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THERMAL DECOMPOSITIONS OF COMPLEXES OF METAL IONS WITH RIBOFLAVIN

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Two kinds of complexes of riboflavin with Zn(II), Co(II), Cu(II), Fe(III), Mg(II) and Ca(II) were synthesized, having metal: ligand molar ratios of 1:1 and 2:1. When heated, these complexes first lose water. Their thermal degradation in static air atmosphere starts at temperatures higher than, equal to, or lower than that observed for free riboflavin degradation. The rates and stages of pyrolysis were related to the structures of the complexes.

Riboflavin (RflH), also known as vitamin B_2, is a yellow pigment. This crystalline, solid-state substance has the chemical structure shown in Fig. 1 and specific physico-chemical properties [1]. Riboflavin 5-phosphate (flavin mononucleotide, FMN) and riboflavin 5-adenosine diphosphate (flavin-adenine dinucleotide, FAD) are prosthetic groups in many enzymes, the flavoprotein enzymes. One of the most important functions of flavoproteins is nonenzymic oxidation-reduction between flavins and pyrimidine nucleotides [1–3]. A number of flavoproteins contain metals ions: iron, molybdenum or copper [1–7]. In these flavoproteins, the bonding sites of the metal ions are situated in the riboflavin isoalloxazine ring. In order to obtain new information on this, we set out to isolate and investigate some solid-state metal ion riboflavinates. The metal ions selected belong among the micro- and macroelements [6–9]: Zn(II), Ni(II), Co(II), Cu(II), Ca(II), Mg(II) and Fe(III).

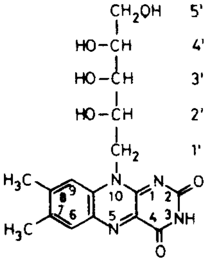

Fig. 1 Riboflavin 7,8-dimethyl-10(1′-D-rybityl) isoalloxazine

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Experimental

Solid-state riboflavinates were prepared by the modified Foye–Lange method [10]. Recrystallization from methanol was performed at the end. The contents of carbon, hydrogen and nitrogen in the prepared complexes were determined by elementary analysis. The contents of metal ions were determined by complexometric titration, nickel(II) by precipitation with dimethylglyoxime, and copper(II) by electrogravimetry.

Digestion of the sample for this purpose was performed by a wet method, with the use of concentrated $HClO_4+HNO_3$ (1 : 1). The content of water was determined by isothermal heating at 120°, IR spectra were recorded with a Specord–71 (Carl Zeiss, Jena) spectrophotometer, using KBr pellets. On the basis of analysis of the IR spectra [12], the following structures were proposed for the compounds obtained (Fig. 2).

Melting points were measured and observations of crystals were performed with a Betins PHMK 78/1781 instrument (VEB Analytic, Dresden).

TG, DTG and DTA curves were recorded simultaneously with a derivatograph (MOM, Budapest). Powdered samples (m_0 = 50 mg) were heated in a ceramic crucible with α-Al_2O_3 within the temperature range from 20 to 1000°, at a constant heating range of 5 or 10 deg/min, in static air atmosphere.

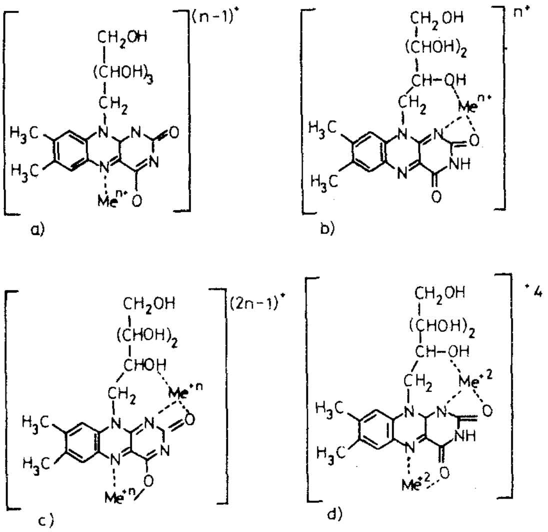

Fig. 2 Metal binding sites in different metal riboflavin-complexes. Molar ratio metal : ligand = 1 : 1; a) transition metals riboflavinates; b) main group metals riboflavinates; molar ratio metal : ligand = 2 : 1; c) transition metal riboflavinates; d) main group metal riboflavinates

