Journal of Thermal Analysis, Vol. 32 (1987) 1051–1062

THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS

VIII. Influence of the structures of complexes $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$ on the course of their thermal transformations

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(Received July 22, 1986)

The paper presents the results of a study of the course of thermal decomposition of complexes $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$, with L = pyrazole, 3,5-dimethylpyrazole, 3,4,5-trimethylpyrazole and indazole. The DTA curves of $Cu(NCO)_2L_2$ show exothermic excursions somewhat below the decomposition temperatures, corresponding to an inner complex nucleophilic addition of a carbon atom (from an NCO group) to the imine nitrogen atom of a pyrazole ligand. In this reaction the carbamoylpyrazolate anion is formed, coordinated to Cu(II). For these reactions the DSC method yielded the following ΔH values: -12.80 kJ mol^{-1} (L = pyrazole), -8.15 kJ mol^{-1} (L = 3,5-dimethylpyrazole), -19.49 kJ mol^{-1} (L = 3,4,5-trimethylpyrazole) and -11.59 kJ mol^{-1} (L = indazole). The course of thermal decomposition for $Cu(NCO)_2L_2$ after the nucleophilic addition is the same as for $Cu(LNCO)_2$. The structure differences between the distortion isomers of $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$ were manifested in the decomposition temperatures and, in some cases, also in the stoichiometry of the decomposition reactions.

The relationship between the structures of coordination compounds in the solid state and the course of their thermal decompositions is one of the fields where further experimental data are still needed. With respect to the great number of factors influencing the course of thermal decomposition, at present it appears impossible to elucidate this relationship theoretically. For the study of the relations between structure and the course of thermal decomposition reactions, it is advantageous to use series of complexes with analogous compositions and

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structures. The complexes at present under study form two such series at room temperature.

Depending on the conditions, complexes of composition $Cu(NCO)_2L_2$ or $Cu(LNCO)_2$ can be prepared from the systems Cu(II)–NCO^-–ligand of the pyrazole type (pyrazole = pz, 3,5-dimethylpyrazole = dmpz, 3,4,5-trimethylpyrazole = tmpz and lbenzopyrazole indazole) = inz). The latter complexes contain the carbamoylpyrazolate anion, which is formed in the coordination sphere of the Cu(II) through a nucleophilic addition between the carbon of an NCO group and the imine nitrogen atom of a pyrazole ligand [1–4]. Pairs of compounds, one of which contains cyanate and pyrazole ligands, while the other contains chelate ligands of carbamoylpyrazolate type, are called co-ligand isomers. Besides co-ligand isomers, distortion isomers [5] of $Cu(NCO)_2L_2$ for L = pz [3] and $Cu(LNCO)_2$ for L = pz, dmpz and tmpz [1–3] have also been prepared.

Since an exothermic peak appears just below the decomposition temperature in the DTA curves for $Cu(NCO)_2L_2$, it was interesting to find out whether this corresponds to the nucleophilic addition reaction in which the complex $Cu(LNCO)_2$ is formed from $Cu(NCO)_2L_2$, and also how the properties of ligand L influence the ΔH value of this reaction. We were also interested in whether, and in what way, the comparatively fine differences in the structures of the distortion isomers of $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$are manifested in the course of their thermal decompositions.

Experimental

The preparation, analytical composition and identification of the complexes under investigation are described in [1–4, 6].

Thermal decomposition was followed on a MOM OD 102 derivatograph. The sample weight was 100 mg, the rate of temperature increase was 5 deg/min, and α-Al_2O_3 was used as reference material. All measurements were made in a dynamic N_2 atmosphere. The ΔH values were obtained on a DSC-2 apparatus (Perkin–Elmer), as averages of at least five measurements. The area enclosed by an exothermic excursion was integrated with a computer coupled to the apparatus. The sample weight was ~ 3 mg, and the heating rate was 5 deg/min. IR spectra were measured with an IR–75 spectrometer (Carl Zeiss, Jena), using the Nujol suspension technique.

