

EXTRACTION OF METAL CHELATES WITH 3,5-HEPTANEDIONE AND 5-METHYL-2,4-HEXANEDIONE

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The extraction of the chelates of Cu(II), Co(II), Ni(II), Fe(III), Be(II), Al(III), Ga(III), In(III), U(VI), Th(IV), Zr(IV) and Hf(IV) with solutions of 3,5-heptanedione and 5-methyl-2,4-hexanedione in benzene was studied. The extraction curves and the calculated values of the extraction constants and $pH_{1/2}$ are given. It has been found that Co, Ni, Zr and Hf are incompletely extracted; the conditions for complete extraction of the other chelates have been found.

In the previous paper¹ the properties of C₇ β -diketones were studied in order to find the most suitable derivative which could be used pure or dissolved in a diluent as a stationary phase in analytical reversed phase partition chromatography, so-called extraction chromatography. On the basis of the dissociation and distribution constants, the diketone solubility in water and the enol content, 5-methyl-2,4-hexanedione (*I*) has been chosen as the most suitable of the diketones studied. 2,4-Heptanedione had very similar properties to *I* and 3-methyl-2,4-hexanedione decomposed on contact with alkaline aqueous solutions, so that only 3,5-heptanedione (*II*) remained for comparison of its extraction properties with the selected diketone, *I*.

Before extraction separation with these reagents could be studied under dynamic conditions, *i.e.* in a column, static extraction was studied. Reagents *I* and *II* have very similar structures from the viewpoint of the formation of extractable chelates and consequently no significant difference in the results obtained in the extraction of metal ions can be expected. However, we studied the extraction of some metal ions with both reagents, since the comparison of the results obtained provides a means for checking their correctness.

This work has been aimed at finding which groups of metal ions can be separated by static extraction of their chelates with the diketone studied and which will have to be separated by extraction chromatography. Extraction of the Cu(II), Co(II), Ni(II), Fe(III), Be(II), Al(III), Ga(III), In(III), U(VI), Th(IV), Zr(IV) and Hf(IV) chelates was studied. For most of these ions it can be assumed that they will be readily extracted on the basis of the results obtained with other β -diketones.

EXPERIMENTAL

Chemicals and instruments: Solutions of metal perchlorates were prepared by dissolving commercial substances (Ni(ClO₄)₂·6 H₂O, E. Merck, Darmstadt), pure metals (at least 99.99%)

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(Fe, Ga, Al, In) oxides (Cu, Co) or carbonates (Be) in a 10% excess of perchloric acid. The solutions of U, Th, Zr and Hf perchlorates were obtained from the nitrates by precipitation with ammonia and dissolution of washed precipitates in a 10% excess of perchloric acid. The stock perchlorate solutions were diluted to a metal concentration of 1–2 mol/l and their pH adjusted to 1 with the acid. The concentrations of the solutions, which have not been prepared from pure metals, were determined gravimetrically², by weighing the oxides (U, Be, Hf, Zr) or chelometrically with murexide or xylenol orange³ (Cu, Co, Ni, Th). Solutions of metal perchlorates for extractions, with concentrations of 10^{-3} – 10^{-4} M, were prepared daily by diluting the stock solutions and their ionic strength was adjusted to $I = 0.1$ (NaClO₄).

Diketones *I* and *II* were prepared and purified by the procedures described earlier¹. They were used for extractions as 0.1M solutions in benzene (*p.a.*), which was not saturated with water. The volume change of the phases after the extraction was neglected.

The extractions were performed in ground-glass stoppered test tubes in rotation, $t = 25 \pm 1^\circ\text{C}$. A PHK 1 pH-meter (Mikrotechna, Prague) and a SEAJ combined electrode (Laboratorní přístroje, Prague) were employed, using the procedures and calibration described earlier¹. The spectrophotometric determinations were carried out on a VSU 2 instrument (C. Zeiss, Jena), the fluorimetric measurements on a Spekol instrument from the same firm with the FK adaptor and the ZV amplifier. Atomic absorption spectrometric determinations were carried out with an AA 5 Varian-Techtron instrument.