Results and discussion

We succeeded in obtaining a series of solid-state complexes of riboflavin with Co(II), Ni(II), Zn(II), Cu(II), Fe(III), Ca(II) and Mg(Ii), with metal : ligand molar ratios M : L = 1 : 1 and 2 : 1. During the synthesis of riboflavin complexes with transition metal ions, a fall in pH was observed, in contrast to the synthesis of the riboflavin complexes of magnesium and calcium. On the basis of this observation, as well as from studies of the IR spectra, we put forward the structures shown in Fig. 2 [12]. The colours of the compounds vary from brown to orange and yellow (see Table 1). The crystals of magnesium and calcium riboflavinates have colours resembling that of free riboflavin. After extraction with acetone, all these compounds were amorphous. Recrystallization from methanol led to small crystals. The efficiency of the synthesis varied from 15 to 90% (see Table 1). The melting points of the compounds were usually lower than that of free riboflavin; only the 1 : 1 riboflavinates of Ni(II) and Zn(II) melted at temperatures higher than 300°.

The thermal curves of the riboflavinates were recorded in static air atmosphere (Fig. 3). The characteristic data and stages of pyrolysis are given in Table 2.

$[NiRfl](OH)\cdot 3.5H_2O$ is thermally more stable that free riboflavin. At the beginning of heating, the evaporation of water is observed. This proceeds in a wide

Table 1 Physical properties of the obtained riboflavinates

Chemical formula	Efficiency, %	Colour	Melting point, °C	Remarks
RflH	—	yellow	280–300	
$[Ni(Rfl)](OH)\cdot 3.5H_2O$	13.5	yellow	350	becoming black without melting
$[Ni_2(Rfl)](OH)_3\cdot 3H_2O$	91.5	orange	220	
$[ZnRfl](OH)\cdot H_2O$	43.6	yellow	>350	
$[Zn_2Rfl](OH)_3\cdot 2.5H_2O$	19.7	yellow	250	becoming black
$[CoRfl](OH)\cdot 0.5H_2O$	61.8	brown	280	
$[Co_2Rfl](OH)_3\cdot 5H_2O$	32.3	brown	250	
$[CuRfl](OH)\cdot 2.5H_2O$	90.0	brown	235	becoming black
$[Cu_2Rfl](OH)_3\cdot 4H_2O$	63.5	brown	260	becoming black
$[FeRfl](OH)_2\cdot 4H_2O$	14.7	brown	259	
$[Fe_2Rfl](OH)_5\cdot 2H_2O$	24.0	brown	250	
$[CaRflH](OH)_2$	35.5	yellow	260	
$[Ca_2RflH](OH)_4$	45.7	yellow	264	
$[MgRflH](OH)_2\cdot 4.5H_2O$	71.3	yellow	282	
$[Mg_2RflH](OH)_4\cdot 2.5H_2O$	48.6	yellow	285	

