

Molecular structure and charge distribution in organometallics of the 4f and 5f elements

I: Dipole moment and charge distribution of the actinoid(IV) tetracyclopentadienides, $An(C_5H_5)_4$

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Abstract

The dipole moments of the tetracyclopentadienides, $An(C_5H_5)_4$, of the lighter actinoids thorium, uranium and neptunium were measured in benzene solution. Although the compounds in the solid state have a quasi- T_d molecular symmetry their dipole moments are not zero, owing to lowering of the molecular symmetry. The origin of the non-zero dipole moments is discussed.

1. Introduction

The rapid expansion in crystallographic investigations of lanthanoid and actinoid organometallics during the past decade has added to our knowledge of the chemical bond and encouraged the theoretical treatment of this class of compounds. It is becoming clear that there is a correlation between charge distribution around the central ion of the molecule of an organometallic compound and its properties in solid state and solution. Coordination number, site symmetry, stabilization of complexes with new ligands, and other important parameters can be exactly calculated. In many cases accurate predictions can be made by using the known crystallographic data of homologous compounds. The crystal structures of several organometallics of the 4f and 5f elements are now available and their crystallographic data can be discussed with respect to many physicochemical properties, *e.g.* solvation and solubility, volatility, reactivity, thermodynamics in solid state and solution etc. The electrical charge distribution, which can be calculated from measurements of the dipole moment, is particularly important, especially for predictions of bond length and angles in different compounds with unknown crystal structure.

When in 1962 Fischer and Hristidu [1] reported on the first synthesis of tetrakis(cyclopentadienyl)uranium(IV), $U(C_5H_5)_4$, they pointed out that the

probable structure of the compound was tetrahedral, because its electrical dipole moment in solution was found to be zero. 12 years later J. Burns [2] after a single-crystal X-ray analysis of the compound showed that the structure of $U(C_5H_5)_4$ is almost tetrahedral. The individual molecule has point symmetry S_4 and the centres of gravity of the four pentahapto-bonded rings form an ideal tetrahedron around the uranium atom.

During the last five years we have measured the dipole moment of more than 250 different organometallic compounds of the lanthanoids and the actinoids with different molecular symmetries (T_d , C_{3v} , C_{2v} , D_{2d} , D_{3h} , D_{3h}) containing the cyclopentadienyl anion $C_5H_5^-$ (Cp^-) as ligand. We report here, as the first part of a series of papers dealing with the correlation between molecular structure and charge distribution in organometallics of the 4f and 5f elements, on the electrical dipole moments and the charge distribution of the highly symmetric $An(C_5H_5)_4$ compounds.

2. Experimental details

All compounds were synthesized by classical preparation methods from the actinoid tetrachlorides (for the synthesis of the plutonium compounds $(Et_4N)_2PuCl_6$ was used) with potassium cyclooctatetraenide or potassium cyclopentadienide in tetrahydrofuran. The dried crude product was extracted several times with pentane before use.

The IR spectra of the compounds pressed into KBr pellets were recorded with a Perkin-Elmer M283 spectrometer ($4000-200\text{ cm}^{-1}$); the far IR (FIR) spectra ($400-40\text{ cm}^{-1}$) of the compounds pressed into polyethylene pellets were recorded with a Beckman FS-720 Fourier spectral photometer.

The dipole moments of the compounds dissolved in benzene were measured with a DM 01 (2 MHz) WTW apparatus.

All manipulations were carried out under inert atmosphere (high purity argon gas with less than 1 ppm oxygen and moisture).

3. Results and discussion

3.1. The molecular structure of $An(C_5H_5)_4$

Actinoid(IV) tetracyclopentadienides, $AnCp_4$, are known of the lighter actinoids protactinium [3], thorium [4], uranium [1] and neptunium [5]. Although only the uranium compound has been characterized by single-crystal X-ray analysis [2], ample experimental evidence shows that all four complexes are isostructural. IR and extended mass spectroscopic investigations for $PaCp_4$ [3] show that this compound exhibits the same molecular symmetry as its homologous compounds of thorium, uranium and neptunium. X-ray powder diffraction performed on $NpCp_4$ [6] leads to the same pattern as UCp_4 . The IR spectra of the compounds are quite similar in the 600–4000

cm^{-1} region [7] as well as in the far IR ($\nu < 400 \text{ cm}^{-1}$), where the skeleton vibrations of the molecule are observed (Fig. 1).

