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Synthesis and Physicochemical Study of Solid Complexes of Ti(IV), Zr(IV), and Zn(II) with Chrysin

J. Pusz, B. Nitka, S. Kopacz, and Ya. I. Korenman

Polytechnic University, Rzeszow, Poland
Voronezh State Technological Academy, Voronezh, Russia

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Abstract—Previously unknown solid complexes of Ti(IV), Zr(IV), and Zn(II) with chrysin were isolated, identified, and studied by thermogravimetric analysis and by UV-Vis, IR, and NMR spectroscopy.

Flavonoids are vegetable dyes absent in animal cells but present in virtually all plants, in particular, in fruits, flowers, leaves, and wood. Flavonoids are methoxy and glycoside derivatives of flavone (2-phenyl-γ-benzopyrone); they contain a system of two aromatic rings linked by a triangular aliphatic chain [1, 2].

Flavonoids containing OH groups at the C atoms in positions 3, 5, 3', and 4' exhibit increased biological activity and form stable complexes with metals. This property is used for treating heavy metal poisonings [3]. Thanks to the complexing power, flavonoids are also used as dyes in textile industry and as reagents for photometric and gravimetric determination of many metals [4].

The best known and most widely used flavonoids are quercetin, morin, rutin, and their sulfo derivatives [5–8]. Less studied is chrysin ([5,7-dihydroxyflavone, $C_{15}H_{10}O_4$), which, similar to the above-mentioned flavonoids, is insoluble in water;, this hinders its use, e.g., in analytical chemistry.

Data on the structure and physicochemical properties of solid metal chrysin complexes are scarce [9]. We have prepared solid complexes of Ti(IV), Zr(IV), and Zn(II) with chrysin, determined their composition, and studied their physicochemical properties.

Previously unknown solid complexes of Ti(IV), Zr(IV), and Zn(II) with chrysin were prepared by mixing hot solutions of the appropriate starting compounds. The complexes are yellow. Their compositions were determined by elemental (Table 1), thermogravimetric, complexometric, and gravimetric analyses and are as follows: $Ti(C_{15}H_9O_4)_4$, $Zr(C_{15}H_9O_4)_4 \cdot 8H_2O$, and $Zn(C_{15}H_9O_4)_2 \cdot 2H_2O$.

The physicochemical properties of the complexes were studied by thermogravimetric analysis (Table 2) and by UV-Vis (Table 3), IR (Table 4), and NMR spectroscopy (Table 5).

The thermal decomposition of chrysin and its Ti(IV), Zr(IV), and Zn(II) complexes was studied in air in the range 293–1273 K. Chrysin is an anhydrous compound and shows no effects due to dehydration in the range 293–553 K. Starting from 578 K, chrysin starts to decompose exothermally in several stages. The decomposition is complete at 1095 K (100% weight loss).

The Zr(IV) and Zn(II) complexes undergo endothermic dehydration in the range 293–593 K; the

Table 1. Analytical data for chrysin and its compounds with Ti(IV), Zr(IV), and Zn(II)[a]

Compound	Color	Found, %				Calculated, %			
		C	H	M[b]	H_2O	C	H	M[b]	H_2O
$C_{15}H_{10}O_4$ (chrysin)	Beige	71.18	3.65	–	–	70.85	3.96	–	–
$Ti(C_{15}H_9O_4)_4$	Yellow	68.33	3.51	4.18	–	67.93	3.42	4.51	–
$Zr(C_{15}H_9O_4)_4 \cdot 8H_2O$	"	57.47	3.52	7.80	10.50	57.78	4.21	7.21	11.56
$Zn(C_{15}H_9O_4)_2 \cdot 2H_2O$	"	59.81	3.16	10.46	6.50	59.45	3.63	10.76	5.94

[a] Derivatographic data. [b] M is metal.

