *(i) Mononuclear Complexes*

Mononuclear complexes of ligands I and II were prepared by stoicheiometric reaction of the ligand