^1H nuclear magnetic resonance [8–10], electron paramagnetic resonance (EPR) [11, 12] and Mössbauer spectroscopic investigations of the neptunium compound [13] give evidence that the homologous compounds are isostructural. The central ion is pentahapto coordinated to four Cp ligands with their centres of gravity on the apices of a tetrahedron.

The exact point symmetry of the molecule is not quite clear. Interpretation of the temperature dependence of the magnetic susceptibility of UCp_4 [14] and analysis of the electronic absorption bands [15] assumes T_d to D_{2d} distortion, while photoelectron spectroscopic studies on $\text{U}(\text{C}_5\text{H}_4\text{CH}_3)_4$ (UCp_4') suggest an S_4 symmetry [16] in agreement with the crystallographic investigations [2]. EPR investigations on polycrystalline NpCp_4 [10, 11] diluted in the diamagnetic ThCp_4 also provide evidence for a deviation from an ideal cubic symmetry.

All four normal vibration modes of a tetrahedral AnCp_4 molecule are Raman active, whereas only two of them are IR active [17]. As shown in Fig. 1, in contradiction to earlier publications [18] three bands appear in the FIR region, an indication of a distortion from the T_d symmetry. The weak absorption band at 250 cm^{-1} (ν_1) may become IR active either through a $T_d \rightarrow S_4 \rightarrow D_{2d}$ lowering of the symmetry or through coupling with lattice

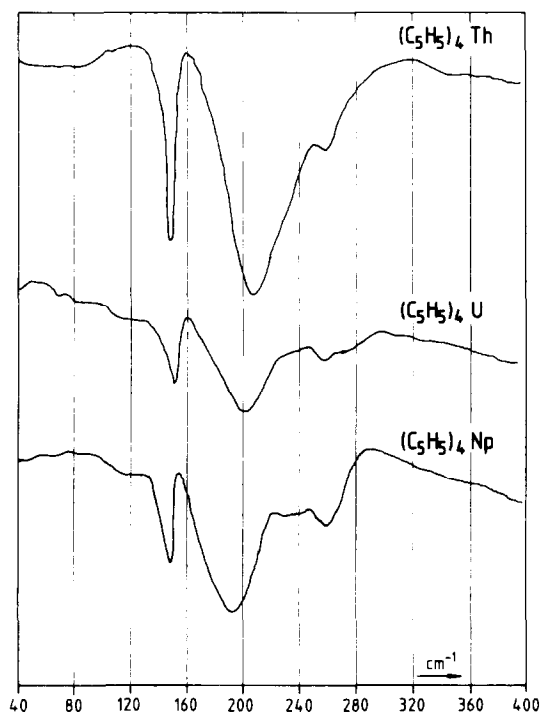
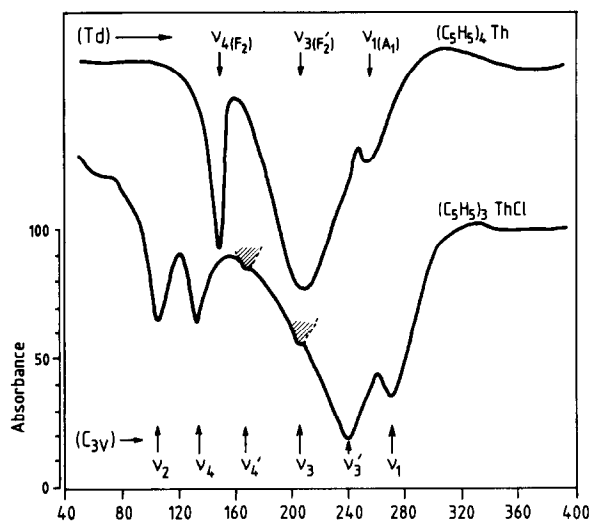


Fig. 1. FIR spectra of actinoid(IV) tetracyclopentadienides (polyethylene pellets).

vibronic frequencies. If one Cp ligand of the AnCp_4 molecule is replaced by a new ligand X, the symmetry of the molecule Cp_3AnX is lowered from T_d to C_{3v} (Fig. 2). Each of the two F terms split to an A_1 and an E term. If a further Cp ligand is replaced by a second ligand X, the symmetry of the molecule Cp_2AnX_2 becomes C_{2v} . The further splitting of the E terms of the C_{3v} symmetry to B_1 and B_2 yields nine normal modes of vibration, only one of which (A_2 from E) is not IR active (Table 1).

