EXTRACTION STUDY OF HAFNIUM COMPLEXES WITH ALIPHATIC HYDROXY ACIDS*

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Hafnium complexes with glycolic, lactic, malic, tartaric, and citric acids were studied in perchlorate medium (1·0—3·0 mol l^{-1} $HClO_4$) by using the competitive extraction method. In the hydroxy acid concentration region 0·01—1·0 or 2·0 mol l^{-1}, complexes with the hafnium-to-ligand ratios 1 : 1 and 1 : 2 (in the case of lactic and malic acids also 1 : 3) were identified and their stability constants determined. One proton is split off during the formation in acidic medium, a five-membered chelate ring being formed with the Hf(IV) cation bonded to the non-dissociated hydroxy group of the ligand.

The ability of Zr(IV) salts to react with hydroxy acids was observed as early as the last century[1]; still there remains much to be elucidated in the chemistry of zirconium and hafnium compounds with these acids. Complicating are here the hydrolytic and polymerization equilibria of the metals, causing the complexes, quite well defined in strongly acidic solutions, to convert in weakly acidic solutions into hydroxo-complexes of the $M(OH)_xL_y$ type[2–7] and ultimately into low soluble, probably polymeric products reported to be zirconyl salts[8,9], which dissolve in excess ligand to give anionic complexes[9]. On the other hand, hydroxy acid media have been used in chromatography not only for mutual separation of zirconium and hafnium[10,11], but also for their separation from other elements[12–15].

As a continuation of our previous study of hafnium complexes with organic ligands[16–18] we have studied in the present work hafnium complexes with some aliphatic hydroxy acids. This was stimulated by the fact that other authors dealing with this topic have confined themselves to the region of low concentrations of the ligands[19,20], where 1 : 1 complexes are formed. Moreover, there are some discrepancies in these studies as to the number of protons split off during the complex formation and associated problems of the structures of complex.

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EXPERIMENTAL

Chemicals. Glycolic acid *puriss.* (Fluka); 1-malic acid for biochemistry (Merck); lactic, tartaric, and citric acids *p.a.* (Lachema). Lithium perchlorate was prepared from technical lithium hydroxide; aluminium and iron were separated during the neutralization, sulphates were removed with barium perchlorate, fluorides by heating solid lithium perchlorate with perchloric acid. The concentrations of the lithium perchlorate and sodium perchlorate solutions were determined alkalimetrically after ion exchange on cation exchanger S in the H cycle. 1-Phenyl-3-methyl-4-benzoylpyrazol-5-one was prepared according to Jensen[21].

The equilibria in the formation of hafnium complexes with hydroxy acids were studied by employing the competitive extraction method using a $^{175+181}$Hf radiotracer[17]. The acidity of the aqueous phase was 1—3 mol l^{-1} $HClO_4$, the ionic strength was held at 2·0 or 3·0 mol l^{-1} by means of $LiClO_4$ or $NaClO_4$. Benzene solution of 1-phenyl-3-methyl-4-benzoylpyrazol-5-one served as the organic phase; its concentration was $1-2 \cdot 10^{-3}$ mol l^{-1}, according to the acidity of the aqueous phase.

The dissociation constants of glycolic and malic acids were determined potentiometrically in 2 mol l^{-1} KNO_3 solutions[17].

Calculations

The hafnium-to-ligand ratios in the complexes were determined from the dependence of the hafnium distribution ratio (D) on the total ligand concentration C_L. The number of protons split off during the complex formation *via* the reaction

$$Hf^{4+} + j\,H_nL \rightleftharpoons Hf(H_{n-i}L)_j^{(4-i)+} + ij\,H^+ \qquad (A)$$

was determined graphically by using the $\varphi(H)$ function introduced previously[17]. The total ligand concentration was chosen so that, according to the log D *vs* C_L dependence, the 1 : 1 complex predominated. For a constant ligand concentration we then have[17]

$$(D_0 D^{-1} - 1)/C_L = \sum_{i=1}^{n} {}^*\beta_1(i\,H)/[H]^i\,, \qquad (1)$$

where D_0 and D are the hafnium distribution ratios in the absence and in the presence of the ligand, respectively, and ${}^*\beta(iH)$ is the equilibrium constant of the reaction (A). The $\varphi(H)$ function is then

$$\varphi(H) = (D_0 D^{-1} - 1)\,[H]/C_L = \sum_{i=1}^{n} {}^*\beta_1(i\,H)/[H]^{i-1}\,; \qquad (2)$$

the slope of its dependence on the hydrogen ion concentration provides the number of protons split off in the reaction (A).