Table 2. Temperatures of thermal decomposition of chrysin and its complexes with Ti(IV), Zr(IV), and Zn(II)[a]

Compound	T_1, K	$T_{\min}^{\mathrm{DTA}}$, K	$T_{\min}^{\mathrm{DTG}}$, K	T_2, K	T_f, K	Final decomposition product
Chrysin	–	–	–	578–1095	1095	–
$Ti(C_{15}H_9O_4)_4$	–	–	–	493–1033	1033	TiO_2
$Zr(C_{15}H_9O_4)_4 \cdot 8H_2O$	293–393	350	353	393–1133	1133	ZrO_2
$Zn(C_{15}H_9O_4)_2 \cdot 2H_2O$	313–593	533	523	593–1183	1183	ZnO

[a] (T_1) Temperature range of dehydration (endothermic effect); (T_2) temperature range of decomposition of the anhydrous compound and combustion of organics to give the final product; ($T_{\min}^{\mathrm{DTA}}$, $T_{\min}^{\mathrm{DTG}}$) temperatures corresponding to the minimum in the DTA and DTG curves; (T_f) temperature of formation of the final product.

Table 3. Parameters of absorption bands[a] of chrysin and its complexes with Ti(IV), Zr(IV), and Zn(II) in methanol; concentrations 3.2×10^{-5}, 7.6×10^{-6}, 7.6×10^{-6}, and 2.1×10^{-5} M, respectively; l 1 cm

Chrysin		$Ti(C_{15}H_9O_4)_4$		$Zr(C_{15}H_9O_4)_4 \cdot 8H_2O$		$Zn(C_{15}H_9O_4)_2 \cdot 2H_2O$	
ν_0	$\varepsilon_{\max}$	ν_0	$\varepsilon_{\max}$	ν_0	$\varepsilon_{\max}$	ν_0	$\varepsilon_{\max}$
31 600	16 775	31 500	33 260	32 000	52 900	32 000	22 380
37 000	40 000	37 000	116 240	37 300	132 200	37 000	55 240
40 500[b]	20 000	40 700[b]	61 120	40 700[b]	66 500	40 500[b]	28095
46 600	44 160	47 400	130 600	47 400	167 400	46 600	56 190

[a] (ν_0) Band center, cm^{-1}; ($\varepsilon_{\max}$) molar extinction coefficient at the band maximum, $l\,mol^{-1}\,cm^{-1}$. [b] Inflection.

Table 4. Vibration bands (cm^{-1}) of the strongest bands in the IR spectra of chrysin and its complexes with Ti(IV), Zr(IV), and Zn(II)

Chrysin	$Ti(C_{15}H_9O_4)_4$	$Zr(C_{15}H_9O_4)_4 \cdot 8H_2O$	$Zn(C_{15}H_9O_4)_2 \cdot 2H_2O$	Assignment[a]
3600–2400	3600–2400	3600–2400	3600–2400	ν_{OH}
1652	1652	1654	1652	$\nu_{C=O}$
1612	1612	1613	1613	$\nu_{C=C}$
1576	1576	1577	1576	
1556	1556	1555	1555	
1500	1500	1499	1499	
1175	1165	1356	1175	δ_{C-H}
908	908	908	908	γ_{C-H}
840	844	843	845	
808	808	807	815	

[a] (ν) Stretching, (δ) in-plane bending, and (γ) out-of-plane bending vibrations.

Ti(iV) complex, which is anhydrous, shows no such effect. At higher temperatures the anhydrous compounds decompose, with burn-out of the organics and formation of metal oxide. The process yielding TiO_2, ZrO_2, and ZnO is complete at 1033, 1133, and 1183 K, respectively.

