

HAFNIUM COMPLEXES WITH MALONIC AND MALEIC ACIDS IN AQUEOUS MEDIUM*

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Hafnium complexes with malonic and maleic acids (H_2L) in perchlorate medium were studied by the competitive extraction method. The formation of the $Hf(HL)^{3+}$ chelates with formation constants of $(9.2 \pm 0.3) \cdot 10^5$ and $(5.9 \pm 0.4) \cdot 10^5 \text{ l mol}^{-1}$ ($2M-HClO_4$) respectively was observed in the ligand concentration region of 0.1–1.0M.

Oxalic acid is known as a very good masking agent for Zr(IV) and Hf(IV) and much effort has therefore been devoted to the investigation of oxalate complexes of these metals^{1–4}. Their high stability makes it possible, under suitable conditions, to keep Zr(IV) and Hf(IV) in solution in the form of defined, non-hydrolyzed chelates $M(\text{oxal})_i^{(4-2i)+}$ in a wide acidity range. The value of i changes from 1–2 for acidic solutions⁵ to 4 in neutral solutions⁶ from which it is possible to isolate the $Zr(\text{oxal})_4^{4-}$ anion in the form of crystalline salts⁷.

The stability of zirconium and hafnium complexes with higher dicarboxylic acids is much lower. This fact has been used in practice to determine μg amounts of oxalic acid in the presence of excess of its homologues based on the masking of the reaction of zirconium with azodyes in 1M-HCl (ref.⁸). However, the composition and stability data of these complexes are not complete. In several papers^{9–11} the existence of zirconium–malonic acid (H_2L) complexes has not even been found. Only Jacimirskij and Rajzman¹² found the formation of a hydrolyzed complex $Zr(\text{OH})_3L^-$ in 0.09–0.35 M-HCl medium by the kinetic method based upon the suppression of the catalytic activity of Zr(IV) in the oxidation of iodide by hydrogen peroxide. In the neutral medium, ZrOL precipitates on addition of potassium malonate to the solution of a Zr(IV) salt, and is then dissolved in the excess of malonate under the formation of a complex the composition of which was determined by electrometric methods¹³ as $ZrOL_2^{2-}$. The dissolution of the zirconium malonate precipitate in malonic acid was attributed to the combined effect of the complex formation and the precipitate peptization¹⁴. The existence of anionic malonate complexes of zirconium is also demonstrated by the sorption of Zr(IV) on the anion exchanger from the malonic acid medium at pH 5 (see¹⁵). The potassium¹⁶ and thalious¹⁷ salts of the complex anion ZrL_4^{4-} have been isolated as solids.

Only conflicting qualitative data^{9,11} are available for zirconium complexes with maleic acid. The potassium salt of the complex anion ZrL_4^{4-} is known¹⁶ in the solid state.

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EXPERIMENTAL

Malonic, maleic, fumaric and perchloric acids and sodium perchlorate (Lachema, Brno) were of reagent grade purity. The following extracting agents were used: di-*n*-butylphosphoric acid (DBP) (Koch and Light, England), *N*-benzoyl-*N*-phenyl-hydroxylamine (BPHA) (Lachema, Brno), 2-theonyl-trifluoroacetone (TTA) (Arcochemie, Berlin) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (BEP) (Lachema, Brno).

Four ml of organic and 4 ml of aqueous phases were agitated, depending on the extracting agent used for 1–3 days in ground stoppered test tubes on a rotary shaking machine¹⁸. The aqueous phase contained HClO₄, eventually also NaClO₄ to make the total ionic strength 1.0 or 2.0, radioactive tracer ¹⁷⁵⁺¹⁸¹Hf of the total hafnium concentration $\leq 10^{-6}$ M (see¹⁸), and the competitive ligand. The preliminary experiments showed that solutions of DBP, BPHA and TTA in benzene gave an identical dependence of the hafnium distribution ratio on the malonic acid concentration. For the sake of better reproducibility, benzene solutions of DBP were used in further experiments with malonate complexes. Their concentration is mentioned further in the text. Benzene solutions of BEP were used to measure the stability constants of the hafnium–maleic acid complex. The distribution ratio of hafnium (*D*) was expressed as the ratio of γ -activities¹⁸ of the aliquot parts of organic and aqueous phases. The values of *D*, in the presence of the competitive ligand, given henceforth are average values from at least two measurements. The values of *D*₀ (in the absence of the competitive ligand) are average values from 5–10 measurements.

