C, is different from either A or B, since H is trans to the group Y and not to CO.

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Registry No. IrCl(CO)(PPh₃)₂, 15318-31-7; IrBr(CO)(PPh₃)₂, 15842-08-7; IrI(CO)(PPh₃)₂, 19472-16-3; IrCl(CO)(PMePh₂)₂,

15318-32-8; IrBr(CO)(PMePh₂)₂, 19354-07-5; IrI(CO)(PMePh₂)₂, 42482-35-9; IrCl(CO)(PMe₂Ph)₂, 21209-82-5; IrBr(CO)(PMe₂Ph)₂, 21209-83-6; IrI(CO)(PMe₂Ph)₂, 21209-87-0; IrCl(CO)(AsPh₃)₂, 23954-42-9; IrCl(CO)(AsMePh₂)₂, 52720-84-0; IrCl(CO)(AsMe₂Ph)₂, 21209-84-7; IrCl(CO)(P-*t*-BuMe₂)₂, 36466-98-5; IrCl(CO)(P-*t*-BuEt₂)₂, 36490-55-8; IrCl(CO)(P(*t*-Bu)₂Me)₂, 34365-68-9; IrCl-(CO)(P(*t*-Bu)₂Et)₂, 34365-70-3; RhCl(CO)(PPh₃)₂, 15318-33-9; RhBr(CO)(PPh₃)₂, 17070-17-6; RhI(CO)(PPh₃)₂, 21006-49-5; RhCl(CO)(AsPh₃)₂, 16970-35-7; RhBr(CO)(AsPh₃)₂, 38581-34-9; RhI(CO)(AsPh₃)₂, 55222-24-7; HCl, 7647-01-0.

Contribution from the Department of Physical Chemistry and Center for Marine Research, "Rudjer Bošković" Institute, Zagreb, Croatia, Yugoslavia

Precipitation and Complex Formation of Zirconium(IV) with Maleic and Phthalic Acids at 25 °C[1a]

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The precipitation of zirconium from aqueous solution of zirconyl chloride (1 mM) and potassium maleate (0.2–100.0 mM) and also with potassium phthalate (0.1–50 mM) was investigated at pH 2–11, at 25 °C, by using the tyndallometric technique. In the precipitation diagram two soluble regions have been observed, where zirconium forms complexes with maleate and phthalate anions. Electrophoretic and pH measurements were used to study soluble complexes. The evidence for the existence of zirconium-hydrolyzed anions has been obtained. In the precipitation region the following precipitates were identified: Zr(OH)₃(OOCCH=CHCOOH) (I), Zr(OH)₃(OOCC₆H₄COOH) (II), and zirconium hydroxide. Infrared spectra were used to characterize the mode of coordination of carboxylate ligands. From physical and infrared spectral data it was concluded that these solid complexes are of polymeric nature.

Introduction

Complexes of zirconium with dibasic carboxylic acids have been studied, as seen in the literature, mostly in a solid form. Complexes having coordinated one[2–4] and two phthalic acid molecules[5] were isolated, but no detailed interpretation of physical and spectral properties has been given. Although Intorre and Martell[6] have been emphasizing for 20 years that very few ligands are known which form water-soluble complexes with zirconium stable at high pH, there was little research in that direction. Zirconium hydrolysis[7,8] and zirconium oxalate[9] have been investigated in detail. Interesting biological experiments with zirconium[10] have inspired us to continue the zirconium research, particularly with respect to the complex formation with oxygen donor ligands such as phthalate and maleate ions.

