

THERMAL ANALYSIS OF COMPLEXES OF CADMIUM CHLORIDE PICOLINE

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The thermal decomposition of the α , β and γ -picoline complexes of cadmium were studied by means of TG-DTG-DTA. In connection with the preparation of the complex compounds, it was established that the ligand number was influenced by the reaction medium. The thermal decomposition took place stepwise, and intermediates were formed which could be isolated with a derivatograph by the "freezing-in" method. The structures and properties of these previously unknown compounds were investigated by far-IR spectroscopy and X-ray powder diffraction.

In investigations of the thermal stabilities of the complexes of various transition metals with 2, 3 or 4-methylpyridine (i.e. α , β , or γ -picoline), the formation of decomposition products characterized by a lower number of ligands than in the original complex has been observed.

The structures and properties of the intermediates of the thermal decompositions were unknown. After earlier investigations [1], cadmium was chosen as the central atom of the complexes in the present case. Thus, difficulties caused by the changing oxidation state could be eliminated, and the uniform composition and reproducibility of the intermediates were ensured. Preparations of these compounds have not been reported in the literature, but by means of thermal analysis the intermediate complexes formed during the decompositions could be isolated with the derivatograph, by the "freezing-in" method.

For the preparation of the new starting compounds products of exactly determined compositions were needed.

For the preparation of the pyridine or picoline complexes of transition metals, four methods have been described in the literature [2–9] (Table 1).

Hause [10] used preparation method A, and obtained 1:1 complexes with α -picoline and 2:1 complexes with β -picoline, while γ -picoline gave an inhomogeneous mixture of 1:2 and 1:4 complexes of cadmium chloride and picoline. In the case of complexes with γ -picoline, ligand numbers of 4 [11] and 3.55 [12] have been reported. Thus, for a given picoline, have been complexes with different

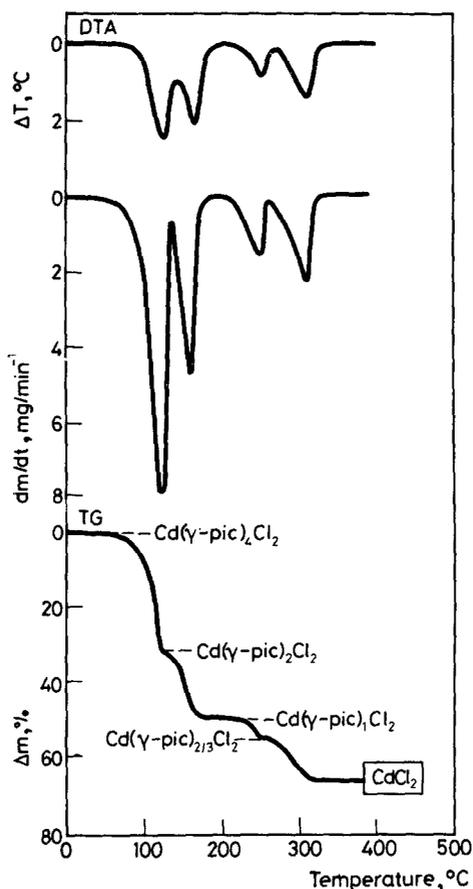


Fig. 1 TG, DTG and DTA curves of $[\text{Cd}(\gamma\text{-pic})_4]\text{Cl}_2$

coordination numbers have been found. We assumed that the nature of the solvent used in the preparation process might influence the composition of the complex.

Experimental

In the preparation of the picoline complexes of cadmium chloride, the solvent was applied in the quality and quantity used by the different authors. The cadmium chloride–picoline mole ratio was in each case 1 : 5. During stirring, the reaction mixture was refluxed for 1.5 h. After cooling of the reaction mixture, the product

Table 1 Preparation methods

CdCl ₂		Reaction medium			
A	Siccum	excess of picoline			
B	Concentrated solution in water	water			
C	Concentrated solution in water	ethanol			
D	Concentrated solution in water	acetone			

Compound	Ligand number, <i>n</i> , depending on the preparation method			
	A	B	C	D
Cd(α -pic) _{<i>n</i>} Cl ₂	1.5	1	1.8	1
Cd(β -pic) _{<i>n</i>} Cl ₂	4	2	2	2
Cd(γ -pic) _{<i>n</i>} Cl ₂	4	4	2	2

was filtered off and dried in a vacuum desiccator. The reaction mixture was processed in the same way in each case.