The intermediates in the thermal decompositions of α and β-$Cu(pzNCO)_2$ were prepared isothermally in a metal block at the temperatures corresponding to the respective steps in the TG curves. The contents of C, N and H were determined by elemental analysis with a Carlo Erba apparatus (Milano). The Cu(II) contents were found by complexometric titration with murexide as indicator after mineralization of the samples.

Results and discussion

Determination of ΔH value for nucleophilic addition in the coordination sphere of $Cu(NCO)_2L_2$

The DTA curves of each of the complexes $Cu(NCO)_2L_2$ at temperatures only a few degrees lower than the decomposition temperature show an exothermic excursion. Since the synthesis study had shown that increased temperature supports the formation of $Cu(LNCO)_2$, it was presumed that the observed exothermic effect accompanies the addition reaction occurring in the inner coordination sphere of $Cu(NCO)_2L_2$. The easiest way to differentiate between the end-bonded linear NCO group and the "bent" one in the carbamoylpyrazolate anion is through their infrared spectra. The vibration most sensitive to differences in the coordination mode of the NCO groups in both kinds of compounds is ν_{as}(NCO); in the IR spectra of cyanato complexes this is observed in the region of ~2200 cm^{-1}, while for the carbamoylpyrazolate complexes, due to their lower bonding order, it is shifted to the region of ~1690 cm^{-1} and prevailingly acquires the character of a C=O vibration. The deformation mode occurs in the region of 600 cm^{-1} for the cyanato complexes, while for the carbamoylpyrazolate complexet out-of-plane and in-plane vibrations of the "bent" NCO group are found at about ~500 and ~750 cm^{-1}. In the spectra of carbamoylpyrazolate complexes a band also appears in the region above 1200 cm^{-1}, corresponding to the newly-formed bond C(NCO)—N(pyrazole ring).

In order to find out whether the exothermic reaction indicates this nucleophilic addition, complexes $Cu(NCO)_2L_2$ were heated for a certain time in sealed tubes at temperatures found from the DTA curves of the respective complexes. The values of the IR absorption band maxima corresponding to the above-mentioned vibrations (Table 1) lead to the conclusion that complexes $Cu(LNCO)_2$ really are formed during the heating of $Cu(NCO)_2L_2$, even though the reaction of a comparatively large amount of substance (heating time 2 hours) in sealed tubes was not completed throughout the whole sample volume.

The nucleophilic addition between the end-bonded linear NCO group and the ligand of pyrazole type takes place in the solid phase, but visual observation under the microscope and also the course of the DSC curve (Fig. 1) indicate that the crystals "soften" before the reaction (the exothermic excursion is preceded by a small, broad endothermic one).

Table 1 Maxima of some absorption bands in IR spectra of $Cu(NCO)_2L_2$ complexes before and after heating

Complex	$\nu_{as}(NCO)$, cm^{-1}	$\nu(C=O)$, cm^{-1}
α-$Cu(NCO)_2(pz)_2$	2218 s 2144 s	1726 m
α-$Cu(pzNCO)_2$	2220 m	1726 vs
$Cu(NCO)_2(dmpz)_2$	2180 s 2230 s	1690 w
$Cu(dmpzNCO)_2$	2180 m 2230 m	1690 s
$Cu(NCO)_2(tmpz)_2$	2224 vs 2173 sh	
$Cu(tmpzNCO)_2$	2180 sh 2210 br, s	1670 br, m
$Cu(NCO)_2(inz)_2$	2227 vs 2242 vs	
$Cu(inzNCO)_2$	2230 sh 2240 m	1710 m

s – strong, vs – very strong, m – medium, w – weak, sh – shoulder, br – broad

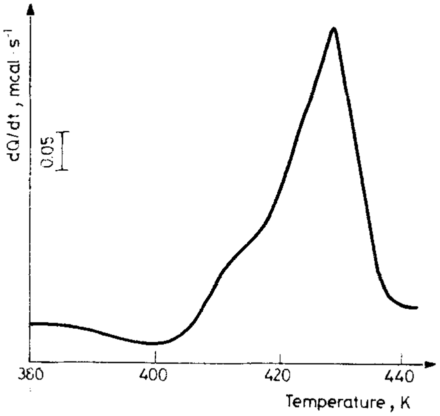

Fig. 1 DSC curve of the $Cu(NCO)_2(pz)_2$

Table 2 Values of ΔH and the temperatures of maxima of exothermic excursions corresponding to the reaction
$Cu(NCO)_2L_2 \rightarrow Cu(LNCO)_2$

