# HALOGENACETIC ACIDS AS SYNERGIC AGENTS IN THE SOLVENT EXTRACTION OF HAFNIUM*

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A synergic effect occurs when hafnium is extracted from 2M-HClO$_4$ medium into solution of N-benzoyl-N-phenylhydroxylamine in organic solvents, in the presence of halogenacetic acids. The magnitude of this effect increases with the increasing number of halogen atoms in the molecule of an acid. The most powerful synergic agent is trichloroacetic acid which increases the distribution ratio of hafnium by 3—4 orders of magnitude. It has been found from the slope analysis and from the distribution of halogenacetic acids that synergism is caused by the extraction of the mixed complex HfL$_3$A (A = CCl$_3$COO$^-$, CF$_3$COO$^-$, CHBr$_2$COO$^-$).

In the course of systematic study of hafnium extraction by chelating agents from 2M-HClO$_4$ medium in the presence of various unidentate ligands it has been found that N-benzoyl-N-phenylhydroxylamine (HL) differs from other extracting agents in that it causes synergism in the presence of phenols[1] or nitrophenols[2]. Hydrogen bonding between phenols or nitrophenols and basic centres of the HfL$_4$ chelate has been suggested as the most likely mechanism of the synergism in these systems. In this paper, the synergic effects which occur in the extraction of hafnium by N-benzoyl--N-phenylhydroxylamine and di-n-butylphosphoric acid in the presence of halogenacetic acids are described.

## EXPERIMENTAL

All details of extraction experiments, the preparation of a stock solution of the $^{175+181}$Hf (IV) tracer and details of radioactivity measurement have been given in previous papers[1,2]. The only difference is that the synergic agent was originally present in the 2M-HClO$_4$ aqueous phase. The composition of the organic phase is mentioned further in the text. The total concentration of hafnium in each extraction experiment was $\leqq 1 \cdot 10^{-6}$M. All extractions were carried out at 20°C in a thermostated room.

The distribution of halogenacetic acids between aqueous 2M-HClO$_4$ and organic phase was determined by the titration of halogenacetic acid in the equilibrated organic phase. Water coextracted with trifluoroacetic acid was determined in the organic phase by the Fischer method.

All solvents used and perchloric acid were of reagent grade purity. Monochloroacetic acid (Xenon, Lodz, Poland), trichloroacetic acid (Reanal, Budapest), monobromo- (Sojuzchimexport,

USSR), dibromo- and monoidoacetic acids (Lachema, Brno), were all of reagent grade purity and were not further purified. Only trifluoroacetic acid (Reachim, USSR) was redistilled and the 71—73°C fraction used. The concentration of all acid solutions was determined by the titration with a standard NaOH solution.

## RESULTS AND DISCUSSION

### Dimerization of Halogenacetic Acids in Benzene

Considering halogenacetic acids (HA) as synergic agents, their distribution between aqueous and organic phases must be taken into account. If we assume that only monomeric acid HA is present in the aqueous phase whereas both monomer and dimer $(HA)_2$ exist in the organic phase, the distribution of HA is then described by the distribution constant of the monomer $K_D = [HA]_{org}[HA]_{aq}^{-1}$ and by the dimerization constant of the acid in the organic phase $K_2 = [(HA)_2]_{org}[HA]_{org}^{-2}$. Making these assumptions, however, hydrated forms of $(HA)$ and $(HA)_2$ in the organic phase[3,4] are neglected. In this paper, the halogenacetic acid equilibria for the system 2M-HClO$_4$/benzene (further used in studies of the synergic extraction of hafnium) have been determined since the literature survey yielded only conflicting data which had been obtained under different conditions[5]. Using the above-mentioned constants and the total equilibrium concentrations of halogenacetic acid in the aqueous and organic phases, for which we can write

$$C_{aq} = [HA]_{aq} \quad \text{and} \quad C_{org} = [HA]_{org} + 2[(HA)_2]_{org} ,$$

it is possible to obtain the constants $K_D$ and $K_2$ from the distribution ratio of the acid[6]

$$D_{HA} = C_{org} C_{aq}^{-1} = K_D + 2K_D^2 K_2 [HA]_{aq} . \tag{1}$$

Similar equation was used for trichloroacetic acid whose dissociation in 2M-HClO$_4$ cannot be neglected

