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The Coordination Chemistry of Trivalent Uranium and Cerium*

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The numerous reports of structurally characterized actinide phosphine complexes [1] have dispensed with the myth that such complexes must be too thermodynamically unstable to exist. However, mere isolation does not address the question of how strong the actinide–phosphine bond is relative to the bonds formed between actinide ions and oxygen or nitrogen donor ligands. In the course of preparatory work, we unexpectedly found that trialkylphosphines quantitatively displaced tetrahydrofuran (thf) from a trivalent uranium coordination sphere; this has led to an examination of the bonding between U(III) and P, N, S and O donor ligands. We discuss here the observation that in solution, $Cp_3U(III)$ preferentially bonds π-accepting ligands such as phosphines and phosphites; in the solid state, the relative strength of the M–L bond is shown to be clearly reflected in the M–L bond length.

The relative affinity of Lewis bases towards the trivalent uranium metallocene $(MeC_5H_4)_3U$ in toluene solution, as determined by monitoring the base exchange reaction below [2], is found to be:

$$Cp_3U{-}L + L' \rightleftharpoons Cp_3UL' + L \quad K_{eq} = \frac{[U{-}L'][L]}{[U{-}L][L']} \tag{1}$$

$PMe_3 > P(OCH_3)_3 > NC_5H_5 > SC_4H_8 \sim OC_4H_8 \sim N(CH_2CH_2)_3CH > CO$. Trimethylphosphine is found to give the most stable coordination complex, followed in base strength by phosphite and pyridine ligands. Tertiary amines, ethers and thioethers are all roughly equivalent in donor capacity; in the competition between thf and CO, measured in a CO saturated toluene solution, roughly 25% of the thf is displaced by CO. When the analogous cerium complexes are studied, there is a significant decrease in the affinity of the metal for phosphine and phosphite donor ligands with respect to pyridine or thf. The postulate that trivalent uranium can act as a π-donor metal is consistent with these measurements, and is supported by the observation that $(Me_3SiC_5H_4)_3U$ bonds to one equivalent of CO in solution and the solid state, greatly reducing the CO stretching frequency [3]. The analogous cerium complexes do not appear to react with CO at ambient pressure. Given the relatively recent isolation of actinide phosphine complexes, it seems surprising that the phosphine ligand will quantitatively displace more conventional oxygen and nitrogen donor ligands from a trivalent uranium coordination sphere.

The equilibrium quotient values are strongly dependent on the steric and electronic properties of the metal coordination sphere. Table I gives equilibrium values for the competition between pyridine and PMe_3 as a function of the $(RC_5H_4)^-$ ligand. Substitution of R = H by an electron-donating methyl substituent enhances the coordinative affinity of the phosphine ligand to U(III), whereas an overwhelming increase in the steric demands of the metal coordination sphere ($R = SiMe_3$) shifts the equilibrium in favor of the smaller pyridine ligand.

The complexes $(MeC_5H_4)_3M{-}L$ (M = U, Ce, and $L = PMe_3$, $P(OCH_2)_3CEt$, and $N(CH_2CH_2)_3CH$) have been crystallographically characterized [4] to examine the possible structural ramifications of this enhanced U–L bonding. Table II gives a list of significant M–L and M–Cp distances for known complexes of the type $Cp_3M{-}L$. The parameter Δ, defined as $\Delta = ([U{-}Cp] - [U{-}L]) - ([M{-}Cp] - [M{-}L])$, accounts for the relative 'ionic radii' of the metal and ligands. If ionic radii could be used to predict M–L bond lengths [5], then $\Delta = 0$; a positive Δ is indicative of a short U–L bond. The ionic radii summation rules clearly hold for the O and N donor ligands, as $\Delta = 0$. However, when the ligand is capable of π-accepting, such as phosphine, phosphite or isocyanide, there is a clear decrease in the length of the U–L bond, as represented by large positive Δ values. The isocyanide comparison is reasonable, as the Me_3Si groups would be expected to lengthen the U–C bond by increasing ligand–ligand repulsions.

TABLE I. Equilibrium Values for the Competition between Pyridine and PMe_3 as a Function of the $(RC_5H_4)^-$ Ligand

Compound	$K_{eq} = \frac{[U{-}PMe_3][py]}{[U{-}py][PMe_3]}$
$(MeC_5H_4)_3U$	180
$(C_2H_5)_3U$	80
$(Me_3SiC_5H_4)_3U$	0.1

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TABLE II. Significant Bond Distances for Known Complexes of the Type $Cp_3M{-}L$

Compound	M–Cp (Å)	M–L (Å)	Δ	Reference
$(C_5H_5)_3La{-}thf$	2.82(4)	2.57(1)	−0.01	6a
$(C_5H_5)_3Pr{-}thf$	2.80(2)	2.56(1)	0.00	6b
$(C_5H_5)_3Nd{-}thf$	2.78(2)	2.54(1)	0.01	6b
$(C_5H_5)_3Gd{-}thf$	2.74(3)	2.494(7)	−0.01	6c
$(C_5H_5)_3U{-}thf$	2.79(3)	2.55(1)		6d
$(MeC_5H_4)_3Ce{-}N(CH_2CH_2)_3CH$	2.85(3)	2.786(4)	0.00	4
$(MeC_5H_4)_3U{-}N(CH_2CH_2)_3CH$	2.82(3)	2.764(4)		4
$(MeC_5H_4)_3Ce{-}PMe_3$	2.82(3)	3.074(6)	+0.07	6e
$(MeC_5H_4)_3U{-}PMe_3$	2.79(3)	2.972(6)		1g
$(MeC_5H_4)_3Ce{-}P(OCH_2)_3Et$	2.82(3)	3.093(3)	+0.09	4
$(MeC_5H_4)_3U{-}P(OCH_2)_3Et$	2.80(5)	2.988(6)		4
$(C_5H_5)_3Pr{-}CNEt$	2.78(2)	2.65(1)	+0.11	6f
$(Me_3SiC_5H_4)_3U{-}CNEt$	2.81(3)	2.57(2)		3

The relative decrease in uranium–ligand bond lengths are consistent with the solution basicity measurements as well as the IR measurements on the CO/RNC complexes, all of which support the contention that U(III) can act as a π-acid.

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