Procedure: A gradually increasing pH of the aqueous phase was adjusted by adding 1M-NaOH from a microburette (capacity 200 μl) to the test tubes containing the aqueous and organic phase

TABLE I
The Methods Employed for the Determination of the Metal Ions^a

Ion	Method, conditions	Reagent	Calibration range ^b p.p.m.
Cu ²⁺	s ^c , 435 nm, CCl ₄	diethyldithiocarbamate	0.25 — 17.5
Fe ³⁺	s, 505 nm, hydroquinone	1,10-phenanthroline	0.1 — 1
Co ²⁺	s, 420 nm	nitroso-R-salt	0.1 — 1
Ni ²⁺	s, 460 nm, K ₂ S ₂ O ₈	biacetyldioxime	0.2 — 2
Be ²⁺	f ^d , 365 nm excit., standard GG 17	morin	0.0035 — 0.03
Al ³⁺	f, 365 nm excit., standard GG 17	8-hydroxyquinoline	0.04 — 0.2
Ga ³⁺	s, 565 nm, C ₆ H ₆	Rhodamine B	0.14 — 1.4
In ³⁺	s, 400 nm, CHCl ₃	8-hydroxyquinoline	1.15 — 11.6
UO ₂ ²⁺	s, 400 nm, CHCl ₃	8-hydroxyquinoline	1.9 — 11.6
Th ⁴⁺	s, 410 nm	morin	0.18 — 0.9
	s, 545 nm	thoron	0.89 — 5.3
Hf ⁴⁺	s, 525 nm	alizarinsulphonate	0.25 — 7.5
Zr ⁴⁺	s, 525 nm	alizarinsulphonate	0.25 — 3

^a According to ref.⁴, ^b linear dependence of the measured signal on the concentration, ^c spectrophotometry, ^d fluorimetry.

TABLE II

The Time Dependence of the Metal Chelate Extractions

Extractant: 0.1M 5-methyl-2,4-hexanedione in benzene. The absorbances in a 1 cm cuvette at the wavelengths specified in Table I are given.

Metal	Analyzed phase	Time						
		5 min	15 min	30 min	1 h	2 h	3 h	4 h
Cu	aq	0.120	0.122	0.082	0.080	0.091	—	—
Fe	aq	0.003	0.002	0.000	0.000	0.000	—	—
Co	org	—	—	0.118	0.124	0.131	0.126 ^a	0.130 ^b
Ni	org	—	—	0.093	0.128	0.136	0.148	0.152
Be	org	30 ^c	40	43	50	52	52	—
Al	aq	66 ^c	64	63	64	64	—	—
Ga	aq	0.056	0.008	0.009	0.010	0.012	0.013	—
In	aq	0.044	0.066	0.073	0.042	0.034	0.041	—
U ^d	org	0.612	0.617	0.609	0.615	0.610	—	—
Th	aq	0.115	0.118	0.117	0.121	0.126	—	—
Hf	aq	0.280	0.280	0.278	0.284	0.280	—	—

^a 3.5 h, ^b 5 h, ^c the fluorimeter scale values, ^d the extract absorbance was measured directly at 362 nm.

TABLE III

The Extraction Constants and $\text{pH}_{1/2}$ Values

M	5-Methyl-2,4-hexanedione					3,5-Heptanedione				
	$c_M \cdot 10^4$ mol . l ⁻¹	i^a	n^b	$\log K_{ex}$	$(\text{pH}_{1/2})_{0.1}$	$c_M \cdot 10^4$ mol . l ⁻¹	i	n	$\log K_{ex}$	$(\text{pH}_{1/2})_{0.1}$
Cu	3.896	7	1.92	-3.41	2.78	3.896	7	1.93	-3.77	2.95
Fe	1.344	15	2.99	-0.75	1.25	2.686	10	3.04	-1.40	1.46
Be	5.326	5	2.06	-4.22	3.05	5.326	9	2.06	-4.62	3.24
Al	1.134	4	3.03	-7.82	3.58	22.69	5	3.10	-7.71	3.49
Ga	4.000	5	3.02	-4.24	2.40	10.00	4	2.69	-3.88	2.44
In	1.265	6	3.34	-7.12	3.13	6.326	6	2.87	-6.33	3.20
U ^c	2.033	9	2.19	-6.71	4.06	2.033	6	2.16	-7.31	4.38
Th	0.3821	6	3.14	—	—	0.3821	8	3.01	—	—