Whereas a large number of Cp_3AnX compounds are known [19], compounds of the class Cp_2AnX_2 with unsubstituted cyclopentadienyl ligands are, for steric and coordinative saturation reasons, not stable [20]. However, compounds of this class can be stabilized by using the bulky pentamethylated cyclopentadienyl anion $\text{C}_5(\text{CH}_3)_5^-$ ($^*\text{Cp}$), and $^*\text{Cp}_2\text{AnX}_2$ compounds have been synthesized for tetravalent thorium ($\text{X} = \text{Cl}$ [21]), uranium ($\text{X} = \text{Cl}$ [22], Br [23]), and for neptunium ($\text{X} = \text{Cl}$ [24, 25]).



	A_1	E	F		F'	
T_d	ν_s	δ_d	ν_d		δ_d	
	(ThCp)	(CpThCp)	(ThCp)		(CpThCp)	
	ν_1	ν_2	ν_3		ν_4	
	A_1	E	A_1	E	A_1	E
C_{3v}	ν_s	δ_s	ν_s	ν_{as}	δ_d	ρ_r
	(ThCl)	(CpThCp)	(ThCp)	(ThCl)	(CpThCp)	(ThCp ₃)
	ν_1	ν_2	ν_3	ν_3'	ν_4	ν_4'

Fig. 2. FIR spectra (reciprocal centimetres) of thorium(IV) tetracyclopentadienide (T_d), and tris(cyclopentadienyl)thorium chloride (C_{3v}), with assignment of the absorption bands.

TABLE 1

Far-IR absorption bands (reciprocal centimetres) of some actinoid cyclopentadienides with different molecular symmetries

$T_d \rightarrow$	A_1	E			F_2			F_2'	
ThCp ₄	256	—			205			146	
UCp ₄	259	—			199			149	
NpCp ₄	258	—			192			148	
$C_{3v} \rightarrow$	A_1	E	A_1	E			A_1	E	
Cp ₃ ThCl	275	105	204	240			135	148	
Cp ₃ UF	273	100	206	235			130	160	
Cp ₃ UCl	275	98	210	242			125	163	
Cp ₃ UOCH ₃	270	105	210	245			145	158	
$C_{2v} \rightarrow$	A_1	A_1	A_2	A_1	B_1	B_2	A_1	B_1	B_2
*Cp ₂ ThCl ₂	245	85	—	326	388	280	270	120	195
*Cp ₂ UCl ₂	246	90	—	329	398	280	269	128	192
*Cp ₂ NpCl ₂	248	91	—	329	397	280	268	127	193

Cp, C₅H₅; *Cp, C₅(CH₃)₅.

3.2. The electrical dipole moment of the AnCp₄ compounds

The permanent electrical moment μ of a compound dissolved in an organic solvent can easily be calculated from the permanent polarization $P_{2\infty}$ and the electronic polarization ${}_D P_E$ using the Debye equation

$$\mu^2 = (9kT/4\pi N_L)(P_{2\infty} - {}_D P_E) \quad (1)$$

where

$$P_{2\infty} = \{(\epsilon_1 - 1)/(\epsilon_1 + 2)\}(1/\rho_1)M_2 + \{3M_1/(\epsilon_1 + 2)^2\}(1/\rho_1)(\epsilon_{12} - \epsilon_1)/x_2 \quad (2)$$

and

$${}_D P_E = \{(\eta_1^2 - 1)/(\eta_1^2 + 2)\}(1/\rho_1)M_2 + \{3M_1/(\eta_1^2 + 2)\}(1/\rho_1)(\eta_{12}^2 - \eta_1^2)/x_2 \quad (3)$$

(M_1 denotes the molecular weight of the solvent, M_2 the molecular weight of the compound under investigation, ϵ_1 the dielectric constant of the solvent, ρ_1 the density of the solvent, ϵ_{12} the dielectric constant of the solution with the mole fraction x_2 for the solved compound, and η the refractive index).

The electrical dipole moment μ of an AnCp₄ molecule, which has an ideal tetrahedral molecular symmetry (T_d) must be zero; it results as the sum of the four partial moments between the central ion An⁴⁺ and each of the four Cp⁻ ligands:

$$\mu_{\text{AnCp}_4} = \sum \mu_{\text{An-centr. } i} = \sum q_i r_{\text{An-centr. } i} = 0.0 \text{ D} \quad (4)$$

where $r_{\text{An-centr. } i}$ denotes the distance between the central ion and the centre of gravity of the i th Cp ring, which is known from the crystallographic analysis of the uranium compound, and q the effective charge of the Cp

ring, which is taken to be $-1e^-$ because of the aromaticity of the pentahapto-bonded ligand.

