

## 4-(2-THIAZOLYLAZO)RESORCINOL AS AN EXTRACTION AGENT

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The distribution of Ag, Cd, Co, Eu, Hf, Ni, Sc and Zn between aqueous solutions of  $\text{HClO}_4$  and  $\text{NaClO}_4$  with an ionic strength of 0.1 or 1–2 (with Hf) and solutions of 4-(2-thiazolylazo)-resorcinol ( $\text{H}_2\text{A}$ ) in isoamyl alcohol was studied. It follows from the study of the dependences of the distribution ratio for the metals on the pH of the aqueous phase and on the analytical and equilibrium concentrations of  $\text{H}_2\text{A}$  in the organic phase that Cd, Ni and Zn are extracted from weakly acidic or neutral aqueous phases in the form of complexes  $\text{M}(\text{HA})_2$  or  $\text{MA}$ ; non-extractable complexes of the  $\text{MA}_2^{2-}$  type are also formed. Cobalt is extracted from weakly acidic aqueous solutions as the  $\text{Co}(\text{HA})_3$  complex. Salts of Ag, Eu and Sc are extracted to a low degree, are adsorbed on the vessel walls and concentrate at the phase boundary. Hf is also poorly extracted into the organic phase from a medium of 1–2M- $\text{HClO}_4$  and 1M-HCl.

4-(2-Thiazolylazo)resorcinol (TAR) is employed in the analytical chemistry of heavy and rare metals as a complexing agent, suitable chiefly for photometric determinations, and as a chelometric indicator<sup>1,2</sup>. Compared to the analogous 4-(2-pyridylazo)-resorcinol (PAR), it is easier to prepare. In the papers published so far employing the liquid extraction method, complex compounds of TAR ( $\text{H}_2\text{A}$ ) with various metals have the character of ion-associates, a suitable organic ammonium salt usually being the cation. The greatest attention has been paid to the extraction of Cd and Co (ref<sup>3,4</sup>); among organic solvents, isoamyl alcohol and methyl isobutyl ketone have been preferred, as  $\text{H}_2\text{A}$  is relatively soluble in these solvents and the organic phase can be employed directly for the determination of the given elements by atomic absorption spectrophotometry. Among reagents analogous to  $\text{H}_2\text{A}$ , 5-(2-thiazolylazo)-2,6-dihydroxypyridine has been used for the extraction of Pd (ref.<sup>5</sup>).

## EXPERIMENTAL

## Chemicals and Apparatus

*p.a.*  $\text{H}_2\text{A}$  from Lachema, Brno was employed; its purity was checked using TLC on MN silica gel G plates (Macharey-Nagel, Hungary) and compared with the substance from Aldrich Co., USA. Stock solutions of the radioactive isotopes,  $^{46}\text{Sc}$ ,  $^{60}\text{Co}$ ,  $^{63}\text{Ni}$ ,  $^{65}\text{Zn}$ ,  $^{109}\text{Cd}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{152+154}\text{Eu}$ , and  $^{175+181}\text{Hf}$ , in the form of the perchlorates or nitrates, were prepared from the commercial substances by diluting more concentrated solutions or by dissolving the oxides in