The effect of maleic acid on the extraction of DBP was studied by the double extraction method using the ¹⁷⁵⁺¹⁸¹Hf radiotracer. Eight ml of $1.5 \cdot 10^{-3}$ M-DBP in benzene were first agitated with a) 8 ml of 2M-HClO₄, and b) 8 ml of 2M-HClO₄ containing 1M-maleic acid. After each extraction had been completed, 4 ml was taken from each organic phase and again agitated with 4 ml of ¹⁷⁵⁺¹⁸¹Hf in 2M-HClO₄. The average of three values of *D* after the double extraction was 1.86 for the extraction without maleic acid, and 1.68 for the extraction in the presence of 1M-maleic acid.

The dissociation constant of maleic acid was determined in the medium of 2.0M-KNO₃ by potentiometric titration using glass electrode G 202 and pH meter 26 with an automatic device Titrigraph (Radiometer, Denmark).

RESULTS AND DISCUSSION

Hafnium–Malonic Acid Complexes

The dependence of log *D* on the total concentration of malonic acid H₂L in 1.0 and 2.0M-HClO₄ is presented in Fig. 1. The graph clearly shows a decrease of *D* from 0.1M-H₂L in 2.0M-HClO₄. In 1.0M-HClO₄ this decrease starts somewhat earlier due to the lower acidity of the medium. The reason why no zirconium–malonate complexes have been found in some papers^{9–11} is obviously a result of the too low ($c \leq 0.01$ M) concentration of H₂L used. Since the measurements using 0.05M-TTA and 0.004M-BPHA in benzene gave identical curves as those in Fig. 1, the decrease of *D* may be attributed to the formation of hafnium–malonate complexes in the aqueous phase and not to the interaction of H₂L with DBP. The latter phenomenon was found in systems containing monocarboxylic acids¹⁹ which cause the decrease of *D* by several orders of magnitude, if DBP is used as the extracting agent; for TTA,

and BPHA, however, the decrease of D under otherwise identical conditions is much smaller.

Both curves in Fig. 1 have slope of only -1 even in regions of the highest H_2L concentrations. This means that the $1:1$ complex predominates in the solution for which, by analogy with the structure of the oxalate complexes, formula *I* could be written. More recent papers on complexes of other cations with malonic acid show, however, also the existence of protonated complexes. A recent potentiometric study of trivalent lanthanides proved the coexistence of malonate and hydrogen malonate complexes in the neutral medium²⁰ in contrast to oxalic acid which forms only normal oxalate complexes²¹. A spectrophotometric study of Al^{3+} , Cu^{2+} , Be^{2+} and UO_2^{2+} chelates with sulphosalicylic and chromotropic acids²² showed that the second proton of the ligand remains bound to the donor oxygen atom of the chelate ring. It has been derived from the correlation of the stability constants with the pK_{a1} values of chelating agents that the chelates of these particular ions with malonic acid have the same structure. It seems therefore more logical to describe the composition of the hafnium chelate in the strong acidic medium as $Hf(HL)^{3+}$ (*II*).

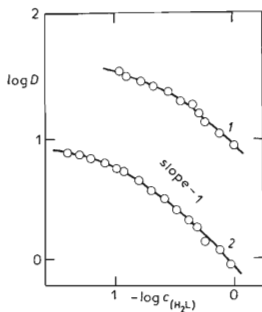


FIG. 1

Dependence of Hafnium Distribution Ratio on the Total Concentration of Malonic Acid

Curve 1: $2.0M-HClO_4$, $1.5 \cdot 10^{-3}M-DBP$ in benzene; 2: $1.0M-HClO_4$, $6.0 \cdot 10^{-4}M-DBP$ in benzene.