^a The range of the series from which the regression coefficients were calculated, ^b the regression line slope; ^c assuming the formation of UO_2L_2 .

($V_{\text{aq}} = V_{\text{org}}$). The contents of the test tubes were shaken until equilibrium was established, the phases were separated and a five-millilitre aliquot was taken from the aqueous or organic phase (or both) for analysis.

Analyses: Both the aqueous and the organic phase were mineralized, because of the presence of excess extracting agent, either by heating with sulphuric acid to white fumes followed by heating with hydrogen peroxide to the formation of a colourless solution, or, more rapidly, by evaporation with nitric and then perchloric acids. In addition to atomic absorption spectrometry, the methods surveyed in Table I were employed for the determination of metal ions in the mineralized solutions.

The time dependence of the extraction of metal chelates with I: The organic and aqueous phases, the pH values of which were always the same for a given element, $I = 0.1$ (NaClO_4), were shaken for various times and after phase separation either the organic or the aqueous phase was analyzed by the methods given in Table I. The results obtained are given in Table II.

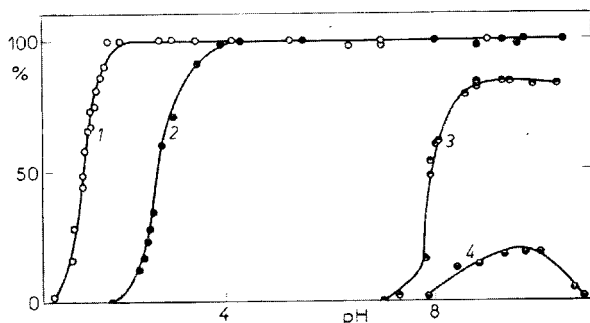


FIG. 1

The Dependence of the Percentage Extraction of Fe(III), Co(II), Ni(II) and Cu(II) with a 0.1M Solution of 5-Methyl-2,4-hexanedione in Benzene on the pH of the Aqueous Phase
 $c_M \approx 10^{-4}M$, 1 Fe, 2 Cu, 3 Co, 4 Ni.

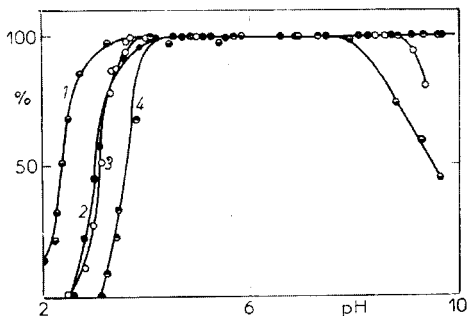


FIG. 2

The Dependence of the Percentage Extraction of Be(II), Al(III), Ga(III) and In(III) with a 0.1M Solution of 5-Methyl-2,4-hexanedione in Benzene on the pH of the Aqueous Phase
 $c_M \approx 10^{-4}M$, 1 Ga, 2 Be, 3 In, 4 Al.

The extraction curves: A selected pH value was adjusted in a mixture of 10 ml of the aqueous phase with 10 ml of the 0.1M reagent solution and the mixture was shaken until equilibrium was established. From the metal concentrations determined, percentage extraction values were calculated and expressed as the extraction curves given in Figs 1–3 for reagent *I* and in Figs 4–6 for reagent *II*.

RESULTS AND DISCUSSION

The time required for extraction equilibration was found only for reagent *I* at a single pH value. We assumed that the extraction kinetics for reagent *II* would be virtually identical because of its properties similar to *I* and the pH value was always chosen so that $E > 50\%$. The analytical methods employed were sufficiently sensitive to detect a 1% change in the original concentration of the metal ions.