acids ( $\text{HfO}_2$ —HF and multiple evaporation with  $\text{HClO}_4$ ,  $\text{Eu}_2\text{O}_3$ — $\text{HNO}_3$ ). They had the following initial activities in  $10^3$  disintegrations/s related to 1 ml of experimental solution and the following concentrations (mol.  $\text{l}^{-1}$ ) in the aqueous phase:  $^{46}\text{Sc}$ : 1.1—3.7,  $5.6 \cdot 10^{-7}\text{M}$ ;  $^{60}\text{Co}$ : 7.4, 8.8.  $10^{-6}\text{M}$ ;  $^{63}\text{Ni}$ : 5.6,  $5 \cdot 10^{-4}\text{M}$ ;  $^{65}\text{Zn}$ : 74—370,  $5 \cdot 10^{-6}\text{M}$ ;  $^{109}\text{Cd}$ : 22.2,  $3.5 \cdot 10^{-10}\text{M}$ ;  $^{110\text{m}}\text{Ag}$ : 7.4,  $6.9 \cdot 10^{-7}\text{M}$ ;  $^{152+154}\text{Eu}$ : 0.48,  $5 \cdot 10^{-8}\text{M}$ ;  $^{175+181}\text{Hf}$ : 25.9,  $4 \cdot 10^{-6}\text{M}$ . The radioactive purity of the isotopes used, except that of Ni, was checked using single-channel spectrometer, Tesla NZQ 714 T and Vakutronic VAM-120 (GDR) with spectrometric crystal SKG 1S, 50.35 mm, and  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  etalons. The  $\gamma$ -radioactivity of the individual liquid samples was measured using a 45.50 mm NaI (TI) well-crystal and a Vakutronic VAM-15D instrument (GDR), the  $\beta$ -activity of  $^{63}\text{Ni}$  was measured on a Tricarb 3375 instrument (Packard, USA) employing liquid scintillators. The aqueous phase pH was measured potentiometrically with an EIL instrument (Electronic Instruments, Richmond, England) using a GHS 23 glass electrode and an RJ-23 saturated calomel reference electrode or with an OP-205 instrument (Radelkis, Hungary) and an OP-711-I/A glass and OP 810 saturated calomel electrode.

### Procedure

The aqueous phase with a volume of 10 ml, containing the appropriate radioactive isotope and solutions of  $\text{HClO}_4$  and  $\text{NaClO}_4$  with an ionic strength of 0.1 (except for Hf, where the ionic strength equalled 1—2 and was adjusted with  $\text{HClO}_4$  and  $\text{NaClO}_4$  or HCl and NaCl), was mixed with 10 ml of an  $\text{H}_2\text{A}$  solution in isoamyl alcohol (iAmOH) and shaken on a rotating shaker for 8 hours at  $20 \pm 1^\circ\text{C}$ ; preliminary experiments showed that this time is quite sufficient for establishment of the extraction equilibria. The phases were separated, the aqueous phase pH was measured and then 5 ml portions were transferred from both phases into glass ampoules for the  $\gamma$ -activity measurement or into 20 ml glass vessels for the  $\beta$ -activity measurement by liquid scintillation.

Distribution of the reagent alone between 1M-(H, Na) Cl and benzene was measured spectrophotometrically using a Spectromom 201 instrument (Hungary) with 1 cm glass cuvettes, diluting part of the aqueous phase aliquot with concentrated perchloric acid in a ratio of 1 : 1. The absorbances were then measured in this medium and compared with a calibration curve obtained under identical conditions. For the measurement of the pH of the aqueous phase, the pH meter was calibrated with standard HCl solutions.

## RESULTS AND DISCUSSION

### *Determination of the $\text{H}_2\text{A}$ Dissociation Constant by the Extraction Method*

The dependence of the  $\text{H}_2\text{A}$  distribution ratio on the aqueous phase pH is given in Fig. 1 for an ionic strength of 1 in a medium of 1M-HCl + NaCl, employing benzene as the organic phase; the dissociation constant,  $K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{A}]}{[\text{H}_3\text{A}^+]}$ , was determined from this dependence. The  $\text{H}_3\text{A}^+$  species was formed by protonation of the hydrogen atom in the heterocyclic nucleus. The higher ionic strength, differing from that commonly employed in the present work was necessitated by the higher  $K_{a1}$  value. Only the molecular form,  $\text{H}_2\text{A}$ , is transferred into the organic phase; it is evident from Fig. 1 that an ion-associate of the type,  $\{\text{H}_3\text{A}^+, \text{Cl}^-\}$  is not extracted into benzene. For the distribution ratio,  $D_{\text{H}_2\text{A}}$ , it then holds that  $D_{\text{H}_2\text{A}} = \frac{[\text{H}_2\text{A}]_{\text{org}}}{[\text{H}_2\text{A}]_{\text{aq}}}$