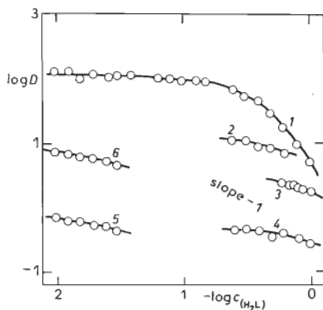
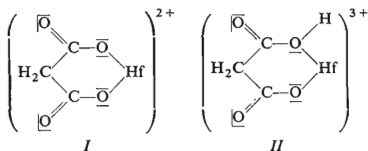


FIG. 2

Dependence of Hafnium Distribution Ratio on the Total Concentration of Maleic and Fumaric Acids for $2.0M-HClO_4$ and Benzene

Curves 1—4: maleic acid, curves 5 and 6: fumaric acid. Curve 1: $1.5 \cdot 10^{-3}M-DBP$, 2: $8 \cdot 10^{-3}M-BPHA$, 3: $6 \cdot 10^{-4}M-BEP$, 4: $2 \cdot 10^{-2}M-TTA$, 5 and 6: $4 \cdot 10^{-4}M-DBP$.



Its existence was proved by the extraction data analysis using a modified method of Day and Stoughton²³. Assuming from Fig. 1 the Hf—ligand ratio in the complex to be 1 : 1, then the total hafnium concentration in the aqueous phase in the presence of malonic acid can be expressed as

$$C_{\text{Hf, aq}} = [\text{Hf}^+] + [\text{Hf}(\text{HL})] + [\text{HfL}] =$$

$$= [\text{Hf}^+] (1 + * \beta(\text{H}) [\text{H}_2\text{L}] [\text{H}]^{-1} + * \beta(2 \text{H}) [\text{H}_2\text{L}] [\text{H}]^{-2}), \quad (1)$$

where Hf(HL) indicates the chelate *II* and $*\beta(\text{H})$ or $*\beta(2 \text{H})$ are equilibrium constants for the formation of the corresponding complexes:

$$* \beta(\text{H}) = [\text{Hf}(\text{HL})] [\text{H}] [\text{Hf}^+]^{-1} [\text{H}_2\text{L}]^{-1}, \quad (2)$$

$$* \beta(2 \text{H}) = [\text{HfL}] [\text{H}]^2 [\text{Hf}^+]^{-1} [\text{H}_2\text{L}]^{-1}. \quad (3)$$

In the above and all following equations charges of ions have been omitted for simplicity. Then:

$$(D_0/D - 1) [\text{H}_2\text{L}]^{-1} = * \beta(\text{H}) [\text{H}]^{-1} + * \beta(2 \text{H}) [\text{H}]^{-2}. \quad (4)$$

Substituting φ for the expression on the left-hand side of equation (4) and defining the additional function $\varphi(\text{H})$ as

$$\varphi(\text{H}) \equiv \varphi[\text{H}] = * \beta(\text{H}) + * \beta(2 \text{H}) [\text{H}]^{-1} \quad (5)$$

we can find the number of liberated protons in the formation of the Hf^{4+} —malonic acid complex from the dependence $\varphi(\text{H})$ on $[\text{H}]$. This has been experimentally studied using the dependence of D on $C_{\text{H}_2\text{L}}$ for various $[\text{H}]$ (1.0, 1.25, 1.50 and 1.75M) at $I = 2$ in HClO_4 — NaClO_4 mixtures using $4 \cdot 10^{-4}$ M-DBP in benzene. The results are given in Table I. It can be seen that $\varphi(\text{H})$ does not depend on $[\text{H}]$ for any value of $C_{\text{H}_2\text{L}}$. It follows that $\varphi(\text{H}) = * \beta(\text{H})$ and that equation (2) governs the hafnium chelate formation. To verify this method an analogous series of measurements

(results not included here) has been carried out on oxalate complexes of hafnium in the region of $1 \cdot 10^{-5} - 1 \cdot 10^{-4} \text{M}$ 10^{-3} ? oxalic acid where the $\text{Hf}(\text{oxal})^{2+}$ complex predominates⁵. In accordance with the structure of these complexes, $\varphi(\text{H})$ is a function of $[\text{H}]$ for any oxalic acid concentration.