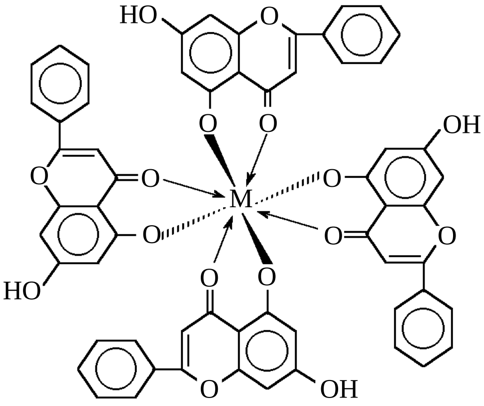
The electronic absorption spectra of the Ti(IV), Zr(IV), and Zn(II) chrysin complexes were measured in methanolic solutions. The electronic absorption spectrum of chrysin in the range 200–700 nm contains two strong bands ($\lambda_{\max}$ 214 and 270 nm) and a weaker band at 316 nm. It is known that these bands are due to $\pi \rightarrow \pi^*$ transitions in the ligand molecule. The band positions in the spectra of the metal chrysin complexes are virtually the same as in the spectrum of free chrysin.

The intensity of the absorption bands of the complexes is higher compared to the free ligand and regularly increases in the order Zn < Ti < Zr. The increased molar extinction coefficients of the complexes are apparently due to changes in the electron density distribution in the benzene and γ-pyrone rings.

The IR spectra of the Ti(IV), Zr(IV), and Zn(II) chrysin compounds are complex (Table 4). No shift of the carbonyl absorption band is observed upon coordination of chrysin with the metals. The other parts of the spectra of free chrysin and its metal complexes also differ insignificantly.

The solid-state NMR spectra of chrysin and its Zr(IV) complex (Table 5) virtually coincide.

Our results, even in combination with published data [10–13], do not allow determination of the coordination mode of chrysin. Available data on complexes of *p*, *d*, and *f* metals with quercetin, morin, and their sulfo derivatives suggest that the corresponding ions are bound via four CO groups and five C–OH groups. Analytical (Table 1) and derivatographic (Table 2) data suggest that chrysin forms characteristic [14] eight-coordinate complexes with Ti(IV) and Zr(IV) and a four-coordinate complex with Zn(II):



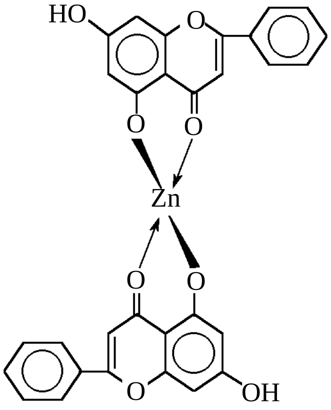


Table 5. Chemical shifts in the ^{13}C NMR spectra (δ_C, ppm) of chrysin and its solid Zr(IV) complex

Assignment	Chrysin, solution in DMSO	Chrysin (Δ^a)	Zr(IV) chrysin complex
C^2	163.50	164.76 (–1.2)	164.58
C^3	105.30	103.17 (+2.1)	103.22
C^4=O	182.00	181.99	181.92
C^5–OH	161.40	160.90	160.90
C^6	99.20	99.19	99.38
C^7–OH	164.50	164.90	164.58
C^8	94.40	94.48	94.36
C^9	159.80	156.94 (+2.9)	156.80
C^{10}	103.90	103.17	103.22
$C^{1'}$	130.80	129.85	130.01
$C^{2'}$	126.50	125.94	125.87
$C^{3'}$	129.30	129.85	130.01
$C^{4'}$	132.16	133.96 (–1.8)	133.77

[a] Δ = δ(solution) – δ(solid state).

EXPERIMENTAL

In physicochemical studies we used a Beckman DU-640 UV-Vis spectrophotometer (the United States), an MOM-3427T derivatograph (Hungary), a Carlo Erba EA-1108 apparatus for elemental analysis (Hungary), a Specord IR-80M spectrophotometer (Germany), a Bruker MSL-300 NMR spectrometer (the United States), a Perkin–Elmer-3100 atomic absorption spectrometer (the United States), and a Radelkis OP-8/1 pH meter (Hungary).