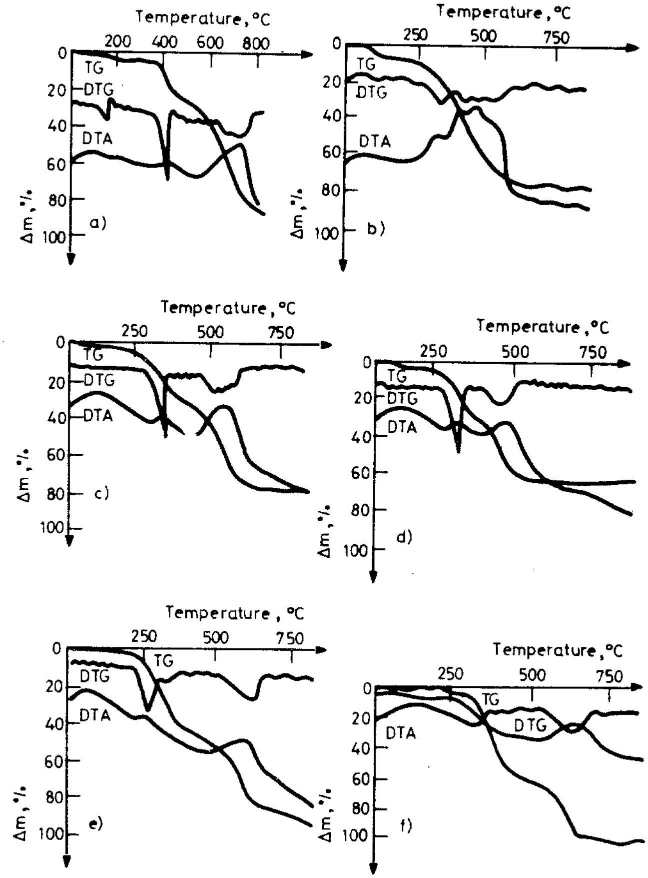

Fig. 3 Simultaneous TG, DTG and DTA curves of riboflavinates in static air atmosphere. m_0 = 50 mg, TG = 50 mg, DTA = 1/5, DTG = 1/5, q = 5 deg/min, T_K = 1000°. a) $[NiRfl](OH) \cdot 3.5H_2O$, b) $[Ni_2Rfl](OH)_3 \cdot 4H_2O$, c) $[FeRfl] \cdot (OH)_2 \cdot 4H_2O$, d) $[Fe_2Rfl] \cdot (OH)_5 \cdot 2H_2O$, e) $[CaRflH] \cdot (OH)_2$, f) $[Ca_2RflH] \cdot (OH)_4$

range of temperature, with a simultaneous decrease in weight, which indicates that the water in this compound, as in the other compounds, is not crystallization water. At 325°, three overlapping stages are observed, which can be resolved only from the changes in rate of weight decrease by DTG. The first stage is very quick and exothermic, the next slower and endothermic, and the last one again quick with a broad exothermic effect, which resembles that for the degradation of riboflavin. The solid residue comprises 14.5% of the initial mass, and elementary analysis indicates that it is pure NiO. $[ZnRfl](OH) \cdot H_2O$ also has a higher thermal stability than that of free riboflavin.

Table 2 Observed stages of thermal decomposition of riboflavinate metal ion in static air atmosphere $m_0 = 50$ mg, $q = 5$ deg/min, Al_2O_3 reference material

Formula	Stage	Temperature, °C		Weight mass, %	Thermal effect
		initial	end		
$[Ni(Rfl)](OH)\cdot 3.5H_2O$	I	80	325	11.5	endo
	II	325	350	14	exo
	III	350	475	19	endo
	IV	475	600	41	exo
$[Ni_2(Rfl)](OH)_3\cdot 3H_2O$	I	80	220	12	endo
	II	220	230	5	exo
	III	230	281	7.5	exo
	IV	281	477	50.5	exo
$[Zn(Rfl)](OH)\cdot H_2O$	I	80	447	6	endo
$q = 10$ deg/min	II	447	530	18	exo
	III	530	880	25	endo
	IV	880	1000	51	exo
$[Zn_2Rfl](OH)_3\cdot H_2O$	I	80	250	12.5	endo
	II	250	262	11	exo
	III	262	400	19	exo
	IV	400	440	18	exo
	V	440	520	17	exo
	VI	905	1000	22.5	endo
$[Co(Rfl)](OH)\cdot 0.5H_2O$	I	80	85	2	endo
	II	85	280	17	exo
	III	280	422	19	endo
	IV	422	600	47	exo
$[CoRfl](OH)_3\cdot 5H_2O$	I	50	250	13	endo
	II	250	285	11	exo
	III	285	350	10	endo
	IV	350	447	43	exo
$[CuRfl](OH)\cdot 2.5H_2O$	I	20	100	4	endo
	II	152	156	10	exo
	III	235	250	10	exo
	IV	250	290	10	exo
	V	290	320	11	exo
	VI	320	420	38	exo
$[Cu_2Rfl](OH)_3\cdot 4H_2O$	I	20	250	12	endo
	II	250			
$[FeRfl](OH)_2\cdot 4H_2O$	I	20	250	10	endo
	II	250	290	20	exo
	III	290	400	15	endo
	IV	400	500	41	exo

Table 2 Cont.

