Solid-State Structure of Tris-Cyclopentadienide Uranium(III) and Plutonium(III)

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Dedicated to Gottfried Huttner on the occasion of his 80th birthday

Abstract: The organometallic tris-cyclopentadienide actinide(III) (AnCp3) complexes were first reported about 50 years ago. However, up until now, only the NpCp3 solid state structure has been studied. Here we report on the solid state structures of UCp3 and PuCp3, which are isomorphous with the Np analogue. The structural models are supported by theoretical calculations and compared to their lanthanide homologues. The observed trends in changes of bond lengths might be indicative for an increased covalency in the bonding in the tris-cyclopentadienide actinide(III) complexes (AnCp3) compared to their lanthanide homologues.

The organometallic actinide chemistry with cyclopentadienyl ligands was developed in Karlsruhe and Munich by the pioneering work of E. O. Fischer, F. Baumgartner, and B. Kanellakopulos together with P. Laubereau, then of the National Laboratories at Oak Ridge.

The oxidation state I-III is not the most stable for all actinides. Nevertheless the solvent free non-stabilized tris-cyclopentadienide actinide(III) complexes AnCp3 were reported 50 years ago,[1][2] a few years after the first reports on the AnCp2 complexes.[3] Type LnCp3 (Ln: lanthanide) complexes not stabilized by Lewis base adduct formation have been previously studied.[4] However, as the first example of an non-stabilized AnCp3 complex, the synthesis and solid-state structure of NpCp3 has only recently been published.[5] This was followed by the first report on a structurally characterized organometallic Pu4 complex Pu(Cp3(TMS)3), and its reduced Pu3 analogue[6] and then the first report on a Pu6 organometallic plutonocene derivative.[6]

Fifty years after the first reports, the structures of the UCp3 or PuCp3 complexes are still unknown. This is because even in the case of the adduct free LnCp3 complexes, high quality single crystals are not easily obtained. Indeed different forms are sometimes observed depending on the crystallization conditions.[7] In case of the actinides, additionally, aging of solids is observed: after some weeks of storage they show drastically decreased solubility.[8] This effect is however less noticeable when pure single crystalline material is stored.

Here, we close the knowledge gap on the solid-state structures of AnCp3 (An: U, Pu). Comparing them to the structures of NpCp3 and related LnCp3 complexes offers the opportunity to gain a more detailed insight in the bonding. This is important for the understanding of 4f or 5f electron behaviour and differences therein.

UCp3 was prepared by reductive elimination of chloride from UCp3Cl with sodium amalgam in diethylether. PuCp3 was obtained from the direct reaction of PuCl3 with a slight excess of KCp. Both were purified by filtration and evaporation of the solvent followed by extraction with pentane or pentane/Et2O mixtures. The IR spectroscopic data reveal a fingerprint consistent with that previously reported for UCp3 and PuCp3.[1b,c,6] The 2H NMR spectra of UCp3 show one single resonance at δH = −15.60 ppm ([D3]THF) or −13.62 ppm ([D3]MeCN) for the formed adducts under these conditions, which are in agreement with literature-known values.[7] The cross-peak for the CH C-atom is observed at low field at 272.4 ppm in the 13C frequency resulting in an overall comparable situation as observed in the bis-TMS substituted uranocene derivative in[7b] (Figure S1). The NMR spectroscopic investigations on PuCp3 are the 4th example of a Pu organometallic complex for which a proton resonance is reported and the 2nd complex on which multi-dimensional NMR spectroscopy was performed.[5,6] In [D3]benzene there is one resonance observed for [PuCp3(thf)] at 11.59 ppm (in good agreement with the values reported in Ref. [5]) giving rise to a cross-peak in the CH correlated spectrum at 81.4 ppm (Figure S2). This is a sign that the Cp rings are in equilibrium due to fast chemical exchange in the sample. It seems that in all Pu organometallic complexes reported up to now the chemical shifts observed for the proton as well as for the 13C resonances appear in the same range independently on the oxidation state of the metal being +II, +III, or +IV.[5,4,7b]
and PuCp residues; this Cp ring is \(\eta^1,\eta^1\)-coordinated (bridging
atom C11, Figure 1). This results in the polymeric zig-zag struc-
ture motif which is known from the complexes LnCp,[9] We
can exclude an interaction on the base of a \(\mu-\eta^1,\eta^1\)-coordinated
bridging cyclopentadienyl group as described earlier[10] for
the AnCp complexes also for all LnCp complexes whose solid
state structures we have determined in the past years resulting
in low temperature high quality datasets.[6] A coordination
environment of four Cp rings three establishing
\(\eta^1\) and one \(\eta^1\)-coordination is also established in [K\(\text{NpCp}_2\)]
the KCP adduct to NpCp.[4] A symmetrical bonding of the \(\eta^1\)-coordinated Cp rings is produced (mean Np-Ct
251 pm, see footnote Table 1) together with a closer interaction to the \(\eta^1\)-