The compounds prepared are sparingly soluble in water, acetone, ethanol, chloroform and benzene. The percentage yields reflect the more or less poor solubilities of the compounds in the solvents used as reaction media. On the other hand, the compounds can be recrystallized from dimethylformamide or dimethylsulfoxide without ligand exchange. The cadmium contents of the compounds prepared were determined by means of complexometric titration and atomic absorption, and on the basis of their TG curves.

Results

The percentage yields, cadmium contents and ligand numbers of the compounds containing the same ligand and prepared in different reaction media are listed in Table 2.

For the α -picoline complexes, only the compound with ligand number 1 was earlier known (this was explained by steric reasons). It was found here that, the nature of the reaction medium affects the composition of the product formed (Tables 1 and 2). Depending on the preparation method, compounds with fractional ligand number were also formed; these are presumably mixtures of compounds with ligand numbers 1 and 2. Thermal investigations proved on the basis of the TG curve and the high initial peak temperature that the fractional coordination number cannot originate from α -picoline bound by sorption. This finding was supported by the TG-DTG-DTA curves of the product recrystallized from dimethylformamide, the thermal analysis of which yielded the same results as those on the original compound.

Table 2 Characteristic data of the preparation method and complex compounds

Compound	Method	Yield, %	Content	Number of ligands (<i>n</i>), from the Cd content
Cd(α -pic) _{<i>n</i>} Cl ₂	A	87.0	345	1.5
	B	79.6	561	1
	C	94.0	360	1.8
	D	76.0	582	1
Cd(β -pic) ₂ Cl ₂	A	100	211	4
	B	94.1	320	2
	C	82.3	300	2
	D	80.7	285	2
Cd(γ -pic) _{<i>n</i>} Cl ₂	A	100	196	4
	B	94.8	202	4
	C	83.6	325	2
	D	79.2	290	2

When methods A and C were applied at the given production parameters, the composition of the product could be reproduced. Thus, in all probability, further variation of the reaction parameters would permit preparation of the product with ligand number 2.

It can be established from the data in Table 2 that for the β -picoline complex method A give the most favorable percentage yield. The highest ligand number value was also attained in this case, whereas only a product with ligand number 2 was obtained with preparation methods B, C and D. These findings explain why certain authors state that for β -picoline the highest attainable ligand number is only 2.

Data concerning the γ -picoline complexes are contained in Table 2. The values are similar to those of the complexes formed with β -picoline. In this case too, the highest percentage yield and ligand number 4 could be achieved with method A at a γ -picoline excess. However, here method B also permitted formation of the compound with ligand number 4.

As concerns the effect of the reaction medium on the quantitative composition of the complex formed, the following statements can be made:

1. Depending on the nature of the picoline used as ligand, the coordination number may change from 1 to 4 in the direction of α -picoline to γ -picoline, because of the decreasing steric hindrance.

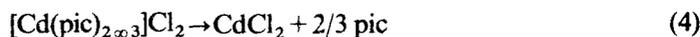
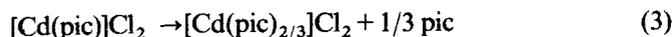
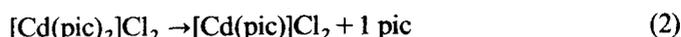
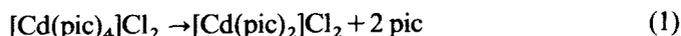
2. At constant other reaction parameters, the nature of the reaction medium may also decisively influence the value of the ligand number for a given ligand.