Complex	ΔH, kJ · mol^{-1}	T_{max}, K
$Cu(NCO)_2(pz)_2$	-12.80 ± 0.58	385.8
$Cu(NCO)_2(dmpz)_2$	$-\ 8.15 \pm 0.64$	377.3
$Cu(NCO)_2(tmpz)$	-19.49 ± 0.66	388.9
$Cu(NCO)_2(inz)_2^2$	-11.59 ± 0.72	431.8

The ΔH values found for the nucleophilic reaction (Table 2) are markedly lower than the energy of the C—N bond usually given in the literature. We presume that a considerable portion of the liberated energy is used for the rearrangement of the crystal and molecular structure required by the new bonding conditions.

Of the studied complexes, $Cu(LNCO)_2(dmpz)_2$ gave the lowest ΔH value, though due to the $+I$ effect of the two methyl groups there should be a higher electron density on the imine nitrogen of this ligand than on the same nitrogen atom in the pyrazole molecule. In fact, however, the addition reaction for this complex takes place only when the starting complex $Cu(LNCO)_2(dmpz)_2$ contains at least a small admixture of its co-ligand isomer $Cu(dmpzNCO)_2$. When isomerically pure $Cu(LNCO)_2(dmpz)_2$ is heated at 370 K, the sample undergoes melting, ΔH_{melt} being 14.38 kJ mol^{-1}. The addition reaction for 3,5-dimethylpyrazole is assumed to be retarded by steric hindrance of the ligand itself, or by other factors, since the properties of $Cu(LNCO)_2(dmpz)_2$ differ significantly from those of the other complexes $Cu(NCO)_2L_2$ [6]. For 3,4,5-trimethylpyrazole the steric hindrance is apparently overcome by the $+I$ effect of the third methyl group and the ΔH value is the highest of those for the discussed complexes. In this connexion it is interesting that, while the complex $Cu(NCO)_2(pz)_2$ is converted to $Cu(pzNCO)_2$ rapidly, even at room temperature, $Cu(NCO)_2(tmpz)_2$ appears to be very stable against isomerization at this temperature. This finding is in agreement with the fact that a distorted tetrahedral structure [4] of the coordination polyhedron is assumed for this complex, which means unfavorable geometrical conditions for nucleophilic addition. Thus, it is presumed that, when $Cu(NCO)_2(tmpz)_2$ is heated, a further distortion of the coordination polyhedron takes place towards a square-planar ligand arrangement, which from a geometrical respect is the most favorable for nucleophilic addition. Therefore, the small endothermic excursions preceding the exothermic ones in the DSC curves may also cover changes in the structure of the coordination polyhedron of the starting compound, inevitable for the course of this reaction.

The lower ΔH value for L = indazole is probably caused by steric hindrance. With regard to the very good reproducibility of the determined values of ΔH (the standard deviations of the measurements are 3–8%), we may assume that under the conditions of measurement of the DSC curves the nucleophilic addition reaction took place practically completely in the inner coordination sphere of $Cu(NCO)_2L_2$.

Study with a derivatograph of the course of thermal decomposition of the complexes $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$

The pairs of distortion isomers prepared from the system Cu(II)—NCO^-—pyrazole, i.e. α and β-$Cu(NCO)_2(pz)_2$ and α and β-$Cu(pzNCO)_2$, differ mainly in the degree of deformation of their coordination polyhedra: a higher distortion degree was found for the β isomers [2]. In contrast with other Cu(II) complexes, for which it was found that an increasing degree of tetragonal distortion of the coordination polyhedron was accompanied by an increase in the decomposition temperature [7], for these isomer pairs a lower decomposition temperature was found for the β isomers (Table 3). We therefore assume that other, mainly macrostructural factors cause a relative lowering of the thermal stability of the β isomers as compared with those of α-$Cu(NCO)_2(pz)_2$ and α-$Cu(pzNCO)_2$.