$/[\text{H}_3\text{A}^+] + [\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]$ , the square brackets with subscript org and without a subscript denoting the equilibrium concentrations in the organic and aqueous phases, respectively. As the dissociation constant of the —OH group of resorcinol in the *para* position with respect to the azo group is  $K_{a2} = [\text{H}^+][\text{HA}^-]/[\text{H}_2\text{A}] = 10^{-6.23}$  and the constant for the —OH group in the *ortho* position is  $K_{a3} = [\text{H}^+][\text{A}^{2-}]/[\text{HA}^-] = 10^{-9.44}$  (see ref.<sup>6</sup>) the last two terms in the denominator in the equation for the  $D_{\text{H}_2\text{A}}$  value can be neglected assuming that the pH of the aqueous phase does not exceed a value of 4.0 during the study of the  $D_{\text{H}_2\text{A}} = f(\text{pH})$  dependence. If the distribution constant is defined as  $K_D(\text{H}_2\text{A}) = [\text{H}_2\text{A}]_{\text{org}}/[\text{H}_2\text{A}]$ , then the reagent distribution ratio can be expressed by the relationship,  $D_{\text{H}_2\text{A}} = K_D(\text{H}_2\text{A})/(1 + [\text{H}^+]/K_{a1})$ . The  $D_{\text{H}_2\text{A}} = f(\text{pH})$  dependence can then be expressed by a simple curve and the intercept of its linear parts (Fig. 1) gives the value  $\text{p}K_{a1}$  1.56. This value is in good agreement with the work of Stanley and Cheney<sup>7</sup>, but differs from the earlier papers<sup>6,8</sup>. The value of  $K_D(\text{H}_2\text{A}) = 10^{1.79}$ , obtained from Fig. 1, is roughly twice that obtained in ref.<sup>4</sup>, but the aqueous phase employed in the latter work contained 0.03M acetate buffer. This is in good agreement with the dependence of the ionic strength value in the aqueous phase on the value of the distribution constant for organic reagents.

#### Optimum Conditions for Metal Extraction

In choosing the organic solvent, several factors were considered: a)  $\text{H}_2\text{A}$  solubility in the organic phase, b) the metal distribution ratio in the absence of  $\text{H}_2\text{A}$ , c) the metal distribution ratio in the presence of  $\text{H}_2\text{A}$  at a defined analytical concentration.

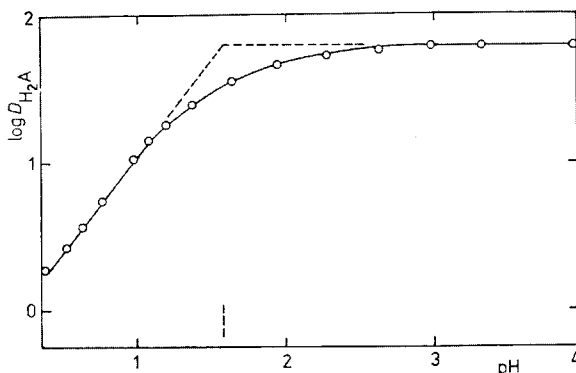


FIG. 1

Distribution of  $\text{H}_2\text{A}$  between 1M-(H, Na)Cl and Benzene in Dependence on the pH of the Aqueous Phase

$$c_{\text{H}_2\text{A}} = 1 \cdot 10^{-4} \text{M}, I = 1.$$

On evaluation of the properties of the organic solvents which were available it was found that best results are obtained when isoamyl alcohol is used. The suitability of this organic solvent is enhanced by the fact that complexes extracted into it can be determined by atomic absorption photometry with direct intake of the organic solvent into the photometer flame<sup>3</sup>. Cyclohexanone, methyl cyclohexanone and methyl isobutyl ketone were not suitable because of their poor selectivity and their greater ability to extract metals in the absence of  $H_2A$  and benzene because of the poor solubility of  $H_2A$ . We stated in previous papers<sup>3,4</sup> that benzene creates difficulties in atomic absorption determinations of metals. An undesirable coloured flame was formed when a Perkin-Elmer 290 instrument was used.

*Extraction of Cd, Ni and Zn complexes.* The dependence of the logarithm of the distribution ratio for these three metals on the pH of the aqueous phase is given in Figs 2 and 3; it can be seen that the extraction curves exhibit a maximum. This maximum becomes more pronounced and shifts to more acidic regions with increasing analytical concentration of  $H_2A$  (Fig. 3); the maximum slope of the left-hand part of the extraction curves reaches a value of 2 and decreases down to a value of  $-4$  with Cd. The slope analysis of the  $\log D_M = f(\log c_{H_2A})$  dependence at a constant aqueous phase pH was chiefly directed to determining the composition of the negatively charged non-extractable cadmium complexes; the following results were

