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Volatile β-Diketonates of Neptunium(IV) and (VI)

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Abstract

A series of new volatile β-diketonates of Np(IV) (in the unsolvated form and as adducts) and Np(VI) (as adducts) have been synthesized. The compounds isolated were identified by IR and NMR spectroscopy and chemical analysis. The sublimation capability of the substances was studied. Some Np(VI) complexes are shown to suffer partial or complete decomposition (depending mainly on the Np–neutral ligand bond strength) with partial formation of Np(IV) chelates during sublimation. The structure of the complexes (including geometrical isomerism) and stoichiometry of adduct formation were studied by NMR spectroscopy. From mass spectrometry, the composition of the complexes in the gas phase as well as their fragmentation schemes have been established. The temperature dependence of the saturated vapour pressure of a series of chelates was determined.

Introduction

The interest shown at the present time in the volatile coordination compounds of actinides is based on the possibility of their use in the processes of fractional sublimation [1,2], deposition of metal-containing films [3] and for the other purposes. The β-diketonates are among the best-studied volatile coordination compounds. Volatile β-diketonates of uranium(IV) and (VI) have been extensively studied [4–6]. As for neptunium, volatile neptunium(IV) β-diketonates have been studied but not in depth [3], and the analogous neptunium(VI) complexes were not known until recently. The first communication concerning the synthesis of volatile neptunium(VI) (neptunyl) β-diketonates appeared in 1984 [7].

In the present work results are given of the investigation of volatile β-diketonates of neptunium(IV) and (VI) and their adducts. In the case of neptunium(IV) chelates, the stoichiometry of adduct formation in solution has been especially studied, because this subject has received little coverage in the literature, not only for neptunium(IV) but also for its analogues uranium and thorium(IV). According to the fragmented data [8,9], the stoichiometry of adduct formation of β-diketonates of actinides(IV) depends on the nature of the β-diketone. In contrast, in the case of uranyl complexes the β-diketonates form adducts with neutral ligands of 1:1 composition only in the wide basicity range of β-diketonates and neutral ligands [10–12].

In our work the following β-diketones containing alkyl and trifluoromethyl substituents (R groups) were chosen as for investigation: hexafluoroacetylacetone ($CF_3COCH_2COCF_3$, H(hfaa)); pyvaloyltrifluoroacetone ($C_4H_9{}^tCOCH_2COCF_3$, H(ptfa)); trifluoroacetylacetone ($CH_3COCH_2COCF_3$, H(tfaa)); and dipyvaloylmethane ($C_4H_9{}^tCOCH_2COC_4H_9{}^t$, H(thd)). In this series the basicity of the β-diketonate anions spans a wide range. Trimethylphosphine oxide ($(CH_3)_3PO$, tmpo), dimethylmethylphosphonate ($(CH_3O)_2CH_3PO$, dmmp), trimethylphosphate ($(CH_3O)_3PO$, tmp), tetrahydrofuran ($(CH_2)_4O$, thf) and water served as neutral ligands.

Synthesis of Compounds and their Sublimation Behaviour

The exchange reaction between stoichiometric amounts of Cs_2NpCl_6 (70–80 mg) and K(ptfa) in aqueous solution was used for the synthesis of $Np(ptfa)_4$. The grey–green solid precipitate was washed twice with water and dried *in vacuo*. $Np(ptfa)_4$·tmpo was synthesized likewise with the addition of a 3-fold amount of tmpo into the original Cs_2NpCl_6 solution. $Np(hfaa)_4$ was obtained by triple extraction from aqueous Cs_2NpCl_6 solution (80–100 mg in 5–6 ml of water) with toluene–cyclohexane (*ca.* 1:1) solution of H(hfaa) (*ca.* 2-fold excess). The extracts were brought together and evaporated *in vacuo* to dryness. Adducts of $Np(hfaa)_4$ with tmp and tmpo were obtained by mixing $Np(hfaa)_4$ extract with a 3-fold ligand excess and evaporating to dryness *in vacuo* (*ca.* 10 Pa) (method A). The adduct of $Np(hfaa)_4$ with tmpo was obtained also by mixing sublimed $Np(hfaa)_4$ with equimolar amounts of tmpo in toluene (method B).

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In order to obtain $NpO_2(ptfa)_2$ adducts, a 3-fold excess of the neutral ligand and then a stoichiometric amount of freshly prepared aqueous solution of K(ptfa) were added to the aqueous solution of rubidium neptunyl trinitrate (50–70 mg in 2 ml of water) containing 1–2 mg of potassium persulphate. The dark-brown precipitate was washed twice with water and dried *in vacuo*. $NpO_2(tfaa)_2$ adducts were synthesized by a similar method. In the case of $NpO_2(hfaa)_2$ adducts, the synthesis was performed by extraction from solution of *ca.* 50 mg $RbNpO_2(NO_3)_3$ in 2 ml of water with a solution of the β-diketone and neutral ligand (*ca.* 3-fold excess) in 2 ml of toluene. In the absence of a neutral ligand (synthesis of $NpO_2(hfaa)_2$ hydrate) extraction was performed three times and the extracts were combined. The solvent was removed *in vacuo*. Synthesis of $NpO_2(thd)_2$ adducts was performed by the reaction of $RbNpO_2(NO_3)_3$ with sublimed K(thd) in absolute ethanol in the presence of the neutral ligand. After removing the precipitated $(Rb,K)NO_3$, the solution was evaporated to dryness *in vacuo*.

All the crude products were subjected to vacuum sublimation. The sublimation temperatures of Np(IV) chelates are listed in Table I. $Np(ptfa)_4$ sublimes without decomposition. During sublimation of $Np(hfaa)_4$ the condensation of a small amount of a colourless liquid was observed. The latter can be removed by treatment of the sublimate *in vacuo* over *ca.* 1 h without warming, but partial loss of the desired product takes place.

According to the NMR data the sublimates do not contain traces of Np(V) or (VI) compounds or organic compounds. $Np(ptfa)_4$ is not hydrated in air to an appreciable extent, but $Np(hfaa)_4$ is hygroscopic and should be handled in a dry atmosphere.