By extraction single crystals are obtained suitable for X-ray
diffraction analyses (Figure 1, all experimental details see the
Supporting Information). Both compounds, UCp3 and PuCp3,
form crystals that are isomorphic to the NpCp analogue.[6] For
Cm and Bk, the cell parameters have been identified by
Debye–Scherrer analyses together with a series of LnCp com-
plexes[1a,b] all containing one axis doubled. Also discussed are
some structures of LnCp complexes with comparable cell para-
ters, maybe containing one axis doubled but also with an
identical reduced cell.[3] Most of these structures show disorder
of the Cp rings, and data collection was performed at room
temperature. Both these factors prevent a good determination
of the atom positions concerned, which leads to high standard
deviations in distances and angles and makes any discussion
on a significant level more difficult (see Baisch et al.[12]). There-
fore we performed our diffraction analyses at a temperature of
100 K in order to collect datasets of good quality. We describe
the systems as orthorhombic Cmc2, with \(a \approx 14.15, b \approx 8.70,\)
and \(c \approx 9.60 \text{ Å},\) which corresponds to a monoclinic reduced cell of
\(a \approx 8.30, b \approx 9.60,\) and \(c \approx 8.30 \text{ Å with } \beta \approx 116.5^{\circ}\) (rounded
values from all three data sets). The monoclinic cell has been
used before to describe LaCp3[4c] and PrCp3[3b] whereas the
orthorhombic cell was applied in the case for one PrCp3 structure
which has been deposited at the CCDC[5a] but the space group
reported is with Pbnm different from our findings.

We are now convinced that at least in the cases for the
three actinide complexes AnCp3 (An: U, Np, Pu) the description
in the orthorhombic space group Cmc2, is best, as in the mon-
oclinic reduced cell for the refinement a disorder must be in-
troduced which is not the case in the orthorhombic cell. This
leads for the monoclinic case in the refinement with identical
crystallographic independent cell volume to nearly double the
refined parameters but higher R values. As the two com-
pounds UCp3 and PuCp3 form the same structure, only PuCp3
is depicted representatively in Figure 1.

In the sphere of the metal all Cp rings show \(\eta^1\)-coordination.
The Lewis acidity of the actinides causes the formation of one
additional \(\eta^1\)-coordination to one Cp ring of a neighboured

Table 1. Selected bond lengths [pm].

|        | UCp3 | NpCp3 | PuCp3 |
|--------|------|-------|-------|
| M–C(\(\eta^1\)) | 278.1(23) | 281.4(15) | 283.0(12) |
| M–Ct | 293.7(23) | 289.4(15) | 288.8(12) |
| M–Ct2 | 241.6 | 241.9 | 239.2 |
| M–Ct3 | 260.4/260.8 | 256.1/258.7 | 256.5/257.4 |
| M–Ct4 | 265.8–274.7; 270.1 | 266.8–273.6; | 264.4–272.0; |
|       |       | 270.3(4) | 267.9(4) |
| M–Ct5 | 279.4–293.7; 287.2(4) | 278.9–292.2; | 276.9–291.5; |
|       |       | 284.3(4) | 283.9(4) |

Standard deviations in parentheses only for dedicated bonds not for cal-
culated ideal positions or ranges. Ct\(3c\): idealised position of center of Cp
ring. [a] First value for \(\eta^1\), \(2\text{nd}\) value for \(\eta^1\)-coordination. [b] Cp ring closer to the
An. [c] Cp rings more distant to the An. [d] mean value.

