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THERMOGRAVIMETRIC INVESTIGATION OF THE DECOMPOSITION OF AQUO-ACIDO COMPLEXES UNDER QUASI-ISOTHERMAL AND QUASI-ISOBARIC CONDITIONS

II. EDTA CHELATES: $M_IM_{II}L \cdot 6H_2O$

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The dehydration of some isostructural EDTA chelates $MgNiL \cdot 6H_2O$, $MgCoL \cdot 6H_2O$, $MgCuL \cdot 6H_2O$ and $MnCuL \cdot 6H_2O$, was studied by thermogravimetry under quasi-isobaric and quasi-isothermal conditions. In the TG curves four decomposition periods can be distinguished. The inflexion points of the curves probably refer to the transitional formation of the intermediates $M_IM_{II}L \cdot 5H_2O$, $M_IM_{II}L \cdot 2H_2O$ and $M_IM_{II}L \cdot H_2O$.

In the first part of our publication [1] we reported results obtained in investigations of the dehydration processes of different EDTA chelates of the type: $M_IM_{II}L \cdot 9H_2O$. We performed our investigations with a non-conventional thermogravimetric technique under quasi-isothermal and quasi-isobaric conditions [2, 3].

In the present paper we wish to report observations made in connection with the dehydration of the EDTA chelates $MgNiL \cdot 6H_2O$, $MgCoL \cdot 6H_2O$, $MgCuL \cdot 6H_2O$ and $MnCuL \cdot 6H_2O$, which had been investigated earlier by dynamic thermoanalytical methods [4, 5].

Experimental

Instrument

A Q-Derivatograph (Hungarian Optical Works, MOM, Budapest) was used by means of which thermoanalytical investigations can be performed under conventional [6] and quasi-isothermal and quasi-isobaric conditions [2, 3].

Experimental conditions

Curves 1–4 in Figs 1–4 were traced by applying a quasi-isothermal heating programme (0.5 mg weight change min) and four different types of sample holders, i.e. the labyrinth crucible [2, 3], the conventional crucible of the Derivatograph, either covered or uncovered, and the polyplate sample holder [6] in the sequence of curves 1–4 respectively. It was found that the partial pressure of the gaseous decomposition products in contact with the solid sample changed in the above sequence as follows: p_{gas} = 0.01, 0.05, 0.2 and 1 atm respectively [1]. For the sake of comparison, the TG curve (curve 5) is shown by a dotted line in the figures. This curve was obtained in the conventional way by using the uncovered crucible and a heating programme of 5°/min. The TG, DTG, and DTA curves in Fig. 5 demonstrate the whole thermal decomposition similarly in the uncovered crucible and under dynamic heating conditions. All experiments were carried out in the presence of air.

Chemicals

The method of preparation [7] of the binuclear chelates is rather simple, since if two different metal EDTA chelates are brought together in an aqueous solution, then their binuclear complex will be precipitated:

$$M_2^IL + M_2^{II}L = 2M^IM^{II}L \cdot 6H_2O$$

After filtering-off of the precipitate it is washed with water and alcohol and dried at room temperature.

Results and discussion

The investigated complexes $MgNiL \cdot 6H_2O$, $MgCoL \cdot 6H_2O$, $MgCuL \cdot 6H_2O$ and $MnCuL \cdot 6H_2O$ are binuclear, isostructural octodentate chelates of the type

$$[M_I(H_2O)_4O_IO_{II}]\,[M_{II}L] \cdot 2H_2O$$

where O_I and O_{II} are the carbonyl oxygens of the EDTA carboxylic group.

These analogous structures are probably responsible for the fact that the dehydrations of all four chelates took place in a very similar way, and differences between them can only be found in the values of their transformation temperatures.

In the TG curves of the four chelates (curves 1 in Figs 1–4), obtained by applying the quasi-isothermal heating programme and the labyrinth sample holder, four sections can be distinguished uniformly. First one mole of water escapes, an intermediate of composition $M_IM_{II}L \cdot 5H_2O$ being formed.