Experimental Section

Zirconium oxychloride octahydrate, ZrOCl₂(H₂O)₈, was used to make a stock solution. It was analyzed for zirconium by complexometric titration with titriplex III. Solutions of maleic acid (0.2 mol dm⁻³), potassium hydrogen phthalate (0.5 mol dm⁻³), phthalic acid (0.1 mol dm⁻³), and potassium hydroxide (0.5 mol dm⁻³) were prepared from Merck, Darmstadt, p.a. chemicals. For determination of precipitation diagrams, the method described earlier by Težak et al.[11]

Table I. Chemical Composition of the Precipitate Formed between Zr(IV) and Maleic Acid at Different pH Values

[Zr], mM	[maleic acid], mM	[KOH], mM	pH	% found C	% found H	% found Zr
1	40	40	2.2	17.09	2.48	35.08
1	4	9	3.75	9.57	2.47	44.99
1	2	6.5	4.2	7.85	2.38	46.27
10	20	30	2.3	16.07	2.52	36.01
10	20	40	2.6	15.25	2.55	36.80
10	20	60	5.5	12.23	2.51	42.65
10	20	80	6.6	8.57	3.04	47.77

was used. For quantitative determination of the composition of the solid phases, precipitates were left to settle and then filtered, washed with water, and dried in a desiccator.

In electrophoretic experiments, a solution of radioactive zirconium was used. The solutions of ⁹⁵Zr(⁹⁵Nb) were prepared from the original solution of ⁹⁵Zr(⁹⁵Nb) in oxalic acid (The Radiochemical Centre Ltd., Amersham), by evaporation to dryness, with addition of concentrated nitric acid and hydrogen peroxide several times.[12] After evaporation, the appropriate supporting electrolyte was added to the residue. The specific activities of these solutions were 1 μCi/20 μL (20 μL was the solution volume applied at the starting point of each electrophoretic strip).

Turbidity measurements, used in precipitation studies, were performed with a Zeiss tyndallometer attached to a Pulfrich photometer. For infrared spectra, a Perkin-Elmer 257 spectrophotometer was used (KBr pellets and Nujol mulls). X-ray photographs were taken in 0.3-mm capillaries, with a Philips 57.54-mm camera and an exposure time of 1.5 h.

The electrophoretic experiments were performed as described previously,[13] except that the temperature of the gasoline was maintained constant by means of an ultrathermostat.[14,15] The concentration of potassium hydrogen maleate and potassium hydrogen phthalate varied from 1 × 10⁻² to 4 × 10⁻² mol dm⁻³. The details of the experimental conditions were published earlier.[16]

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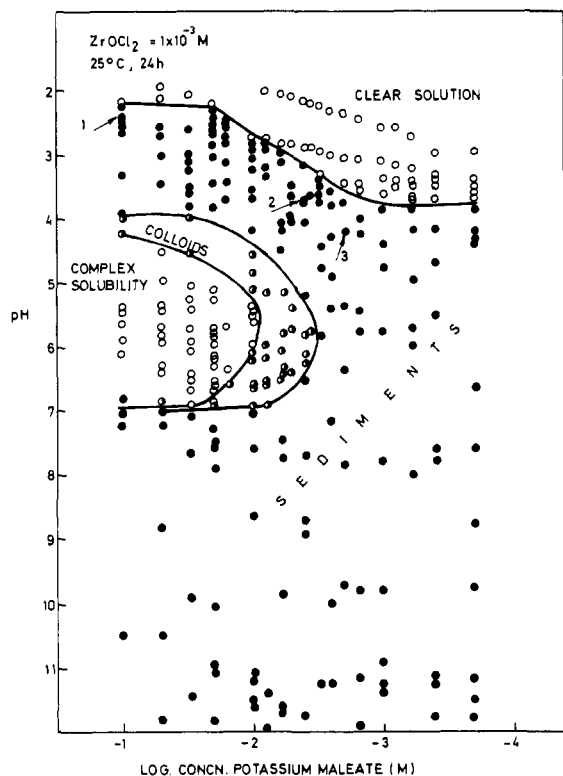
Figure 1. Precipitation diagram of zirconium salts formed in potassium maleate solutions at different pH values (25 °C, 24-h aging).