After mineralization of organic phases containing Co, Ni, Th and U, results lower than would correspond to material balance were sometimes found; this may be caused by volatility of the β -diketonates. The metal contents in the organic phases were then calculated from the difference of the original amount of metal and its content in the equilibrium aqueous phase. Mineralization of the uranyl β -diketonates was difficult. Although colourless and transparent solutions were obtained by repeated treatment with nitric and perchloric acids, they turned yellow again on pH adjustment to 6–7.

It follows from the $E = f(\text{pH})$ dependence that complete extraction with a 0.1M solution of reagent *I* is achieved for the metal ions (as perchlorates) in the following pH ranges (the corresponding values for a 0.1M solution of *II* in benzene are given in parentheses): Fe(III) 2.1–9.0 (2.5–8.7); Cu(II) 4.0–10.5 (4.2–10.1); Be(II) 4.2–9.6 (4.4–9.4); Al(III) 4.1–9.6 (4.8–7.7); Ga(III) 4.1–7.9 (5.2; a precipitate was formed in the aqueous phase at $\text{pH} > 7.7$); In(III) 3.7–8.6 (4.0–6.3); U(VI) 4.9–7.4 (4.9–7.0); Th(IV) 3.8–8.9 (3.8–9.3). This dependence could not be studied for Zr(IV), since a solid phase separated at the boundary of the two phases. The other metal ions were partially extracted. The pH values at E_{\max} and the E_{\max} values for reagent *I* are as follows (the same data for *II* are given in parentheses): Co(II) pH 8.6–10.3, 82% (8.6–10.6, 70%); Ni(II) pH 10, 19% (9.4, 6.5%); Hf(IV) pH 1.78, 86% (1.65, 49%).

If the degree of extraction of the metal ions studied with reagents *I* and *II* is compared with that for metal acetylacetonates⁵, it is found that incomplete extraction occurred with the same metals in both cases. However, reagents *I* and *II* completely extract aluminium and copper, while a 0.1M acetylacetonone solution in benzene extracts at most 90% Al and 90% Cu. The pH range, within which the metal extraction is complete, is broader for reagents *I* and *II* than for acetylacetonone.

The extraction curves for Fe(III), Al(III), Co(II) and Ni(II) with *II* have also been studied by Koshimura and Okubo⁶. The pH ranges for complete or maximum extraction which they found could have been affected by competing complexation equilibria of the ions with acetates of borates contained in the buffer solutions. Still,

their pH range values agree with those found here, except for Fe(III), where we have found a broader pH range for complete extraction (2.5–8.7) than the cited authors (pH 2.5–5), and for Al(III), where our range is narrower than theirs (4.5–11). In view of the protolytic reactions of these ions, we consider our values to be more accurate, which is also verified by comparison with similar values for acetylacetone.

The $E = f(\text{pH})$ dependence was recalculated to $\log D = f(\text{pH})$. From the linear portion of this dependence, corresponding to the equation, $\log D = \log K + n \text{pH}$, where $K = K_{\text{ex}}[\text{HL}]_{\text{org}}^n$, the K and n values were found by regression analysis. The

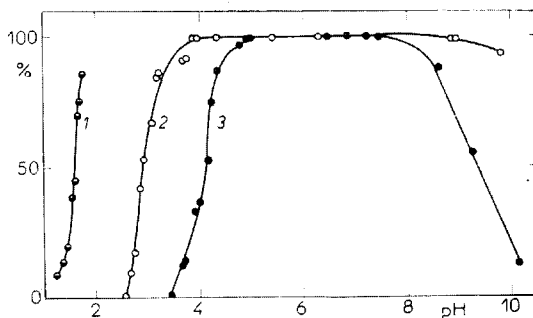


FIG. 3

The Dependence of the Percentage Extraction of Hf(IV), Th(IV), and U(VI) with a 0.1M Solution of 5-Methyl-2,4-hexanedione in Benzene on the pH of the Aqueous Phase
 $c_M = 10^{-3} - 10^{-4} \text{M}$, 1 Hf, 2 Th, 3 U.

