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## ALKYLINDENYL ORGANOACTINIDES: SYNTHETIC CHEMISTRY, CHARACTERIZATION AND PHYSICAL PROPERTIES

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### Summary

Tris(1-ethylindenyl)actinide chloride and tris(1,4,7-trimethylindenyl)-actinide chloride (An = U and Th) have been prepared and characterized by chemical analysis and mass spectrometry. The electronic, infrared, Raman and NMR spectra have been recorded. No major steric hindrance was detected and the alkylindenyl groups appear mainly as *pentahapto* bonded to the actinide. The spectroscopic measurements are consistent with the single crystal X-ray structure of tris(1,4,7-trimethylindenyl)uranium chloride. The magnetic susceptibility of the uranium compounds has been measured between 2 and 300 K.

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### Introduction

The synthesis and characterization of a number of indenyl organoactinides such as  $(\eta^5\text{-C}_9\text{H}_7)_3\text{AnX}$  [1–5],  $(\eta^5\text{-C}_9\text{H}_7)_3\text{An}$  [6–7] and  $(\eta^5\text{-C}_9\text{H}_7)\text{AnX}_3 \cdot n\text{L}$  [8–9], where X = halide and L = ligand, have been reported. Some new compounds,  $(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{AnCl}$  and  $(1,4,7\text{-}(\text{CH}_3)_3\text{-C}_9\text{H}_4)_3\text{AnCl}$ , have been prepared. Their properties were compared with those of well known alkylcyclopentadienylactinide halides [10–13]. Interest in the alkylindenide ligand lies in its ability to donate by complex formation more electron density to the cation. Moreover, these compounds are generally more soluble and more easily crystallizable than those with  $\text{C}_9\text{H}_7^-$  or  $\text{C}_5\text{H}_5^-$  ligands. They are also preferable for the interpretation of the NMR spectra.

### Experimental

#### General

The synthesis and manipulation of all the organometallic compounds were

carried out in a glove box under highly purified argon ( $\text{H}_2\text{O} < 1 \text{ ppm}$ ,  $\text{O}_2 < 1 \text{ ppm}$ ). All solvents were thoroughly dried and were distilled under argon immediately before use. Elemental analyses were performed by the Analytical Laboratories, Engelskirchen, West Germany.

### 1-Ethylindene

A solution of freshly distilled indene (0.5 mol) in dry ethyl ether (400 ml) was introduced into a 1000 ml three necked flask equipped with a condenser, a gas-inlet tube, a dropping funnel and a magnetic stirrer. 0.5 mol of butyllithium in hexane was slowly added under argon. The resulting solution was mixed with a large excess (4/1) of ethyl bromide in ethyl ether. After stirring overnight, the ether layer was separated, washed with water (250 ml) and dried over calcium sulfate. The ether was pumped off and the residue distilled twice under vacuum (yield 80%). The purity of the compound was checked by NMR spectrometry, gas-liquid chromatography coupled with mass spectrometry and by infrared

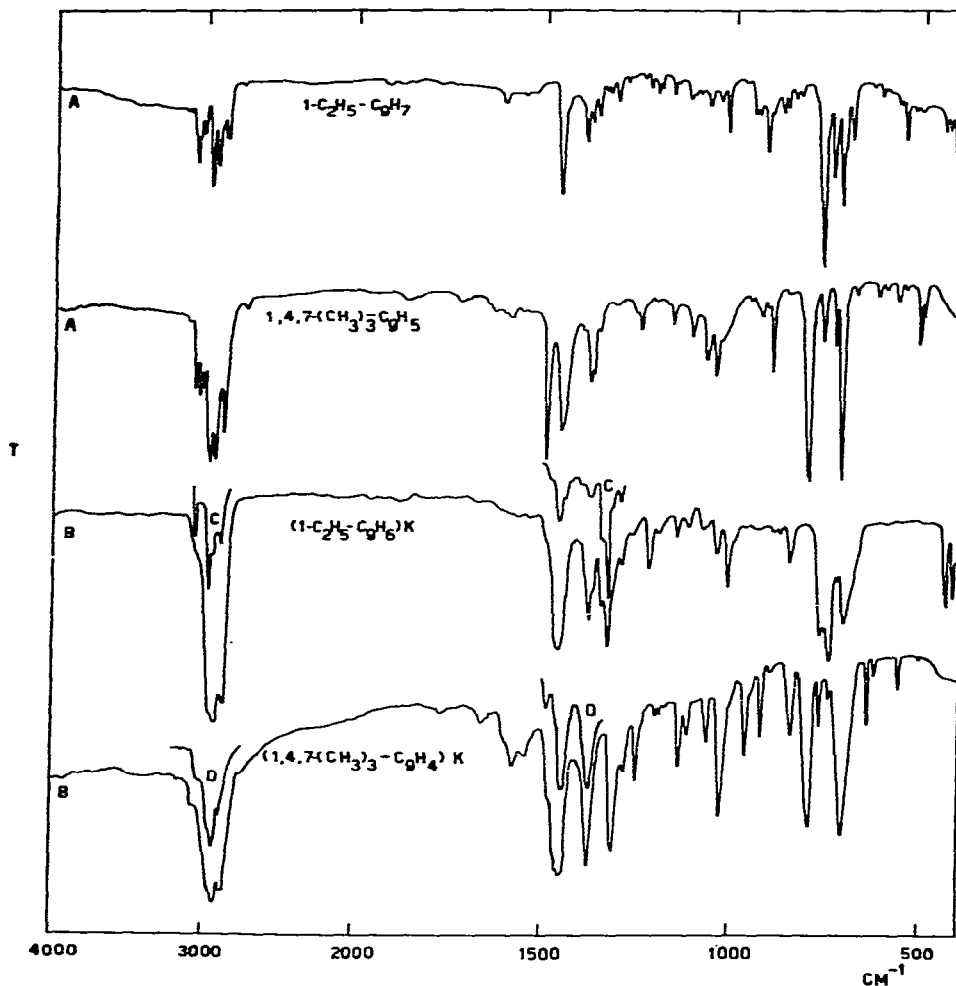


Fig. 1. Infrared spectra. A: Liquid sandwiched between KBr plates; B: Nujol mull; C: Hexachlorobutadiene mull; D: Poly(chlorotrifluoroethylene) mull.

spectroscopy (Fig. 1). The detected impurities (<0.1%) were 3-ethylindene and indene [14,15].