The equilibrium constants of complex formation according to equation (A), ${}^*\beta_j(iH)$, were determined from the equation

$$(D_0 D^{-1} - 1) = \sum_{i,j} {}^*\beta_j(i\,H)\,C_L^j/[H]^{ij} \qquad (3)$$

corrected for hydrolysis of hafnium. The values of the equilibrium constants for monomeric hydrolysis of hafnium determined by Peshkova and Pen An (ref.[22]) for $Hf(OH)_x^{(4-x)+}$ com-

plexes ($x = 1-4$) were obtained from measurements in weakly acidic or neutral solutions, where the various Hf(IV) ionic species may not be in a true thermodynamic equilibrium. Therefore, the use of these constants has not been recommended[23]. According to current views[24,25], the extent of monomeric hydrolysis of Hf(IV) and Zr(IV) in strongly acidic solutions is considerably lower than as assumed before, and in solutions in 0·5—4·0 mol l^{-1} $HClO_4$ only the first hydrolytic complex $Hf(OH)^{3+}$ exists. The most reliable seems to be the constant $K_h = [Hf(OH)][H]/[Hf] = 0{\cdot}08 \pm 0{\cdot}03$ determined potentiometrically at 25°C (ref.[24]); this value was also used throughout the present work. Eq. (*3*) corrected for the occurrence of the $Hf(OH)^{3+}$ complex in the aqueous phase is

$$*D \equiv (D_0 D^{-1} - 1)(1 + K_h/[H]) = \sum_{i,j} *\beta_j(i\,H)\, C_L^j/[H]^{ij} . \qquad (4)$$

Formation of mixed $Hf(OH)(H_{n-i}L)_j$ complexes was not considered because under the conditions applied in this work ($C_{Hf} \approx 10^{-6}$ mol l^{-1}, $C_{H^+} \geqq 1{\cdot}0$ mol l^{-1}) the fraction of the $Hf(OH)^{3+}$ complex in the absence of the complexing ligand is as low as 5%.

After splitting off of one proton, Eq. (*4*) simplifies to

$$*D = \sum_j *\beta_j(1\,H)\,(C_L/[H])^j . \qquad (5)$$

The $*\beta_j(1\,H)$ constants in Eq. (*5*) were determined graphically by the method of Day and Stoughton[26]. The stability constants then were obtained from the realation $\beta_j(1\,H) = *\beta_j(1\,H)/K_a^j$, where K_a is the dissociation constant for the corresponding proton in the H_nL acid.

RESULTS

The dependences of log *D* on the total ligand concentration are shown in Figs 1 and 2. Table I gives some of the calculations of the $\varphi(H)$ function for determination of the number of split off protons, Table II lists the equilibrium constants of the complex formation $*\beta_j(1\,H)$ and the stability constants $\beta_j(1\,H)$. The distribution curves for the complexes calculated from the stability constants are plotted in Fig. 3.

As Table I demonstrates, the $\varphi(H)$ function of glycolic acid for $C_L = 0{\cdot}08$ mol l^{-1} is independent of the acidity, hence one proton is split off during the 1 : 1 complex formation in 1·0—2·0 mol l^{-1} $HClO_4$ solutions. The $*\beta_j(1\,H)$ constants were determined for $j = 1$ and 2 for the region of $C_L = 0{\cdot}04 - 1{\cdot}0$ mol l^{-1} by using the values of curve *1*, (Fig. 1). For $C_L > 1{\cdot}0$ mol l^{-1}, Eq. (*5*) indicates also formation of a higher complex, probably of the 1 : 3 composition; its equilibrium constant was not determined because of lack of sufficient experimental data in this region. The stability constants were calculated by employing the value $K_a = 2{\cdot}29 \cdot 10^{-4}$ (2 mol l^{-1} KNO_3)