Adducts of $Np(ptfa)_4 \cdot x$tmpo, $Np(hfaa)_4 \cdot y$tmp and $Np(hfaa)_4 \cdot z$tmpo also sublime without decomposition, neutral ligands being retained in the sublimates. NMR analysis gives $x = y = 1$ (see Table II; for more details on the NMR data, see below). The sublimation of $Np(hfaa)_4 \cdot z$tmpo obtained by method A gives $1 < z < 2$ according to NMR analysis, and by method B, $z = 1$.

TABLE I. Sublimation Temperatures of Np(IV) Chelates (°C, at 0.2 Pa)

Neutral ligand	β-Diketonate ligand	
	ptfa	hfaa
—	120–130	30–35
tmp		70–80
tmpo	120–130	85–100 (method A) 80–90 (method B)

Neptunyl β-diketonate adducts exhibit complex behaviour during sublimation. In some cases heating of the samples *in vacuo* is accompanied by partial or full reduction of the neptunyl with formation of volatile Np(IV) chelates and nonvolatile residue. NMR analysis shows that nonsublimed samples do not contain impurities of the lower valence states of neptunium. Thus, it is heating *in vacuo* that leads to reduction of Np(VI) β-diketonates and this is followed by joint sublimation of Np(IV) and (VI) compounds. The complexes $NpO_2L_2 \cdot S$ and NpL_4 (with L = ptfa, S = dmmp, tmp; L = tfaa, S = tmp; L = thd, S = tmpo) are condensed in one zone of a sublimation tube but $NpO_2(hfaa)_2 \cdot S$ (S = thf, H_2O) and $Np(hfaa)_4$ occur in a different zone. The estimated values of the molar fractions of the Np(IV) complex in the sublimate are presented in Table III. Thus, after vacuum sublimation of neptunyl β-diketonates, the individual forms of $NpO_2(hfaa)_2 \cdot S$, $NpO_2(ptfa)_2 \cdot$tmpo and $NpO_2(tfaa)_2 \cdot$tmpo were iso-

TABLE II. Relative Proton Signal Intensities in PMR Spectra of Np(IV) and (VI) β-Diketonate Adducts (calculated values in parentheses)[a]

Compound	CH	CH_3	$C(CH_3)_3$	$POCH_3$	PCH_3	OCH_2CH_2	OCH_2CH_2
$Np(ptfa)_4 \cdot$tmpo	1		8.7(9)		2.11(2.25)		
$Np(hfaa)_4 \cdot$tmp	1			2.45(2.25)			
$Np(hfaa)_4 \cdot$tmpo	1				2.35(2.25)		
$NpO_2(thd)_2 \cdot$tmpo	0.07(0.06)		1		0.23(0.25)		
$NpO_2(ptfa)_2 \cdot$tmpo	1		9.21(9)		4.56(4.5)		
$NpO_2(ptfa)_2 \cdot$dmmp	0.09(0.11)		1	0.30(0.33)	0.14(0.17)		
$NpO_2(ptfa)_2 \cdot$tmp	0.09(0.11)		1	0.52(0.5)			
$NpO_2(tfaa)_2 \cdot$tmpo	0.32(0.33)	1			1.95(1.5)		
$NpO_2(tfaa)_2 \cdot$tmp	1	3.17(3.0)		4.42(4.5)			
$NpO_2(hfaa)_2 \cdot$tmpo	1				4.8(4.5)		
$NpO_2(hfaa)_2 \cdot$tmp	1			5.1(4.5)			
$NpO_2(hfaa)_2 \cdot$thf	1					2.00(2.0)	2.12(2.0)

[a] The intensity of the methine proton signal was taken as a unit (in the case of its overlap with the other signals, the intensity of the R group signal was taken as a unit).

TABLE III. Vacuum Sublimation Temperatures of Np(VI) Chelates (°C, at 0.2 Pa) and Approximate Mole Fraction of Np(IV) in Sublimate (%, in parentheses)

Neutral	β-Diketonates			
	thd	ptfa	tfaa	hfaa
H_2O		120–130 (100)		50–60 (70)
thf				50–60 (40)
tmp	180–190 (100)	110–120 (25)	120–130 (10)	55–65 (0)
dmmp		110–120 (10)		
tmpo	150–160 (30)	120–130 (0)	130–140 (0)	70–80 (0)

lated. The data of Table III show that the extent of decomposition of neptunyl β-diketonate adducts during sublimation increases as the basicity of neutral ligand decreases and the basicity of the β-diketonate anions increases; *i.e.* as the bond strength of neptunium with the neutral ligand is decreased.

The consequence of this observation is that the necessary condition for the stabilization of neptunyl β-diketonates is the presence of strong neutral ligands and that the unstable unsolvated form NpO_2L_2, arising from thermal decomposition of the adduct in a vacuum, is decomposed.

In contrast to the neptunyl compounds, unsolvated uranyl β-diketonates are sufficiently stable and volatile. For instance, $UO_2(ptfa)_2$ is formed in high yield by heating $UO_2(ptfa)_2{\cdot}H_2O$ in a vacuum and sublimes without decomposition at 160–170 °C [11]. In the case of the stronger oxidizer neptunyl, the unsolvated form is not formed because of neptunium(VI) reduction.

The IR spectra of neptunyl β-diketonate adducts contain ν_{as} NpO_2^{2+} bands in the 900–950 cm^{-1} region (Table IV). In the spectrum of $NpO_2(ptfa)_2{\cdot}$tmpo the nature of the ν_{as} NpO_2^{2+} splitting into two components of equal intensity is as yet not clear. This splitting may be caused by Fermi resonance, for example.

The line intensity ratio of β-diketonate and neutral ligand protons in the NMR spectra of Np(VI) complexes shows an adduct composition of 1:1 Table II).

The sublimed Np(VI) adducts free of appreciable amounts of impurities as well as unsolvated Np(IV) β-diketonates were analysed for neptunium content by potentiometric titration [13] (see Table V). The results of these analyses confirm the 1:1 composition of Np(VI) β-diketonate adducts.