### 1,4,7-Trimethylindene

1) *3,4,7-Trimethylindan-1-one*. A mixture of *p*-xylene (50 g), crotonic acid (50 g) and polyphosphoric acid (500 g) was stirred at 100°C for 2 h. The solution, which became progressively red, was poured into ice and then steam distilled. After extraction with benzene (3 × 50 ml), the organic layer was distilled. The 90–100°C fraction (3 Torr) was collected and distilled again (100°C, 3 Torr) (yield 35%). The infrared and NMR spectra agreed with literature data [16,17].

2) *3,4,7-Trimethylindan-1-ol*. This compound was obtained by slow reduction of 3,4,7-trimethylindan-1-one (0.05 mol) with LiAlH<sub>4</sub> (0.015 mol) in ether. After careful decomposition of the excess LiAlH<sub>4</sub>, the alcohol was extracted with ether, dried over sodium sulfate and crystallized from ether. The yield is excellent (90%).

3) *1,4,7-Trimethylindene*. 3,4,7-trimethylindan-1-ol (0.04 mol) dissolved in benzene (500 ml) was dehydrated by refluxing with 100 mg of toluene-4-sulfonic acid for 2 h. After concentration, the residue was dried over sodium sulfate and distilled twice under vacuum (85°C, 1 Torr, yield 50%). Three peaks were observed in the gas chromatogram. The two peaks, representing less than 1% of the main peak were identified by coupled chromatography-mass spectrometry as isomers of trimethylindene (Table 1, Fig. 1).

### Tris(*n*-alkylindenyl)actinide chloride

All new compounds were prepared by the following method. The potassium 1-ethyl- or the potassium 1,4,7-trimethyl-indenide (9 mmol, Fig. 1) and uranium or thorium tetrachloride (3 mmol) were dissolved in 150 ml of tetrahydrofuran (THF) at room temperature. The solution was stirred for at least two days. KCl was filtered off and THF evaporated under vacuum at room temperature. The residue was extracted with *n*-pentane for two weeks. Slow cooling of the extracts produced single crystals of the four compounds (yield 50%). The analytical results are shown in Table 2.

TABLE 1

PARTIAL MASS SPECTRA OF TRIMETHYLINDENE (70 eV, INLET TEMPERATURE 225°C)

<i>m/e</i>	Main peak/ R.I. <sup>a</sup>	Peak 2/ R.I. <sup>a</sup>	Peak 3/ R.I. <sup>a</sup>	Ion
158	61	57	52	(CH <sub>3</sub> ) <sub>3</sub> C <sub>9</sub> H <sub>5</sub> <sup>+</sup>
143	100	100	100	(CH <sub>3</sub> ) <sub>2</sub> C <sub>9</sub> H <sub>5</sub> <sup>+</sup>
141	24	31	31	C <sub>11</sub> H <sub>9</sub> <sup>+</sup>
128	53	61	56	(CH <sub>3</sub> )C <sub>9</sub> H <sub>5</sub> <sup>+</sup>
115	18	27	20	C <sub>9</sub> H <sub>7</sub> <sup>+</sup>

<sup>a</sup> Relative intensity.

TABLE 2  
ANALYTICAL RESULTS <sup>a</sup> (%)

Compounds	Color	C	H	An	Cl
(1-C <sub>2</sub> H <sub>5</sub> -C <sub>9</sub> H <sub>6</sub> ) <sub>3</sub> ThCl	Yellow	56.37(56.86)	4.90(4.77)	33.3(33.29)	5.2(5.09)
(1-C <sub>2</sub> H <sub>5</sub> -C <sub>9</sub> H <sub>6</sub> ) <sub>3</sub> UCl	Brown	55.92(56.37)	5.06(4.73)	33.8(33.85)	4.9(5.04)
(1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> ThCl	Yellow	58.45(58.44)	5.31(5.31)	31.4(31.36)	4.8(4.79)
(1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> UCl	Dark brown	58.24(57.97)	5.32(5.27)	31.7(31.91)	4.8(4.75)

<sup>a</sup> Calculated values are given between brackets.

### Physical measurements

Infrared spectra were recorded on a Perkin-Elmer model 125 and 580B and a Polytec FIR 30. The hexachlorobutadiene, the poly(chlorotrifluoroethylene) and the Nujol were degassed before the preparation of the mulls. The potassium trimethylindenide reacts with the hexachlorobutadiene and was dispersed in poly-(chlorotrifluoroethylene). Raman spectra were recorded with the instrument previously described [18]. Samples were examined as single crystals in sealed Lindemann capillaries. The furnace used for recording Raman spectra at high temperatures is similar to the one previously described [19]. The inside however was modified in order to insert a large nickel block, machined to provide the necessary windows. A heating nickel-chrome wire is wrapped around the block with proper electrical insulation. Except for the windows, the block is completely surrounded by a water cooled brass jacket. For relatively low temperature work (up to 400°C), the Pyrex Raman cell consists of square tubing fitted in an aluminium cylinder which is inserted into the nickel block. This new design combines high light gathering power, thermal radiation rejection, and temperature stability. Electronic spectra were recorded on a Cary 17 spectrophotometer. Mass spectra were obtained with a Varian MAT-112. The magnetic susceptibility of the uranium compounds was measured between 2 and 300 K with a Faraday balance calibrated with CuSO<sub>4</sub> · 5 H<sub>2</sub>O, HgCo(SCN)<sub>4</sub>, (NH<sub>4</sub>)Fe(SO<sub>4</sub>)<sub>2</sub> · 12 H<sub>2</sub>O and Fe(SO<sub>4</sub>)<sub>2</sub> · 7 H<sub>2</sub>O. <sup>1</sup>H spectra were determined on a Cameca spectrometer at 250 MHz.