Results

Figure 1 represents the ground plan of the precipitation diagram of zirconium salts in the presence of potassium maleate. Turbidity was measured as a function of pH and log [potassium maleate] for the constant concentration of $ZrOCl_2$, equal to 1×10^{-3} mol dm^{-3} 24 h after mixing the precipitation components. The precipitation diagram is quite similar to the one determined for zirconium oxalate.[9] In the acid region, zirconium maleate is more soluble than zirconium oxalate. The range of complex solubility in excess of ligand is greater for zirconium oxalate. Precipitates were isolated for characterization in the presence of a high excess of maleic acid (sample no. 1) and in the presence of a small excess of maleate (sample no. 2 and no. 3), for the concentration of $ZrOCl_2$ equal to 1 $\times 10^{-3}$ mol dm^{-3}. For higher concentration of $ZrOCl_2$ equal to 1×10^{-2} mol dm^{-3}, complexes were isolated in the presence of a small excess of maleate but at various pH values. The experimental conditions and the results of chemical analyses are presented in Table I. In the pH region lower than pH 3, the precipitate was of a defined composition corresponding to $Zr(OH)_3(OOCCH=CHCOOH)$. At pH >3, the hydrolysis of zirconium takes place.[7] Table I also shows that, in the presence of maleate in a small excess, a continuous higher percent of zirconium in the precipitate was found. Soluble complexes were formed in the presence of an excess of maleate.

In order for some idea about the composition of the soluble region to be obtained, a typical titration experiment is presented in Figure 2.

The two titration curves are compared. Curve 1 presents the titration curve of pure potassium maleate solution while curve 2 illustrates the same solution, only with the addition of $ZrOCl_2$, equal to 1×10^{-3} mol dm^{-3}. The difference, Δ, in the pH between the two curves compared at the zero ad-

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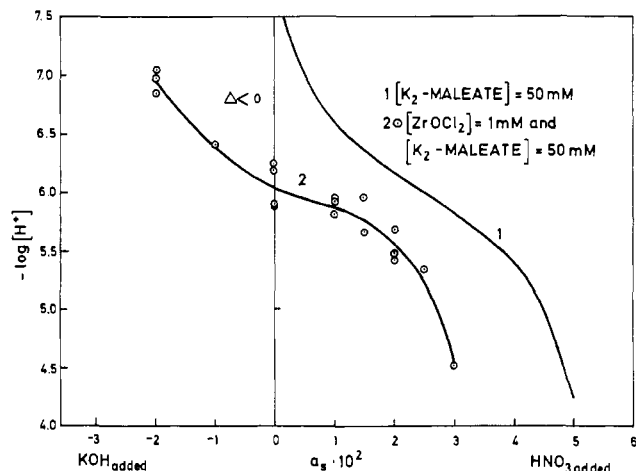

Figure 2. (1) Titration curve of potassium (50 mM) which was titrated with KOH and HNO_3. (2) Titration curve of potassium maleate of the same concentrations as in curve 1, except that all solutions contain 1 mM of zirconyl chloride.

Table II. Electrophoretic Mobilities

$10^2 \times$ [potassium maleate], mol dm^{-3}	aging of the system, days	$10^4 \times$ electrophoretic mobilities, cm^2 V^{-1} s^{-1}
1	0	0
	7	0, +1.4
2	0	0, +1.4
	7	0, +2.6
3	0	0, +1.4
	7	0, +2.6
4	0	0, +1.4
	7	0, +2.6

dition of acid or base can be due to the metal ion added. The value $\Delta < 0$ means that there is an additional hydrolysis of the $Zr(OH)_2^{2+}$ central group.[17]

For an investigation of the charge of soluble complexes of zirconium maleate, the electrophoretic experiments have been performed, and the experimental data are presented in Table II.