TABLE IV. Frequencies of ν_{as} NpO_2^{2+} in IR Spectra of Np(VI) β-Diketonate adducts (cm^{-1})

Neutral	β-Diketonate		
	ptfa	tfaa	hfaa
tmpo	926, 912	919	932
dmmp	930		
tmp			943
thf			946
H_2O	942, 930sh[a]		950

[a] Unsublimed sample.

TABLE V. Neptunium Content in Chelates

Complex	Neptunium content (%)	
	Calculated	Found
$Np(ptfa)_4$	23.3	23.5
$Np(hfaa)_4$	22.2	22.7
$NpO_2(ptfa)_2{\cdot}$tmpo	31.6	31.5
$NpO_2(tfaa)_2{\cdot}$tmpo	35.5	34.7
$NpO_2(hfaa)_2{\cdot}$tmpo	30.6	30.4
$NpO_2(hfaa)_2{\cdot}$tmp	28.8	28.5
$NpO_2(hfaa)_2{\cdot}$thf	31.4	30.9
$NpO_2(hfaa)_2{\cdot}H_2O$	33.8	32.8

NMR Investigation of Neptunium(IV) and (VI) β-Diketonates in Solution

The NMR analysis procedure is described in ref. 14. The paramagnetism of Np(IV) and (VI) together with the short electronic relaxation times (narrow lines in NMR spectra) result in high spectrum sensitivity to the neptunium valence form, coordination sphere composition and geometrical arrangement of the ligands around the central ion. The ^1H and ^{19}F chemical shifts of the complexes investigated are presented in Table VI.

NMR Spectra of Neptunium(VI) Chelates

In all investigated complexes the high-field paramagnetic shifts of the signals of all ^1H and ^{19}F nuclei are mostly pseudo-contact in nature. All signals experience splitting at ambient or lowered temperatures, which can be accounted for by the following reasons:

(a) *cis–trans* Isomerism of chelates with unsymmetrical β-diketones (Fig. 1).

(b) Non-equivalence of position of β-diketonate R groups with respect to the neutral ligand.

(c) Deviation of the complex structure from ideal pentagonal-bipyramidal configuration with planar position of the β-diketonate and neutral ligands.

TABLE VI. ^1H (ppm in the strong field relative to TMS) and ^{19}F (ppm relative to F_2) Chemical Shifts in NMR Spectra of the Investigated Complexes at the Temperature of Maximum Signal Resolution

Complex	T (K)	CH	$C(CH_3)_3$	CH_3	CF_3	PCH_3	$POCH_3$	thf
$NpO_2(hfaa)_2\cdot tmpo$	298	+3.21			509.9^{a}	+1.61		
$NpO_2(hfaa)_2\cdot tmp$	273	+4.97			511.9^{a}		+1.08	
$NpO_2(hfaa)_2\cdot thf$	291	+2.27			509.6^{a}			+4.11
								+6.11
$NpO_2(hfaa)_2\cdot H_2O$	298	+0.48			511.1^{a}			
$NpO_2(tfaa)_2\cdot tmpo$	253	+1.66		+7.20	507.5	+0.77		
				$\underline{+8.09^{b}}$	$\underline{506.2}$			
				+8.40				
$NpO_2(ptfa)_2\cdot tmpo$	298	+0.03	+2.50		504.4	+0.68		
		$\underline{+0.28}$	$\underline{+3.10}$		$\underline{504.6}$	$\underline{+0.92}$		
		+0.61	+3.32		505.1	+1.10		
$NpO_2(ptfa)_2\cdot dmmp$	223	+2.42	+4.02		$\underline{505.1^{c}}$	+2.82	+0.48	
			$\underline{+5.11}$		505.6^{c}		$\underline{+1.51}$	
			+5.33					
$NpO_2(ptfa)_2\cdot tmp$	213	+0.52	+3.71		506.9^{c}		$\underline{+0.70}$	
			$\underline{+5.03}$		$\underline{506.2^{c}}$		−0.38	
			+5.11					
$NpO_2(tfaa)_2\cdot tmp$	253	+2.03	+7.72		507.8		+0.45	
			$\underline{+8.91}$		$\underline{506.8}$			
			+9.09					
$NpO_2(ptfa)_2\cdot H_2O$	263	+3.35	+0.52		507.5^{c}			
		$\underline{+3.92}$						
$NpO_2(thd)_2\cdot tmpo$	273	−0.71	+1.51			+0.44		
			+2.02					
$Np(hfaa)_4$	297	−7.69			504.0			
$Np(hfaa)_4\cdot tmp$	293	−7.54			502.6		−0.57	
$Np(hfaa)_4\cdot tmpo$	293	−6.32			503.5	−0.97		
$Np(hfaa)_4\cdot 2tmpo$	253	−6.18			502.5	−3.28		
		−0.33			505.4			
$Np(ptfa)_4$	298	−8.35	+0.70		501.1			
$Np(ptfa)_4\cdot tmpo$	298	−7.55	−0.65		499.5	+2.70		
$Np(ptfa)_4\cdot dmmp$	298	−7.70	−0.60		501.1	+2.55	+0.20	
$Np(tfaa)_4$	298	−7.89		+3.76	499.4			
$Np(thd)_4$	298	−8.19	+0.53					

[a] ^{19}F signal is not split at this temperature. [b] The *cis* isomer signal is underlined. [c] At 298 K.

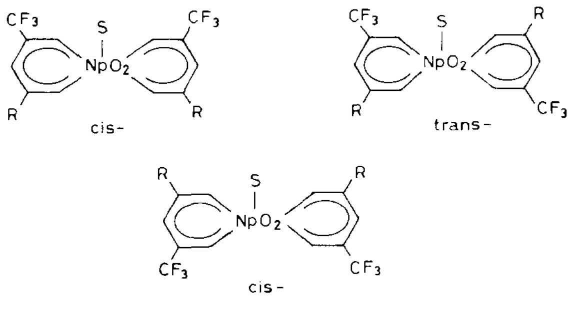

Fig. 1. Possible isomers of unsymmetrical neptunyl β-diketonate adducts (S = neutral ligand, R = CH_3 or $C_4H_9^t$).