### Results and discussion

Details of the mass spectra of the new compounds are shown in Table 3. No ions were observed with *m/e* ratio larger than the parent ion. As previously reported for (η<sup>5</sup>-C<sub>9</sub>H<sub>7</sub>)<sub>3</sub>AnX [1,5], the R<sub>2</sub>AnCl<sup>+</sup> ion (R = ethylindenyl or trimethylindenyl) gives the strongest mass peak. No AnCl<sup>+</sup> or An<sup>+</sup> ions were found. No peak corresponding to (1-C<sub>2</sub>H<sub>5</sub>-C<sub>9</sub>H<sub>6</sub>)<sub>n</sub>An<sup>+</sup> was observed, showing that in monoalkyl indenyl derivatives, as in the indenyl derivatives [1], the halide is more firmly bonded to the actinide than in trimethylindenyl compounds, in which the corresponding peak can be detected.

### Vibrational spectra

1. 4000–400 cm<sup>-1</sup> region. Comparison of the spectra of 1-ethylindene and 1,4,7-trimethylindene with those of the corresponding potassium indenides

TABLE 3  
PARTIAL MASS SPECTRA (62 eV)<sup>a</sup>

(1-C <sub>2</sub> H <sub>5</sub> -C <sub>9</sub> H <sub>6</sub> ) <sub>3</sub> ThCl Inlet temperature 175°C			(1-C <sub>2</sub> H <sub>5</sub> -C <sub>9</sub> H <sub>6</sub> ) <sub>3</sub> UCl Inlet temperature 175°C			(1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> ThCl Inlet temperature 260°C			(1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> UCl Inlet temperature 280°C		
m/e	R.i. <sup>b</sup>	Ion	m/e	R.i. <sup>b</sup>	Ion	m/e	R.i. <sup>b</sup>	Ion	m/e	R.i. <sup>b</sup>	Ion
697	0.1	C <sub>33</sub> H <sub>33</sub> ThCl <sup>+</sup>	703	0.1	C <sub>33</sub> H <sub>33</sub> UCl <sup>+</sup>	739	0.1	C <sub>36</sub> H <sub>39</sub> ThCl <sup>+</sup>	745	0.1	C <sub>36</sub> H <sub>39</sub> UCl <sup>+</sup>
553	100	C <sub>22</sub> H <sub>22</sub> ThCl <sup>+</sup>	559	100	C <sub>22</sub> H <sub>22</sub> UCl <sup>+</sup>	704	0.1	C <sub>36</sub> H <sub>39</sub> Th <sup>+</sup>	710	0.1	C <sub>36</sub> H <sub>39</sub> U <sup>+</sup>
445	2.7	C <sub>13</sub> H <sub>17</sub> ThCl <sup>+</sup>	451	3.2	C <sub>13</sub> H <sub>17</sub> UCl <sup>+</sup>	582	100	C <sub>24</sub> H <sub>26</sub> ThCl <sup>+</sup>	588	100	C <sub>24</sub> H <sub>26</sub> UCl <sup>+</sup>
409	29	C <sub>11</sub> H <sub>10</sub> ThCl <sup>+</sup>	416	53	C <sub>11</sub> H <sub>11</sub> UCl <sup>+</sup>	546	2.6	C <sub>24</sub> H <sub>26</sub> Th <sup>+</sup>	552	1.0	C <sub>24</sub> H <sub>26</sub> U <sup>+</sup>
287	8	C <sub>22</sub> H <sub>21</sub> <sup>+</sup>	287	54	C <sub>22</sub> H <sub>21</sub> <sup>+</sup>	425	17	C <sub>12</sub> H <sub>13</sub> ThCl <sup>+</sup>	431	47	C <sub>12</sub> H <sub>13</sub> UCl <sup>+</sup>

<sup>a</sup> Only <sup>35</sup>Cl has been considered. <sup>b</sup> R.I.: Relative intensity.