One proton is also split off during formation of Hf(IV) complexes with lactic acid in 2 mol l^{-1} $HClO_4$ solution, which is in agreement with the results of the study of Hf(IV) sorption on a cation exchanger in the same medium[19]. The 1 : 3 complex formation is more pronounced as compared with the case of glycolic acid. The $*\beta_2(1\,H)$ constant had not to be determined by graphical extrapolation thanks to the fact that the function obtained from Eq. (*5*) for calculation of $*\beta_2(1\,H)$ (ref.[26])

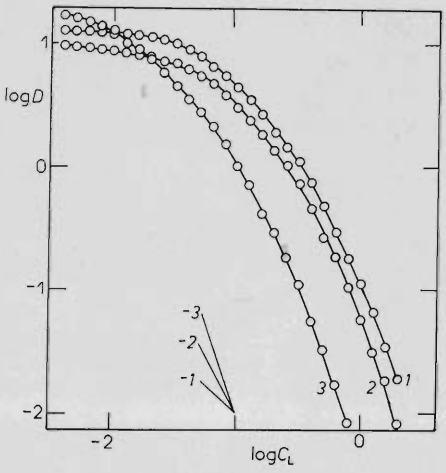


FIG. 1

Dependence of the hafnium distribution ratio on the total ligand concentration. $C_{HClO4} = 2{\cdot}0$ mol l^{-1}. Acids: *1* glycolic, *2* malic, *3* lactic

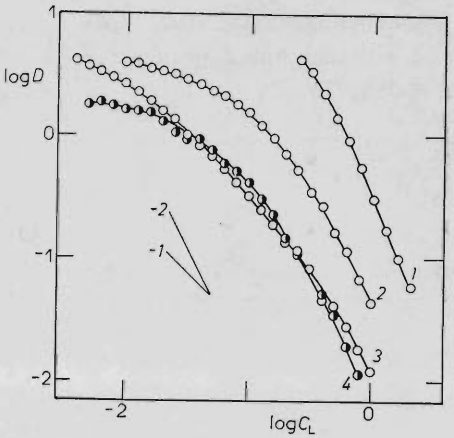
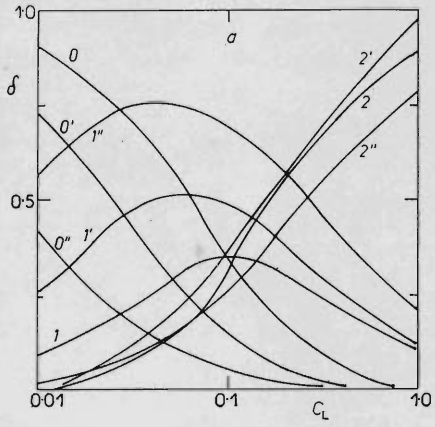


FIG. 2

Dependence of the hafnium distribution ratio on the total ligand concentration. *1* Tartaric acid, 1 mol l^{-1} $HClO_4$; *2* tartaric acid, 3 mol l^{-1} $HClO_4$; *3* citric acid, 2 mol l^{-1} $HClO_4$; *4* tartaric acid, 2 mol l^{-1} $HClO_4$



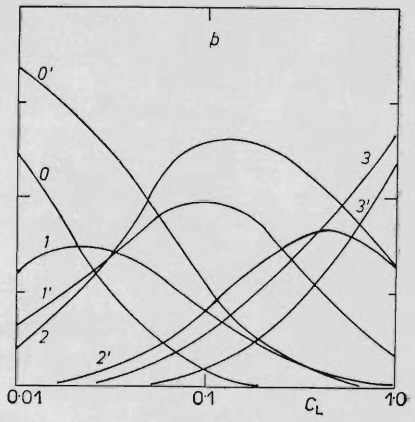


FIG. 3

Distribution curves of the $Hf(HL)_j^{(4-j)+}$ complexes in 2 mol l^{-1} $HClO_4$. The curve numbering refers to the *j* coefficient values; *A*: *0*, *1*, *2* — glycolic acid, *0'*, *1*, *2'* — tartaric acid, *0''*, *1''*, *2''* — citric acid; *B*: *0*, *1*, *2*, *3* — lactic acid, *0'*, *1'*, *2'*, *3'* — malic acid

was constant in the $C_L = 0{\cdot}05-0{\cdot}25$ mol l^{-1} region and yielded thus the $*\beta_2(1\,H)$ value directly. The subsequent rise of the function at higher ligand concentrations is accounted for by the formation of the 1 : 3 complex; the equilibrium constant of the latter was determined graphically from the $*D/(C_L/[H])^3$ *vs* $1/(C_L/[H])$ plot[18]; the dependence was linear in the region $C_L = 0{\cdot}2-1{\cdot}0$ mol l^{-1}, confirming thus the

