

COMPLEXES OF HAFNIUM WITH DIANTIPYRINYLMETHANE IN 2M-HCl MEDIUM*

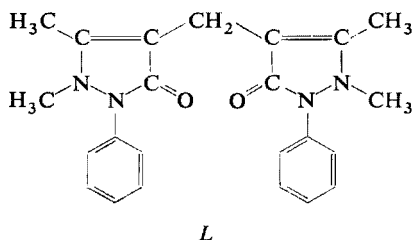
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Received November 16th, 1974

Hafnium complexes with diantipyrylmethane (L) were studied by competitive extraction method in 2M-HCl medium. Complexes HfL_2^{4+} and HfL_3^{4+} with stability constants of $\beta_2 = (2.5 \pm 0.5) \cdot 10^7 \text{ l}^2 \text{ mol}^{-2}$ and $\beta_3 = (1.6 \pm 0.1) \cdot 10^{11} \text{ l}^3 \text{ mol}^{-3}$ are formed. Diantipyrylmethane acts in these complexes as a bidentate oxygen-containing ligand forming an eight membered chelate ring in the hafnium chelates.

Diantipyrylmethane (L) forms colourless complexes with zirconium and hafnium in solution; they were studied by competitive spectrophotometry¹⁻³. Their stability is quite high and is comparable with *e.g.* the stability of the complexes of nitrilotriacetic and phosphoric acid in 1M-HCl (ref.⁴), and causes interference in the photometric determination of titanium⁵. In order to make the data so far published¹⁻⁴ more accurate, competitive extraction method in 2M-HCl medium was used in the present paper to study the hafnium complexes with this ligand.



EXPERIMENTAL

Diantipyrylmethane was prepared by condensation of antipyrine with formaldehyde⁶ as a monohydrate. As extractants, 2-thenoyltrifluoroacetone (Arcochemie, Berlin, GDR), di-*n*-butylphosphoric acid (Koch and Light, England) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HA), prepared according to Jensen⁷, were employed. Benzene and hydrochloric acid were of reagent grade quality.

* Part XIX in the series Extraction of Hafnium; Part XVIII: This Journal 40, 1711 (1975).

An indicator solution, ^{181}Hf in 10M-HCl, was prepared from a stock solution in 10M- HClO_4 (ref.⁸). An aliquot portion was diluted to an acidity of 1M- HClO_4 and ^{181}Hf was extracted twice into 0.1M-TTA in benzene. The combined extracts were diluted with benzene to a concentration of 0.01M-TTA and back-extracted twice with 10M-HCl. The combined back-extracts (^{181}Hf in 10M-HCl) were finally freed of dissolved TTA by repeated shaking with benzene.

The methods employed for extraction experiments and the radioactivity measurement have been described in previous communications^{8,9}. The aqueous phase contained diantipyrylmethane and $^{181}\text{Hf(IV)}$ in 2M-HCl medium (L is insoluble in HClO_4) and was shaken with benzene solutions of the extractants overnight. The phase volumes were 4 ml. The distribution ratio of hafnium (D) was expressed in terms of the ratio of the γ -activities measured in 2 ml aliquot parts of the organic and aqueous phases after the extraction.

Back-extraction experiments were carried out in order to determine the distribution of L as follows: 10 ml 0.1M-L in 2M-HCl were shaken with 10 ml benzene. After the extraction, 2 ml $6 \cdot 10^{-3}\text{M-HA}$ in benzene were added to 2 ml of the benzene phase and this solution was used as the organic phase for the extraction of ^{181}Hf from 2M-HCl. A $\log D$ value equal to 1.15 was found as an average from three determinations. According to Fig. 1, this value corresponds to an overall L concentration of $\leq 1.5 \cdot 10^{-4}\text{M}$ in the second extraction, *i.e.* the concentration of L transferred into benzene during the first extraction. Hence the distribution ratio of L is $\leq 1.5 \cdot 10^{-3}$ for the benzene-2M-HCl system; therefore, the distribution of L was neglected in further considerations.

