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THERMAL DECOMPOSITION OF DICITRATOBORATES

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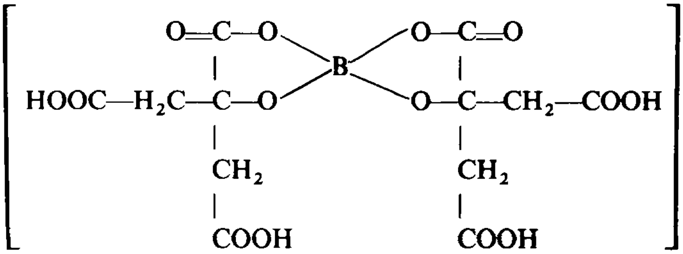
The thermal decompositions of dicitratoborates $M^I[B(C_6H_6O_7)_2]\cdot nH_2O$ (n = 0–2, M^I = Rb, K, Li, NH_4) and $M^{II}[B(C_6H_6O_7)_2]_2\cdot 8H_2O$ (M^{II} = Co, Ni, Mn, Cu, Zn, Cd) were investigated by means of TG, DTA and DTG methods. It was found that these thermal decompositions involve three successive stages: dehydration, the endothermal decomposition of the ligand, and oxidation of the residual organic component. The volatile products of decomposition in each stage were detected by means of gas chromatography. The method of TG-curve transformation into the curve dm/dT vs. m, where m is the loss of weight at each moment of time, was used for a more detailed study of dehydration. The optimal conditions for TG-curve modification were found.

The dicitratoborates $M^I[B(C_6H_6O_7)_2]\cdot nH_2O$, where n = 0–2, and M^I = Li, K, NH_4, Rb, and $M^{II}[B(C_6H_6O_7)_2]_2\cdot 8H_2O$, where M^{II} = Zn, Cd, Co, Mn, Cu were synthesized earlier [1–3]. The complex anion was found to be:



In the dicitratoborate octahydrates of *d* elements, six molecules of water are coordinated to the cation, the remaining two being bonded by hydrogen-bonds to the complex anion [4, 5].

This work deals with the dehydration and thermal decomposition of the above dicitratoborates.

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Measuring methods

The thermoanalytical curves were recorded with an OD–102 derivatograph, using a small standard crucible or plate crucible (4 plates), at a heating rate of 2.5–10 deg/min, with a samples weight of 100–200 mg, in an air atmosphere and with evacuation of the volatile products. Since the samples swell up and spray out, Al_2O_3 was used as filler in a ratio of 10 : 1 to sample weight and reference substance. The volatile products of decomposition were detected by means of gas chromatography. The samples were heated to the temperature of the end of each stage of decomposition, and the volatile products were introduced into a (ABX–07 chromatograph) heat conductivity detector with a combined column, half of which was filled with zeolite Na*X* 0.2–0.5 mesh and the other half with Polysorb–1.

Thermoanalytical curves were also taken with a Q-derivatograph in quasi-isothermal small standard crucible and quasi-isobaric labyrinth crucible regimes.

For a detailed study of the dehydration stage, the TG curve was transformed according to [6] into the curve dm/dT *vs.* m (MDTG curve), where m is the weight loss of the sample at the given moment of time. The TG curve was recorded with an OD–102 derivatograph or Q-derivatograph in the dynamic regime (293–523 K). The sensitivity of the thermobalance was 0.25 mg per scale unit, and the heating rate was 1.25 deg/min. The small standard crucible was used without filling, and the reference substance was Al_2O_3. The scanning rate was 8.8 mm/min, the atmosphere was air, and the volatile products were not evacuated. Two drums were used to ensure rapid change of the photopapers. When the Q-derivatograph was used, the scanning rate was 20 mm/min. In separate experiments, the reproducibility of the results (T, m) and their dependence on the heating rate, the weight of the sample, and the form of the crucible were determined. The reproducibility of the results is shown in Table 1 on the example of the dehydration of cobalt dicitratoborate. The standard deviation S of the peak temperatures of the MDTG curve does not exceed 3 K, and that of the weight loss does not exceed 0.25 mol of water. The type of derivatograph does not influence the reproducibility of the results. With the use of plate crucibles, the reproducibility of the weight loss is worse; this is easy to explain in terms of the increase of spultering of the substance from the plates. Increase of the heating rate leads to an increase of the peak temperature, which is in agreement with the theory of thermal analysis. The weight of the sample has a much lower influence.