3. It follows from the above two statements that optimization of the reaction parameters is needed for the preparation of a product with desired ligand number,

and the selection of an appropriate reaction medium is of primary importance. The course of the reaction is influenced by the polarity of the solvent used as reaction medium, while the solubility of the products formed in the reaction medium depends on their ligand number.

The picoline complexes of cadmium chloride are decomposed by heat in a solid-gas phase reaction. This process took place in several well-defined steps, and the picoline ligand left the system as picoline, without burning.

Schematic decomposition equations:



From the product with ligand number 4, 2 ligands are first split off according to Eq. (1), then 1 molecule of picoline leaves the compound (Eq. (2)), but the most interesting step of the whole decomposition is the process characterized by general equation (3), whereby a new complex with fractional ligand number could be prepared.

The thermal analysis of compounds containing different picolines showed that the thermal decomposition process is independent of the preparation method. This permits the conclusion that the products always separate in an identical crystal form, and decomposition always proceeds in the same way for a given ligand number.

Thus, the decomposition process is not affected by nature of the ligand, but by the coordination number. The decomposition steps of identical stoichiometry peak temperatures are shifted towards higher temperatures in the sequence $2 < 3 < 4$ -picoline (Fig. 2).

The starting complexes and their thermal decomposition products were investigated by far-infrared spectroscopy to acquire information on their bond structures and steric structures (Table 3).

Independently of the nature of the ligand, for complexes with ligand number 4 a doublet was always observed (e.g. in the case of β -picoline at 217 and 225 cm^{-1}). This doublet indicates octahedral symmetry at a picoline coordination number of 4. As the metal-chlorine bond vibrations can be assigned to higher frequencies, and the Cd-N ligand bonds to lower frequencies, these data prove the *cis* symmetry of the octahedron. On the other hand, the four different metal-ligand vibrations indicate a distorted octahedron.

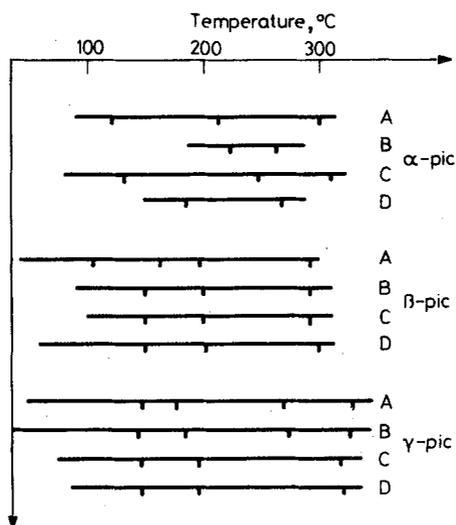


Fig. 2 DTG peak temperatures of the decomposition steps (see Eqs (1-4))

For the compounds containing two molecules of ligands, bands appearing in the $120\text{--}157\text{ cm}^{-1}$ frequency range prove the same crystal structure as above, with a trans-annular arrangement, where the vibration of the Cd-Cl bond appears as a singlet. The increase in the value of $\nu_{\text{Cd-Cl}}$ (230 cm^{-1}) can be attributed to the change in the coordination number.

When the ligand number is 1, the characteristic bands of the Cd-Cl bond appear at 202 and 226 cm^{-1} , and the metal-ligand band at 174 cm^{-1} . Two kinds of Cd-Cl band appear; thus, the lower value proves the existence of a chlorine bridge bond, while that at 226 cm^{-1} can be assigned to chlorine not participating in the secondary bond. The frequency ratio of the weaker and stronger bonds is 0.90, on the basis of which a dimeric structure can be presumed, in good agreement with data in the literature.

For compounds with fractional ligand number, the Cd-Cl frequency appears at 227 cm^{-1} , while a broad absorption band at 191 cm^{-1} can be assigned to the Cd-N bond. This broadened absorption band indicates a multinuclear polymeric structure.

The effects of the anion (Cl, Br and I) and of the nature of the ligand (methylpyridine, ethylpyridine, halogenated pyridine and aminopyridine) on the thermal decompositions were also studied. The results obtained will be reported in another publication.