Formula	Stage	Temperature, °C		Weight mass, %	Thermal effect
		initial	end		
$[Fe_2Rfl](OH)_5 \cdot 2H_2O$	I	20	250	10	exo-endo
	II	250	280	17	exo
	III	280	330	10	endo
	IV	330	450	32	
$[MgRflH](OH)_2$	I	280	300	21	exo
	II	300	360	15	exo
	III	360	500	10	endo
	IV	500	650	45	exo
$[Mg_2RflH](OH)_4$	I	280	300	26	endo-exo
	II	300	440	24	endo
	III	440	630	35	exo
$[CaRflH](OH)_2$	I	260	280	20	exo
	II	280	450	26	endo
	III	450	600	42	exo
$[Ca_2RflH](OH)_4$	I	260	280	16	exo
	II	280	550	26	endo
	III	550	620	35	exo

When the second metal ion is coordinated by riboflavin at N(1), C(2)O and C(2')O, this changes the thermal stability dramatically. After the evaporation of water at about 230–250° the thermal degradation of the ligand starts. As for free riboflavin [11], this begins with changes in the ribityl side-chain. This stage is accelerated by the coordination of metal ion at this site. This may explain the observations that every compound which involves coordination of metal ions to the ribityl side-chain is usually less stable than the free ligand. We propose that the first metal ion of metals belonging to the main groups, i.e. Ca(II) and Mg(II), coordinates first at the ribityl side-chain, which accords with the observations of their thermal stabilities. There are no compounds of Mg(II) and Ca(II) more stable than riboflavin itself. The thermal decompositions of both these compounds suggest rather weak bonds between the ligand and the metal ion. The 1 : 1 Co(II) and Ni(II) compounds have about the same thermal stability as riboflavin, while the compounds with L : M = 1 : 2 have lower stabilities.

The compounds with copper(II) display an accelerated rate of decomposition. This is well observed for one copper ion in the compound. In the presence of two copper ions, the thermal degradation of the complex resembles an explosion. This may be due to the redox activity of this ion.

Conclusions

Only [ZnRfl](OH)·H_2O and [NiRfl](OH)·$3.5H_2O$ have higher decomposition temperatures than that of pure riboflavin [11].

Coordination of a metal ion to the ribityl side-chain of riboflavin causes the decomposition to start at a lower temperature, and also to accelerate the rate of decomposition. The process of decomposition usually ends earlier than for free riboflavin.

Divalent transition metal ions such as Ni(II) and Zn(II) form the most thermally stable complexes in this group. The Fe(III) complex of riboflavin probably has a rigid structure, which would result in a decreased persistence. Copper(II) ions catalyse the thermal destruction of copper(II) complex.

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Zusammenfassung — Es wurden zwei verschiedenartige Komplexe von Riboflavin mit Zn(II), Co(II), Cu(II), Fe(III), Mg(II) und Ca(II) mit einem molaren Metall-Ligandenverhältnis von 1 : 1 und 2 : 1 dargestellt. Beim Erhitzen geben diese Komplexe zuerst Wasser ab. Ihre thermische Zersetzung beginnt in unbewegter Luftathmosphäre bei einer Temperatur, die entweder mit der für die Zersetzung freien Riboflavins übereinstimmt, größer oder kleiner als diese ist. Die Abschnitte und Geschwindigkeit der Pyrolyse werden mittels der Struktur der Komplexe erläutert.

Резюме — Получены два типа комплексов рибофлавина с двухвалентными цинком кобальтом, медью, магнием, кальцием и трехвалентным железом с молярным соотношением металл : лиганд равным 1 : 1 и 2 : 1. При нагревании комплексы первоначально теряют воду. Термическое разложение комплексов в статической атмосфере воздуха начинается при темпетауре выше или ниже, чем разложение свободного рибофлавина. Стадии и скорости разложения комплексов связаны с их структурой.