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CHARACTERIZATION OF SOME MIXED COMPLEX COMBINATIONS OF Ni(II) WITH PICOLINES FROM THERMOGRAVIMETRIC DATA

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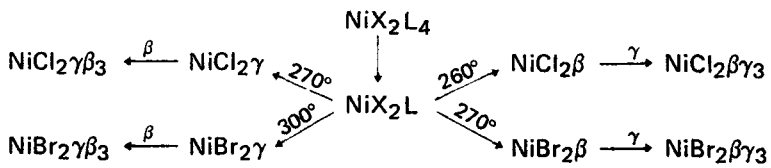
New mixed complex combinations of Ni(II) with γ and β-picoline were synthesized and characterized by means of thermogravimetry under dynamic temperature conditions. The formation of these complex combinations was confirmed, the structure-thermostability dependence was established, and a mechanism for the thermal degradation was proposed.

In previous papers [1–3] the thermal behaviour of some complex combinations of the type NiX_2L_4, where X denotes Cl or Br and L = γ or β-picoline, was studied under dynamic temperature conditions. The decomposition was found to proceed stepwise, which suggested the possibility of preparing complex combinations of Ni(II) with both γ- and β-picoline.

Experimental

Complexes of the types $NiX_2\beta$ and $NiX_2\gamma$ were separated thermally and new complexes were synthesized by treating them with γ- and β-picoline, respectively. The separating temperatures, depending on the natures of X and L, were established from the thermogravimetric data. The synthesis procedure and the temperatures for the complex separations are given in the following scheme:



The complex NiX_2L_4 was submitted to dynamic heating at 10 deg/min until the formation temperature of NiX_2L was reached. The separating complex was treated with a picoline excess. The complexation with γ-picoline was performed by stirring for 30 minutes at room temperature. The complexation with β-picoline takes place

under heating. The complex + picoline mixture was heated for 30 minutes in a flask provided with a reflux condenser. The complexes were separated by filtration and then washed with ethyl alcohol and ether.

Four mixed Ni-picoline complexes were synthesized and characterized by thermogravimetry. The analyses were performed on a MOM-Budapest derivatograph with recording of the weight losses (TG), the derivative (DTG), the differential thermal analysis (DTA) and the temperature increases (T). The thermal curves were recorded in air at a heating rate of 10 deg/min. In order to obtain comparable data, the same sensitivities for TG (10 mg), DTG (1/10) and DTA (1/10) and sample weight of about 100 mg were maintained.

Results and discussion

The thermal curves were recorded under the above conditions for the mixed complex combination and for the parent complexes of Ni(II) with γ-picoline and β-picoline, respectively.

The DTG and TG curves of $NiCl_2\gamma_3\beta$ and $NiCl_2\gamma_4$ are depicted in Fig. 1.

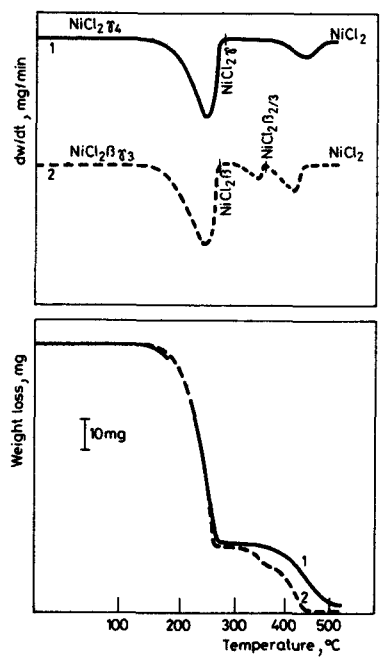


Fig. 1 DTG and TG curves of $NiCl_2\gamma_4$ (1) and $NiCl_2\gamma_3\beta$ (2)