The following conditions were selected as optimum: sample weight 245 mg, heating rate 1.25 deg/min, Q-derivatograph in the dynamic regime, scanning rate 20 mm/min, and thermobalance sensitivity 0.25 mg per scale unit.

Table 1 The reproducibility of results of the TG-curves modification on the example of dehydration of $Co[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$

Type of apparatus		Temperature of maxima				The loss of weight (mol H_2O) at temperatures of minima				
		I	II	III	IV	I	II	III	IV	
OD–102	1	—	385.4	395.9	430.0	—	2.9*	3.0	2.0	* Is not taken in account at deviation calculating
	2	—	385.5	394.7	429.0	—	2.6*	3.3	2.1	
	3	381.0	389.0	398.7	432.0	1.2	2.1	2.7	2.0	
	4	378.0	385.2	395.2	425.5	1.0	2.0	2.6	2.3	
Q-derivatograph	5	—	388.0	396.9	428.0	—	3.0*	2.8	2.1	
	6	381.6	390.9	397.8	—	0.8	2.3	2.8	—	
	7	385.0	390.0	399.9	432.9	0.9	2.0	3.1	2.0	
	S	*2.87*	*2.02*	*1.90*	*2.71*	*0.13*	*0.14*	*0.25*	*0.12*	
	$\overline{\Delta x}$	4.56	2.50	1.76	2.84	0.21	0.22	0.23	0.13	

Results and discussion

Details on the thermal decompositions of the dicitratoborates are given in Table 2, and the thermoanalytical curves are depicted in Figs 1, 4 and 6. The thermal decompositions exhibit successive stages: 1) Dehydration in one or several steps; 2) endothermal decomposition of the ligand; 3) oxidation of the residual organic component.

The dehydration of the dicitratoborates of alkali metals and ammonia usually occurs in one step and is not connected with the appearance of liquid phase, but the dehydration of the dicitratoborates of *d* elements occurs in several steps, the substance dissolving in the water of crystallization evolved when the heating rate is 2.5–10 deg/min, and the end of dehydration is masked by the beginning of decomposition of the ligand. The dehydration occurs without the appearance of liquid phase when the heating rate is 1.25 deg/min or less.

The dehydration leads to complete destruction of the crystal structure, but when dissolution does not take place the complex anion seems to remain. With the method of TG-curve transformation, several steps are found in the dehydration of dicitratoborates of *d* elements. There are 3–4 steps for the Co and Cd salts, and 5 steps for the Zn salt. These involve the loss of 3, 3 and 2 mol of water (Fig. 2). The first dehydration step is sometimes split into two, with the loss of 1 and 2 mol of water (Co), or the second step is split (Zn), with the loss of 2 and 1 mol of water

Table 2 Thermal decomposition of dicitratoborates
(Derivatograph OD–102, heating rate 2.5 K/min, sample weight 100–200 mg, small standard crucible, the filling and reference substance Al_2O_3, atmosphere air)