The stability constant of the $\text{Hf}(\text{HL})^{3+}$ complex can now be obtained from competitive extraction equilibria using the equation

$$(D_0/D - 1) [\text{HL}]^{-1} = \beta(\text{Hf}(\text{HL})), \quad (6)$$

where $\beta(\text{Hf}(\text{HL})) = [\text{Hf}(\text{HL})] [\text{Hf}]^{-1} [\text{HL}]^{-1}$. Since the acidic proton in the HL anion is bound by a strong chelate bonding²⁴, one can assume that the chelate *II* is formed from malonic acid by substitution of that particular chelate-bonded proton. The second ionization constant ($\text{p}K_{a2}$) of malonic acid describes its dissociation²⁵. The concentration of the HL anion has therefore been calculated from the expression

$$[\text{HL}] = K_{a2} C_{\text{H}_2\text{L}} [\text{H}]^{-1}, \quad (7)$$

where $C_{\text{H}_2\text{L}}$ is the total concentration of malonic acid. The anion HL, as defined by equation (7), corresponds to a hypothetical ionization equilibrium in which only the less acidic, chelate-bonded proton has dissociated from the H_2L molecule. A similar approach was used to solve equilibria of 2,4-dihydroxy-azodyes complexes where in the process of the chelate formation a metal cation is substituted for the less acidic proton of the O-hydroxyl group²⁶. The value of $K_{a2} = 8 \cdot 62 \cdot 10^{-6}$ ($I = 1 \cdot 0$) from reference²¹ was used to calculate the $[\text{HL}]$ according to equation (7). The concentration of the HL anion which had been formed by the ionization of the more acidic

TABLE I
Evidence of the Existence of the $\text{Hf}(\text{HL})^{3+}$ -Complex Using the $\varphi(\text{H})$ Function

$C_{\text{H}_2\text{L}}$ mol l^{-1}	$1 \cdot 0 \text{M} \cdot \text{H}^+$			$1 \cdot 25 \text{M} \cdot \text{H}^+$			$1 \cdot 50 \text{M} \cdot \text{H}^+$			$1 \cdot 75 \text{M} \cdot \text{H}^+$		
	<i>D</i>	φ	$\varphi(\text{H})$	<i>D</i>	φ	$\varphi(\text{H})$	<i>D</i>	φ	$\varphi(\text{H})$	<i>D</i>	φ	$\varphi(\text{H})$
0	10.32	—	—	4.86	—	—	2.65	—	—	1.50	—	—
0.1	4.52	12.3	12.3	2.54	9.00	11.25	1.37	9.40	14.1	0.85	7.65	13.4
0.2	2.94	12.6	12.6	1.91	9.54	11.9	0.95	8.95	13.4	0.59	7.70	13.45
0.4	1.69	12.75	12.75	1.01	9.52	11.9	0.59	8.65	13.0	0.39	6.80	11.9
0.6	1.12	13.7 ^a	13.7	0.68	10.25 ^a	12.8	0.41	9.00	13.5	0.28	7.22	12.65
1.0	0.67	15.5 ^a	15.5	0.41	10.8 ^a	13.5	0.26	9.15	13.75	0.17	7.77	13.6

^a Probably indication of the formation of a higher complex.