In the second period of the decomposition this intermediate loses further 3 moles of water. This process was unambiguous and took place according to zero order [1], curves 1 in Figs 1–4 showing the sample temperature to be strictly constant during this decomposition period.

Curves 1 of Figs 1–4 show two further break-points, corresponding to the compositions $M_IM_{II}L \cdot 2H_2O$ and $M_IM_{II}L \cdot H_2O$. It is rather hard to identify the first break-point, but the second can be recognized without difficulty. The third period of the decomposition process took place in a temperature interval of about 10–15° between the above two break-points, demonstrating that this process is not an unambiguous and uniform reaction. A possible explanation of this could perhaps be that in this period of the decomposition not solely the reaction $M_IM_{II}L \cdot 2H_2O = M_IM_{II}L \cdot H_2O + H_2O$ took place, but the decomposition process $M_IM_{II}L \cdot H_2O = M_IM_{II}L + H_2O$ also slowly started, and the decomposition period in question was the resultant of the two reactions.

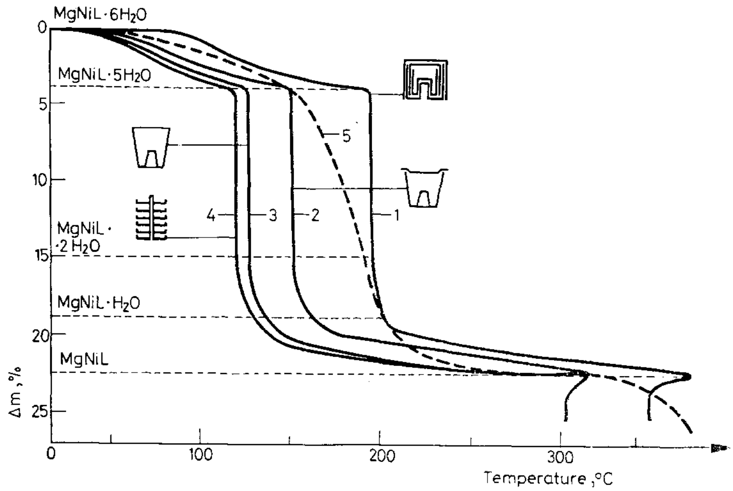

Fig. 1. Dehydration of EDTA chelate MgNiL · $6H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: *ca.* 350 mg. Atmosphere: air.

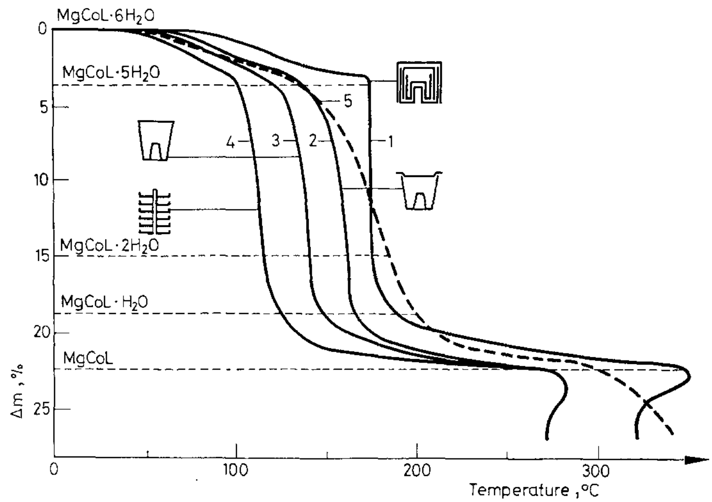

Fig. 2. Dehydration of EDTA chelate MgCoL · $6H_2O$ Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: *ca.* 350 mg. Atmosphere: air.

The last period of the dehydration took place in a broad temperature interval extending over 30–180°.