$$D_{HA}\varphi = K_D + 2K_D^2 K_2 [HA]_{aq} , \tag{2}$$

where $\varphi = (1 + K_a[H^+]^{-1})$. The values of $[H^+]$ and $[HA]_{aq}$ were calculated by successive approximations, as it had been done for mixtures of HNO$_3$ and HClO$_4$ (ref.[7]), using the dissociation constant of CCl$_3$COOH $K_a = 3.0$ for $I = 2.0$ (see[8]). The dependences of $D_{HA}$ on $[HA]_{aq}$ for dibromo- and monohalogenacetic acids according to the equation (1) and for CCl$_3$COOH using the equation (2) were processed by the method of least squares. Thus obtained constants are presented in Table I.

Consistently with a common concept of the distribution of covalent molecules[9], the distribution constants increase in a homologous series of acids with the size of the substituted alkyl group: $CH_2Cl < CH_2Br < CH_2I$; $CH_2Br < CHBr_2$; $CF_3 < < CCl_3$. For trifluoroacetic acid the dimerization constant was not determined and the distribution constant was found by extrapolation of $D_{HA}$ when $[HA]_{aq} \to 0$. In fact the distribution ratio of the acid increases only very little with the increasing acid equilibrium concentration in the aqueous phase which is an evidence that $CF_3COOH$ does not appreciably dimerize in benzene. This is in good agreement with the behaviour of $CF_3COOH$ in dry benzene[10], for which a very low value of dimerization constant $K_2(2 \cdot 6 \text{ l mol}^{-1})$ was found. The comparison with dimerization constants for dry cyclohexane $(192 \text{ l mol}^{-1})$ and $CCl_4$ $(149 \text{ l mol}^{-1})$[10] shows a strong interaction between monomeric $CF_3COOH$ and $\pi$-electron system of benzene. It is therefore not surprising that in the presence of another even stronger base, such as water, in the equilibrium benzene phase, the dimerization is further suppressed. This is also indicated by the co-extraction of water in the presence of $CF_3COOH$ in the system 2M-$HClO_4$/benzene. For 1M-$CF_3COOH$, where $[HA]_{org} = 0 \cdot 0165$M, the equilibrium concentration of water in the organic phase $\approx 0 \cdot 013$M, which approximately corresponds to the presence of $CF_3COOH$ monohydrate which was actually found in moist $CCl_4$ by spectroscopy[11].

*Extraction of Hafnium by N-Benzoyl-N-phenylhydroxylamine in the Presence of Halogenacetic Acids*

Fig. 1 shows synergism and antagonism in the hafnium extraction by benzene solutions of N-benzoyl-N-phenylhydroxylamine (HL) in the presence of monohalogenacetic and dibromoacetic acids. The increase of distribution ratio of hafnium $(D)$ strongly contradicts the acetic acid behaviour in that system. Acetic acid has no effect

TABLE I

Partition Coefficients and Dimerization Constants of Halogenacetic Acids in 2M-$HClO_4$/Benzene System

| Acid | $K_D$ | $K_2$, l mol$^{-1}$ | Acid | $K_D$ | $K_2$, l mol$^{-1}$ |
|---|---|---|---|---|---|
| $CH_2ClCOOH$ | 0·0117 | 67·8 | $CHBr_2COOH$ | 0·153 | 12·8 |
| $CH_2BrCOOH$ | 0·0224 | 42·8 | $CCl_3COOH$ | 0·62 | 3·8 |
| $CH_2ICOOH$ | 0·041 | 343 | $CF_3COOH$ | 0·013[a] | — |

[a] Not corrected for the dissociation of $CF_3COOH$ in the aqueous phase (equation (2)), since the value of $K_a$ for $I = 2 \cdot 0$ is not known.

on $D$ up to the concentration of 1M, whereas at higher concentrations $D$ slightly decreases[12]. The correlation of the synergic effect of $CH_2XCOOH$ acids with their concentration in the organic phase in the synergic maximum is shown in Table II. The same order of magnitude of synergic effect of all acids agrees with both the values of $[HA]_{org}$ calculated using constants from Table I, and the almost identical acidity of acids[13] ($pK_a \approx 3$).