Compound	The type reaction	Thermal effect	The interval of temperature, K	The loss of weight		The volatile products	Nonvolatile rest
				on TG	Calculat.		
$Rb[B(C_6H_6O_7)_2]\cdot 2H_2O$	Dehydration	Endothermal	343–371	6.92	7.02	1.97 mol H_2O	$Rb[B(C_6H_6O_7)_2]$
	Decomposition	Endothermal	463–748	53.20	53.08	CO, CO_2, H_2O	is not determined
	Oxydation	Exothermal	558–793	75.43	75.11	CO, CO_2	$Rb_2O\cdot B_2O_3$
$K[B(C_6H_6O_7)_2]\cdot 2H_2O$	Dehydration	Endothermal	483–513	7.58	7.72	1.96 mol H_2O	$K[B(C_6H_6O_7)_2]$
	Decomposition	Endothermal	513–543	58.60	58.36	CO, CO_2, H_2O	is not detected
	Oxydation	Exothermal	543–773	82.16	82.43	CO, CO_2	$K_3B_3O_6$**
$Li[B(C_6H_6O_7)_2]\cdot 1.5H_2O$	Dehydration	Endothermal	393–433	6.14	6.35	1.44 mol H_2O	$Li[B(C_6H_6O_7)_2]$
	Decomposition	Endothermal	433–565	61.88	61.90	CO, CO_2, H_2O	is not detected
	Oxydation	Exothermal	565–620	88.52	88.30	CO, CO_2	$Li_3B_3O_6$**
$NH_4[B(C_6H_6O_7)_2]\cdot 2H_2O$	Dehydration	Endothermal	373–413	7.84	8.09	1.9 mol H_2O	$NH_4[B(C_6H_6O_7)_2]$
	NH_3 evolution	Endothermal	413–493	11.60	11.90	0.98 mol NH_3	undetected
	Decomposition	Endothermal	493–533	64.50	64.50	CO, CO_2, H_2O	undetected
	Oxydation	Exothermal	533–813	92.83	92.12	CO, CO_2	B_2O_3
$Mn[B(C_6H_6O_7)_2]_2\cdot 8H_2O$	Dehydration	Endothermal	373–408	7.32	7.34	4 mol H_2O	a melt
	Dehydration	Endothermal	408–443	14.64	14.68	4 mol H_2O	$Mn[B(C_6H_6O_7)_2]_2$
	Decomposition	Endothermal	443–533	62.65	62.80	CO, CO_2, H_2O, succinic ac.	undetected
	Oxydation	Exothermal	533–823	86.20	—	CO, CO_2	$Mn_2O_3+B_2O_3$
$Co[B(C_6H_6O_7)_2]_2\cdot 8H_2O$	Dehydration	Endothermal	413	7.20	7.31	4 mol H_2O	a melt
	Dehydration	Endothermal	413–448	14.64	14.62	4 mol H_2O	$Co[B(C_6H_6O_7)_2]_2$

	Decom-position	Endothermal	448–548	62.40	62.55	CO, CO_2. H_2O, succinic ac.	undetected
	Oxydation	Exothermal	548–813	85.45	85.33	CO, CO_2	$CoO\cdot B_2O_3$
$Zn[B(C_6H_6O_7)_2]_2\cdot 8H_2O$	Dehydration	Endothermal	383–413	7.37	7.26	4 mol H_2O	a melt
	Dehydration	Endothermal	413–443	14.34	14.52	4 mol H_2O	$Zn[B(C_6H_6O_7)_2]_2$
	Decom-position	Endothermal	443–543	62.29	62.14	CO, CO_2, H_2O, succinic ac.	undetected
	Oxydation	Exothermal	543–813	85.24	84.27	CO, CO_2	α-ZnB_2O_4**
$Cd[B(C_6H_6O_7)_2]_2\cdot 8H_2O$	Dehydration	Endothermal	388–423	6.69	6.93	4 mol H_2O	a melt
	Dehydration	Endothermal	423–453	13.39	13.86	4 mol H_2O	$Cd[B(C_6H_6O_7)_2]_2$
	Decom-position	Endothermal	453–473	58.95	59.33	CO, CO_2, H_2O succinic ac.	undetected
	Oxydation	Exothermal	573–873	85.24	84.77	CO, CO_2	$CdO\cdot B_2O_3$
$Cu[B(C_6H_6O_7)_2]_2\cdot 8H_2O$	Dehydration	Endothermal	353–403	7.28	7.27	4 mol H_2O	a melt
	Dehydration	Endothermal	403–443	14.57	14.54	4 mol H_2O	$Cu[B(C_6H_6O_7)_2]_2$
	Decom-position	Endothermal	443–513	62.10	62.25	CO, CO_2, H_2O, succinic ac.	undetected
	Oxydation	Exothermal	513–823	86.49	86.55	CO, CO_2	$Cu+B_2O_3$

* Calculated according with equation:

$$Me^{I}[B(C_6H_6O_7)_2]\cdot nH_2O \xrightarrow{-nH_2O} Me^{I}[B(C_6H_6O_7)_2] \xrightarrow{-4(-CH_2COOH)} MeBC_4O_6 \xrightarrow{-CO_2,\,CO} 1/2[Me_2O\cdot B_2O_3]$$

and $Me^{II}[B(C_6H_6O_7)_2]_2\cdot 8H_2O \xrightarrow{-8H_2O} Me[B(C_6H_6O_7)_2]_2 \xrightarrow{-8(-CH_2COOH)} MeB_2C_8O_{12} \xrightarrow{CO,\,CO_2} MeO\cdot B_2O_3$ consequently.

