

THE STUDY OF DEHYDRATION OF DICITRATOBORATES BY MEANS OF
TG- CURVE MODIFICATION

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ABSTRACT

The possibility of the investigation of dehydration processes by means of the modification of TG-curve in the (dm/dT) -m curve is shown at the example of dehydration of octahydrate of dicitratoborate of cobalt. The several (3) stages of dehydration are found in the temperature range not over 430 K, where the DTG-curve shows only one minimum. The reproducibility of results (T,m) and their dependence on the various parameters of experiment were discussed. The dehydration of dicitratoborates of Zn, Cd, Fe (II) is investigated by means of TG-curves modification.

INTRODUCTION

The dicitratoborates of d- elements: $M[B(C_6H_6O_7)_2] \cdot 2 \cdot 8H_2O$ where M- Co, Zn, Cd, Ni, Mn are synthesized earlier [1]. The X-ray analysis shows, that six moles of water belong to the coordination sphera of the cation, but two are linked with the complex anion by means of hydrogen linkages[2]. The thermal decomposition of dicitratoborates includes some successive stages: the dehydration, the endothermal decomposition of the ligand, including the tearing off the endgroups- CH_2COOH and the building in the secondary reactions CO, CO_2 , H_2O and succinic acid, whose are found in the volatile products of decomposition, and oxydation of the rested organic component. The rests of combustion in the major cases are the borates 1: 1[3]. It is impossible to resolve the stages of dehydration on the DTG- curves (fig. 1) and exactly to find the end of dehydration owing to overlapping the effect of the beginning of ligand decomposition. Therefore the method of the TG- curve - modification was applied.

MEASURING METHODS

The TG- curve was recorded by means of Derivatograph OD - 102 and Q - Derivatograph in dynamic regime (293 - 523 K). The sensitivity of the thermobalances was 0,25 mg per scale unit, the heating rate 1,25 K/min. The small standart crucible was used with Al_2O_3 as the reference substance. The scanning rate was

8,8 mm/min (Derivatograph OD - 102). Two drums were used to ensure rapid change of the photopaper, there the curve was written on 2-3 photopapers. When the ϕ - Derivatograph was used the scanning rate was 20 mm/min. The atmosphere - air, the volatile products were sucked away.

To transform the TG- curve the analog signal from the weight adapter was discretized with definite steps and the derivative dm/dT was calculated by means of the computer "Mir-2". The DTG-curve was constructed in the coordinates $(dm/dT)-m$, where

$m = m_0 - m_i$, where m_0 - the initial weight of the sample, m_i - the weight of sample at definite moment of time t .

In separate experiments the reproducibility of the results (T, m) and their dependence on the heating rate, the weight of sample, the form of crucible was determined.

RESULTS AND DISCUSSION

The method of modifying of TG- curves allows to distinguish 3-5 stages of the dehydration (fig. 2, table 1). This is in general the loss of three, three and two molecules of water (dicitratoborates of Fe (II), Cd). The first and second stages sometimes are split in two steps with the loss of first one, then two (dicitratoborate of Co) or the first two, then one (dicitratoborate of Zn) moles of water in each. This shows that the linkages of water to metal in the octahedra $[Me(H_2O)_6]^+$ energetically are not equal.

Table 1

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

Dicitratoborate	The temperatures of maxima, K					The losses of weight at the temperatures of minima, mol				
	I	II	III	IV	V	I	II	III	IV	V
Zn	383	386	389	393	408	1	2	2	1	2
Fe		381,7		390,3	420		3		3	2
Cd		398,7		404,0	452		3		3	2
Co	381,2	383,7		397	430	1	2	3		2

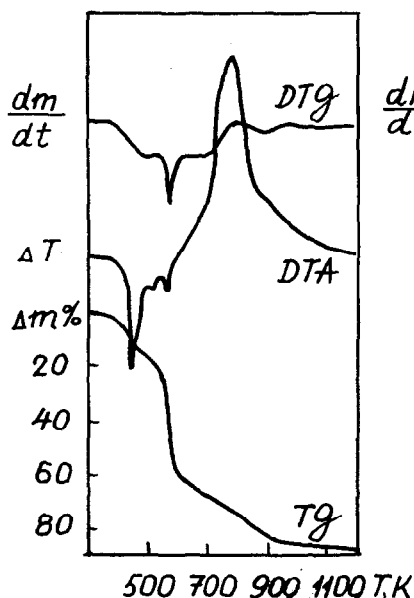


Fig. 1. Thermoanalytical curves of cobaltum dicitratoborate $\text{Co} [\text{B} (\text{C}_6 \text{H}_6 \text{O}_7)_2]_2 \cdot 8 \text{H}_2\text{O}$