TABLE II

Synergic Efficiency of Monohalogenacetic Acids

| Acid | $C_{HA, tot}$ at synergic maximum mol $l^{-1}$ | $D_{max}{}^a$ | $S^b$ | $C_{HA, org}$ mol $l^{-1}$ | $[HA]_{org}$ mol $l^{-1}$ |
|---|---|---|---|---|---|
| $CH_2ClCOOH$ | 1·25—1·60 | 15 | 8·3 | $0·045^c$ | $0·015^c$ |
| $CH_2BrCOOH$ | 1·25 | 13 | 7·3 | $0·096^c$ | $0·028^c$ |
| $CH_2ICOOH$ | 0·8 —1·0 | 10 | 5·5 | $0·41^d$ | $0·024^d$ |

$^a$ Distribution ratio of hafnium at the synergic maximum. $^b$ Synergic effect expressed as $D_{max}/D_0$, where $D_0$ is the distribution ratio of hafnium in the absence of the synergic agent under otherwise indentical conditions, *i.e.* $4 . 10^{-3}$M-HL in benzene ($D_0 = 1·8$). $^c$ For $C_{HA, tot} = 1·25$M, $^d$ for $C_{HA, tot} = 1·0$M.

TABLE III

Solvent Effect on the Synergic Efficiency of $CCl_3COOH^a$

| Solvent | Slope of the linear part of the log $D$ = f(log $C_{HA, tot}$) function | $S^b$ | $D_0$ | $C_{HA, org}{}^c$ mol $l^{-1}$ |
|---|---|---|---|---|
| Cyclohexane | 2·5 | $1·8 . 10^4$ | 0·002 | 0·0008 |
| $CCl_4$ | 2·25 | $3·5 . 10^3$ | 0·068 | 0·0042 |
| Benzene | 1·5 | $9 . 10^2$ | 0·28 | 0·0226 |
| Chlorobenzene | 1·35 | $3·6 . 10^2$ | 0·445 | 0·0125 |
| Toluene | 1·75 | $2·4 . 10^2$ | 0·575 | 0·019 |
| $CHCl_3$ | 1·0—1·5 | $1·5 . 10^2$ | 0·275 | 0·031 |
| Nitrobenzene | — | 4·2 | 0·10 | 0·074 |

$^a$ $[HL]_{tot} = 2 . 10^{-3}$M, in nitrobenzene $[HL]_{tot} = 2 . 10^{-4}$M, $^b$ see legend of Table II, $^c$ $C_{HA, tot} = 0·1$M.

Dibromoacetic acid, the only one of disubstituted acids which was available, shows under identical conditions the synergic effect even at concentrations $< 10^{-2}$M, where with monosubstituted acids the synergism is not yet exhibited (Fig. 1, curve 4). The value of $S = D_{max}/D_0 = 3.3 \cdot 10^2$ ($D_0 = 0.048$, $[HA]_{org} = 0.067$M for $0.63$M-CHBr$_2$COOH, $pK_a = 1.40$, see[14]) was obtained from curve 5 for $1 \cdot 10^{-3}$M--HL. Both the region of the synergic effect (Fig. 2, curve 4) and its magnitude (curve 5) of trifluoroacetic acid are very much like those of CHBr$_2$COOH. For trichloroacetic acid, however, the effect of the full halogen substitution is strongly manifested. The synergism starts at concentrations $<10^{-4}$M and for $1 \cdot 10^{-3}$M-HL the value of $S$ can be estimated as $5.9 \cdot 10^3$ ($D_0 = 0.048$, $[HA]_{org} = 0.164$M for 1M-CCl$_3$COOH, $pK_a = -0.52$, see[8]).

The effect of the solvent on the synergic efficiency of trichloroacetic acid is presented in Table III. Solvents can be arranged into the following series according to their synergic effect: nitrobenzene $<$ CHCl$_3$ $<$ toluene $<$ chlorobenzene $<$ benzene $<$ $<$ CCl$_4$ $<$ cyclohexane. For the calculations of $S$, the values of $D$, which correspond to the total concentration $0.1$M-CCl$_3$COOH, were used. This series, with the exception of benzene, is even more pronounced if we take into account the fact that the equi-
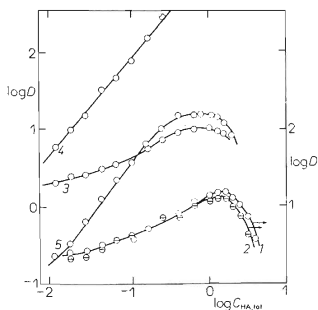