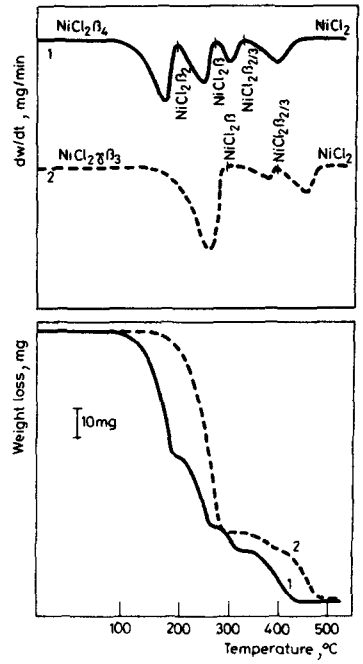


Fig. 2 DTG and TG curves of $NiCl_2\beta_4$ (1) and $NiCl_2\gamma\beta_3$ (2)

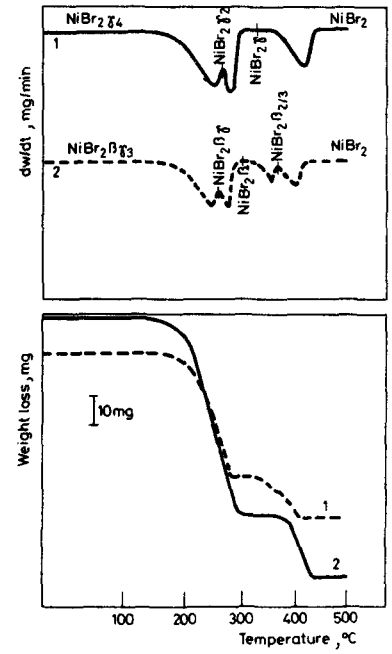


Fig. 3 DTG and TG curves of $NiBr_2\gamma_4$ (1) and $NiBr_2\beta\gamma_3$ (2)

The differences in thermal behaviour suggest the presence of β-picoline in the structure. The first degradation stage is identical for the two complexes, and is followed by a new stage for $NiCl_2\gamma_4$ and by two stages for $NiCl_2\gamma_3\beta$. These stages are characteristic of the thermal degradation of the complex combinations of the type $NiCl_2\beta$.

The complex $NiCl_2\gamma\beta_3$ differs from $NiCl_2\beta_4$ by superimposition of the first two stages in the case of the mixed combination; this suggests the presence of γ-picoline in the molecule (Fig. 2).

Similar results were obtained for the mixed combinations containing bromine. In the case of the complex $NiBr_2\beta\gamma_3$, the appearance of the stages specific for the thermal degradation of $NiBr_2\beta$ confirms the existence of this new compound (Fig. 3).

The complexes $NiBr_2\beta_4$ and $NiBr_2\gamma\beta_3$ differ in the shapes of the DTG and TG curves, which confirms the composition modifications of the molecule, that is the presence of γ-picoline (Fig. 4).

The thermogravimetric characteristics are listed in Table 1.

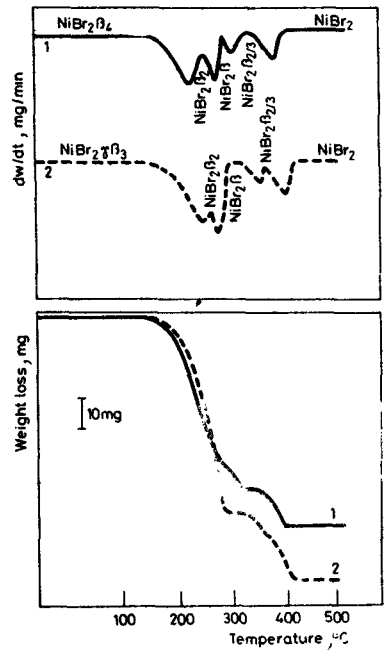


Fig. 4 DTG and TG curves of $NiBr_2\beta_4$ (1) and $NiBr_2\gamma\beta_3$ (2)