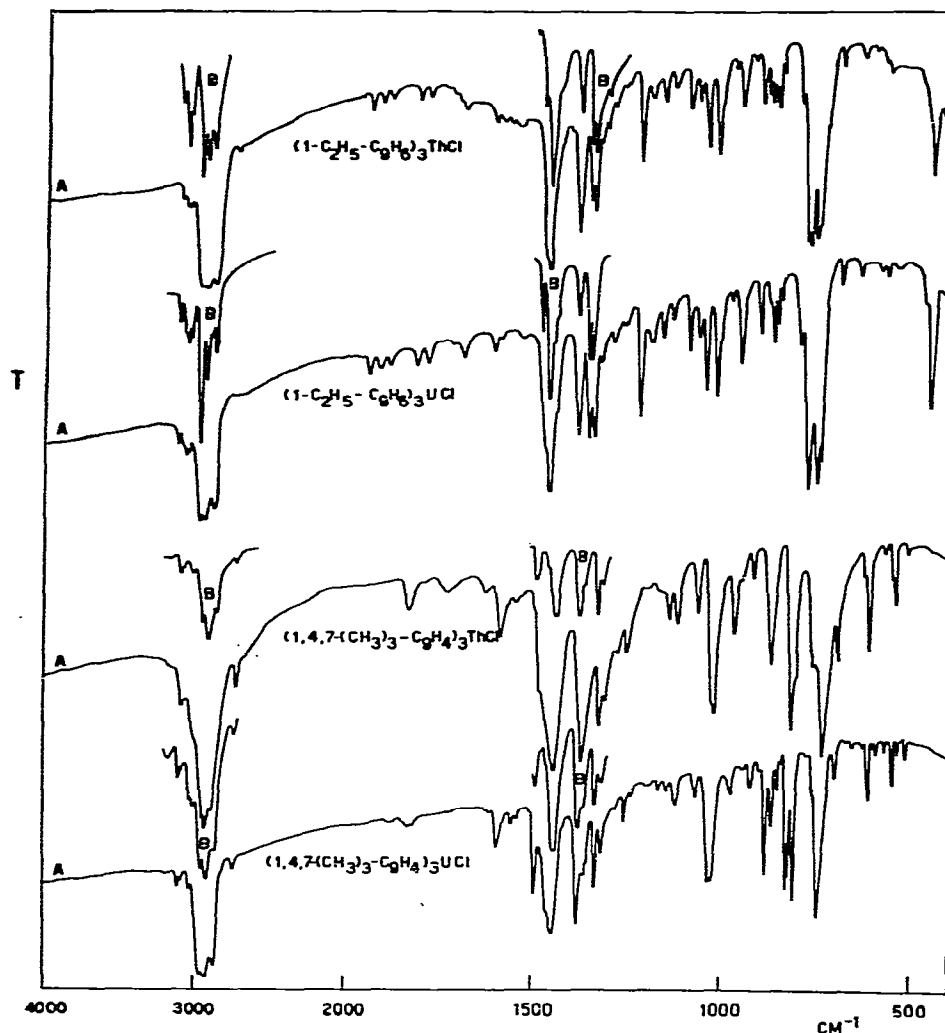


Fig. 2. Infrared spectra. A: Nujol mull; B: hexachlorobutadiene mull.

(Fig. 1), reveals that the main difference is found near  $1315\text{ cm}^{-1}$  where a new strong band appears in the indenides. The corresponding Raman line also has a strong intensity and is polarized [5]. This band has been assigned to C—C stretching vibrations, mainly of the  $C_5$  ring. This vibration is clearly related to the aromatization of the  $C_5$  ring and disappears during the oxidation process of the compounds. In the  $800\text{--}600\text{ cm}^{-1}$  region, the potassium indenides (Fig. 1) show two very intense bands which have been assigned to C—H and C—CH<sub>3</sub> out-of-plane bending vibrations [2–6,20]. These bands are, as expected [21], shifted to higher frequencies ( $30\text{--}40\text{ cm}^{-1}$ ) when the alkyindenyl groups are coordinated to the actinides (Figs. 1 and 2). In tris(trimethyindenyl) actinide chlorides, the structure of the corresponding bands is much more complicated than in trisindenyl analogues [2–6]. This indicates that the interaction between the three substituted indenyl ligands must be important because the

groups are very close, so that there is appreciable vibrational coupling giving a more complicated structure for the out-of-plane vibrations, which are normally more affected by the coordination to a cation than the other vibrations. The vibrational behaviour of the four new compounds appears identical to that of the indenyl actinide compounds [1–6,8]; thus, it seems reasonable to suppose that, as in the indenyl compounds, the  $C_5$  rings of the new ligands are  $\eta^5$ -bonded to the cation. The infrared band observed at  $440\text{ cm}^{-1}$  in trisindenylactinide halides and in tris(1-ethylindenyl)actinide halides is shifted to about  $350\text{ cm}^{-1}$  in tris(trimethylindenyl)actinide halides. This observation confirms the previous assignment [5]; this band corresponds to deformation vibrations of the  $C_6$  ring which are strongly affected by the presence of the two methyl groups in position 4 and 7 [20].

2.  $400\text{--}0\text{ cm}^{-1}$  region. If the indenyl or the n-alkylindenyl groups are regarded as rigid discs [21], then for a  $C_{3v}$  internal symmetry, the skeletal vibrations belong to

$$\Gamma_{\text{vib.}} = 4A_1 + 2A_2 + 6E$$

where  $A_1$  and  $E$  normal vibrations are active in the infrared and Raman spectra. The method of internal coordinates allows us to assign the skeletal vibrations (Table 4).

The inner vibrations are probably observed below  $400\text{ cm}^{-1}$ . The vibrational spectra of four analogous compounds are compared in Table 5. We have obtained very good Raman spectra of trisindenylthorium chloride or tetrahydroborate in molten or vitreous state to determine the polarization of the Raman line, but the other compounds melt at high temperature with decomposition, and under such conditions it is impossible to record good Raman spectra of molten compounds.

For a pure  $C_{3v}$  internal geometry, the vibrational spectra should exhibit ten infrared bands and the same number of Raman lines with four polarized lines (Table 4). In fact, even for trisindenylthorium chloride, which possess a nearly pure  $C_{3v}$  symmetry, only six infrared bands and eight Raman lines, two being polarized, are observed [1–6,8]. Nevertheless, the correlation between the vibrational spectra of the four compounds is quite good (Table 5), and the same internal geometry can be assumed. The polarized Raman line observed at  $277\text{ cm}^{-1}$  ( $283\text{ cm}^{-1}$  in molten or vitreous state), at  $260\text{ cm}^{-1}$  and  $268\text{ cm}^{-1}$  for trisindenylthorium chloride, tris(1-ethylindenyl)thorium chloride and tris(tri-

TABLE 4  
SKELETAL VIBRATIONS OF TETRAHEDRAL  $R_3AnX$

Representation	Approximate type of normal vibrations
$1A_1$	An—X stretching
$1A_1 + 1E$	An—ligand stretching
$1A_1 + 2E$	Ligand—An—X bending and ligand An—ligand bending
$1E$	Ligand—An torsion
$1A_1 + 2E$	Ligand—An—ligand stretching

TABLE 5

VIBRATIONAL SPECTRA OF SOME ORGANOINDENYLTHORIUM COMPOUNDS ( $\nu < 400 \text{ cm}^{-1}$ )