For other pairs of distortion isomers (α and β-$Cu(tmpzNCO)_2$) and co-ligand isomers ($Cu(LNCO)_2(dmpz)_2$, $Cu(dmpzNCO)_2$; α and β-$Cu(tmpzNCO)_2$, α and β-$Cu(NCO)_2(tmpz)_2$), lower decomposition temperatures were found for those

Table 3 Some data on the thermal decomposition of the complexes under study

Complex	T_d, °C	Weight loss, % in the		Weight loss, % calculated for formation of		
		1. step	2. step	A*	B*	C*
α-$Cu(NCO)_2(pz)_2$	131	24	37	24	39	49
β-$Cu(NCO)_2(pz)_2$	115	27				
α-$Cu(pzNCO)_2$	135	25	44			
β-$Cu(pzNCO)_2$	125	27	42			
$Cu(NCO)_2(dmpz)_2$	160	28	46	28	41	45
$Cu(dmpzNCO)_2$	138	24				
$Cu(NCO)_2(tmpz)_2$	(90)	52	64	30	41	44
α-$Cu(tmpzNCO)_2$	125	49	56			
β-$Cu(tmpzNCO)_2$	140	42	58			
$Cu(inzNCO)_2$	160	19	31	31	42	43

* A – $Cu(NCO)_2L$; B – $Cu(NCO)L$; C – $Cu_2(NCO)_2L$

isomers for which a square-planar arrangement can be assumed, i.e. for α-$Cu(tmpzNCO)_2$ and $Cu(dmpzNCO)_2$, or a pseudotetrahedral structure, i.e. $Cu(NCO)_2(tmpz)_2$. This fact is in agreement with the often observed phenomenon of a lowering of the decomposition temperatures of Cu(II) complexes at the transition of polymeric to monomeric structures for substances with comparable compositions [7].

The data of the TG and DTG curves indicate that the stoichiometry of thermal decomposition for all the studied cyanato and carbamoylpyrazolato copper(II) complexes is quite complicated. In the first step of the decomposition reaction, the loss in weight of α and β-$Cu(pzNCO)_2$ corresponds approximately to 1 mole pyrazole for 1 mole compound. By means of the isothermal decomposition of the two complexes up to ~200°, intermediates of the thermal decomposition were prepared in the form of light-green powders, the analytical composition of which corresponds approximately to that of $Cu(NCO)_2(pz)$. The chemical analysis of the decomposition intermediates obtained at 180° indicates that the carbon content decreases more rapidly than the nitrogen content. Therefore, we conclude that the carbamoylpyrazolate ring, and especially its pyrazole part, decomposes to yield $Cu(NCO)_2(pz)$. From the course of the TG curve of $Cu(NCO)_2(pz)_2$, an analogous stoichiometry of decomposition may be assumed. This is understandable with respect to the fact that the decomposition is preceded by a nucleophilic addition, so that in the two cases the same substances are decomposed. Under non-isothermal decomposition conditions the intermediates are unstable, and the TG curves of α and β-$Cu(NCO)_2(pz)_2$ (Figs 2 and 3) and of α and β-$Cu(pzNCO)_2$ (Figs 4 and 5) do not show the corresponding plateau.