FIG. 1

Dependence of Hafnium Distribution Ratio on the Total Concentration of Monohalogen- and Dibromoacetic Acids (HA)

Curve 1: CH$_2$ClCOOH, 2: CH$_2$BrCOOH, 3: CH$_2$ICOOH, 4 and 5: CHBr$_2$COOH. $C_{HL}$ in benzene: Curves 1−4: $4 \cdot 10^{-3}$, 5: $1 \cdot 10^{-3}$M.
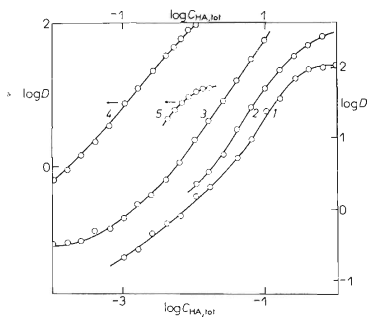
FIG. 2

Dependence of Hafnium Distribution Ratio the Total on Concentration of Trihalogenacetic Acids (HA)

Curves 1−3: CCl$_3$COOH, 4 and 5: CF$_3$COOH. $C_{HL}$ in benzene: curve 1: $4 \cdot 10^{-4}$, 2 and 5: $1 \cdot 10^{-3}$, 3 and 4: $2 \cdot 10^{-3}$M. The upper horizontal scale is for CF$_3$COOH.

librium concentration of $CCl_3COOH$ in the organic phase is inversely proportional to the value of $S$ ($S$ is the highest for cyclohexane, where $[CCl_3COOH]_{org}$ is the lowest). The synergic series of solvents is approximately identical with that of the system Hf(IV)––HL–phenol[1] and is again most likely caused by the interaction of $CCl_3COOH$ with the solvent which affects the activity of the former. The effect is most pronounced for nitrobenzene which almost completely suppresses synergism, similarly as in the system Hf(IV)–HL–picric acid[2]. Here the solvent–$CCl_3COOH$ interaction is obviously considerable as shown also by the formation of molecular complexes of nitrobenzene with $CCl_3COOH$[15].

Even though not all halogenacetic acids have been studied, it is obvious that their synergic effect increases with the degree of substitution of the methyl group, in another words with decreasing dimerization constant and/or increasing acidity. This proves that the synergically active component is the monomeric acid HA.

It has not been possible to determine the number of monohalogenacetic molecules which take part in the formation of the synergic complex from the dependence of log $D$ on the total concentration of the acid. The reason is that the synergism
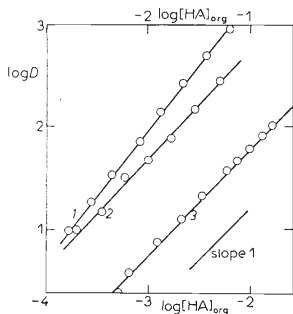


Fig. 3

Dependence of Hafnium Distribution Ratio on the Equilibrium Concentration of Halogenacetic Acids in the Organic Phase

Curve *1*: $CCl_3COOH$, 2: $CHBr_2COOH$ (upper horizontal scale), *3*: $CF_3COOH$ (lower horizontal scale); $2 . 10^{-3}$M-HL in benzene.

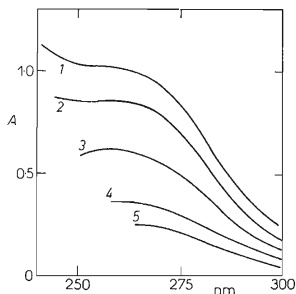Fig. 4

Absorption Spectra of HL in Equilibrium Aqueous Phase after Extraction of $1 . 10^{-3}$M- -HL in $CCl_4$ into 2M-$HClO_4$ in the Presence of $CCl_3COOH$

$[CCl_3COOH]_{tot}$ and $[HL]_{aq}$: curve *1*: 0, $2·15 . 10^{-4}$; 2: 0·025, $1·82 . 10^{-4}$; *3*: 0·10, $1·3 . 10^{-4}$; *4*: 0·40, $7·7 . 10^{-5}$; *5*: 1·0M, $5·4 . 10^{-5}$M.