Curves 2–4 in Figs 1–4 are of similar course as curves 1. Accordingly, it seems that in every case the decomposition was practically the result of the same

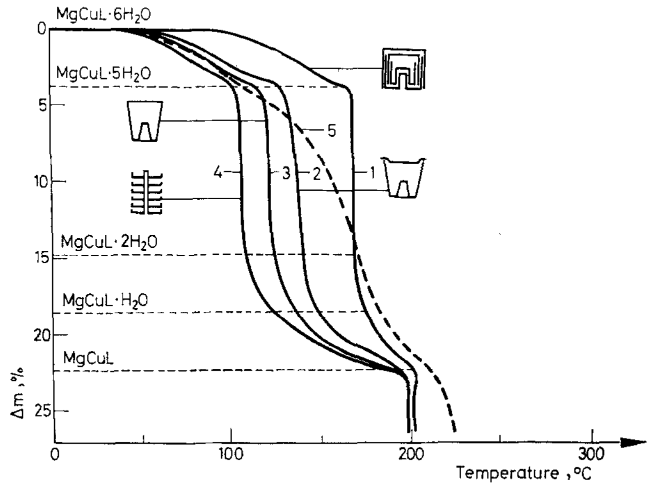

Fig. 3. Dehydration of EDTA chelate MgCuL · $6H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: *ca.* 350 mg. Atmosphere: air.

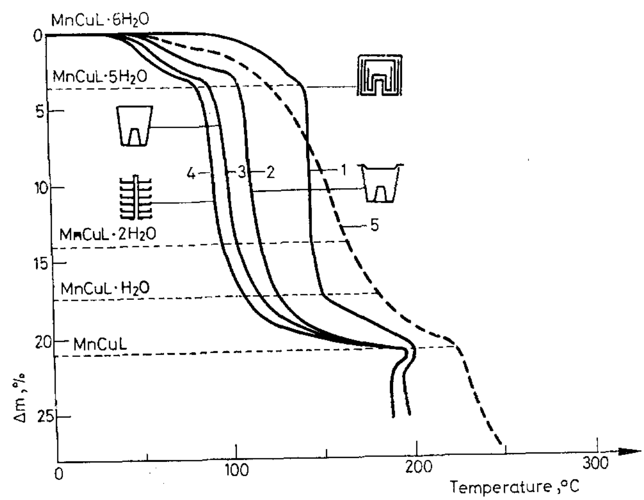

Fig. 4. Dehydration of EDTA chelate MnCuL · $6H_2O$. Sample holder: curve 1: labyrinth; curve 2: crucible with lid; curve 3: crucible without lid; curve 4: polyplate. Heating programme: curves 1–4: quasi-isothermal. Weight of sample: *ca.* 350 mg. Atmosphere: air.

partial reactions and their mechanisms between the courses of these were also very similar.

A significant shift can be found between the course of these curves. However, the temperatures of the second decomposition period increased in the sequence of the applied sample holders along with the increased partial pressure of the water vapour in the vicinity of the sample. This also proves that the reaction