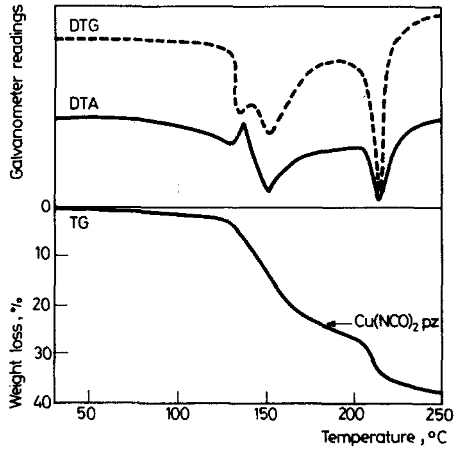

Fig. 2 DTA, DTG and TG curves of α-$Cu(NCO)_2(pz)_2$

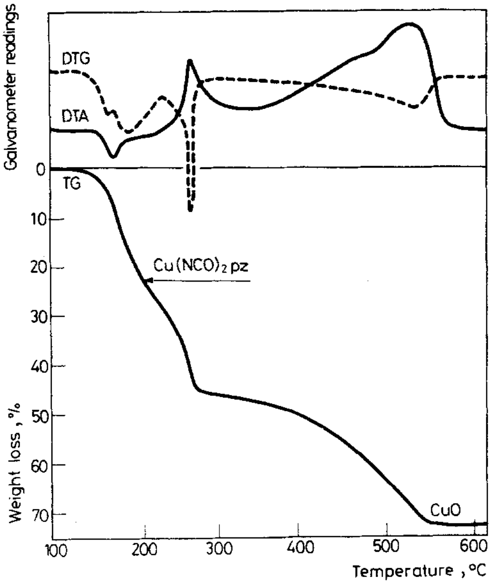

Fig. 3 DTA, DTG and TG curves of α-Cu(pzNCO)$_2$

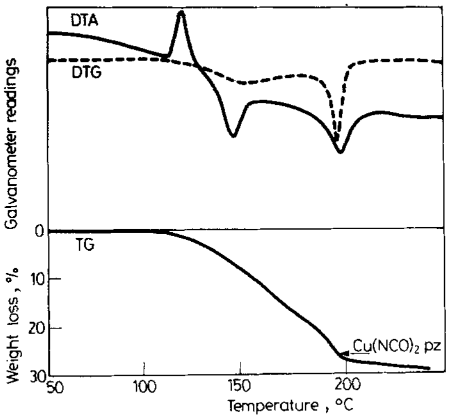

Fig. 4 DTA, DTG and TG curves of β-Cu(NCO)$_2$(pz)$_2$

The TG curves indicate that the decompositions of Cu(NCO)$_2$(dmpz)$_2$ and Cu(dmpzNCO)$_2$ lead to an intermediate of composition Cu(NCO)$_2$(dmpz), which is unstable under the given experimental conditions, however (Figs 6 and 7). The decomposition of this intermediate continues with an exothermic reaction, in which the reduction of Cu(II) to Cu(I) probably takes place and the further