RESULTS

Fig. 1 shows the dependence of $\log D$ on the concentration of L in the aqueous phase. Because of the small distribution ratio for L, its overall concentration can be considered to be its equilibrium concentration. It is evident that the curves have similar shapes for all three extractants. Therefore interaction of L with the extractants can be

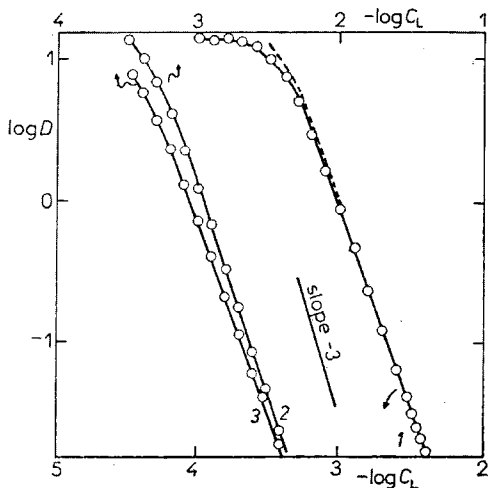


FIG. 1

The Dependence of the Distribution Ratio of Hafnium on the Overall Diantipyrylmethane Concentration

2M-HCl-benzene system. Curve: 1 $3 \cdot 10^{-3}\text{M-HA}$; solid line calculated assuming the existence of the 1:2 and 1:3 complexes; dashed line calculated assuming the existence of the 1:3 complex; 2 $7.5 \cdot 10^{-2}\text{M-TTA}$; 3 $1.5 \cdot 10^{-3}\text{M-DBP}$.

excluded, as is also indicated by the low distribution ratio L , and the decrease in D with increasing concentration of L can be ascribed to the formation of competing complexes of hafnium in the aqueous phase.

The curve for $3 \cdot 10^{-3}$ M-HA was used in the following calculations, because of its good reproducibility. The D values given are averages from 3–5 determinations. As hafnium forms chlorocomplexes HfCl^{3+} and HfCl_2^{2+} in 2M-HCl (ref.¹⁰), the decrease in D with increasing concentration of L must be expressed by the equation

$$D_0/D = (1 + \sum_{i=1} \beta_i [L]_i + \sum_{j=1} \beta_{j,\text{Cl}} [\text{Cl}]_j) / (1 + \sum_{j=1} \beta_{j,\text{Cl}} [\text{Cl}]_j), \quad (1)$$

where D_0 is the distribution ratio of hafnium in 2M-HCl in the absence of L and β_i and $\beta_{j,\text{Cl}}$ are the stability constants for the hafnium complexes with L and chloride ions, respectively. The values of the polynomial, $\sum_{i=1} \beta_i [L]^i$, denoted as φ and calculated using the values, $\beta_{1,\text{Cl}} = 2 \cdot 2 \text{ l mol}^{-1}$ and $\beta_{2,\text{Cl}} = 0 \cdot 95 \text{ l}^2 \text{ mol}^{-2}$ (ref.¹⁰), are given in Table I.

The sharp decrease in D from the lowest concentrations of L and approaching

TABLE I

The Competitive Extraction Equilibrium in the Hf^{4+} -Diantipyrylmethane System

$C_L \cdot 10^{3a}$	D_{Hf}	φ	$\varphi[\text{L}]^{-3} \cdot 10^{-11}$	$\varphi' \cdot 10^{-7}$
0.316	10.27	8.2	2.60	3.1
0.400	7.69	14.1	2.20	2.3
0.500	5.13	25.7	2.14	2.1
0.63	2.93	51.8	2.07	2.8
0.80	1.64	100	1.95	2.6
1.00	0.892	190	1.90	2.7
1.26	0.473	370	1.85	2.8
1.60	0.242	730	1.78	2.4
2.00	0.128	1 390	1.74	2.2
2.50	0.068	2 610	1.67	—
3.00	0.0425	4 200	1.55	—
3.16	0.0336	5 300	1.68	—
3.25	0.0312	5 720	1.66	—
3.50	0.0249	7 150	1.66	—
3.75	0.0218	8 200	1.56	—
4.00	0.0171	10 450	1.63	—

^a In mol . l⁻¹.