** Identified by X-ray analysis.

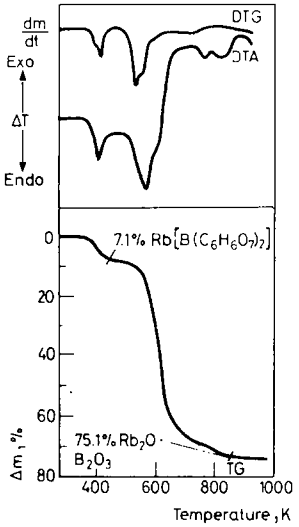

Fig. 1 The thermoanalytical curves of $Rb[B(C_6H_6O_7)_2] \cdot 2H_2O$

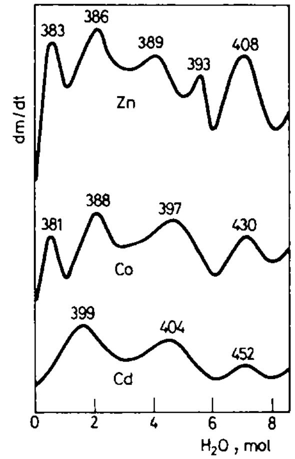

Fig. 2 The dehydration of dicitratoborates of *d*-elements $Me[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$ by MDTG data

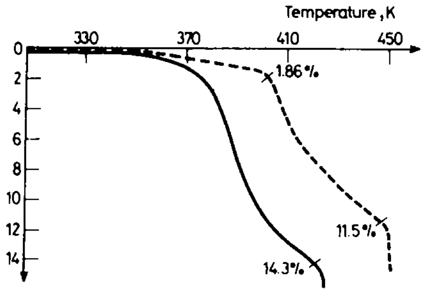

Fig. 3 Thermal decomposition of $Co[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$ under a) quasiisothermal (the small standard crucible); b) quasiisothermal and quasiisobaric (the labyrinte crucible) conditions (dotted line)

(Table 3). This shows that the linkages of the water to the metal in the octahedral $[M(H_2O)_6]$ are energetically not equal.

The TG curves obtained under quasi-isothermal and quasi-isobaric conditions (Fig. 3) are substantially different from the TG curves obtained under dynamic conditions. Under quasi-isothermal conditions, 5 mol of water are lost at 371–401 K and 2.77 more up to 431 K. The end of dehydration is masked by the decomposition of the ligand, which occurs isothermally at 431 K. In the quasi-isobaric regime, all the processes take place at much higher temperature: dehydration at 350–443 K, decomposition of the ligand quite isothermally at

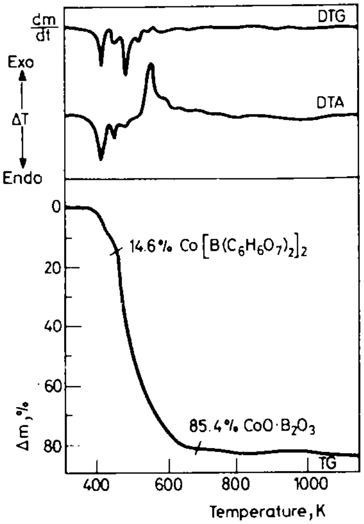

Fig. 4 The thermoanalytical curves of $Co[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$

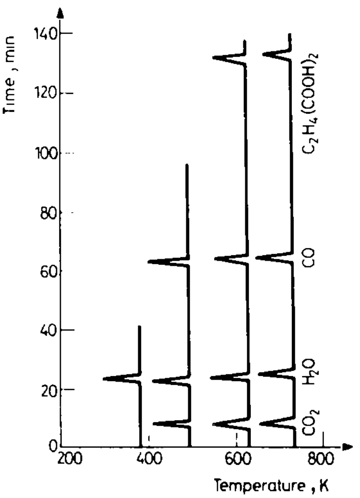

Fig. 5 The volatile products of decomposition of $Co[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$ at 373–673 K

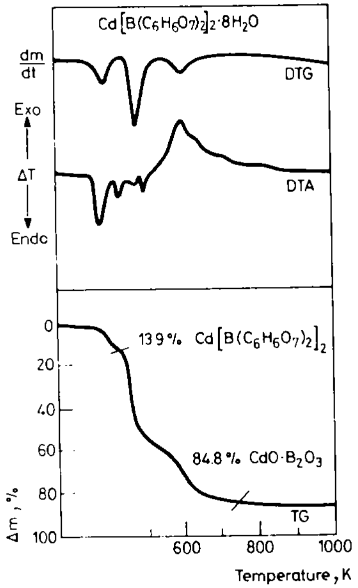

Fig. 6 The thermoanalytical curves of $Cd[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$