At the constant concentration of zirconium, 1×10^{-3} mol dm^{-3}, the potassium maleate concentration was changed. The electrophoretic mobilities show the presence of anionic complexes and uncharged compounds. The electrophoretic mobilities of anionic complexes changed from $u = +1.4 \times 10^{-4}$ cm^2 V^{-1} s^{-1}, measured immediately after the mixing, to $u = +2.6 \times 10^{-4}$ cm^2 V^{-1} s^{-1} for 7 day old systems. In comparison of the electrophoretic mobilities of zirconium maleate complexes with the zirconium oxalate complexes[9] at the same metal:ligand ratio, the electrophoretic mobilities of zirconium maleato complexes are approximately equal to $u/2$ of zirconium oxalato complexes.

However, the exact composition of zirconyl maleato complexes formed in the soluble region has not yet been completely determined, but we assume that it might be the $Zr(OH)_4$-$(OOCCH=CHCOO)^{2-}$ ion. It was not possible to isolate this complex in a solid form.

Figure 3 represents the ground plan of the precipitation diagram of zirconium salts in the presence of potassium phthalate. Turbidity was measured as a function of pH and log [potassium phthalate], also for $ZrOCl_2$, equal to 1×10^{-3} mol dm^{-3}.
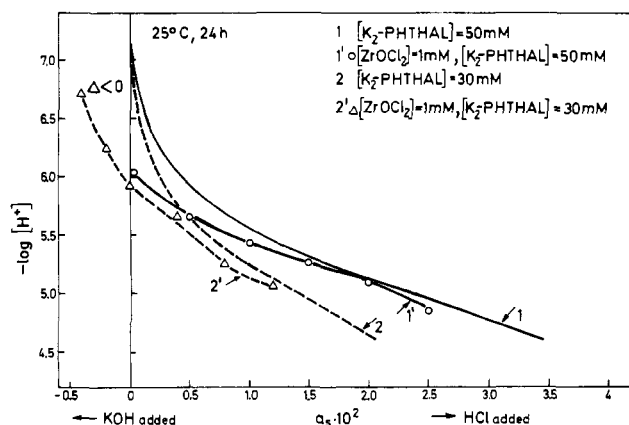
In the acid region, zirconium phthalate is less soluble than zirconium maleate and shows a similar solubility to zirconium

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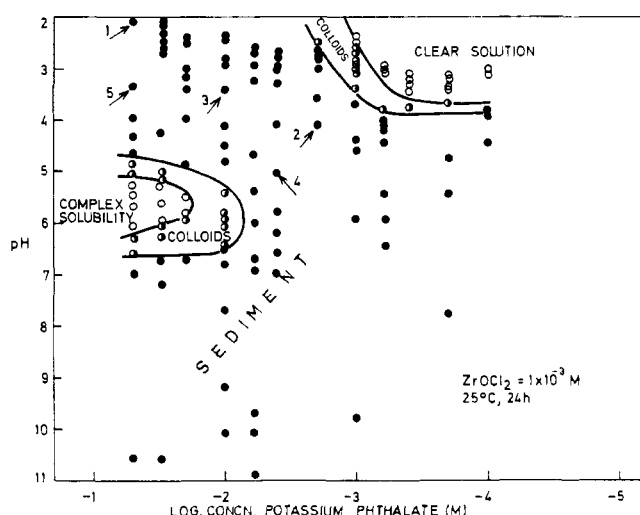
Figure 3. Precipitation diagram of zirconium salts formed in potassium phthalate solutions at different pH values (25 °C, 24-h aging).

Figure 4. Titration curves of potassium phthalate: (1) 50 mM; (2) 30 mM, which was titrated with KOH and HCl. Curves 1' and 2' are titration curves of potassium phthalate of the same concentrations as in curves 1 and 2, except that all solutions contain 1 mM zirconyl chloride.

oxalate.[9] At higher pH values in high excess of phthalate, soluble complexes are formed in a very narrow pH region. Several typical precipitates were isolated, and a conclusion similar to that for maleate was reached. In high excess of phthalate the precipitates were of a defined composition—$Zr(OH)_3(OOCC_6H_4COOH)$. In small excess of phthalate and at pH >3, the hydrolysis of zirconium took place, and the continuous increase of zirconium percentage was observed with the pH increase.