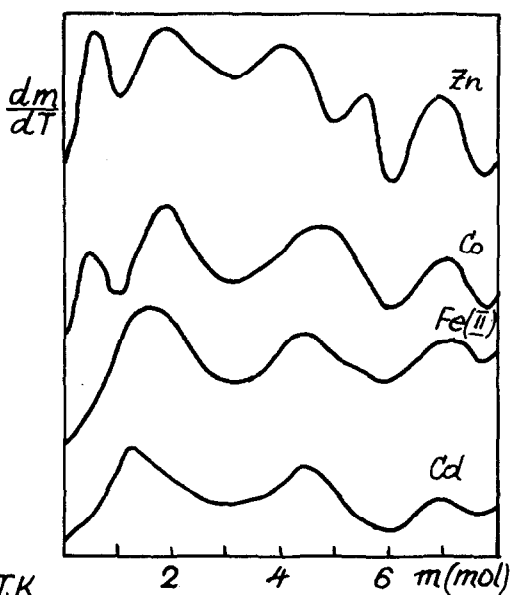


Fig. 2. Modified TG-curves of $\text{M} [\text{B} (\text{C}_6 \text{H}_6 \text{O}_7)_2]_2 \cdot 8 \text{H}_2\text{O}$ M- Zn, Co, Fe, Cd

The reproducibility of results is shown in table 2 on the example of cobaltum dicitratoborate. The standard deviation s at the temperatures of maxima is not greater than 3 K, of weight losses in each stage-not greater than 0,2 mol H_2O . The type of derivatograph has not influence on the reproducibility of results. The use of plate-crucibles changes the temperatures within in the range of deviations, but the weight loss reproducibility becomes worse. The increase of heating rate leads to the tendency of the growth of the temperatures of the maxima and minima of the modified curve. The change of the weight of sample by the use of plate-crucibles and connected change of the sensitivity of thermobalances does not lead to substantial change of temperatures and loss of weight in the stages of dehydration.

Table 2

The reproducibility of results of the TG- curve modification on the example of dehydration of $\text{Co}[\text{B}(\text{C}_6\text{H}_6\text{O}_7)_2]_2 \cdot 8\text{H}_2\text{O}$.

Type of apparatus	N	Temperature of maxima, K				The loss of weight, (mol H_2O) at the temperatures of minima,			
		I	II	III	IV	I	II	III	IV
Derivatograph OD-102,	1	385,4		395,9	430,0	-	2,9 ^x	3,0	2,0
	2	385,5		394,7	429,0	-	2,6 ^x	3,3	2,1
scanning rate 8,8 mm/min	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
Derivatograph Q-1500,	5	-	388,0	386,9	428,0	-	3,0 ^x	2,8	2,1
	6	381,6	390,9	397,8	-	0,8	2,3	2,8	-
scanning rate 20 mm/min	7	385,0	390,0	399,9	432,9	0,9	2,0	3,1	2,0
	S	2,87	1,97	1,75	2,71	0,71	0,17	0,10	0,12
	S _m	1,43	0,88	0,66	1,11	0,08	0,09	0,04	0,05
	2S _m	2,86	1,76	1,32	2,22	0,16	0,18	0,08	0,10

x- Is not taken in account at deviation calculating

CONCLUSIONS

The optimal conditions of getting the modified TG- curve of dicitratoborates $\text{Me}[\text{B}(\text{C}_6\text{H}_6\text{O}_7)_2]_2 \cdot 8\text{H}_2\text{O}$ in the region of dehydration are: weight of sample 245 mg, heating rate 1,25 K/ min, the use of Q-Derivatograph in dynamic regime, the scanning rate 20 mm/min, small standart crucible, the sensitivity of thermobalance 0,25 mg per unit of scale.

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