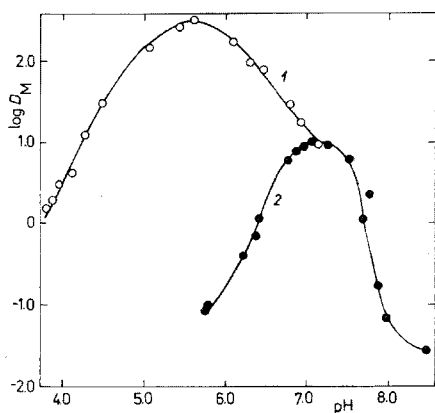


FIG. 2

Distribution of Nickel and Cadmium between a Solution of  $H_2A$  in Isoamyl Alcohol and  $0.1M (H, Na)ClO_4$  and  $NaOH$

$c_{H_2A} = 1 \cdot 10^{-2}M$ , nickel  $\circ$ ,  $2 \cdot 10^{-3}M$ , cadmium  $\bullet$ .

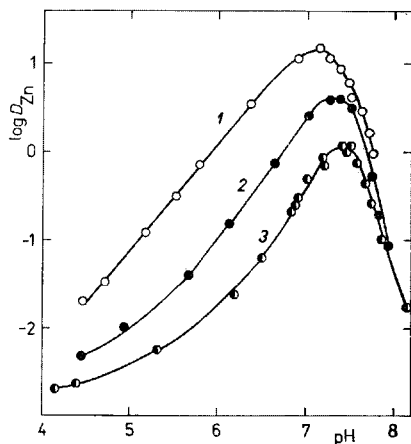


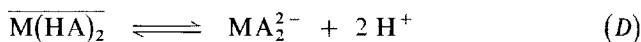
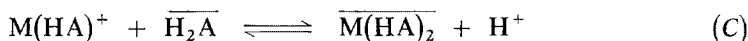
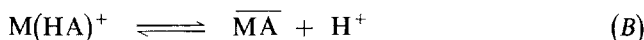
FIG. 3

Distribution of Zinc between a Solution of  $H_2A$  in Isoamyl Alcohol and  $0.1M (H, Na)ClO_4$

$c_{H_2A} = \circ 1 \cdot 10^{-2}M$ ,  $\bullet 2 \cdot 10^{-3}M$ ,  $\bullet 5 \cdot 10^{-4}M$ .

obtained: Cd – pH 7.30, slope 1.1; pH 7.50, slope 1.5; pH 7.8, slope 1.8; Zn – pH 6.2, slope 1.8.

The extraction of cadmium at pH 8.3 in the presence of  $2 \cdot 10^{-3} \text{M-H}_2\text{A}$  and  $3 \cdot 10^{-1} \text{M-tri-n-octylamine}$  was also studied. The  $\log D_{\text{Cd}}$  value increased by two units compared with the original value, obtained in the absence of tri-n-octylamine. On the basis of the above data, the following schemes can be proposed for the extraction of Cd, Ni and Zn:



*i.e.* stepwise complex formation is assumed and only neutral particles pass into the organic phase (indicated by a horizontal line in the scheme), provided a large organic ion enabling the formation of an extractable ion associate is not present. The above scheme enables definition of the extraction constant  $K_{\text{ex},1} = [\overline{\text{MA}}]_{\text{org}} [\text{H}]^2 / [\text{M}] \cdot [\text{H}_2\text{A}]_{\text{org}}$ , or  $K_{\text{ex},2} = [\overline{\text{M}(\text{HA})_2}]_{\text{org}} [\text{H}]^2 / [\text{M}] [\text{H}_2\text{A}]_{\text{org}}^2$ , the value of  $\log K_{\text{ex},1}$  equals, for Cd:  $-11.0 \pm 0.2$ , for Zn:  $-10.4 \pm 0.2$ , for Ni:  $-5.5 \pm 0.2$ . The value