TABLE II
Competitive Extraction Equilibria of Hafnium–Malonate Complexes

C_{H_2L} mol l ⁻¹	1.0M-HClO ₄			2.0M-HClO ₄		
	<i>D</i>	[HL] · 10 ⁻⁷	β(Hf(HL)) · 10 ⁻⁵	<i>D</i>	[HL] · 10 ⁷	β(Hf(HL)) · 10 ⁻⁵
0	9.57 ^a	—	—	47.3 ^a	—	—
0.037	7.23	3.19	10.2	—	—	—
0.047	7.09	4.05	8.64	—	—	—
0.057	6.52	4.91	9.52	—	—	—
0.074	6.07	6.38	9.04	—	—	—
0.093	5.43	8.02	9.52	35.4	4.01	8.35
0.106	5.37	9.14	8.56	32.1	4.57	10.25
0.144	4.38	12.4	9.50	29.9	6.20	9.52
0.19	3.72	16.4	9.58	28.4	8.20	8.10
0.25	3.15	21.5	9.50	24.6	10.7	8.62
0.32	2.59	27.6	9.74	21.05	13.8	9.06
0.40	2.20	34.5	9.70	19.9	17.2	8.02
0.45	1.70	38.8	11.9	16.9	19.4	9.26
0.52	1.40	48.8	12.0	14.0	24.4	9.76
0.71	1.21	61.2	11.3	11.2	30.6	10.5
0.93	0.92	80.2	11.6	9.68	40.1	9.71

^a *D*₀.

proton was neglected because $K_{a1} = 2.56 \cdot 10^{-3}$ (see²¹) and its concentration is therefore much smaller than C_{H_2L} . The calculation for the curves in Fig. 1 is presented in Table II. For 1.0M-HClO₄ β(Hf(HL)) was determined as the average of the values in the 0.037 – 0.40M-H₂L region as $(9.4 \pm 0.15) \cdot 10^5$ l mol⁻¹. Its increase at higher values of C_{H_2L} indicates the formation of the Hf(HL)₂²⁺ complex. For 2.0M-HClO₄ the value of β(Hf(HL)) = $(9.2 \pm 0.25) \cdot 10^5$ l mol⁻¹ as the average from the 0.093 – 0.93M-H₂L region was obtained.

Hafnium–Maleic Acid Complexes

In this case (Fig. 2, curve 1), the behaviour of DBP is completely different from that of the other extracting agents. The multiple extraction shows that the steeper decrease of *D* can be at least partly caused by the decrease of the distribution ratio of DBP in the presence of maleic acid. Similar is the behaviour of fumaric acid (curves 5, 6). The fact that the same relationship between *D* and the maleic acid concentration is observed for the other three extracting agents (curves 2–4) makes it possible to attribute it to the competitive formation of maleinate

complexes. The decrease of D is relatively small and becomes obvious at $[H_2L] > 0.1M$. This is in contrast to the data of Connick and McVey⁹ who have found for the system TTA-2M-HClO₄ that in the presence of 0.05M-maleic acid, 25% of ⁹⁵Zr in the aqueous phase is complexed. In the concentration region presented in Fig. 2, the slope does not even reach the value of -1 , so that one can assume the coexistence of Hf⁴⁺ ions and, by analogy with malonate complexes, the Hf(HL)³⁺ complex. By using the same approach as in case of malonate complexes, the stability constant was determined from extraction data for $6 \cdot 10^{-4}M$ -BEP in benzene ($D_0 = 0.131$) in 0.56 – 1.0M-H₂L to be $\beta(Hf(HL)) = (5.9 \pm 0.4) \cdot 10^5 l mol^{-1}$. From the dissociation constants of maleic acid²⁵ it seems obvious that its HL⁻ anion is more stabilized in the chelate ring than that of malonic acid. The value of $K_{a2} = 2.5 \cdot 10^{-6}$ ($I = 2.0$), which had been determined potentiometrically, was used to calculate the maleic acid HL⁻ anion concentration.

The Schwarzenbach's model²⁷ of the chelate effect derives from the speculation that the chelate ring is formed in two steps. In the first step the bidentate ligand is linked to the central atom by one donor atom. The other end of the molecule with the second donor atom remains free and the probability of its coordination to the metal ion decreases with the increasing number of atoms between both donor groups. The same magnitude of the $\beta(Hf(HL))$ values for malonic and maleic acids is, however, not in accordance with this model. The explanation may be offered by the *cis*-structure of maleic acid which keeps both donor groups at short distance. The ring closure is therefore more likely to take place which results in the stabilization of the maleic acid chelate.

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