The actions of factors (a) and (b) should theoretically lead to splitting of the R group signals and splitting of the methine protons into four signals (two of them, with equal intensity, refer to the *trans* isomer, and one signal refers to each of the two *cis* isomers). The actually observed spectra (e.g. Fig. 2), as in the case of analogous uranyl complexes [15, 16], show that only one of two possible *cis* isomers exists. By analogy with the known structure of the adduct of uranyl thenoyltrifluoroacetonate with trioctylphosphine oxide [17], the realization of a *cis* isomer with neutral ligand position between the two CF_3 groups can be postulated. The signals of the neutral ligands split into two, their intensity ratio being equal to the intensity ratio of the central signal of the R groups (*cis* isomer) to the sum of the side signals (*trans* isomer).

The large difference between the paramagnetic shifts of the R group signals reaches 1.4 ppm and greatly exceeds the value of the splitting for diamagnetic uranyl analogues, showing that the positional non-equivalence is accompanied by differences in geometrical position of the resonating nuclei around the paramagnetic centre, *i.e.* factor c, making

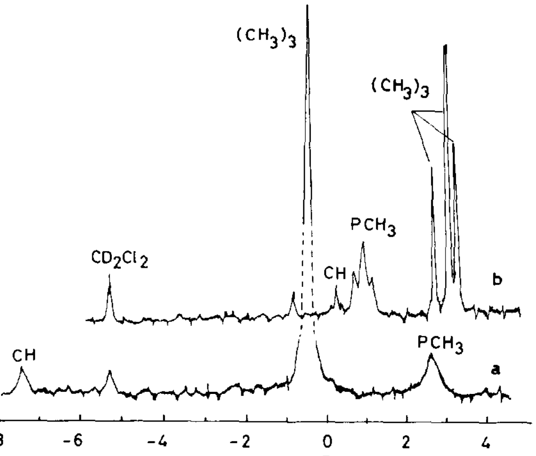

Fig. 2. PMR spectra of $Np(ptfa)_4 \cdot tmpo$ (a) and $NpO_2(ptfa)_2 \cdot tmpo$ (b) at 298 K (solvent CD_2Cl_2). Signal assignments are shown on the figure.

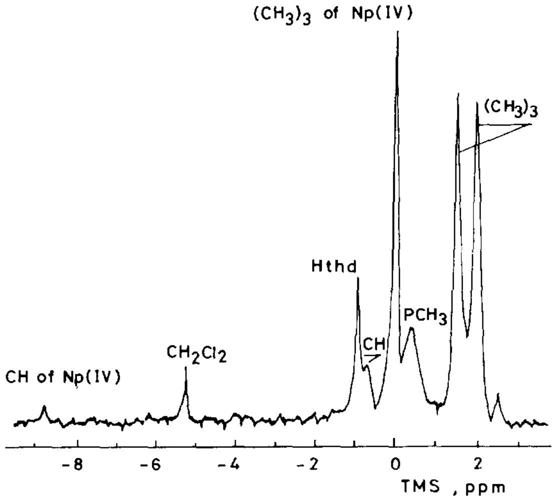

Fig. 3. PMR spectrum of sublimed $NpO_2(thd)_2 \cdot tmpo$ at 273 K (solvent CD_2Cl_2). Signal assignments are shown on the figure.

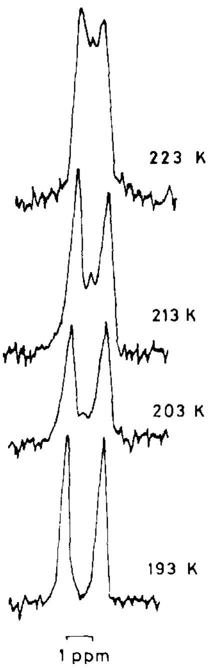

Fig. 4. ^{19}F NMR spectrum of sublimed $NpO_2(hfaa)_2 \cdot tmp$ (solvent CD_2Cl_2).

the determining influence on the relative chemical shift act together with factors (a) and (b).

Two types of chelate ring distortion can be pointed out: (1) bending around the O···O line leading to a change of position of both R groups and methine protons, and (2) rotation around the Np···CH axis leading to a change of position of R groups only. Since the isomerism is not expressed or is poorly expressed on the methine proton signals, the conclusion can be drawn that the distortion of the first type is nearly the same in all isomers and that the distortion of the second type accounts for the differences in shifts. This distortion may be caused by interligand repulsion in the neptunyl group equator, leading to deviation of the ligand donor atoms from the equatorial plane. The middle position of the *cis* isomer signal with respect to the *trans* isomer ones shows that the structure of the *cis* isomer is not planar, with the chelate rings being similarly distorted; in the *trans* isomer one ring is more and the other one less distorted than in the *cis* isomer [14].

In the case of chelates with symmetrical β-diketones, non-equivalence of the positions of the R groups with respect to the neutral ligand should cause splitting of their signals into two equal intensity bands, which is in fact the case (Fig. 3). But here again the large value of the splitting points to a difference also in the spatial position of the R groups with respect to the paramagnetic centre. Such a difference may arise, for instance, from a simultaneous occurrence of both types of distortion. But in the spectrum of $NpO_2(hfaa)_2 \cdot tmp$ (CD_2Cl_2 solvent) a third signal is observed between the two signals of the non-equivalent CF_3 groups (Fig. 4), the intensity of which decreases with decreasing temperature (there is no splitting of the CH signals over all the temperature range). In our opinion, this is explained by the existence of two isomeric forms of adduct $NpO_2(hfaa)_2 \cdot tmp$ being in dynamic equilibrium with each other (such a phenomenon is known for uranyl analogues in the solid phase [18, 19] and in solution [20]). The form to which the central signal relates is characterized by spatial equivalence of all four CF_3 groups; *i.e.* the distortion of the second type does not seem to exist. Considering the interligand repulsion as the cause of rotation of the chelate rings, the occurrence of the symmetrical 'unrotated' form in the complex with the least basic β-diketonate anion (hfaa) becomes clear. It should be noted also that the symmetrical isomer was found in $NpO_2(hfaa)_2 \cdot H_2O$ as well, but was absent in the adduct with the more basic ligand (tmpo). Further, the symmetrical isomer of $NpO_2(hfaa)_2 \cdot$tmp disappeared when the solvent CD_2Cl_2, which decreases electronic density on the oxygen atoms due to H-bonds, was substituted by toluene.