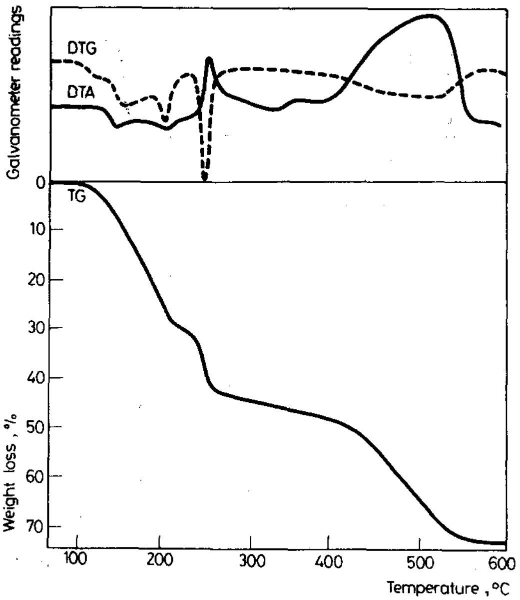

Fig. 5 DTA, DTG and TG curves of β-Cu(pzNCO)$_2$

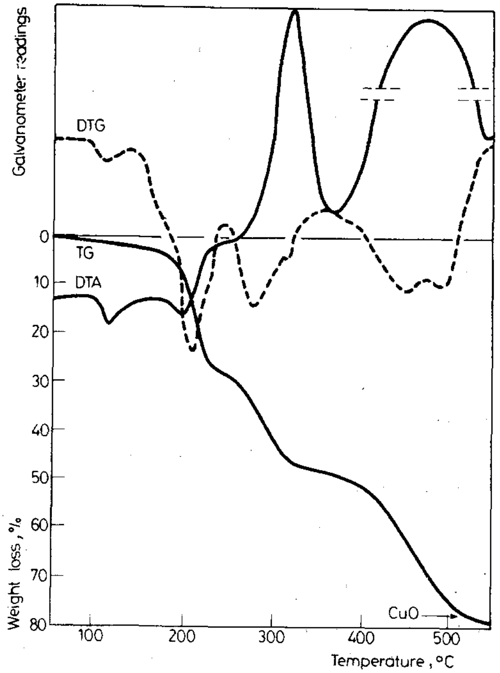

Fig. 6 DTA, DTG and TG curves of Cu(NCO)$_2$(dmpz)$_2$

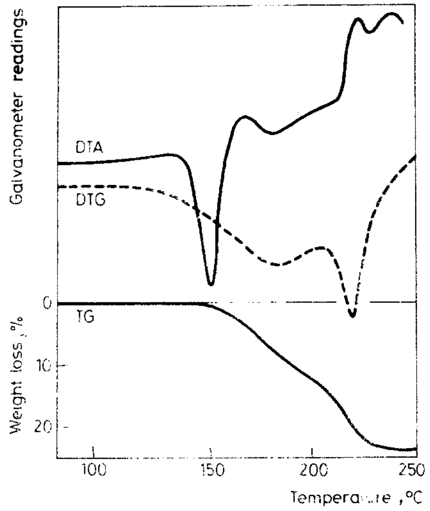

Fig. 7 DTA, DTG and TG curves of $Cu(dmpzNCO)_2$

Table 4 Analytical composition of intermediates of thermal decomposition of α- and β-$Cu(pzNCO)_2$

Complex	Temperature of decomposition, °C	Weight loss, %	Analytical composition, %			
			Cu	C	N	H
α-$Cu(pzNCO)_2$	180	17.30	26.73	30.73	28.08	2.85
	200	22.87	28.66	29.74	26.53	2.44
β-$Cu(pzNCO)_2$	180	12.00	22.62	31.14	28.84	2.84
	200	23.88	28.44	30.47	26.91	2.61

Calculated for $Cu(NCO)_2(pz)$: MW = 215.71 g mol^{-1}, Cu – 29.40%, C – 29.46%, N – 25.96%, H – 1.87%

decomposition intermediate has the composition $Cu_2(NCO)_2(dmpz)$. On the other hand, in the decomposition of $Cu(NCO)_2(pz)$ the loss in weight is greater than corresponds to the formation of $Cu(NCO)(pz)$, but is smaller than corresponds to the formation of $Cu_2(NCO)_2(pz)$.

The stoichiometry of decomposition of $Cu(tmpzNCO)_2$ and $Cu(NCO)_2(tmpz)_2$ is so complicated (Figs 8 and 9) that it is not possible to describe it on the basis of the TG curve.

In conclusion, it may be stated that the stoichiometry of thermal decomposition of $Cu(NCO)_2L_2$ and $Cu(LNCO)_2$ is due to the exothermic isomerization $Cu(NCO)_2L_2 \rightarrow Cu(LNCO)_2$. The decomposition temperatures, which under the