TABLE I

Determination of the number of detached protons from the φ(H) function

C_{H^+}	D_O	D	φ(H)
Glycolic acid, $C_L = 0{\cdot}08$ mol l^{-1}, $C_{(H+Na)ClO_4} = 2{\cdot}0$ mol l^{-1}			
2·00	16·1	6·37	38·3
1·75	26·0	9·5	38·2
1·50	44·7	14·5	39·0
1·25	75·3	23·2	35·0
1·00	129	32·8	36·8
Lactic acid, $C_L = 0{\cdot}04$ mol l^{-1}, $C_{(H+Na)ClO_4} = 2{\cdot}0$ mol l^{-1}			
2·00	1·31	0·26	202
1·80	1·89	0·33	213
1·60	2·69	0·43	210
1·40	4·90	0·61	246
1·20	8·23	1·00	217
1·00	13·17	1·27	234
Tartaric acid, $C_L = 0{\cdot}025$ mol l^{-1}, $C_{(H+Na)ClO_4} = 2{\cdot}0$ mol l^{-1}			
2·00	16·65	9·85	55·2
1·75	26·4	14·23	60·0
1·50	49·3	18·9	96·7
1·25	98·0	31·8	104
1·00	160	48·3	92·2
Tartaric acid, $C_L = 0{\cdot}01$ mol l^{-1}, $C_{(H+Na)ClO_4} = 3{\cdot}0$ mol l^{-1}			
3·00	4·98	4·37	41·9
2·80	6·06	5·09	53·4
2·60	7·57	6·26	54·4
2·40	10·30	8·74	51·9
2·20	13·26	10·72	52·1

occurrence of the 1 : 2 and 1 : 3 complexes in this region. The stability constant was calculated with $K_{a1} = 2{\cdot}34 \cdot 10^{-4}$ determined in 1 mol l^{-1} $NaClO_4$ solution[27].

Application of Eq. (2) to 0·04 mol l^{-1} malic acid again confirmed the splitting off of one proton. For $i = 1$, Eq. (5) showed that the $^*D/(C_L/[H])$ function for $C_L = 0{\cdot}004 - 0{\cdot}08$ mol l^{-1} is constant, hence represents directly the $^*\beta_1$(1 H) value. The $^*\beta_2$(1 H) value could be similarly determined without extrapolation to zero ligand concentration as the average value of corresponding function in the region $C_L = 0{\cdot}125 - 0{\cdot}30$ mol l^{-1}. The $^*\beta_3$(1 H) constant was determined in the same manner as that of lactic acid. NMR study of malic and 1-methoxysuccinic acids[28] evidenced that in the former acid, intramolecular hydrogen bonds involving the hydroxy group are insignificant; the carboxy group nearer to the hydroxy group can be thus considered more acidic and the stability constant can be calculated by employing the malic acid dissociation constant $K_{a1} = 5{\cdot}50 \cdot 10^{-4}$ ($K_{a2} = 3{\cdot}40 \cdot 10^{-5}$, both values for 2·0 mol l^{-1} KNO_3).