[1] Lewis acidity of the actinides causes the formation of one
polymeric zig-zag structure of which is known from the complexes LnCp3.[9] We can exclude an interaction on the base of a \(\mu-\eta^1,\eta^1\)-coordinated bridging cyclopentadienyl group as described earlier[10] for the AnCp complexes also for all LnCp complexes whose solid
state structures we have determined in the past years resulting
in low temperature high quality datasets.[6] A coordination
environment of four Cp rings three establishing
\(\eta^1\) and one \(\eta^1\)-coordination is also established in [K\(\text{NpCp}_2\)]
the KCP adduct to NpCp.[4] A symmetrical bonding of the \(\eta^1\)-coordinated Cp rings is produced (mean Np-Ct
251 pm, see footnote Table 1) together with a closer interaction to the \(\eta^1\)-
tion. As the η<sup>1</sup>-π-coordinated Cp ring approaches the An<sup>II</sup> ion centres the η<sup>1</sup>-interaction to the μ-η<sup>1</sup>,η<sup>1</sup>-coordinated C atom decreases. This results in an elongation of the bond length M-C(μ-η<sup>1</sup>) from 278(2) for UCP₃ over 281(2) for NpCP₃ to 283(1) pm for PuCP₃ (Table 1). This increase of ≈5 pm describes a trend; the high standard deviations disable to make a clear statement based only on experimental data. However, over the series of the three complexes the elongation of the η<sup>1</sup>-interaction to the μ-η<sup>1</sup>,η<sup>1</sup>-coordinated C atom of ≈5 pm seems to be about twice as much as that observed for the corresponding lanthanide complexes [see Figure S3, left]. So in the case of the complexes MCP₃ this bond might possibly be regarded as an indicator for changes in the metal electronic environment.

This is because the outer orbitals of the actinide ions in AnCP₃ reach out far enough to establish a good interaction to the π-coordinated Cp rings at the given distance demonstrating again the high coordinative flexibility of both the Cp rings and the actinide ions. This hypothesis is supported by the results from DFT calculations we performed using a dimeric molecular model of selected Ln and An complexes reducing the structural motif to a negatively charged unit (CP₃-M-CP-M-CP₃<sup>−</sup>) with the central Cp ring in the bridging position (details see Supporting Information and Figure S3). The geometry optimisations reproduced the η<sup>1</sup>,η<sup>1</sup>-coordination of the bridging Cp ring, confirming that this unique interaction belongs to the basic bonding properties of the complexes and is not enforced by the packing effects. Similarly, the competitive nature of η<sup>1</sup>,η<sup>1</sup>-interactions are confirmed by the calculations, the results reflecting the already described changes in the M–C distances. During the geometry optimisations we observed that the system is very flexible; it exhibits a flat potential energy hyperface. Hence slight changes in force can cause significant changes in the structure in the η<sup>1</sup>–M–C distances. Another significant clue on the bonding was the verified importance of the 4f subshell for the Ln–Cp donor–acceptor interactions, calculations using the 4f-in-core Ln pseudopotentials failed to reproduce the characteristic change of the η<sup>1</sup>-Ln–Cp distances. On the other hand, the experimentally suggested gradual change in the M–C bond lengths for η<sup>2</sup>- and η<sup>1</sup>-coordinated Cp rings across the 4f/5f rows were only partially reproduced by the calculations. The probable reason lies in the already mentioned flat potential energy surface and the dimeric model structure (size limited by technical problems in the calculations) being unable to account for long-range cooperative or solid-state effects.

Our experimental results described here close the knowledge gap on the solid state structure of the long known complexes PuCP₃ and UCP₃. They indicate that covalency in AnCP₃ is higher than in LnCP₃ (at least for the here reported minor actinide complexes), which is in agreement with theoretical considerations. Series comparing experimental data of transition metal or lanthanide complexes to their actinide analogues together with theoretical calculation showed in other cases as well: 5f and or 6d orbital contribution contributes to covalency in the bonding of actinide complexes. It is influenced by the interchange between the metal ions and the ligands.

With this background it seems promising to compare as well the cyclohexylisonitrile adducts AnCp₃(CNC₆H₄) to those of the corresponding lanthanides. The IR CN-stretching vibration of the isonitrile ligand is an excellent sensor on its binding mode and forces which enables the detection of differences between the lanthanides and actinides in their complexes M Cp₃(CNC₆H₄).<ref>1c,12</ref>

### Crystallographic data

CCDC 570389 (PuCP₃) and 1570390 (UCP₃), contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. For further information, please see the Supporting Information.

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### Conflict of interest

The authors declare no conflict of interest.

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