$$M_IM_{II}L \cdot 5H_2O = M_IM_{II}L \cdot 2H_2O + 3H_2O$$

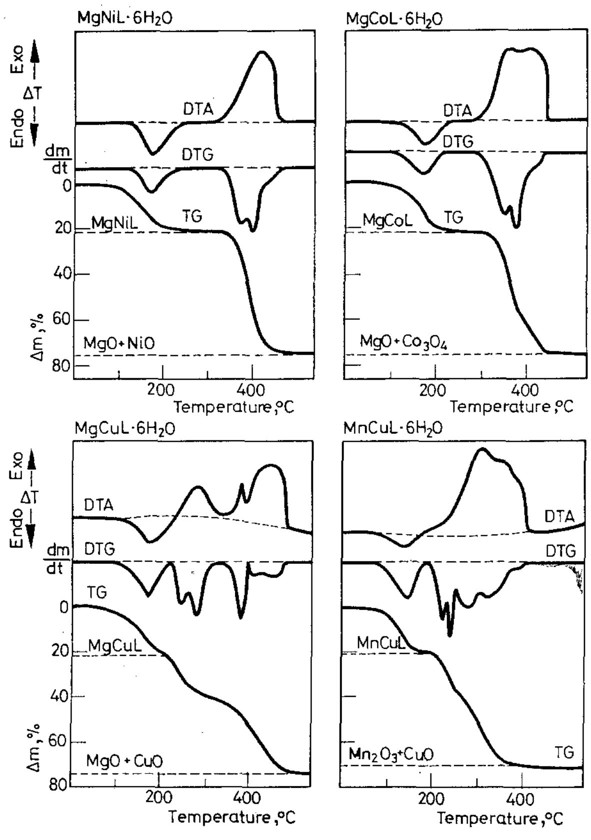

Fig. 5. TG, DTG and DTA curves of EDTA chelates. Sample holder: crucible without lid. Heating programme: dynamic, 5°/min. Weight of samples: *ca.* 350 mg. Atmosphere: air

is actually a process leading to equilibrium. In spite of this in this decomposition period the sample temperature did not become constant, even transitionally. This can probably be explained by supposing that under the given conditions not solely the above reaction took place, but the next two partial dehydration processes started too. Accordingly, the relevant section of curves 2–4 in Figs 1–4 represents the resultant of more than one partial reaction.

Curves 1 of Figs 1·4 show the decomposition temperatures of the intermediates $M_IM_{II}L \cdot 5H_2O$ and $M_IM_{II}L$ to decrease without exception in the sequence:

Mg Ni complex > Mg Co complex > Mg Cu complex > Mn Cu complex; this simultaneously also expresses the stability sequence of these chelates.

The curves obtained under the conventional experimental conditions do not offer much information about the partial reactions taking place during the thermal decomposition of the compounds in question. All the curves traced by using the dynamic heating programme and the open crucible (curves 5 in Figs 1–4) show the dehydration of the investigated chelates as a one-step process.

The TG, DTG and DTA curves obtained for the overall decomposition of the chelates (Fig. 5) are not characteristic; this is understandable, since they are the resultants of many complicated partial processes.

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Résumé — On a étudié par thermogravimétrie, en conditions quasi-isobares et quasi-isothermes, la déshydratation de plusieurs chélates de l'EDTA isostructuraux: $MgNiL \cdot 6\,H_2O$ $MgCoL \cdot 6\,H_2O$, $MgCuL \cdot 6\,H_2O$ et $MnCuL \cdot 6\,H_2O$. On peut distinguer quatre étapes de décomposition sur les courbes TG. Les points d'inflexion des courbes se rapportent probablement à la formation transitoire de produits intermédiaires de composition $M_IM_{II}L \cdot 5\,H_2O$, $M_IM_{II}L \cdot 2\,H_2O$ et $M_IM_{II}L \cdot H_2O$.

Zusammenfassung — Die Dehydratisierung einiger isostruktureller EDTA-Chelate, wie $MgNiL \cdot 6\,H_2O$, $MgCoL \cdot 6\,H_2O$, $MgCuL \cdot 6\,H_2O$ und $MnCuL \cdot 6\,H_2O$ wurde thermogravimetrisch unter quasi isobaren und quasi isothermen Bedingungen untersucht. In den TG-Kurven können vier Zersetzungsabschnitte unterschieden werden. Die Inflexionspunkte der Kurven beziehen sich wahrscheinlich auf die Übergangsbildung intermediärer Produkte der Zusammensetzungen $M_IM_{II}L \cdot 5\,H_2O$, $M_IM_{II}L \cdot 2\,H_2O$ und $M_IM_{II}L \cdot H_2O$.

Резюме — Термогравиметрическим путем при квази-изобарных и квази-изотермических условиях была изучена дегидратация некоторых изоструктурных ЕДТА хелатов: $MgNiL . 6H_2O$, $MgCoL . 6H_2O$, $MgCuL . 6H_2O$ и $MnCuL . 6H_2O$. На кривых ТГ можно выделить четыре периода разложения. Точки инфлексии на кривых, вероятно, обусловлены образованием переходных промежуточных продуктов разложения $M_IM_{II}L. 5H_2O$, $M_IM_{II}L. 2H_2O$ и $M_IM_{II}L. H_2O$.