Figure 4 illustrates two typical titration experiments, for two different phthalate concentrations. The difference $\Delta <$ 0 means that there is an additional hydrolysis of the $Zr(OH)_2{}^{2+}$ central group. For an investigation of the charge of the soluble complexes of zirconium phthalate, the electrophoretic experiments have been performed, and experimental data are presented in Table III.

At constant concentration of zirconium, 1×10^{-3} mol dm^{-3}, the potassium phthalate concentration was changed. The electrophoretic mobilities show the presence of anionic complexes and uncharged compounds. The electrophoretic mobilities do not remain constant with the increase of ligand concentration for 0 day old systems as was the case with the zirconium maleato complexes; however, for 7 day old systems they remain constant.

It was not possible to isolate the complex in the solid form

Table III. Electrophoretic Mobilities

$10^3 \times$ [potassium phthalate], mol dm^{-3}	aging of the system, days	$10^4 \times$ electrophoretic mobilities, cm^2 V^{-1} s^{-1}
1	0	0, +1.4
	1	0, +3.2
	7	0, +2.8
2	0	0, +1.5
	1	0, +3.1
	7	0, +2.8
3	0	0, +1.6
	1	0, +3.1
	7	0, +2.8
4	0	0, +2.0
	1	0, +2.6
	7	0, +2.9

Table IV. Analytical Data

compd	% found			% required		
	C	H	Zr	C	H	Zr
$Zr(OH)_3(OOCCH=$ CHCOOH) (I)	17.07	2.48	35.08	18.67	2.35	35.45
$Zr(OH)_3(OOCC_6H_4-$ COOH) (II)	30.53	3.12	29.58	31.26	2.62	29.68

Table V. Infrared Spectra^a (cm^{-1})

$Zr(OH)_3(OOCCH=CHCOOH)$	$Zr(OH)_3(OOCC_6H_4COOH)$
3420 s, b	3400 s, b
1708 sh	1695 m
1655 sh	1605 sh
1565 s	1546 s
	1490 w
	1445 w
1441 s	1415 s
1390 sh	
1313 m	1298 w
1183 w	1162 w
	1143 w
1100 w	1088 w
985 w	1040 vw
905 w	
855 vw	750 m
840 w	712 w
634 s	650 m

^{a} Key: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; vw, very weak; b = broad.

nor was it possible to perform the potentiometric titration for equilibrium constant determination in such a limited concentration range.

Isolated solid complexes of zirconium maleate and phthalate are presented in Table IV, containing experimental data and theoretical values. They are white, amorphous solids, insoluble in both cold and hot water, as well as in all common organic solvents. They have been further characterized with use of the IR spectra presented in Table V.

The mode of coordination of carboxylate ligands can be obtained from the IR spectra (Table V). Both complexes exhibit a strong absorption band in the region 3300–3600 cm^{-1}, corresponding to the Zr–OH stretchings.[18] The broadness of this band indicates the presence of a strong hydrogen bonding.

The most significant information about the mode of coordination of maleic and phthalic acids can be obtained from the analysis of absorption region of carboxyl groups presented in Table VI.

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Table VI. Characteristic COO⁻ Frequencies (cm⁻¹)

compd	ν_a^- (COO⁻)	ν_s^- (COO⁻)	Δ
$C_4H_4O_4$	1590	1432	158
$Zr(OH)_3(OOCCH=CHCOOH)$	1565	1441	124
$C_8H_8O_4$	1684	1403	281
$Zr(OH)_3(OOCC_6H_4COOH)$	1546	1415	131

There is a very close similarity in the position of ν_a(COO⁻) and ν_s(COO⁻) in complex I and in the free maleic acid. The position of these bands could indicate that, besides coordinated carboxyl group, also the uncoordinated one is present at the same time. The same was observed with complex II. Further, the separation of ν_a(COO⁻) − ν_s(COO⁻) in this complex is comparable to that in the free ligand (Table VI).