The difference between isomerism in $NpO_2(hfaa)_2$ adducts and *cis–trans* isomerism should be stressed. In the first case there are two conformations of the same complex which rather smoothly and reversibly convert into each other, depending on the temperature and solvent. On the other hand, *cis* and *trans* isomers are actually different complexes. They do not exhibit any signs of mutual exchange, their ratio depends neither on temperature nor on solvent. Furthermore, during sublimation (which is accompanied by decomposition) they behave as independent chemical compounds: the *trans* isomer is less stable and therefore its content in the sublimates of $NpO_2(ptfa)_2 \cdot$dmmp, $NpO_2(ptfa)_2 \cdot$tmp and $NpO_2(tfaa)_2 \cdot$tmp is lowered with respect to nonsublimed samples.

NMR Spectra of Neptunium(IV) Chelates: Stoichiometry of Adduct Formation

The isomerism of unsolvated chelates of actinoid(IV) compounds is known to be observed in their NMR spectra. The nature of this isomerism results in different types of polyhedra for the particular complex that is established (e.g. $U(thd)_4$ [8]), or in different positional isomers within the frames of one polyhedron (e.g. $U(fod)_4$ [21]). When an additional ligand is coordinated, the number of isomers as well as non-equivalent positions in the complex may increase further. But in the course of an investigation of the chelates $Np(hfaa)_4$, $Np(ptfa)_4$ and their adducts with one molecule of neutral ligand, no signs of splitting of the signals of CF_3, $C_4H_9^t$ and CH groups were found in the NMR spectra. This can be explained by the energetic proximity of different possible isomers of the Np(IV) complexes as well as the chelates $U(thd)_4$ and $U(fod)_4$. As a result, a decrease in temperature to 183–188 K would be necessary for their observation, but this is impossible because of the fast decrease in solubility of the complexes in CD_2Cl_2 even at temperatures of 253–233 K.

It should be noted that stereoisomers of neptunyl β-diketonates are observed in the NMR spectra at relatively high temperatures (253–298 K and higher). This shows that they are separated by essentially higher energetic barriers than the isomers of Np(IV) chelates, despite the greater thermodynamic stability of the latter. Obviously, such a difference is caused by the greater rigidity of the actinyl ion coordination polyhedron, hindering mutual conversion of isomeric forms.

Special attention was paid to the study of the stoichiometry of adduct formation of Np(IV) chelates. $Np(thd)_4$ was earlier shown not to form adducts [8] (the position of $C(CH_3)_3$ and CH signals did not change with addition of the neutral ligand). In the $Np(ptfa)_4$–tmpo and $Np(hfaa)_4$–tmp systems adducts of 1:1 composition are formed. Further addition of neutral ligands does not change the position nor the relative intensity of the signals of the β-diketone and coordinated ligand. The signals of the coordinated and free neutral ligands are fully resolved at 278 K in the case of $Np(ptfa)_4 \cdot$tmpo + tmpo, and at an ambient temperature in the case of $Np(hfaa)_4 \cdot$tmp + tmp. Adduct formation of Np(IV) chelates is accompanied by an increase in the coordination number (CN) of Np from 8 to 9 (no signs of chelate ring opening in monosolvates were observed). The structures of adducts of tetrakis-β-diketonates with CN 9 are known for thorium and are considered as monocapped square antiprisms [22] or tricapped trigonal prisms [23].

In the $Np(hfaa)_4$–tmpo system, which contains a β-diketonate ligand of low basicity in connection with a highly basic neutral ligand, the interaction is not limited to monosolvate formation. With an excess of tmpo, formation of the second complex is observed, to which the signals of ^{19}F at 505–506 and 502 ppm (intensity ratio *ca.* 1:6), methine protons at 6.0–6.5 and 0–2 ppm (intensity ratio *ca.* 1:2.5) and coordinated tmpo at 3.0–3.5 ppm (intensity ratio $P(CH_3)_3$: ΣCH *ca.* 5.5:1) are attributed by the authors. On the basis of the NMR spectra (Fig. 5) the complex is assumed to have the composition $Np(hfaa)_4 \cdot 2$tmpo, one of the chelate rings being opened and the hfaa ligand becoming monodentate. The ^{19}F signal of lower intensity should be attributed here to the 'farther' CF_3 group of the monodentate ligand. This assumption is supported by the small value of the paramagnetic shift of this signal. The ^{19}F signal of the 'nearer' CF_3 group of the monodentate ligand probably coincides with the signals of the bidentate hfaa ligands.

Upon decreasing the temperature, in the presence of a large excess of neutral ligand, the NMR spectrum shows the reversible formation of a $Np(hfaa)_4 \cdot 3$tmpo complex with two opened chelate rings. This is confirmed by the following facts:

(1) with decreasing temperature, redistribution of intensities between the signals of the coordinated and free tmpo in favour of the former takes place, the total intensity of the CH signals remaining constant;

(2) the gradual levelling of the intensities of the fluorine signals up to a 1:3 ratio is observed, which is reached at 213 K and probably is a limiting value.