$(\eta^5\text{-C}_9\text{H}_7)_3\text{ThBH}_4$			$(\eta^5\text{-C}_9\text{H}_7)_3\text{ThCl}$			$(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{ThCl}$		$(1,4,7\text{-(CH}_3)_3\text{-C}_9\text{H}_4)_3\text{ThCl}$	
Infra-red	Raman		Infra-red	Raman		Infra-red	Raman solid	Infra-red	Raman solid
	solid	molten or vitreous state		solid	molten or vitreous state				
390m	390m	390vw	383m	388vw	380vw	—	—	378w	378w
—	366vw	366vw, P	—	—	—	—	367vw	—	—
—	—	—	—	—	—	—	—	348m	345m
—	316vw	312vw	310vw	316w	310w	—	323vw	330w	325m
307w	307w	306w	—	300w	—	306m	302s	304w	303s
—	—	—	276s	277m	283m, P	—	273w	—	—
—	—	—	—	—	—	262s	260w	265m	268vs
—	240s	240s, P	—	246m	235m, P	—	—	248vs	248vs
—	—	—	—	—	—	—	—	234(sh)	235(sh)
223vs	224w	228w	228s	227m	227w	—	—	—	—
—	—	—	—	—	—	212vs	211m	—	—
—	—	—	—	—	—	—	—	195w	190s
180m	179m	—	—	176m	180vw	—	182w	—	—
—	163s	165m	—	166vs	156m	—	159s	166w	156m
—	—	—	—	125s	—	117vw	119s	—	117m(sh)
118vw	116s	—	116s	107vs	—	107vw	107vs	109w	111cs
103w	102s	104s	—	93vs	94vs	103vw	87vs	98vs	84m
—	53m	—	—	—	—	—	59s	—	—
—	39s	—	—	—	—	—	—	—	38s
—	35s	—	—	—	—	—	—	—	—

vw: very weak; w: weak; m: medium; s: strong; vs: very strong; sh: shoulder; P: polarized.

methylindenyl)thorium chloride, respectively, undoubtedly corresponds to the Th—Cl stretching vibration. Its Raman intensity seems to be rather sensitive to the cation environment. As expected, this line is not observed in the Raman spectrum of the tetrahydroborate derivative (Table 5). This Th—Cl stretching vibration is observed at  $297 \text{ cm}^{-1}$  in  $\text{ThCl}_4$  [22,23]; It was not possible to record the Raman spectrum of the uranium analogues, the laser beam being absorbed by the strongly colored uranium derivatives. The U—Cl vibration is assigned to an infrared band at  $267 \text{ cm}^{-1}$  for tris(1-ethylindenyl)uranium chloride and also for tris(trimethylindenyl)uranium chloride.

A strong absorption band around  $240 \text{ cm}^{-1}$  is observed in all the indenyl and n-alkylindenyl derivatives [2–6,8]. The study of the Raman spectrum of molten compounds with polarized light displays clearly two lines, one polarized. This observation confirms the hypothesis of Aleksanyan and coworkers [24] who noted a very strong Raman line between 200 and  $240 \text{ cm}^{-1}$  in the spectra of triscyclopentadienyllanthanides(III), and suggested that it is due to the superposition of two or more transitions. The metal—C<sub>5</sub> ring stretching vibration is assigned to the strong polarized line around  $240 \text{ cm}^{-1}$  in indenyl compounds,  $211 \text{ cm}^{-1}$  in tris(1-ethylindenyl) compounds and  $190 \text{ cm}^{-1}$  in tris(trimethylindenyl) derivatives.

A weak polarized line is observed at  $366 \text{ cm}^{-1}$  in trisindenylthorium tetrahy-



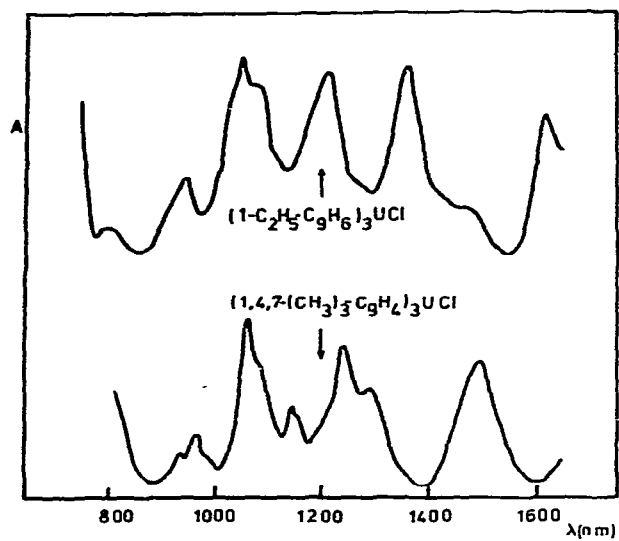


Fig. 3. Electronic spectra (THF solution).

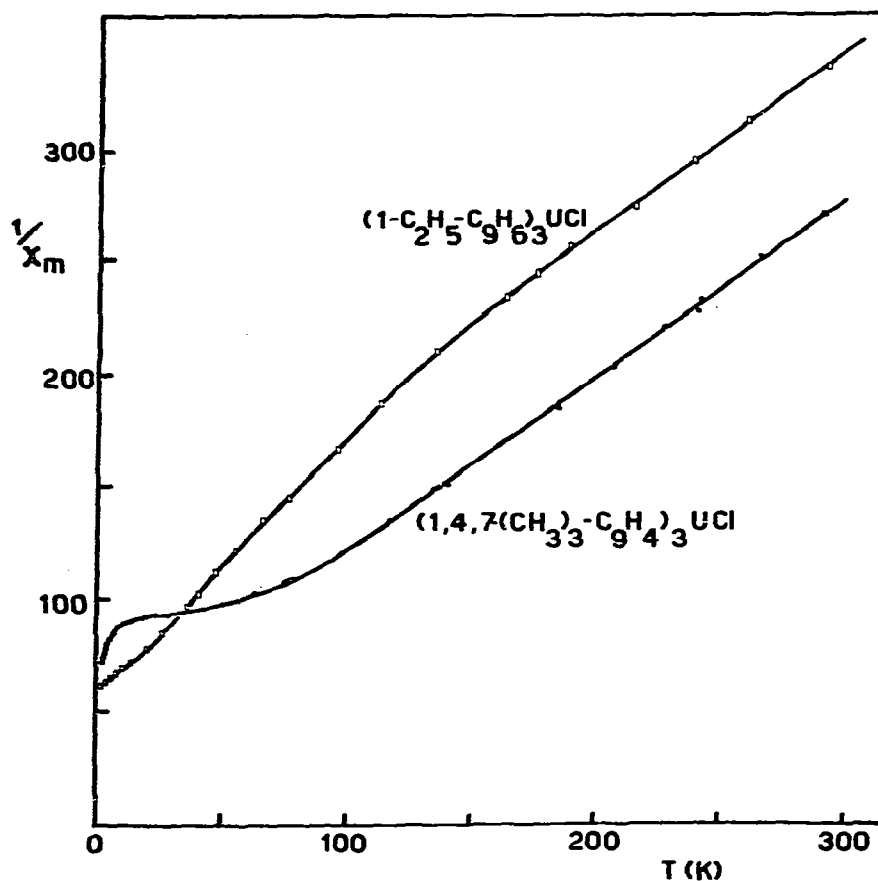


Fig. 4. Magnetic susceptibility.