For the determination of the number of split off protons in the case of tartaric acid, the concentration was chosen $C_L = 0{\cdot}025$ mol l^{-1} in 2·0 mol l^{-1} $HClO_4$ (Table I). Although the 1 : 1 complex predominates in such conditions, the shape of the φ(H) function indicated the splitting of off two protons. This, however, for the 1 : 1 complex would imply the formation of a seven-membered ring chelate, or dissociation of a proton from the hydroxy group: we rather assume that the φ(H) function was not constant because with lowering acidity the equilibrium shifted in favour of the 1 : 2 complex. The dependence of D on C_L was therefore measured also in 3·0 mol l^{-1} $HClO_4$ (Fig. 2, curve 2) and the dependence of the φ(H) function

TABLE II

Equilibrium and formation constants of Hafnium complexes with hydroxy acids in 2·0 mol l^{-1} $HClO_4$ solutions

Acid	$^*\beta_j$(1 H)			β_j(1 H)		
	$j = 1$	$j = 2$	$j = 3$	$j = 1$	$j = 2$	$j = 3$
Glycolic	20[a]	367 ± 17	—	$8{\cdot}7 \cdot 10^4$	$7{\cdot}0 \cdot 10^9$	—
Lactic	95[a]	6 160 ± 310	$2{\cdot}5 \cdot 10^{4a}$	$4{\cdot}1 \cdot 10^5$	$1{\cdot}1 \cdot 10^{11}$	$2{\cdot}0 \cdot 10^{15}$
Malic	36 ± 2	290 ± 17	$1{\cdot}1 \cdot 10^{3a}$	$6{\cdot}5 \cdot 10^4$	$9{\cdot}6 \cdot 10^8$	$6{\cdot}6 \cdot 10^{15}$
Tartaric	70 ± 6	1 050 ± 80	—	$4{\cdot}8 \cdot 10^4$	$4{\cdot}8 \cdot 10^8$	—
Tartaric[b]	63 ± 3	970 ± 20	—	$6{\cdot}0 \cdot 10^4$	$8{\cdot}8 \cdot 10^8$	—
Citric	274 ± 5	2 100 ± 155	—	$2{\cdot}15 \cdot 10^5$	$1{\cdot}3 \cdot 10^9$	—

The limits denote the confidence intervals for $\alpha = 0{\cdot}05$. [a] Values determined by graphical extrapolation; [b] 3·0 mol l^{-1} $HClO_4$.

on acidity, at the ionic strength 3·0 mol l^{-1} (Table I). In such circumstances one proton is split off during the formation of Hf(IV) tartrate complexes, and the same mechanism can be assumed in 2·0 mol l^{-1} $HClO_4$; this was confirmed by an analogous graphical analysis for $C_L = 0{\cdot}25-2{\cdot}0$ mol l^{-1} and $C_{H^+} = 1{\cdot}0$ mol l^{-1}, where two protons were found to be split off. Since in this region the 1 : 2 complex is formed (Fig. 2, curve *1*), this implies splitting off of one proton from each ligand. The equilibrium constants were determined, similarly as in the case of malic acid, with extrapolation for the $C_L = 0{\cdot}01-0{\cdot}1$ and $0{\cdot}4-1{\cdot}0$ mol l^{-1} regions in 3·0 mol l^{-1} $HClO_4$ and the $C_L = 0{\cdot}02-0{\cdot}1$ and $0{\cdot}2-0{\cdot}8$ mol l^{-1} regions in 2·0 mol l^{-1} $HClO_4$. Formation of the third tartrate complex was not observed. The K_{a1} dissociation constant values of tartaric acid for the pertinent ionic strengths were taken from ref.[29].

The determination of the number of detached protons for citric acid gave the same results as in the case of tartaric acid. With the ionic strengths 2·0 and 3·0 mol l^{-1}, the $\varphi(H)$ function was constant in the regions 1·4–2·0 mol l^{-1} $HClO_4$ and 1·6 to 3·0 mol l^{-1} $HClO_4$, respectively. The equilibrium constants of the complex formation were determined analogously as in the case of tartaric acid. The pertinent functions were constant in the regions $C_L = 0{\cdot}005-0{\cdot}016$ and $0{\cdot}63-1{\cdot}0$ mol l^{-1}, respectively. The third complex was not observed to form. The value $K_{a1} = 1{\cdot}26 \cdot 10^{-3}$ in 2 mol . l^{-1} $NaClO_4$ (ref.[30]) was used for the calculation of the stability constants.