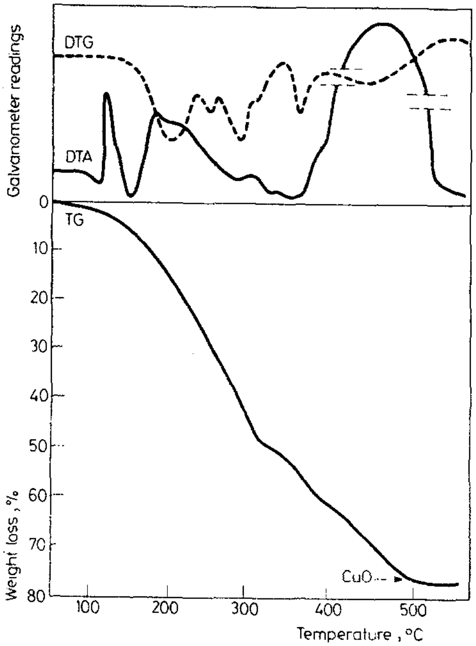

Fig. 8 DTA, DTG and TG curves of Cu(NCO)$_2$(tmpz)$_2$

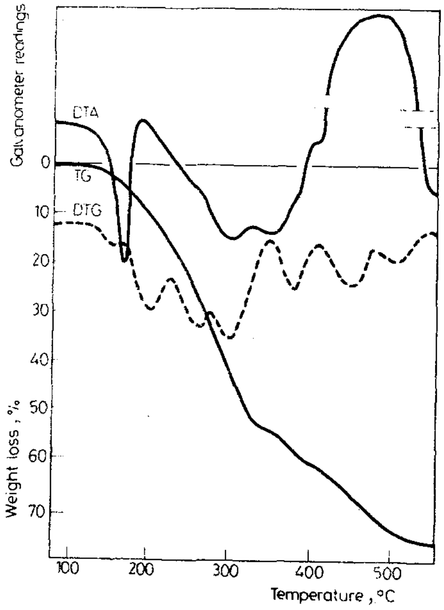

Fig. 9 DTA, DTG and TG curves of Cu(tmpzNCO)$_2$

experimental conditions (on the derivatograph) overlap with the initial temperatures of the isomerization reactions, are influenced by the compositions of the respective complexes and also by the structures of their coordination polyhedra. The bonding and steric properties of ligand L strongly influence the ΔH values of the isomerization reactions and also the decomposition stoichiometries of the studied complexes.

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Zusammenfassung — Der Verlauf der thermischen Zersetzung der Komplexe $Cu(NCO)_2L_2$ und $Cu(LNCO)_2$ mit L = Pyrazol, 3,5-Dimethylpyrazol, 3,4,5-Trimethylpyrazol und Indazol wurde untersucht. Die DTA-Kurven von $Cu(NCO)_2L_2$ zeigen etwas unterhalb der Zersetzungstemperaturen exotherme Effekte, die einer inneren komplexen nukleophilen Addition eines Kohlenstoffatoms (von einer NCO-Gruppe) an das Iminstickstoffatom eines Pyrazol-Liganden entsprechen. In dieser Reaktion wird das an Cu(II) koordinativ gebundene Carbamoylpyrazolat-Anion gebildet. Für diese Reaktionen wurden mit der DSC-Methode folgende ΔH-Werte erhalten: $-12{,}80$ $kJ \cdot mol^{-1}$ (L = Pyrazol), $-8{,}15$ $kJ \cdot mol^{-1}$ (L = 3,5-Dimethylpyrazol), $-19{,}49$ $kJ \cdot mol^{-1}$ (L = 3,4,5-Trimethylpyrazol) und $-11{,}59$ $kJ \cdot mol^{-1}$ (L = Indazol). Nach der nukleophilen Addition zeigt $Cu(NCO)_2L_2$ den gleichen thermischen Zersetzungsverlauf wie $Cu(LNCO)_2$. Die Strukturunterschiede zwischen den Distortionsisomeren von $Cu(NCO)_2L_2$ und $Cu(LNCO)_2$ manifestieren sich in der Zersetzungstemperatur und, in einigen Fällen, auch in der Stöchiometrie der Zersetzungsreaktion.

Резюме Представлены результаты термического разложения комплексов $Cu(NCO)_2L_2$ и $Cu(LNCO)_2$, где L = пиразол, 3,5-диметилпиразол, 3,4,5-тьирметилпиразол и индазол. ДТА кривые комплексов $Cu(NCO)_2L_2$ ниже температур их разложения показали экзотермические октлонения, вызванные внутрикомплексным нуклеофильным присоединением атома углерода (от группы NCO) к азоту иминогруппы пиразола. При такой реакции образуется карбамоилпиразолат-анион, координационно связанный с двухвалентной медью. Метод ДСК позволил определить для этих реакций следующие значения ΔH: для пиразола — $-12{,}80$ кдж/моль, для 3,5-диметилпиразола — $-8{,}15$ кдж/моль, для 3,4,5-триметилпиразола — $-19{,}49$ кдж/моль и для индазола — $-11{,}59$ кдж/моль. Процесс термического разложения этих комплексов после нуклеофильного присоединения атома углерода, тот же самый как и для $Cu(LNCO)_2$. Структурные различия между этими двумя изомерами проявляются в их температурах разложения и в некоторых случаях — в стехиометрии реакций разложения.