droborate. Its assignment is not obvious, but it could be related to ligand-thorium-tetrahydroborate deformation vibrations. A band at  $140\text{ cm}^{-1}$  has been associated [24] with the linear combination of tilting movements of the three cyclopentadienyl rings in  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Ln}$ .

A strong band and Raman line in the  $105\text{--}85\text{ cm}^{-1}$  region (Table V) is observed in the indenyl and alkylindenyl compounds; it is not polarized. It is possible that this absorption is also due to the tilting movement of the indenyl moieties; the lowest frequency is noted for the heaviest ligand.

#### Electronic spectra

Figure 3 shows the near infrared spectra in the  $800\text{--}1650\text{ nm}$  region of tris(1-ethylindenyl)uranium chloride and tris(trimethylindenyl)uranium chloride in tetrahydrofuran solution. The thorium analogues showed no absorption in this region. As in  $(\eta^5\text{-C}_9\text{H}_7)_3\text{UX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CH}_3 \dots$  [1–6]), a group of three sharp bands with low extinction coefficients ( $\epsilon < 100$ ) is observed in the  $1000\text{--}1400\text{ nm}$  region. It is clear that the cation environment must be nearly the same in all these types of indenyl compounds since they have approximately the same electronic spectra. In the octahedral cyclopentadienyl and indenyl uranium compounds, the absorption spectra are quite different [8,23,25].

#### Magnetic susceptibility

The magnetic susceptibilities of the two new uranium compounds have been measured between 2 and 300 K, using a Faraday balance (Fig. 4). The thorium compounds are diamagnetic. The susceptibility was corrected for the diamagnetic contribution of the constituents.

$(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{UCl}$  follows the Curie-Weiss law between 150 and 300 K ( $\theta = -130\text{ K}$ ). The effective magnetic moment ( $\mu_e = 2.84 \sqrt{\chi_m(T - \theta)}$ ) is  $3.18 \pm 0.03\text{ BM}$ . The same value is obtained for  $(1,4,7\text{-}(\text{CH}_3)_3\text{-C}_9\text{H}_4)_3\text{UCl}$  ( $3.17 \pm 0.03\text{ BM}$ ) which follows the Curie-Weiss law between 100 and 300 K ( $\theta = -108\text{ K}$ ). When we compare the magnetic behaviour of the two uranium compounds with the magnetism of the cyclopentadienyl analogues [27], we observe that tris(trimethylindenyl)uranium chloride shows qualitatively the same magnetic behaviour as  $(\eta^5\text{-C}_5\text{H}_5)_3\text{UCl}$ , which is well known to have a tetrahedral structure with a rather strong trigonal distortion [27].  $(1\text{-C}_2\text{H}_5\text{-C}_9\text{H}_6)_3\text{UCl}$  possesses probably a purer  $T_d$  symmetry.

#### Crystal structure

The crystal structure of tris(trimethylindenyl)uranium chloride has been established [28] and is illustrated in Fig. 5.

The chlorine and the five-membered rings of the three trimethylindenyl ligands are arranged almost symmetrically about the cation. The coordination polyhedron is a distorted tetrahedron. The main difference between the structure of the new compound and the structure of the other indenyl actinide complexes [1,7,9] lies in the position of the  $\text{C}_6$  rings: the  $\text{C}_2$  axes of the indenyl skeleton are always oriented towards the  $\text{U}\text{--}\text{Cl}$  axis, while it is nearly perpendicular to this  $\text{U}\text{--}\text{Cl}$  axis in tris(trimethylindenyl)uranium chloride.

The bonding possibilities in this type of compound include a mainly *tri-*

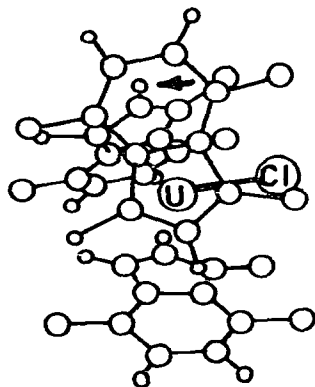


Fig. 5. Structure of tris(1,4,7-trimethylindenyl)uranium chloride.

*hapto* or *pentahapto* mode for the  $C_5$  ring of the indenyl ligand. If we compare (Table 6) the distance between carbon of the  $C_5$  ring and uranium for different indenyl derivatives, we observe that the average distance between bridged carbon—uranium (2.91 Å) is longer than the non-bridged carbon—uranium distance (2.72 Å). On the other hand, the average C—C distance in the  $C_5$  rings is 1.42 Å for tris(trimethylindenyl)uranium chloride, 1.41 Å for trisindenyluranium and 1.43 Å for  $(\eta^5-C_9H_7)UBr_3 \cdot THF \cdot (C_6H_5)_3PO$  [1,7,9,28]. These values are within the range expected for conjugated ring systems. The shorter bonds between uranium atom and carbon in the 1,2,3-ring positions in the  $C_5$  rings for the new uranium compound do not necessary support a model involving 1,2,3-*trihapto* indenyl coordination. This feature may be attributed to steric interactions between the 1,4,7-trimethylindenyl moieties.