Table 3 Data of far-IR spectra of $\text{Cd}(\beta\text{-picolin})_n\text{Cl}_2$

$n=4$	$n=2$	$n=1$	$n=2/3$	
	101 cm^{-1}	102 cm^{-1}	95 cm^{-1}	
121 cm^{-1} distorted symmetry	121 cm^{-1} transplanar octahedral symmetry	125 cm^{-1}		
140 cm^{-1} distorted symmetry	143 cm^{-1}		132 cm^{-1}	
160 cm^{-1} distorted symmetry	157 cm^{-1} transplanar octahedral symmetry		165 cm^{-1}	
191 cm^{-1} octaeder cis symmetry	189 cm^{-1}	174 cm^{-1}	191 cm^{-1} $\nu\text{Cd-N}$ broad band polymeric structure	
$\left\{ \begin{array}{l} 217 \text{ cm}^{-1} \\ \text{doublet} \\ \text{octahedral} \\ \text{symmetry} \\ 225 \text{ cm}^{-1} \end{array} \right.$		202 cm^{-1} chlorine bridge	$\left. \begin{array}{l} \\ \\ \\ 227 \text{ cm}^{-1} \end{array} \right\}$	$\nu\text{Cd-Cl}$
	230 cm^{-1} singulet	226 cm^{-1} free chlorine dimer structure		

References

- G. Liptay, A. Borbély-Kuszmán and G. Nagy, *J. Thermal Anal.*, 32 (1988) 91.
- J. R. Allan, D. N. Brown and R. H. Nuttal, *J. Chem. Soc.*, A8 (1966) 1031.
- N. Hudruc, L. Odochian and J. A. Schneider, *J. Thermal Anal.*, 6 (1974) 17.
- F. Reizenstein, *Z. Anorg. Allg. Chem.*, 11 (1896) 254.
- J. Vymetal, *Coll. Chech. Chem. Commun.*, 30 (1965) 2134.
- H. Langfelderová, L. Macásková, M. Melnik and J. Gazo, *Z. Anorg. Chem.*, 445 (1978) 214.
- K. Wojcieckovski and J. Szadowski, *J. Prem. Chem.*, 59 (1980) 498.
- C. T. Mortimer and I. S. McNaughton, *Thermochim. Acta*, 10 (1974) 125.
- J. Vymetal and P. Tvarazek, *Z. Anorg. Allg. Chem.*, 351 (1967) 100.
- J. E. Hause and A. L. Rohner, *Thermochim. Acta*, 19 (1977) 119.
- J. E. D. Davies and K. T. Holmes, *J. Mol. Struct.*, 42 (1977) 59.
- E. Segal and D. Fatu, *Introduction to Non-isothermal Kinetics (in Roumanian)*. Editura Academiei Republicii Socialiste Romania, Bucurest, 1983.

Zusammenfassung — Der thermische Zersetzungsprozess der Komplexverbindungen von Cadmiumchlorid mit α -, β - oder γ -Picolin wurde durch simultane TG–DTG–DTA im Derivatograph untersucht. Die Ligandenzahl der Komplexverbindungen wird durch das Reaktionsmedium bei der Präparation beeinflusst. Die thermische Zersetzung erfolgt stufenweise, Zwischenprodukte konnten mittels Derivatograph durch die „Einfriermethode“ isoliert werden. Struktur und Eigenschaften dieser bisher unbekannt Verbindungen wurden durch Fern-IR-Spektroskopie und Röntgenpulverbeugung untersucht.

Резюме — Методом ТГ–ДТГ и ДТА изучено термическое разложение комплексов кадмия с α -, β - и γ -пиколинами. Установлено, что число лигандов в комплексах зависит от реакционной среды. Термическое разложение протекает ступенчато, а образующиеся при этом промежуточные продукты были выделены методом «замораживания». Строение и свойства этих ранее неизвестных соединений были исследованы длинноволновой ИК спектроскопией и рентгено-структурным анализом.