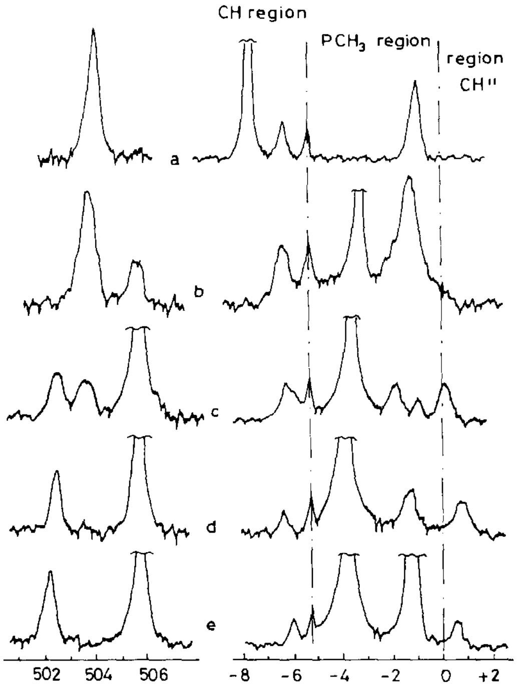

Fig. 5. ^{19}F NMR (left) and PMR (right) spectra of $Np(hfaa)_4$ + n tmpo system with n and temperature (K) correspond to: (a) 0.2 and 296; (b) 1.6 and 253; (c) 2.6 and 243; (d) 3.4 and 223; (e) 4.8 and 233.

The proton and fluorine shifts of analogous nuclei in the $Np(hfaa)_4 \cdot 2tmpo$ and $Np(hfaa)_4 \cdot 3tmpo$ complexes are practically equal. Thus, adduct formation of $Np(hfaa)_4$ and tmpo, although not stopping at the monosolvate step, is not accompanied by an increase in CN beyond 9.

On the whole, a significant increase in adduct formation ability of Np(IV) β-diketonates can be noted as the β-diketonate anion basicity decreases: $Np(thd)_4$ does not form adducts [8]; $Np(ptfa)_4$ and $Np(tta)_4$ [9] containing one fluorinated substituent in the β-diketonate anion form adducts with 1:1 composition and a change in Np CN from 8 to 9 is observed; in the case of $Np(hfaa)_4$, which has the strongest neutral ligand used, the adducts of higher composition can be formed (probably with partial opening of the chelate rings and Np CN remaining as 9). The influence of such factors as R group volume is less essential since adduct formation takes place neither for dipyvaloylmethanates nor for acetylacetonates of actinides(IV) [8].

Mass Spectrometric Study of Np(IV) and (VI) β-Diketonates

Mass spectra (MS) were recorded on an MS-30 mass spectrometer at 50–1400 mass range and ionizing electron energy of 70 and 25–15 eV. The sample was introduced directly into the source. The source temperature was 60–100 ℃. The results are shown in Tables VII and VIII in which only peaks of metal-containing ions having a relative intensity of more than 3% (at least for one of the compounds) are given. Ion precursors were determined from the respective metastable ions.

Peaks assigned to the undissociated form of the adduct were absent in the MS of $Np(ptfa)_4 \cdot tmpo$, even when the ionizing electron energy was lowered to 15 eV. On the contrary, in the MS of $Np(hfaa)_4 \cdot tmpo$, which contains the less basic anion, the peaks

TABLE VII. Mass Spectra of Neptunium(IV) Chelates at 70 eV

Number	Ion	Relative intensity (%)			Ion-precursor (number)
		L = hfaa	L = hfaa, S = tmpo	L = ptfa, S = tmpo	
1	$NpL_4 \cdot S^+$				
2	$(NpL_4 \cdot S - F)^+$		5		
3	NpL_4^+	14	6	6	
4	$(NpL_4 - F)^+$	3	1	1	
5	$NpL_3 \cdot S^+$		100		
6	NpL_3^+	100	42	100	3, 4
7	$(NpL_3 - CF_2)^+$	4	2		6
8	$NpL_2F \cdot S^+$		9		5
9	NpL_2F^+	38	17	13	6, 7
10	$(NpL_2F - CF_2)^+$	19	10	8	9
11	$NpF_2L \cdot S^+$		10		
12	NpF_2L^+	13	6	7	10
13	$NpFL^+$	2	2	4	
14	$(NpF_2L - CF_2)^+$	16	9	7	12
15	$NpF_3 \cdot S^+$		14		

TABLE VIII. Mass Spectra of Neptunium(VI) Chelates at 70 eV (peaks of Np(IV) chelate fragmentation are not presented)

Number	Ion	Relative intensity (%)				Ion-precursor (number)
		L = hfaa, S = H_2O	L = hfaa, S = thf	L = ptfa, S = tmpo	L = tfaa, S = tmpo	
1	$NpO_2L_2{\cdot}S^+$		10	10	19	
2	$(NpO_2L_2{\cdot}S - C_4H_9)^+$			16		
3	$(NpO_2L_2{\cdot}S - CF_3)^+$		5			
4	$NpO_2L_2^+$	43	27	1	4	
5	$(NpO_2L_2 - CF_3)^+$	56	45		2	
6	$(NpO_2L{\cdot}S)^+$		51	100	100	1
7	$NpOFL^+$	13	17[b]		1	4
8	NpO_2LH^+			5		
9	NpO_2L^+	100	100	5	9	5, 6
10	$(NpOFL - CF_2)^+$	13	17			
11	$(NpO_2L - CF_2)^+$	7	9			
12	$(NpO_2L - CF_3)^+$	61	62		4	9
13	$NpO_2F{\cdot}S^+$		3		2	6
14	$NpOF{\cdot}S^+$				6	
15	$NpO_2{\cdot}S^+$		18	43	34	6
16	NpF_3^+	8	10			
17	$NpOF_2^+$	7	12			
18	NpO_2F^+	5	7			
19	NpF_2^+	11	13			
20	$NpOF^+$	16	30		3	
21	NpO_2^+	54	95	8	12	15

[a] Peaks of binuclear ions $(NpO_2)_2(hfaa)_n^+$ (n = 1, 2, 3) are found in $NpO_2(hfaa)_2{\cdot}H_2O$ MS with 1% intensity. [b] Coincides with the $(NpO_2L{\cdot}S - CF_3)^+$ peak.

of the undissociated form (e.g. $Np(hfaa)_3{\cdot}tmpo^+$) had a high intensity and in sum (in the first scans) exceeded the peak intensity of the unsolvated form.