Table 3 The dehydration of $Me[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$ by the data of modified thermogravimetric analysis

Dicitratoborate	The temperature of the pike, K					The loss of weight at the temperature of minima, mol of water				
	I	II	III	IV	V	I	II	III	IV	V
Zn	383	386	389	393	408	1	2	2	1	2
Cd	—	399	—	404	452	—	3	—	3	2
Co	381	388	—	397	430	1	2	—	3	2

443–447 K, and three steps of dehydration can be distinguished. At 350–401 K 0.73 (~ 1) mol of water is lost, at 401–433 K 4 mol more, and at 438–443 K 1.3 mol more (altogether 6 mol). The last 2 mol of water are lost isothermally, together with the beginning of decomposition of the ligand.

The thermal destruction of the ligand consists in the splitting off of the $—CH_2COOH$ groups, which undergo secondary transformations in which CO, CO_2 and H_2O are evolved and succinic acid is formed:

$$2\,(—CH_2COOH) \rightarrow HOOCCH_2CH_2COOH$$

It seems that this process takes place at 433–448 K, but succinic acid is found in the volatile products of decomposition only at temperature higher than its boiling point (503 K). In the DTA curves of some dicitratoborates (Fig. 6), endothermal minima are seen at 458 and 503–506 K, which can be connected with the melting and boiling points of succinic acid. Decarboxylation and C—C bond rupture are endothermal, while the oxidation of CH_2 to CO, CO_2 and H_2O involves exothermal processes; the DTA curve reveals an overall endothermal effect, corresponding to a weight loss in the TG curve equal to the loss of weight if all the $—CH_2COOH$ end-groups are split off.

The last stage of decomposition is the oxidation of the residual organic component. In the volatile products of decomposition at this stage, only CO and CO_2 are identified. The residue after combustion at 773–813 K is in most cases $M_2O \cdot B_2O_3$ or $MO \cdot B_2O_3$. The residue from the Li or K salt is the metaborate $M_3B_3O_6$, while that from the Zn salt is α-ZnB_2O_4; these products were identified by X-ray analysis. $CoO \cdot B_2O_3$ is X-ray amorphous. For the Cu(II) and Mn(II) salts, mixtures of B_2O_3 with metallic Cu or Mn_2O_3 were found. The ammonium salt gave only B_2O_3.

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Zusammenfassung — Die thermische Zersetzung von Dicitratboraten der allgemeinen Formeln $M^I[B(C_6H_6O_7)_2] \cdot nH_2O$ (n = 0–2; M^I = Rb, K, Li, NH_4) und $M^{II}[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$ (M^{II} = Co, Ni, Mn, Cu, Zn, Cd) wurden mittels TG, DTA und DTG untersucht. Es wurde gefunden, daß die thermische Zersetzung dieser Verbindungen in drei Schritten verläuft: Dehydratisierung, endotherme Zersetzung des Liganden und Oxydation des organischen Rückstandes. Die flüchtigen Zersetzungsprodukte eines jeden Stadiums wurden gaschromatographisch detektiert. Zur detailierten Untersuchung der Dehydratisierung wurden die TG-Kurven zu Kurven transformiert, in denen dm/dT gegen m dargestellt ist, wobei m der Gewichtsverlust zu einer gegebenen Zeit ist. Die optimalen Bedingungen für die TG-Kurvenmodifikation wurden festgestellt.

Резюме — Методами ТГ, ДТГ, ДТА изучено термическое разложение дицитратоборатов $Me^I[B(C_6H_6O_7)_2] \cdot nH_2O$, где n = 0–2, и $Me^{II}[B(C_6H_6O_7)_2]_2 \cdot 8H_2O$, где Me^I = Rb, K, Li, NH_4, Me^{II} = Co, Ni, Zn, Cd, Mn, Cu. Выявлены три последовательных этапа термического разложения: дегидратация, эндотермическое разложение лиганда и окисление оставшейся органической составляющей. Газохроматографически определен состав летучих продуктов разложения на каждом этапе. Для детального изучения дегидратации применен метод преобразования кривой ТГ в кривую $\frac{dm}{dT} - m$ (МДТГ). Выявлены оптимальные для преобразования кривой ТГ условия эксперимента.