In contrast to the cyclooctatetraenides, $An(COT)_2$, of thorium, uranium, neptunium and plutonium with D_{8h} symmetry for which we measured the dipole moments and found them to be zero, the measured dipole moments of the investigated $AnCp_4$ compounds (Table 2) are small but not zero, as it would be expected for an ideal tetrahedral arrangement of the four Cp^- ligands around the tetravalent actinoid cation.

The non-zero dipole moment can be interpreted as evidence for a small deviation from the ideal T_d symmetry. In such a case the four rings cannot be equal with respect (a) to their distance from the central ion, and/or (b) to the tetrahedral angle.

In both cases the dipole moment can be calculated taking into account a C_3 symmetry axis for the individual molecule:

$$\mu = q_1 |r_{An-centr.1}| - \sum q_i |r_{An-centr.i}| \sin(\Phi - 90^\circ) \quad (5)$$

The centre of the first ring (Cp_1) lies on the C_3 axis of the molecule, while the centres of the three other rings (Cp_i) are symmetrically arranged on a plane lower than the An ion and perpendicular to the C_3 axis (Fig. 3). In the first of the above mentioned cases the $Cp_1-An-Cp_i$ angle Φ remains at 109.5° (tetrahedral) and the distance $An-Cp_1$ for the first Cp^- is longer (*e.g.* 269.9 pm in the uranium compound) than the corresponding distance of the three other rings measured by crystallographic analysis (253.8 pm in UCp_4). In the second case the distances remain as found in the crystallographic investigation but the tetrahedral arrangement of three rings is flattened by small change in the angle Φ .

The deviation from the ideal T_d symmetry of the dissolved molecule may have its origin in the two possible vibrations schematically presented

TABLE 2

Measured dipole moments and calculated distances of the tetracyclopentadienides of the lighter actinoids

Compound	μ ($\pm 0.05D$)	Case (a) ($\Phi = 109.5^\circ$)		Case (b)	
		An- Cp_1 distance (pm)	An- $Cp_{i=2-4}$ distance (pm)*	An- $Cp_{i=1-4}$ distance (pm)*	Φ (deg)
Th Cp_4	1.18	283.3	258.8	258.8	107.6
U Cp_4	0.77	269.9	253.8	253.8	108.3
Np Cp_4	1.13	275.3	251.8	251.8	107.6
Th Cp_4'	1.42	289.5	260.0	260.0	107.2
U Cp_4'	1.02	276.2	255.0	255.0	107.8

*The distance $An-Cp_i$ was calculated from the $U-Cp_i$ distance and the difference of the ionic radii r_i of the tetravalent actinides: $r_{An-Cp_i} = r_{U-Cp_i} + r_{An} - r_U$.

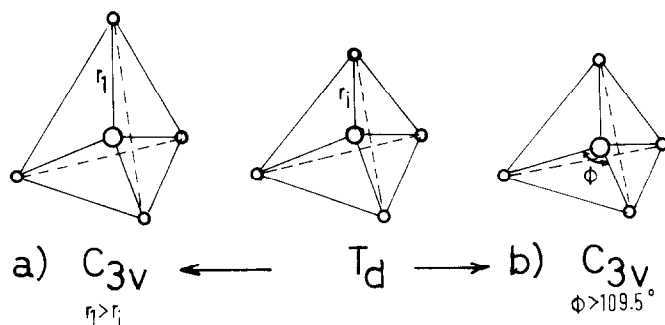


Fig. 3. Distortion of the T_d symmetry of the $AnCp_4$ compounds.

in Fig. 3. The frequency of this vibration must be lower than the frequency of the apparatus (2 MHz) used for the measurements of dielectric constants. Distances and angles in the compounds investigated, for the two possible cases as they can be calculated from the measured dipole moments, are summarized in Table 2. It is evident that the assumption of an $An-Cp_1$ distance about 16 pm longer than that calculated from the crystallographic data cannot be realistic; such a distance is too long for a stable electrostatic interaction between the central ion and the Cp^- anion.

However, concerning the case (b), a small deviation (about 2°) of the angle Φ from the tetrahedral angle can easily explain the experimental dipole moment. In reality both cases may be involved simultaneously in the vibration mode of the molecule.

4. Conclusions

In this paper we have demonstrated that careful measurements of physicochemical parameters in solution can give important information on the molecular structure of the dissolved compound.

It would be interesting to check the predictions concerning distances and angles of Table 2 of the two homologous compounds of thorium and neptunium. Attempts to grow single crystals of the compounds are now in progress.

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