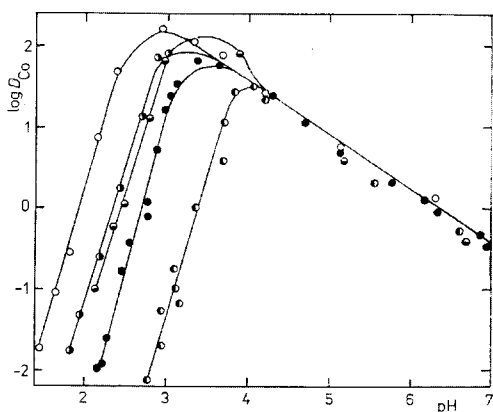


FIG. 4

Distribution of Cobalt between Solutions of  $\text{H}_2\text{A}$  in Isoamyl Alcohol and  $0.1 \text{M-(H, Na)ClO}_4$   
 $c_{\text{H}_2\text{A}} = \circ 1 \cdot 10^{-2} \text{M}$ ,  $\bullet 5 \cdot 10^{-3} \text{M}$ ,  $\blacksquare 2 \cdot 10^{-3} \text{M}$ ,  $\circ 5 \cdot 10^{-4} \text{M}$ ,  $\bullet 2 \cdot 10^{-3} \text{M}$  in the presence  
of  $1 \cdot 10^{-2} \text{M}$  picric acid.

of  $\log K_{ex,2}$  for zinc equals  $-7.9 \pm 0.2$ . In the calculation, the value of the equilibrium concentration of  $H_2A$  in the organic phase was replaced by the analytical concentration, because the distribution constant of  $H_2A$  between  $iAmOH$  and the aqueous phase  $K_D(H_2A) = 10^{3.08}$ , as follows from work<sup>4</sup>, and  $c_{H_2A} \gg c_M$ . The stability constants of the  $M(HA)^+$  and  $M(HA)_2$  complexes in the aqueous phase,  $\beta_n = [M(HA)_n]/[M][HA^-]^n$ , can be calculated from the extraction curves using common methods<sup>9</sup>. The fact that the uncharged complex with the composition  $MA$  must be considered with all three metals renders the calculation so complicated that it was abandoned.

**Extraction of Co.** In contrast to the previous three metals, this extraction proceeds in weakly acidic aqueous media (Fig. 4). It is also necessary to bear in mind that, in the presence of atmospheric oxygen, divalent cobalt is easily oxidized to trivalent in aqueous solutions in the presence of azodyes<sup>10</sup>, which was observed in some further extraction studies<sup>11-13</sup>. It can be concluded from the shape of the extraction curves and the slope analysis that cobalt passes into the organic phase according to the scheme



where the value of  $K_{ex,3} = [Co(HA)_3]_{org} [H^+]^3 / [Co^{3+}] [H_2A]_{org}^3 = 0.3 \pm 0.1$ .

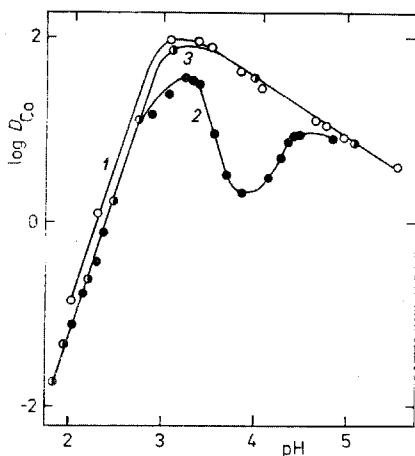


FIG. 5

Distribution of Cobalt between a Solution of  $5 \cdot 10^{-3} M$ - $H_2A$  in Isoamyl Alcohol and a Solution of  $(H, Na)ClO_4$

Ionic strength:  $\circ$  1.0,  $\bullet$  0.1,  $\bullet$  0.01.

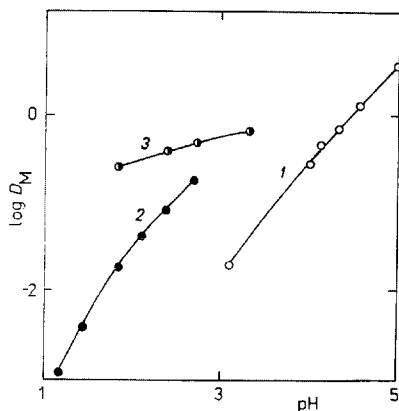


FIG. 6

Distribution of Europium, Scandium and Silver between a Solution of  $1 \cdot 10^{-2} M$ - $H_2A$  in Isoamyl Alcohol and  $0.1 M$ - $(H, Na)ClO_4$

$\circ$  Eu,  $\bullet$  Sc,  $\bullet$  Ag.