### NMR spectral

An analysis of the proton NMR spectra of 1,4,7-trimethylindene and of its potassium complex throws some light on the dynamic behaviour of  $(1,4,7-(CH_3)_3-C_9H_4)_3ThCl$  in solution.

Representation 250 MHz NMR spectra of the potassium and thorium complexes are shown in Fig. 6. The main spectral features obtained for these compounds and for the ligand are summarized in Table 7 and compared with the corresponding data reported for indene [1] and 1-methylindene [29]. The assignment of the NMR peaks of the ligand 1,4,7-trimethylindene from their relative areas and splitting patterns is straightforward. The NMR spectrum of the potassium complex was assigned by comparison with the spectrum of 1-methylindenyllithium as reported by Taylor and Rakita [29]. The coupling constants  $J_{2-3}$  (3.2 Hz) and  $J_{5-6}$  (6.8 Hz) we obtained are in close agreement with those calculated by these authors. The assignment of the three methyl peaks or of protons H(5)—H(6) may have to be reversed, but this is of minor interest for the discussion that follows.

As shown in Fig. 6, tris(1,4,7-trimethylindenyl)thorium chloride exhibits only one peak for each type of proton. At ordinary temperature the three

TABLE 6  
STRUCTURE DATA FOR INDENYL COMPOUNDS

Compounds	( $\eta^5$ -C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> UCl [1]	( $\eta^5$ -1,4,7-(CH <sub>3</sub> ) <sub>3</sub> C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> UCl [28]	( $\eta^5$ -C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> U [7]	( $\eta^5$ -C <sub>9</sub> H <sub>7</sub> )UBr <sub>3</sub> · THF · Ph <sub>3</sub> PO [9]
U-Cl( $\sigma$ ) bond (Å)	2.593(3)	2.601(3)	—	—
Avg <sup>a</sup> U-C distance (Å) (C <sub>5</sub> ring)	2.78	2.79	2.79	2.76
Range U-C distance (Å) (C <sub>5</sub> ring)	2.67-2.89	2.66-2.93	2.73-2.85	2.70-2.80
Avg <sup>a</sup> U-C distance (Å) (C-C bridged)	2.86	2.91	2.81	2.80
Avg <sup>a</sup> U-C distance (Å) (C-C non-bridged)	2.72	2.72	2.78	2.73
Center Plane-U-Center (°)	105	118	123	
Plane angles (°)	112	117	122	
	120	118	115	
Center Plane-U-Cl (°)	108	119		
angles (°)	107	100		
	105	104		

<sup>a</sup> Averaged.

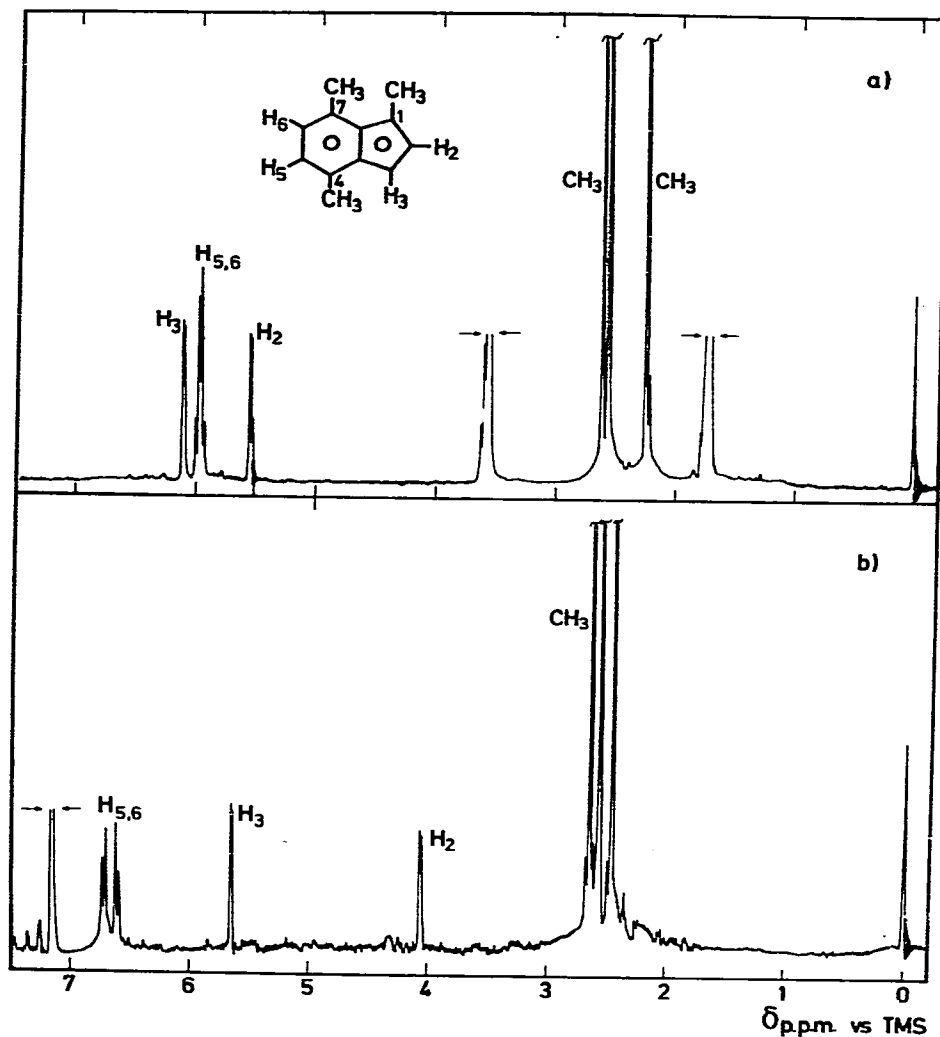


Fig. 6. 250 MHz proton NMR spectra of a) 1,4,7-trimethylindenidepotassium (TDF), b) tris(1,4,7-trimethylindenyl)thorium chloride (C<sub>6</sub>D<sub>6</sub>). The solvent peaks are indicated by arrows.