DISCUSSION

Composition and Stability of Complexes

The values of the stability constants for the glycolic acid complexes cannot be compared with published data, since studies of hafnium complexes with glycolic acid[5,7] only covered the $Hf(OH)_2L^+$ complex forming at pH > 0 by reaction of the L^- anion with the $Hf(OH)_3^+$ cation; moreover, the existence of the latter is questionable[23], and there even are discrepancies in the kinetic measurement results[3]. In fact, an equally stable analogous complex has been found to form with phenylacetic acid, although phenylacetate is not capable of formation of a chelate ring and thus the stability of its complex should be essentially lower than that of the glycolate.

Lactate complexes of Hf(IV) have been studied[19] by means of sorption on cation exchanger in 2 mol l^{-1} $HClO_4$ at $C_L = 0{\cdot}003-0{\cdot}28$ mol l^{-1}. In accordance with our results, the 1 : 1 complex has been identified at $C_L \leqq 0{\cdot}12$ mol l^{-1}, with the equilibrium constant $^*\beta_1(1\,H) = 110$. For $C_L = 0{\cdot}2$ mol l^{-1}, the results of the work[19] also point to the formation of higher complexes, which, however, have not been evaluated. The stability of Hf(IV) complexes with lactic acid, found in the present work, owing to the +I effect of the CH_3 group on the hydroxy group exceeds that for glycolic acid and at the same time is consistent with the stability of Hf(IV) complexes with 2-methyllactic acid[31] ($\beta_1(1\,H) = 10^6-10^7$, $\beta_2(1\,H) = 10^{11}-10^{12}$),

where the additional increase in stability is contributed by the +I effect of the second CH_3 group.

The results obtained for Hf(IV) complexes with malic acid agree – as to the composition of the complexes and regions of their existence – with the data of Ryabchikov and coworkers[19], who identified the 1 : 1 complex in 2 mol l^{-1} $HClO_4$ at C_L = 0·0064–0·1 mol l^{-1}; in the equilibrium constant value, however, there is a disagreement, since according to [19], $*\beta_1(1\,H) = 67$ (in the paper[19] there is given the constant $K_{f1} = 33{\cdot}7$, related to the $*\beta_1(1\,H)$ constant through $K_{f1} = *\beta_1(1\,H)/[H]$). In view of the good agreement of the constants for glycolic acid, we are unable to offer an explanation of this difference.

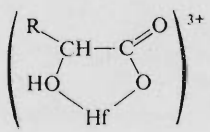
For the first tartrate complex, too, our results agree well with those of Ryabchikov and coworkers[19], who were able to prove its existence in 2·0 mol l^{-1} $HClO_4$ at C_L = = 0·013–0·10 mol l^{-1}. However, the value $*\beta_1(1\,H) = 97{\cdot}2$, obtained from ion exchange data[19], again agrees with our value only within the order of magnitude.

The splitting off of one proton during the formation of the $Hf(H_2L)_j$ citrate complexes in acidic solutions is consistent with the results arrived at by investigating zirconium citrate complexes in nitric acid solutions by extraction with tributylphosphate[32]. The value $*\beta_1(1\,H) = 350$ determined from the sorption of hafnium on ion exchanger[19] is again higher than our value.

The $\beta_1(1\,H)$ values indicate that the stability of the complexes under study decreases in the order lactate > citrate > glycolate > malate > tartrate. This order agrees with that obtained in the work[19], if the K_{f1} values given there are converted into the $\beta_1(1\,H)$ values. A higher stability of the citrate complexes as compared with the tartrate complexes has been observed also for zirconium[19,33,34]. On the whole, the $\beta_1(1\,H)$ constant values obtained by the ion exchange method[19] are 1·1–1·6 times higher than those obtained in the present work. Correlation of the stability constants of the complexes with the ligand pK_a values (Fig. 4) does not yield a single straight line. Obviously, in addition to the basicity, other factors play a role in the complex formation as well.

Structure of the Complexes

The results of measurements for glycolic and lactic acids indicate that in view of the splitting off of one proton, the structure of the HfL^{3+} complex can be represented as the five-membered ring chelate *I* with coordinated hydroxy group (R = H and CH_3 in glycolic and lactic acids, respectively).