Because dissociation of an OH-group in the *para* position of the  $H_2A$  molecule can be ignored in weakly acidic aqueous media to pH 4.0, constants  $\beta_n$ , defined above, could be calculated. This was, however, prevented by the decrease in the extraction curves, visible in their right part. This decrease cannot be attributed to hydrolysis of cobalt alone and was not explained in this work. The decrease is also dependent on the magnitude of the ionic strength  $I$  in the aqueous phase (Fig. 5); it has an analogous shape for  $I = 1.0$  to  $0.1$  but increases for  $I = 0.01$ . The effect of the analytical concentration of cobalt on its distribution ratio at a given pH and  $c_{H_2A}$  appears to be a constant dependence of  $\log D_{Co}$  at  $c_{Co} \leq 2 \cdot 10^{-5} M$ . At higher Co concentrations a decrease in  $D_{Co}$  occurs; for  $c_{H_2A} = 1 \cdot 10^{-2} M$  and  $c_{Co} = 2.2 \cdot 10^{-4} M$ , pH 1.90,  $\log D_{Co}$  decreases by 0.6; at pH 4.22 it decreases by as much as two units. This confirms the assumed formation of polymers in the aqueous phase.

Further, the effect of adding picric acid (HP) in dependence on the pH of the aqueous phase was studied (Fig. 4). In regions corresponding to the existence of cationic complexes of the  $Co(HA)^{2+}$  and  $Co(HA)_2^+$  type in the presence of  $1 \cdot 10^{-2} M$ -HP, the original value of  $D_{Co}$  increases by one order in the pH region 2.1–2.9 through formation of more extractable ion associates  $\{Co(HA)_n^{m+}, P_m^-\}$ . HP alone does not extract cobalt.

The extraction of Eu, Sc and Ag was studied in dependence on the acidity of the aqueous phase for  $c_{H_2A} = 1 \cdot 10^{-2} M$  (Fig. 6). For all three studied metals it is without practical significance as the  $D_M$  values are small. It is accompanied by adsorption on the vessel walls and in the interface, for Eu at  $pH \geq 5.0$ , for Sc at  $pH \geq 2.7$  and for Ag at  $pH \geq 3.4$ , caused both by the low stability of the complex and by the formation of hydrolytic products.

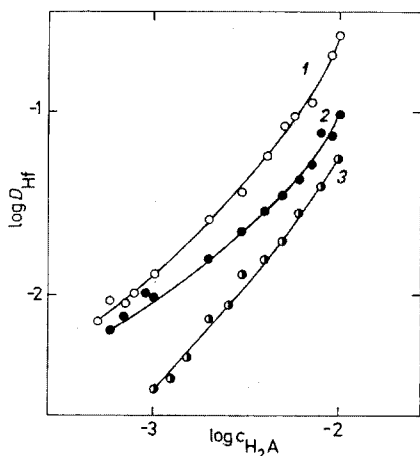


FIG. 7

Distribution of Hafnium between a Solution of  $H_2A$  in Isoamyl Alcohol and 1.2M- $HClO_4$  or 1M-HCl

Aqueous phase: ○ 1M- $HClO_4$ ,  
● 2M- $HClO_4$ , ◐ 1M-HCl.

*Extraction of Hf.* The distribution ratio  $D_{\text{Hf}}$  has low values in the studied interval of analytical concentrations of  $\text{H}_2\text{A}$  in 1–2M- $\text{HClO}_4$  and 1M- $\text{HCl}$  media (Fig. 7) and it follows from the slope analysis that 1 : 1 and 1 : 2 complexes are most important in the aqueous phase. The complexes of hafnium have a positive charge. Consequently we assume that, similar to the extraction of hafnium with some acidic organophosphorus reagents<sup>14,15</sup>, extractable ion associates of the type  $\{\text{Hf}(\text{H}_2\text{A})_n^{4+}, \text{X}_4^-\}$  are formed, where  $\text{X}^-$  is the anion of a mineral acid. In the studied region of analytical concentrations of  $\text{H}_2\text{A}$ , formation of 1 : 3 and 1 : 4 complexes cannot be considered and the stability of the hafnium complexes formed will not be particularly large.

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