is weak and at higher acid concentrations antagonism becomes dominant (Fig. 1). Neither are these dependences applicable to other acids because their slope values are not integral numbers and change continuously. Fig. 3 shows the linear dependences of log $D$ (values for $2 . 10^{-3}$M-HL are from Fig. 2 and those for $4 . 10^{-3}$M-HL from Fig. 1) on the equilibrium concentration of monomeric acid HA in the organic phase for $CCl_3COOH$, $CF_3COOH$ and $CHBr_2COOH$ with the corresponding slopes of 1·35, 1·0 and 1·2 respectively. This proves that one molecule of $CF_3COOH$ takes part in the formation of the synergic complex. This conclusion may also be extended to $CCl_3COOH$ and $CHBr_2COOH$. The corresponding values of slopes of curves in Fig. 3 are somewhat higher since for their determination dimerization constants from Table I were used and consequently the presence of hydrated forms of HA or $(HA)_2$ in the organic phase has not been considered.

While the dissociation of monohalogen- ($pK_a$ 3, see[13]) and dibromoacetic acid ($pK_a = 1·4$, see[14]) may be neglected in the 2M-$HClO_4$ medium, and the value of $[H^+]_{equil} = 2·0$M, in case of $CCl_3COOH$, however, the acidity changes if the acid concentration is increased in a mixture with 2M-$HClO_4$. An estimate has been made how such a change affects the slope values in Fig. 3. The equilibrium concentration $[H^+]$ was calculated by successive approximations, as it had been done in the calculation of $K_D$ and $K_2$ of trichloroacetic acid. In curve 1 in Fig. 3, the point with the highest $[CCl_3COOH]_{org}$ corresponds to the following composition of the aqueous phase: 2·0M-$HClO_4$ + 0·25M-$CCl_3COOH$. Through successive approximations, the value of $[H^+]_{equil} = 2·15$M is obtained which makes the value of $D$ lower. The function log $D = f(log [HL]_{tot})$ has the slope of 2·0 for 0·25M-$CCl_3COOH$. Thus the corresponding deviation in log $D$ is approximately 0·06 which does not appreciably exceed error limits in the experimental determination of $D$. With decreasing concentration of $CCl_3COOH$ this effect is further reduced (e.g. in 0·1M-$CCl_3COOH$ $[H^+]_{equil} = 2·06$ and $\Delta$ log $D = 0·03$), so that the changes of $[H^+]_{equil}$ do not practically affect the slope value of curve 1 in Fig. 3. The same situation holds for curve 3 for $CF_3COOH$ at lower concentrations of the acid. Nevertheless, more accurate calculation for higher concentrations is not possible since the value of dissociation constant is not known for higher ionic strength. It may, however, be estimated considering the thermodynamic value of the constant, which is quoted in the limits $4-8$ mol l$^{-1}$ (see[16]), that even for the highest concentrations used, viz. 1·0M-$CF_3COOH$, the value of $\Delta$ log $D$ will not exceed 0·15−0·2. Such a change would result in the increase of the slope value to 1·2. Other papers[17,18], however, quote the thermodynamic value of dissociation constant as <2, which again would make the corresponding change of the slope value negligible.

The functions of log $D$ vs log $C_{HL, tot}$ in the presence of halogenacetic acids are straight lines whose slopes have lower values than that for the system benzene/2M- -$HClO_4$ for which the value of 2·7 (see[1]) has been found. The following values of slopes have been determined: 2·4 for 1·0M-$CF_3COOH$, 0·63M-$CH_2ClCOOH$ and