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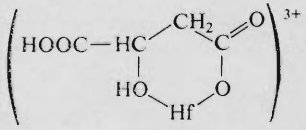


II

Such structure has been identified spectroscopically in Zr(IV) and Hf(IV) glycolate[35] and lactate[26] complexes isolated in the solid state, and is consistent with the high pK_a value of the hydroxy group of the ligands.

The structure *I* can be assumed also for complexes with other ligands. In the case of malic (R = HOOC—CH_2—) and citric acids, the formation of a similar six-membered ring chelate *II* is also feasible, but these rings have been for a long time known[37] to be less stable. In the case of bivalent cation complexes with bidentate nitrogen ligands the difference in the stability amounts to 2–3 orders of magnitude[38,39], and the stability also decreases considerably on going from the Hf(IV) chelate with oxalic acid[40] to that with malonic acid[17]. According to some authors[41,42], the lower stability of the complexes of 2-hydroxycarboxylic acids is due to chelate rings not being formed at all. The structure *II* is ruled out even by the mere fact that the stability of the Hf(IV) chelate with citric acid is higher than that of the glycolic acid chelate.

As found by Ryabchikov and coworkers[20], two protons are split off during the formation of the first tartrate complex in 1·0–1·6 mol l^{-1} $HClO_4$. Inasmuch as the hydroxy group of tartaric acid does not release a proton in such conditions ($pK_a \approx$ $\approx$ 16, ref.[43]), a chelate with participation of both carboxylic groups would imply the occurrence of a seven-membered ring (*III*), which, however, the authors themselves do not consider very likely, also with regard to the fact that under the same conditions they did not observe formation of hafnium complexes with succinic acid[19]. (For the same reasons, the formation of malic and citric acids chelates with participation of two carboxy groups can be ruled out as well.) Still the authors have not rejected this structure altogether, although they have offered no explanation for the splitting off of two protons. We suppose that the results may be affected by the above-mentioned shift in the equilibria and that only the chelate *I* is formed, dis-

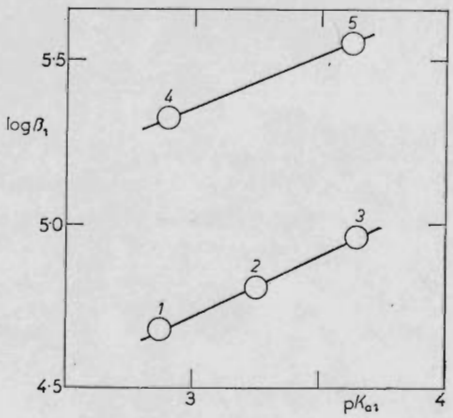
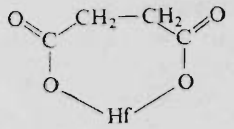


FIG. 4

Correlation of the stability constants β_1(1 H) with the pK_{a1} values of the H_nL acids. Acids: *1* tartaric, *2* malic, *3* glycolic, *4* citric, *5* lactic

sociation of the second proton from the $M(H_3L)^{3+}$ chelate only taking place in weakly acidic solutions[44].



III

The problem of formation of 1-hydroxy acids chelates has also been discussed for trivalent lanthanoid ions. Based on an analysis of their stability constants, Manning has suggested[45] that in lanthanoid complexes with glycolate the ligand is monodentate. Citrate complexes, on the other hand, have been found appreciably more stable as compared with the acetate complexes, which is in favour of the formation of chelate[46]. Such a comparison cannot be so far made for the hafnium complexes because of lack of the stability constant for the $Hf(OOC.CH_3)^{3+}$ complex. However, it can be claimed that hydroxycarboxylates form chelates, based on a mere qualitative comparison of extraction of Hf(IV) in the presence of monocarboxylic and hydroxycarboxylic acids, respectively: while acetic acid does not suppress the extractability of zirconium[47] and hafnium[48] by chelating agents even in concentration 1 mol l^{-1}, the results of the present work (Figs 1 and 2) as well as of earlier studies[19,20] indicate clearly that the OH group at the α carbon of the carboxylic acid affects the stability of the complex appreciably, which can be ascribed to chelation. From this point of view the conclusions concerning Zr(IV) complexes with glycolic[49] and lactic[50] acids in weakly acidic solutions, according to which the ZrO^{2+} cation is bound to monodentate ligands, appear to be incorrect.

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