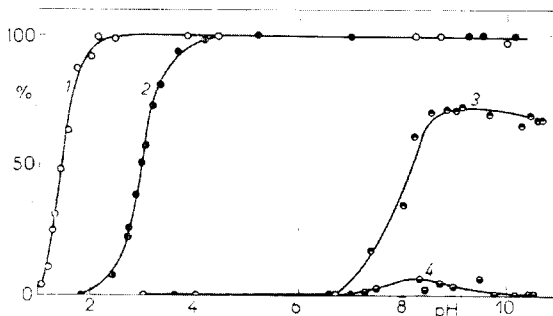


FIG. 4

The Dependence of the Percentage Extraction of Fe(III), Co(II), Ni(II) and Cu(II) with a 0.1M Solution of 3,5-Heptanedione in Benzene on the pH of the Aqueous Phase
 $c_M \approx 10^{-4} \text{M}$, 1 Fe, 2 Cu, 3 Co, 4 Ni.

values of $K_{ex} = [ML_n]_{org}/[M^{n+}]_{aq} [HL]_{org}^n$ were calculated from the relation for K , into which the original reagent concentration in the organic phase, $c_{HL,org}$, was substituted for I , since for $pH < 9$ and neglecting the amount of the reagent bound in complex ML_n it holds that $c_{HL,org} = [HL]_{org}$ with a difference smaller than 0.01. $c_{HL,org}$. For reagent *II*, which is more soluble in water than *I* (ref.¹), its equilibrium concentration in the organic phase was calculated from the relationship, $[HL]_{org} = c_{HL,org}/(1 + K_D^{-1})$, where K_D is the distribution constant of *II*; this relationship also holds with the above accuracy for $pH < 9$. A linear $\log D$ vs pH dependence was observed for all the ions studied for $pH < 5$. The K_{ex} values calculated, together with the slope values, n , and the $(pH_{1/2})_{0.1}$ values for both reagents are given in Table III.

The K_{ex} values found in this work for extraction of Cu(II), Fe(III) and Al(III) differ significantly from those published by Koshimura and Okubo⁶. These authors ad-

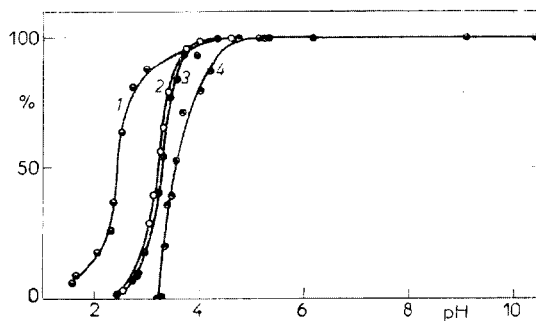


FIG. 5.

The Dependence of the Percentage Extraction of Be(II), Al(III), Ga(III) and In(III) with a 0.1M Solution of 3,5-Heptanedione in Benzene on the pH of the Aqueous Phase
 $c_M \approx 10^{-4}M$, 1 Ga, 2 In, 3 Be, 4 Al.

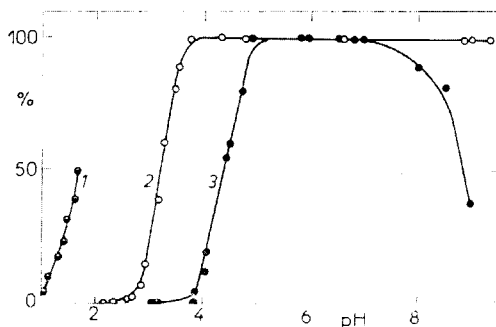


FIG. 6

The Dependence of the Percentage Extraction of Hf(IV), Th(IV) and U(VI) with a 0.1M Solution 3,5-Heptanedione in Benzene on the pH of the Aqueous Phase
 $c_M = 10^{-3} - 10^{-4}M$, 1 Hf, 2 Th, 3 U.

justed the pH values with buffer solutions of unspecified concentrations. It should also be mentioned that the dissociation constant values for *II* determined by us¹, which was close to the values obtained by other authors, differs from the value given by Koshimura and Okubo.