0.025M-CCl$_3$COOH, 2.15 for 0.1M-CCl$_3$COOH and 1.95 for 1.0M-CCl$_3$COOH.
The relation between the slope value and the increasing concentration of the synergic
agent is inverse to that of phenol[1]. Since the slope of the function log $D$ vs log $[HL]_{tot}$
gives the difference in the average number of ligands L$^-$ coordinated to the Hf(IV)
ion in the organic and aqueous phases ($\bar{n}_{org} - \bar{n}_{aq}$) the easiest interpretation of the
decrease in the slope value on increasing the concentration of halogenacetic acid
(especially of CCl$_3$COOH) would therefore be in the increase of $\bar{n}_{aq}$, in another
words in the increase of the degree of complexation of Hf(IV) in the aqueous phase.
This is, however, in contrast with the spectrophotometric measurement of the HL
distribution (Fig. 4) which shows that with increasing concentration of CCl$_3$COOH
the equilibrium concentration of HL in the aqueous phase decreases and hence also
$\bar{n}_{aq}$, decreases (CCl$_4$ was used for these measurements since benzene absorption would
interfere with the photometric determination of HL). The fact that with the increasing
concentration of CCl$_3$COOH the distribution ratio of HL increases ($[HL]_{aq}$ decreases)
is characteristic for an interaction of both components in the organic phase[19]. This
interaction is also proved by higher solubility of HL in CCl$_4$ in the presence of
CCl$_3$COOH. It may be assumed that the carboxylic hydrogen is bonded to the tertiary
nitrogen atom of HL (e.g. the formation constant of the molecular complex of
CCl$_3$COOH with N,N′-dimethylaniline in benzene is 5.5 . 10$^2$ l mol$^{-1}$, see[20]). Such
interaction could not, however, be proved by infrared spectroscopy because the
region of valence vibrations of the N—H—O group (2500−2800 cm$^{-1}$ in such
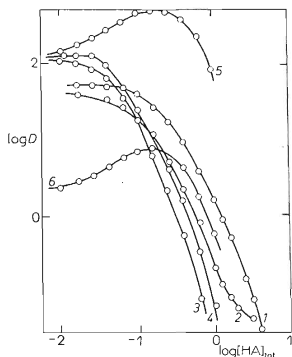complexes[21]) is overlapped by the region of the O—H and O—H—O vibrations.



Fig. 5

Dependence of Hafnium Distribution Ratio
on the Total Concentration of Halogenacetic
Acids for the Extraction by Di-n-butylphos-
phoric Acid in Benzene

Curve 1: CH$_2$ClCOOH, 2: CH$_2$BrCOOH,
3: CHBr$_2$COOH, 4: CCl$_3$COOH, 5 and 6:
CF$_3$COOH. [DBP]$_{tot}$; curve 1—5: 1.5 . 10$^{-3}$,
6: 5 . 10$^{-4}$M.

*Extraction of Hafnium by Di-n-butylphosphoric Acid in the Presence of Halogen-acetic Acids*

Fig. 5 shows the effect of halogenacetic acids on the extraction of hafnium by di-n--butylphosphoric acid (DBP) into benzene from 2M-HClO$_4$. The shape of the curves is basically identical to that of unsubstituted monocarboxylic acids. The antagonism, which has been discussed earlier[12], takes place in most cases. Exceptional is CF$_3$COOH (curves *5* and *6*) which shows a slight but well developed synergism before the region of antagonism. Since there is a continuous transition between both phenomena, and the interaction constants of DBP with CF$_3$COOH are not known, the synergism has not been further studied.

*Origin of Synergism in the Extraction Using N-Benzoyl-N-phenylhydroxylamine*

Two interpretations of the synergism in the system Hf(IV)–HL–halogenacetic acid can be suggested. The first one is analogous to the synergism of phenols[1] and nitro-phenols[2] and is based on the addition of the acid to the HfL$_4$ chelate through hydrogen bond. In this case $\bar{n}_{org} = 4$. Owing to the decrease of $[HL]_{aq}$ and hence also of $\bar{n}_{aq}$ in the presence of halogenacetic acid (Fig. 4), the slope of the log $D = f(\log [HL]_{tot})$ function should, with the increasing concentration of halogenacetic acid, increase from the value of 2·7 (see[1]). This type of synergism may therefore be rejected.

The second explanation seems to be more likely. It is based on the substitution of one L$^-$ anion in the HfL$_4$ chelate with the formation of a HfL$_3$A complex. If the latter one coexists in the organic phase with the original chelate HfL$_4$, then the value of $\bar{n}_{org}$ would decrease from 4 to 3 with the increasing concentration of the synergic agent. The observed trend of the slopes of the log $D = f(\log [HL]_{tot})$ functions might then be interpreted considering the change of $\bar{n}_{aq}$ being less significant than that of $\bar{n}_{org}$. This mechanism does not contradict general chemical properties of hafnium and zirconium. In contrast to the M(IV)–OAryl bond, the bond M(IV)–OOCR is stable even in the presence of water. Recently a number of defined complexes of zirconium and hafnium with this bond (*e.g.* with trichloroacetic acid[22]) have been isolated from aqueous solutions.

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