In the case of acetic acid,[18] oxydiacetate,[19,20] and methoxyacetate[21] complexes, it has been found that the same separation is comparable to that existing in the free ligand, when the carboxyl group acts as a bridge between the two metal atoms. If this result can be applied also in the case of complexes with dicarboxylic acids, then it seems reasonable to conclude that the coordinated COO⁻ group in complex I could be a bridge between the two zirconium atoms, raising the coordination number of zirconium and providing the polymeric nature of this complex.

In the absorption spectrum of complex II, in addition to the strong absorption band at 1546 cm⁻¹, there is a nicely resolved band at 1695 cm⁻¹ corresponding very likely to the uncoordinated carboxyl group. The separation between the asymmetric and symmetric stretching frequencies of the coordinated COO⁻ group is smaller than that in the free phthalic acid (Table VI) but greater than 100 cm⁻¹. For the carboxyl group acting as a bidentate ligand toward the same metal atom, this separation was found to be smaller than 100 cm⁻¹.[18] This result suggests the bridging of the COO⁻ group in both complexes: complex I and complex II.

Inspection of the infrared spectra in the region 1050–800 cm⁻¹ shows that these complexes do not exhibit the absorption band corresponding to Zr=O vibrations, which was found earlier in the spectrum of $ZrOCl_2$ salt prepared from nonaqueous solvents.[22]

Furthermore, infrared spectra are not so explicit in differentiating OH from O bridges between the two metal atoms. In the spectra of these complexes in the region 800–625 cm⁻¹, there is a band of medium intensity that could represent OH bridges in these complexes.

According to physical and infrared spectral data, we are inclined to conclude that (a) both complex I and complex II are polymeric in nature, (b) the polymerization occurs either through a COO⁻ group or through OH bridges or through both of them, and (c) this polymerization is responsible for the amorphous nature and the insolubility as strong as that observed.

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High-Spin, Five-Coordinate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Linear, Pentadentate Keto Iminato Ligands

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Over 35 transition-metal complexes of Ni(II), Co(II), and Cu(II) with pentadentate Schiff base ligands derived from various β-diketones (Hacac, Htfac, Hbenac, and p-XHbenac) and triamines (DPT, MeDPT, and PhDPT) have been isolated and characterized. All of the Ni(II) and Co(II) complexes are high-spin, five-coordinate species with average μ_{eff} values of 3.3 and 4.3 μ_B, respectively. The Cu(II) complexes have experimental μ_{eff} values of ~1.9 μ_B. Visible spectral results on all samples and EPR studies on the Cu(II) complexes indicate that the new compounds are five-coordinate with geometries intermediate between TBP and SP. The Co(II) derivatives bind dioxygen reversibly in solution.

Introduction

Over the past several years, we have been studying the oxygen reactivity of Co(II) complexes containing tetradentate keto iminato and thio iminato ligands.[1–3] Work in our laboratory as well as in several others[4] has shown that bonding of dioxygen by such complexes in low-temperature solutions involves activation of the metal ion with a Lewis base to form a five-coordinate precursor (eq 1) followed by dioxygen coordination (eq 2). One obvious drawback to these types of

$$Co(lig) + B \rightleftharpoons Co(lig) \cdot B \qquad (1)$$

$$Co(lig) \cdot B + O_2 \rightleftharpoons Co(lig) \cdot B \cdot O_2 \qquad (2)$$
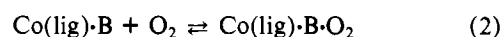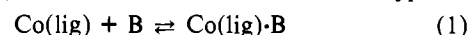
systems is that the excess Lewis base normally used in the

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