indenyl ligands are thus involved in the same kind of ligand-to-metal bonding. From a comparison of spectrum (b) in Fig. 6 with the spectrum of trisindenylthorium chloride [1], it is readily concluded that one NMR peak, which can be correlated to hydrogens 2 or 3 (doublet,  $\delta = 4.08$  ppm,  $J(2-3) = 3.6$  Hz) occurs at particularly high fields. Cotton and Marks [30] reported that bis-(1-*monohapto*indenyl)mercury is stable at low temperatures, and that the NMR peak of the proton bound to the carbon atom to which the Hg atom is also attached appears at 3.8 ppm. However, the observation of a proton peak at about the same position in the case of the thorium complex must not be taken as evidence in favour of a *monohapto* type of bonding; such a bonding can be ruled out on the basis of a) the near identity of  $J_{2-3}$  in the potassium and the

TABLE 7  
 PROTON NMR CHEMICAL SHIFTS ( $\delta$ )<sup>a</sup> OF INDENE, 1-METHYLINDENE AND 1,4,7-TRIMETHYLINDENE AND OF SOME OF THEIR ORGANOMETALLIC DERIVATIVES

	$\delta_1$	$\delta_2$	$\delta_3$	$\delta_4$	$\delta_5$	$\delta_6$	$\delta_7$	$\delta(\text{CH}_3(1))$	$\delta(\text{CH}_3(4,7))$
Indene	3.01	6.53	6.34						
(C <sub>9</sub> H <sub>7</sub> )Li <sup>b</sup>	5.96	6.50	5.95		(6.71)	(7.4)	(7.51)		
(C <sub>9</sub> H <sub>7</sub> ) <sub>3</sub> ThCl <sup>c</sup>	5.84	6.34	5.84	7.18	7.71	7.71	7.18		
1-CH <sub>3</sub> -C <sub>9</sub> H <sub>7</sub> <sup>d</sup>	3.32	6.71	6.35			(7.3)		1.19	
1-CH <sub>3</sub> -C <sub>9</sub> H <sub>6</sub> Li <sup>b</sup>	—	5.69	6.20	7.50	6.82	6.81	7.49	2.20	
1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>5</sub> <sup>e</sup>	3.44	6.74	6.34	—	6.90	6.83	—	1.22	2.29
1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> K <sup>f</sup>	—	5.54	6.10	—	5.97	6.00	—	2.24	2.54, 2.58
(1,4,7-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>9</sub> H <sub>4</sub> ) <sub>3</sub> ThCl <sup>g</sup>	—	4.08	5.66	—	6.60	6.72	—	2.47	2.55, 2.63

<sup>a</sup> Chemical shifts are in ppm, downfield from TMS. <sup>b</sup> In THF, see ref. 30. <sup>c</sup> In THF, see ref. 1. <sup>d</sup> In CDCl<sub>3</sub>, see ref. 30. <sup>e</sup> In CDCl<sub>3</sub>. <sup>f</sup> In THF. <sup>g</sup> In C<sub>6</sub>D<sub>6</sub>.

thorium complexes, b) the absence of temperature variation in the NMR spectra and c) the crystallographic structure described above.

The abnormal shift of one of the protons belonging to the five-membered ring of the ligand is considered to arise from the rigidity of the thorium complex. Molecular models indicate that rotation of the indenyl moieties around the metal–ring bonds is virtually impossible because of the heavily crowded environment of the metal ion. The methyl groups seem to prevent the free rotation of the ligands. Because Laubereau et al. [1] reported that the replacement of lithium by thorium in indenyl complexes leads to a greater shielding of the protons 2 and 3, it will be tentatively assumed that the doublet at 4.08 ppm is due to H(2) while proton H(3) would absorb at 5.66 ppm. A careful examination of the crystallographic structure (see Fig. 5) leads to the conclusion that proton H(2) is located above and near to the middle of the benzene ring belonging to the adjacent indenyl moiety. (For clarity, a proton H(2) is indicated by an arrow in Fig. 5). Proton H(2) is thus subjected to a strong shielding effect arising from the magnetic anisotropy of the benzene ring in its immediate vicinity. Although this is only an approximation, the solid state structure of the thorium complex will be assumed to remain unchanged in solution. From the crystallographic coordinates, it is easy to compute  $z$  and  $\rho$ , the cylindrical coordinates relative to the six-fold axis of the benzene ring. The mean values of these coordinates calculated for the three protons H(2), each one belonging to a different indenyl group are  $z = 1.7$  and  $\rho = 0.4$  (in benzene radius unit = 1.397 Å). According to the theoretical treatment developed by Haig and Mallion [31], a ring current effect of 0.93 ppm upfield should then be expected. It can be assumed that the replacement of lithium by thorium will cause the same shift for an indenyl complex and for its substituted analogues; the experimental shift due to the anisotropy of the benzene ring then amounts to 1.30 ppm. A similar calculation in the case of proton H(3) yields the coordinates  $z = 2.2$  and  $\rho = 1.5$ , and consequently an upfield shift of 0.22 ppm should be observed [31]. The experimental shift is 0.33 ppm. For both protons H(2) and H(3) the agreement between the theoretical and experimental values is considered satisfactory, taking into account the crudeness of the structural model and the uncertainties in the computation of the magnetic anisotropy of aromatic systems [31].

From the interpretation of the NMR spectra, it is inferred that the trimethylated indenyl ligands are not rotating around the metal–ring bonds on the NMR time scale, in contrast to observation for simpler actinide organometallics [1].

## Conclusions

The coordination of the *n*-alkylindenyl ligands around the tetravalent actinides is interpreted on the basis of vibrational, magnetic, NMR, absorption and crystallographic studies in terms of *pentahapto* indenyl groups with some distortions from a pure tetrahedral structure. The attempt to isolate pure bis-(*n*-alkylindenyl)actinide dichloride failed. It is now clear that even bulky *n*-alkylindenyl ligands do not inhibit the formation of tris(*n*-alkylindenyl)-actinide halides [26].

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