Table 1 Thermogravimetric characteristics of the complex combinations

NiX_2L_4	W_∞, %									
	Overall weight losses		step I		step II		step III		step IV	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
$NiCl_2\beta_4$	74.30	73.38	37.13	34.68	18.58	19.35	6.19	6.45	12.38	12.90
$NiCl_2\gamma_4$	74.30	72.36	55.73	54.47	18.58	17.88	–	–	–	–
$NiCl_2\beta\gamma_3$	74.30	73.77	55.73	55.32	6.19	6.14	12.38	12.29	–	–
$NiCl_2\gamma\beta_3$	74.30	73.57	55.73	55.28	6.19	6.09	12.38	12.19	–	–
$NiBr_2\beta_4$	63.01	60.00	31.48	30.00	15.75	14.16	5.24	5.41	10.50	10.41
$NiBr_2\gamma_4$	63.01	62.50	31.48	31.25	15.75	15.27	15.75	15.28	–	–
$NiBr_2\beta\gamma_3$	63.01	59.37	31.48	29.69	15.75	14.58	5.24	4.68	10.50	10.41
$NiBr_2\gamma\beta_3$	63.01	62.50	31.48	31.25	15.75	15.28	5.24	5.55	10.50	10.42

The overall weight losses, as well as those observed for individual decomposition stages, confirm the existence of the mixed complex combinations and suggest the following thermal degradation mechanism:

$NiCl_2\beta_4 \longrightarrow NiCl_2\beta_2 \longrightarrow NiCl_2\beta \longrightarrow NiCl_2\beta_{2/3} \longrightarrow NiCl_2$

$NiCl_2\gamma_4 \longrightarrow NiCl_2\gamma \longrightarrow NiCl_2$

$NiCl_2\beta\gamma_3 \longrightarrow NiCl_2\beta \longrightarrow NiCl_2\beta_{2/3} \longrightarrow NiCl_2$

$NiCl_2\gamma\beta_3 \longrightarrow NiCl_2\beta \longrightarrow NiCl_2\beta_{2/3} \longrightarrow NiCl_2$

$NiBr_2\beta_4 \longrightarrow NiBr_2\beta_2 \longrightarrow NiBr_2\beta \longrightarrow NiBr_2\beta_{2/3} \longrightarrow NiBr_2$

$NiBr_2\gamma_4 \longrightarrow NiBr_2\gamma_2 \longrightarrow NiBr_2\gamma \longrightarrow NiBr_2$

$NiBr_2\beta\gamma_3 \longrightarrow NiBr_2\beta\gamma \longrightarrow NiBr_2\beta \longrightarrow NiBr_2\beta_{2/3} \longrightarrow NiBr_2$

$NiBr_2\gamma\beta_3 \longrightarrow NiBr_2\beta_2 \longrightarrow NiBr_2\beta \longrightarrow NiBr_2\beta_{2/3} \longrightarrow NiBr_2$

In order to establish the structure-thermostability dependence, the energy of activation was estimated by means of the Freeman–Carroll [4] differential method (Table 2).

Table 2 Energies of activation of the decomposition steps

NiX_2L_4	Energy of activation, kJ/mol			
	step I	step II	step III	step IV
$NiCl_2\beta_4$	76	148	225	178
$NiCl_2\gamma_4$	70	172	–	–
$NiCl_2\beta\gamma_3$	88	287	191	–
$NiCl_2\beta_3\gamma$	87	370	231	–
$NiBr_2\beta_4$	87	294	383	266
$NiBr_2\gamma_4$	84	191	159	–
$NiBr_2\gamma\beta_3$	80	478	–	357
$NiBr_2\beta\gamma_3$	96	382	151	410

The energies of activation for low conversion degrees indicate an increased thermostability of the mixed complex combinations in comparison with the parent NiX_2L_4 complexes. A significant increase in the activation energies of the intermediates is also observed.

The application of thermogravimetry under dynamic temperature conditions allowed the synthesis of new complex combinations, as well as the establishment of the structure-thermostability dependence.

References

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4 E. S. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.

Zusammenfassung — Neue gemischte Komplexkombinationen von Ni(II) mit γ- und β-Picolin wurden synthesisiert und thermogravimetrisch charakterisiert. Die Bildung dieser Komplexe wurde nachgewiesen, die Abhängigkeit zwischen Struktur und Thermostabilität ermittelt und ein Mechanismus für den thermischen Abbau vorgeschlagen.

Резюме — Синтезированы и термогравиметрически охарактеризованы в условиях динамической температуры новые смешанные комплексы двухвалентного никеля с γ- и β-пиколином. Подтверждено образование этих комбинированных комплексов, установлена зависимость термоустойчивости их от структуры и предложен механизм термического разложения.