In the experiments, we used the following chemicals: $TiCl_4$, density 1.73 g cm^{-3}; $ZnCl_2$, analytically pure grade; zinc metal, analytically pure grade; $ZrOCl_2 \cdot 8H_2O$, pure grade; chrysin, pure grade; Na_2EDTA, analytically pure grade; potassium metal, analytically pure grade; dimethyl sulfoxide (DMSO), analytically pure grade; sulfuric acid, 0.05 M; concentrated perchloric acid; concentrated hydrochloric acid; concentrated aqueous ammonia; Xylenol Orange, 1 : 100 mixture with NaCl; methanol, analytically pure grade; and 96% ethanol, analytically pure grade.

Initial solutions. A 1.0 M Ti(IV) solution was prepared by diluting the required amount of $TiCl_4$ with double-distilled water. A 0.038 M Zr(IV) solution was prepared by dissolving $ZrOCl_2 \cdot 8H_2O$ in sulfuric acid. A 0.5 M $ZnCl_2$ solution was prepared by dissolving $ZnCl_2$ in ethanol. The saturated solution of chrysin in ethanol was prepared on heating.

A 0.2 M solution of K in ethanol was prepared by gradual addition of 0.7820 g of K metal to 100 ml of

96% ethanol; the resulting solution was filtered. The reference solution containing 0.0150 M Zn(II) was prepared by dissolving 1.9613 g of Zn metal in 30 ml of HCl; the volume was brought to 2.0 l with double-distilled water.

A 0.0150 M solution of Na_2EDTA was prepared by dissolving 11.1672 g of the salt in 0.2 l of double-distilled water. The solution concentration was determined by titration with a zinc reference solution in the presence of Xylenol Orange.

Synthesis of the complexes. To prepare the Ti(VI) and Zr(IV) chrysin complexes, solutions of metal salts in amounts corresponding to the metal-to-ligand ratio M : L = 1 : 4 were added with heating and stirring to 200 ml of a saturated aqueous-ethanolic solution of chrysin. The mixtures were cooled, an ammonia solution was added to pH 6–7, and the precipitates were filtered off, washed several times with water and aqueous ethanol (1 : 1), centrifuged, and dried in air at room temperature.

To prepare the Zn(II) chrysin complex, a reference solution of $ZnCl_2$ in amount corresponding to the ratio M : L = 1 : 2 was added with stirring to 300 ml of a hot saturated solution of chrysin containing a solution of K in ethanol. The precipitate was centrifuged, washed several times with aqueous ethanol (1 : 1), and dried in air at room temperature.

Identification of the complexes. The composition and structure of the complexes were determined by elemental and thermogravimetric analysis and by UV-Vis, IR, and NMR spectroscopy.

The content of C and H in the complexes was determined by a standard gravimetric procedure with an apparatus for elemental analysis.

The metal percentage was determined complexometrically (EDTA titration) after decomposition of the complexes with perchloric acid, gravimetrically (after combustion at 1193–1213 K), and by atomic spectroscopy (after decomposition with perchloric acid).

Thermal decomposition of chrysin and its Ti(IV), Zr(IV), and Zn(II) complexes was studied in the temperature range 293–1273 K. Samples were heated at a rate of 1 deg min^{-1} in air; the device sensitivity levels were as follows: Ti(IV) compounds, TG 100 mg, DTG 1/5, DTA 1/10; Zr(IV) compounds, TG 200 mg, DTG 1/5, DTA 1/3; and Zn(II) compounds, TG 200 mg, DTG 1/10, and DTA 1/10.

The electronic absorption spectra of Ti(IV), Zr(IV), and Zn(II) chrysin complexes were taken in methanol (Table 3). The IR spectra (KBr pellets) were recorded in the range 4000–400 cm^{-1}. The frequencies of selected absorption bands in the IR spectra are listed in Table 4.

The ^{13}C NMR spectra of chrysin and its solid Zr(IV) complex were recorded at 75.5 MHz. Measurement conditions: rotor diameter 4 mm, frequency 7.4 kHz, contact time 3 μs, spectral width 20 kHz. The chemical shifts were measured relative to the CO signal of glycine (176.03 ppm) and recalculated relative to TMS (Table 5).

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