To the extraction of the individual ions it can be added:

Copper(II): The theoretical value of slope n of the regression straight line was found. Up to pH < 3.01 (or 3.19 for *II*), Cu^{2+} ions predominate in the aqueous phase; at higher pH the CuL^+ complex starts to form and the extracted species is apparently CuL_2 .

Iron(III): In this case the theoretical slope was also found. At pH > 9 (or 8.7 for *II*), a slight decrease in percentage extraction was observed ($\approx 3\%$), which might be caused by partial hydrolysis of Fe^{3+} . A different and unusual shape of the *Fe(III)* extraction curve was obtained by Koshimura and Okubo, who found that the percentage extraction decreases down to 60% at pH > 6 and then increases again with increasing pH (at pH ≈ 12 , $\approx 70\%$).

Cobalt(II), *nickel(II)*: The incomplete extraction observed can be caused by incomplete displacement of water molecules from the hydration shell of the aquo-ions by reagent HL. The percentage extraction increases when a more concentrated extractant is employed.

Beryllium(II): Be^{2+} ions predominate in the solution at pH < 3.6; at higher pH, the BeL^+ complex begins to form.

Aluminium(III): The linear log D vs pH dependence has the theoretical slope value at pH < 3.5; at higher pH (3.5–5.5) the slope decreases to $n = 1$, so that in this range the AlL_2^+ species predominates in the aqueous phase. Slopes of less than 3 have also been found by other authors for complexes of trivalent metals with β -diketones^{6–8}.

Galium(III), *indium(III)*: The theoretical slopes were obtained for the two ions at pH < 2.7 or 3.6, respectively (2.7 or 3.4 for reagent *II*). At pH > 8 (reagent *I*) or 5.2 (reagent *II*) for Ga and pH > 8.5 (*I*) or 6.3 (*II*) for In, reactions of the ions with hydroxide ions take place.

Uranium(VI): The slopes found for the two reagents differed somewhat from the theoretical value. At pH > 7.4 (*I*) or 7 (*II*), the percentage extraction decreased due to side reaction with OH^- ions. The K_{ex} value given in Table III is calculated assuming that the UO_2L_2 complex is extracted. In extraction with acetyl acetone, extraction of the $\text{UO}_2\text{L}_2 \cdot \text{HL}$ complex has also been demonstrated^{5,9}. We did not determine the complex composition in the organic phase. If a species of this composition were extracted, log K_{ex} would equal -5.71 (*I*) or -6.31 (*II*).

Thorium(IV): The K_{ex} value was not calculated, since the theoretical slope was not obtained in the studied pH range. In a pH range of 2.7–3.2 (I) or 2.7–3.5 (II) $n = 3$, so that species ThL^{3+} predominates in the aqueous phase under these conditions. The same n value has been calculated by other authors⁷ for extraction of Th with acetylacetone.

Zirconium(IV), hafnium(IV): Complete extraction of the two metals could not be attained. A colourless crystalline substance (tetragonal bipyramids) was observed at the phase boundary at $c_{Zr} = 1.4 \cdot 10^{-4}M$ and pH 1.2–1.5, the amount of which increased with increasing pH of the aqueous phase and which did not disappear even on prolonged shaking. Because of the pH range in which the work was carried out (pH < 1.8), precipitation of hydroxides or hydroxy salts of the two metals cannot be assumed; moreover, the crystalline character of the precipitate is not characteristic of those compounds.

From the K_{ex} values it can be presumed that stationary extraction with either of the two reagents can separate the following pairs of metals, without masking and in the presence of concentrations of the same order of magnitude: Cu—Ni, Cu—Co, Fe—Al, Fe—In, and Fe—U. Extraction chromatography will have to be employed for separations of other metal pairs or for samples with metal contents of different orders of magnitude.

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