of the curve to the tangent with a slope of -3 at high concentrations of L indicate that a complex with a $Hf : L$ ratio equal $1 : 3$ predominates in the aqueous phase. Therefore, $\varphi = \beta_3[L]^3$ as a first approximation, and the stability constant β_3 can be determined from the relationship $\beta_3 = \lim_{[L] \rightarrow \infty} (\varphi/[L]^3)$. It can be seen from Table I that the term $\varphi/[L]^3$ is independent of $[L]$ for $[L] > 2.5 \cdot 10^{-3} M$ and the average of its values yields the constant, $\beta_3 = (1.6 \pm 0.1) \cdot 10^{11} l^3 mol^{-3}$. The extraction curve calculated using this constant is in good agreement with the experimental curve for $[L] > 10^{-3} M$; at lower concentrations, the calculated D values are somewhat higher. This indicates the presence of a lower complex. If it is assumed that this is HfL_2^{4+} , its stability constant can be determined from the function, $\varphi' = (\varphi - \beta_3[L]^3)/[L]^2$, neglecting the first complex, HfL^{4+} . It can be seen from Table I that function φ' is actually constant at lower concentrations of L , verifying the existence of the HfL_2^{4+} complex and indicating that the HfL^{4+} complex, if it is formed at all under the given conditions, is present at a very low concentration and is imperceptible by the present method. (The difference between the experimental and calculated curves cannot be explained by assuming the existence of the HfL^{4+} and HfL_3^{4+} complexes, as the appropriate function, $(\varphi - \beta_3[L]^3)/[L]$ is not constant at low ligand concentrations). The average of the values of function φ' gives the stability constant for complex HfL_2^{4+} , $\beta_2 = (2.5 \pm 0.5) \cdot 10^7 l^2 mol^{-2}$. The literature^{1,3} quotes the values, $\beta_2 = 3.2 \cdot 10^{11} l^2 mol^{-2}$ and $\beta_3 = 8.3 \cdot 10^{16} l^3 mol^{-3}$ for zirconium. We have no explanation for this discrepancy.

DISCUSSION

The composition of the hafnium complexes with diantipyrylmethane with $Hf : L$ ratios of $1 : 2$ and $1 : 3$, found in the present paper, is in good agreement with the results of the study of complexes of this ligand with zirconium by competitive spectrophotometry¹⁻³. Babko and coworkers have found ZrL_2^{4+} and ZrL_3^{4+} complexes in media $0.05-1M-HCl$. Complexes with a metal-to-ligand ratio of $1 : 3$ are also formed by zirconium in $0.04-1M-HCl$ and hafnium in $0.04-0.5M-HCl$ with a derivative of L , bis-(1-*p*-sulphophenyl-2,3-dimethyl-5-pyrazolonyl)methane¹¹.

Babko and Shtokalo² assume that zirconium complexes with diantipyrylmethane are cationic complexes of the amocomplex type, with metal-to-nitrogen coordination. The presence of two oxygen atoms in the molecule of L and much greater tendency of $Zr(IV)$ and $Hf(IV)$ to form $M-O$ bonds rather than $M-N$ ^{12,13}, however, render this assumption rather improbable. It has been verified by IR spectroscopy¹⁴ that, in complexes of zirconium and of other metals with antipyrine, the metal is coordinated to the antipyrine carbonyl group. Busev and coworkers¹⁵ have also found that, in salts of diantipyrylmethane of the type of $(LH^+)_2OsCl_6$, it is the oxygen atom of L that is protonized; the authors ascribe a structure to the LH^+ cation containing a chelate intramolecular hydrogen bond with the proton

bound to both carbonyl groups. It is therefore probable that L acts as a bidentate ligand in the complexes of zirconium and hafnium. Our experiments with antipyrine as a competing ligand are in agreement with this assumption; under conditions identical with those given in Fig. 1, antipyrine does not cause a decrease in the hafnium distribution ratio. This fact excludes the existence of the M—N bond in the studied complexes since the two ligands are equivalent from the point of view of the metal-to-nitrogen coordination.

The fact that the 1 : 1 complex was not detected is interesting from the point of view of stepwise complex formation in solution, which usually proceeds according to statistical laws by stepwise addition of ligands to the central atom. It occurs relatively rarely that some intermediate is missing in the series, M, ML, ..., ML_N; this has mostly been encountered with halide complexes of heavy metals^{16,17}, where some complexes, usually with an odd number of coordinated ligands, have unstable steric configuration and consequently are not formed in solution. However, this is rather exceptional with bidentate ligands and the complexes with L are the only examples of this kind for zirconium and hafnium. The studied chelates are further interesting from the point of view of the existence of the uncommon eight-membered chelate ring, which is probably stabilized by the ligand structure. Similar stabilization was found with the seven-membered ring of the hafnium chelate with maleic acid¹⁸.

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Translated by M Štulíková.