Adducts having more than a 1:1 stoichiometry were not found. Introduction of a mixture of the complex and excess tmpo into the source gave only monosolvate peaks, peaks of the unsolvated form, free tmpo and unidentified decomposition products.

The MS of Np(IV) β-diketonate adducts allows one to extend correlations in adduct formation of β-diketonates and tmpo obtained for solutions from NMR spectra, to behaviour in the vapour phase:

Chelate	Adduct 1:1		Higher adducts	
	in solution	in gas	in solution	in gas
$Np(thd)_4$	no			
$Np(ptfa)_4$	yes	no	no	
$Np(hfaa)_4$	yes	yes	yes	no

In the MS of $NpO_2(ptfa)_2{\cdot}tmpo$ and $NpO_2(tfaa)_2{\cdot}tmpo$ peaks of the undissociated form predominate. This shows the greater Lewis acidity of $NpO_2(ptfa)_2$ in comparison with $Np(ptfa)_4$. Peaks of the dissociated form have a low intensity and are appreciably weaker than even the corresponding peaks in the MS of the uranyl analogues [24]. This can be explained by a fast chemical decay of the unstable unsolvated form in the source. Such side chemical processes in the source may be the cause of the appearance of Np(IV) chelate peaks in the MS of neptunyl chelates (the samples had no Np(IV) impurity).

In the MS of $NpO_2(hfaa)_2{\cdot}H_2O$ and $NpO_2(hfaa)_2{\cdot}thf$, peaks of Np(IV) and Np(VI) forms were present with comparable intensity. This is in accordance with the behaviour of these complexes on vacuum sublimation.

The hydrated $NpO_2(hfaa)_2$ form was not found in the MS even at an ionizing electron energy as low as 15 eV, but in $NpO_2(hfaa)_2{\cdot}thf$ MS peaks of the solvated and unsolvated forms were observed with comparable intensity. Probably the unsolvated $NpO_2(hfaa)_2$ is more stable than $NpO_2(ptfa)_2$ and $NpO_2(tfaa)_2$.

As far as the fragmentation of neptunium chelates is concerned, Np(IV) chelates undergo fragmentation mainly by way of removal of even-electron particles after removal of the first β-diketonate ligand. This fragmentation route is typical of metal chelates which are difficult to reduce to the lower valence state [25] and corresponds to preservation of the central ion formal valence during fragmentation. Indeed, Np(IV) can be reduced to Np(III) only by strong reductors (formal redox potential Np(IV)/Np(III) +0.155 V in 1 M $HClO_4$ [26]). On the contrary, neptunyl chelate fragmentation occurs mainly via removal of the first β-diketonate ligand. This fragmentation route is typical of easily reduced metal chelates and corresponds to reduction of the central ion formal valence [25]. The peaks of the forms corresponding to the retention of the formal valence state (VI) of the central ion after removal of the first β-diketonate ligand are absent for neptunium or are much weaker than for uranyl. This difference is in accordance with redox potentials of these ions (formal redox potentials in 1 M $HClO_4$: NpO_2^{2+}/NpO_2^+ +1.137 V, UO_2^{2+}/UO_2^+ +0.063 V [26]).

Tensimetric Study of Neptunium (IV) and (VI) β-Diketonates

The flow method with spectrophotometric determination of the amount of transported neptunium was chosen for measuring the temperature dependence of the saturated vapour pressure of Np(IV) and (VI) chelates. The main advantages of this method consist in its high sensitivity (the lowest limit of the measured pressure was *ca.* 0.1 Pa), the possibility of measurements when purification from volatile substances is incomplete (traces of free β-diketone, neutral ligand, solvent) and partial decomposition of the specimen in the condensed phase takes place (provided that the volatile decomposition products do not contain neptunium). The latter demand means that only such Np(VI) chelates can be investigated which do not form Np(IV) chelate impurities on sublimation in the carrier gas flow.

As was mentioned earlier, only $NpO_2(hfaa)_2$·tmp, $NpO_2(hfaa)_2$·tmpo, $NpO_2(tfaa)_2$·tmpo and $NpO_2(ptfa)_2$·tmpo are sublimed in a vacuum without decomposition. But preliminary experiments have shown that only $NpO_2(hfaa)_2$·tmpo sublimes in a helium flow at atmospheric pressure without decomposition and formation of volatile Np(IV) chelate impurity. The decomposition to Np(IV) could not be suppressed also when $NpO_2(hfaa)_2$·thf was sublimed in the flow of helium saturated with thf vapour.

Thus, for the Np(VI) complexes, only the pressure of $NpO_2(hfaa)_2$·tmpo was determined. In the case of Np(IV) complexes, $Np(ptfa)_4$, $Np(ptfa)_4$·tmpo, $Np(hfaa)_4$ and $Np(hfaa)_4$·tmpo were investigated. Tensimetric data for $Np(fod)_4$ (fod = $C_3F_7COCHCOC_4H_9^t$) [27] and $Np(thd)_4$ [3] were obtained earlier.

In order to measure vapour pressure, a sample (in the form of benzene solution) was placed on the glasswool tampon in the saturator. The dried helium flow passed through the saturator which had been heated to the required temperature. In the case of $Np(hfaa)_4$, which hydrates in air, the carrier gas was saturated with H(hfaa) vapour at 0 °C to prevent hydrolytic decomposition causing low and irreproducible results.

The specimen vapour was condensed on the cooled finger. The volume of carrier gas was determined by collection in the measuring flasks over water. The apparatus construction allowed the quick substitution of finger-condensers. The condensate was washed off and determined photometrically as an arsenazo(III) complex of Np(IV) [28]. Np(VI) was preliminary reduced to Np(IV) by Fe(II) solution in the presence of sulphamic acid. The vapour pressure of the neptunium complex was calculated assuming monomeric complex composition in the gas phase. This assumption was confirmed by the absence of complex association in a donor-passive solvent such as CD_2Cl_2 (NMR data).

The results are given in Table IX and Figs. 6 and 7. $Np(hfaa)_4$ appeared to be the most volatile complex. In the series of Np(IV) β-diketonates, the volatility is lowered when perfluoroalkyl groups are substituted by alkyl ones: $Np(hfaa)_4 > Np(ptfa)_4$, $Np(fod)_4 > Np(thd)_4$. This is in accordance with the known correlations for the other metal β-diketonates [29, 30].

The introduction of the neutral ligand (tmpo) substantially lowers the $Np(hfaa)_4$ volatility. Apparently, the neutral ligand increases the weight of the chelate molecule and makes it polar. In the case of $Np(ptfa)_4$, the introduction of the neutral ligand into the complex also lowers volatility. But the vapour

TABLE IX. Temperature Dependence of Saturated Vapour Pressure of Neptunium(IV) and (VI) Chelates (Pa)

Chelate	A[a]	B[a]	Temperature range (K)	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/mol K)
$Np(hfaa)_4$	4241 ± 150	12.64 ± 0.42	314–375	81 ± 3	154 ± 7
$Np(hfaa)_4$·tmpo	5234 ± 231	14.33 ± 0.61	353–404	100 ± 4	178 ± 12
$Np(ptfa)_4$	5573 ± 135	14.56 ± 0.34	374–424	106 ± 3	183 ± 7
$NpO_2(hfaa)_2$·tmpo	4708 ± 151	12.47 ± 0.39	370–418	90 ± 3	143 ± 7
$UO_2(hfaa)_2$·tmpo	4928 ± 148	13.06 ± 0.37	376–424	94 ± 3	154 ± 7

[a] A and B are the coefficients of equation $\lg p = -\dfrac{A}{T} + B$.

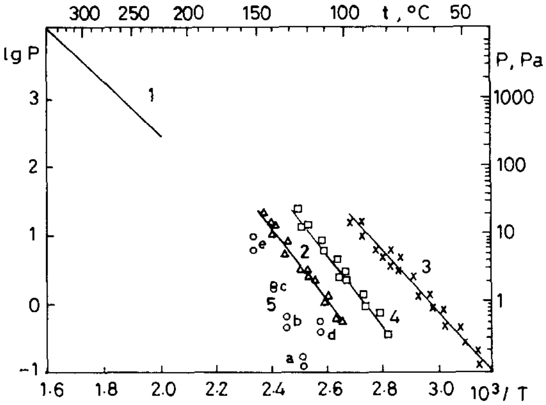

Fig. 6. Temperature dependence of saturated vapour pressure of: (1), $Np(thd)_4$ [3]; (2) △, $Np(ptfa)_4$; (3) ×, $Np(hfaa)_4$; (4) □, $Np(hfaa)_4$·tmpo; (5) ○, $Np(ptfa)_4$·tmpo; a, b, c, d, e is the sequence of measurements.

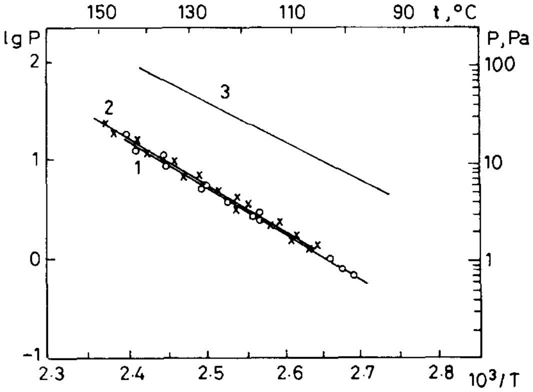

Fig. 7. Temperature dependence of saturated vapour pressure of: (1) ○, $NpO_2(hfaa)_2$·tmpo; (2) ×, $UO_2(hfaa)_2$·tmpo; (3), $UO_2(hfaa)_2$·tmp [31].

TABLE X. Temperatures (K) Corresponding to the Chosen Saturated Vapour Pressure Values for Np(IV) and Uranyl Chelates

Chelate	$p = 1$ Pa	$p = 10$ Pa	$p = 10^2$ Pa	$p = 10^3$ Pa	References
$Np(hfaa)_4$	336	364	399[a]		This work
$UO_2(hfaa)_2$	394	415	439[a]		31
$Np(ptfa)_4$	382	411	444[a]		This work
$UO_2(ptfa)_2$	420	446	476		32
$Np(thd)_4$			475[a]	540	3
$UO_2(thd)_2$	430	450	472	524	32

[a] Extrapolated values.

pressure measurements tended to show a systematic rise in consecutive measurements. This can be explained by adduct dissociation and formation of free tmpo and more volatile unsolvated chelate.

The adduct $NpO_2(hfaa)_2$·tmpo is less volatile than $Np(hfaa)_4$·tmpo. Vapour pressures of $NpO_2(hfaa)_2$·tmpo and $UO_2(hfaa)_2$·tmpo are equal over all the investigated temperature range within experimental error.

It should be noted that $Np(ptfa)_4$ and especially $Np(hfaa)_4$ are considerably more volatile than the corresponding unsolvated uranyl chelates (Table X). This fact is explained by the existence of the latter ones in the form of stable polymers being partly retained even in the gas phase. $Np(thd)_4$ and $UO_2(thd)_2$ which is monomeric in the gas phase have similar vapour pressures.

Conclusions

Np(IV) chelates are volatile both in the unsolvated form and in the form of their adducts, which are formed only by β-diketonates with electron-withdrawing substituents. Volatile Np(VI) chelates have not been obtained in the unsolvated form and sublime only as adducts. The adduct stability towards decomposition to Np(IV) in the sublimation process increases as the bond strength of the neptunium atom with the neutral ligand increases. So, the increase of neutral ligand basicity, on the one hand, prevents adduct decomposition to Np(IV) but, on the other hand, reduces its volatility (see ref. 6). Increasing β-diketonate anion basicity is unfavourable for both the volatility and adduct stability upon sublimation. Thus, the greater oxidizing ability of Np(VI) leads to a decrease in the number of volatile and thermostable complexes progressing from uranyl to neptunyl.

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