

SOME APPLICATIONS OF THERMAL ANALYSIS TO THE COORDINATION CHEMISTRY

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The behaviour of complexes of the type MeD_2I_2 ($Me = Co$, $D =$ acetylacetonone or benzoylacetonone, $I =$ imidazole and derivatives in the course of the stepwise thermal degradation is different. In the case of $D =$ acetylacetonone in the first step acetylacetonone is split off. At $D =$ benzoylacetonone the decomposition starts with the partial elimination of the heterocyclic ligands.

In β -position unsubstituted nickelacyclic complexes from type $(bipy)Ni(CH_2CH_2CH_2COO)$ decompose by a reductive elimination and separating of CO_2 forming a '(bipy)Ni'-intermediate. A single reductive decoupling is hindered by blocking up the β -position.

Opposite to the high thermal stability of the trimesityl aluminium the intermediates $Almes_2Cl$ and $AlmesCl_2$ show with decreasing amounts of mesityl groups and increasing content of halogene, respectively, a significant decreasing thermal stability.

The thermal degradation of nickelchelates of alkylsubstituted chinolin-8-ol starts with the dehydration followed by a different separation of the ligands as a function of the chain-length and the position of the substituents of the ligands.

Keywords: complexes, coordination chemistry

Introduction

In the classical monographs on coordination compounds only few pages are dedicated to the solid state reactions of these compounds. Most of the assertions to the behaviour and properties of coordination compounds were created by investigations of the reactions in solution.

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The judgement of the thermal stability of solid complex compounds is usually carried out by the estimation of the heat of the reaction from the metal salts with the ligands.

Experimental investigations of the thermal stability of complex compounds, as well known, go back to caloric measurements of Ephraim and Biltz [1] at the beginning of the twentieth century. The reaction enthalpy of amoniacates and hydrates from this measurements allowed a good evaluation of the thermal stability. The thermochemistry of complex compounds has been mainly created by Klemm, Spacu and Heiber [2, 4].

These problems have been essentially completed by the investigations of Jatzimirski and by a monography in 1951 summarizing his presentations of the thermal stability of complex compounds [5].

Thermal analysis nowadays plays an important role in studying the structure and properties of metal complexes. This is mainly due to the fact, that thermal decomposition reactions of coordination compounds are ligand substitution reactions in the solid state, the leaving ligand being substituted by originally outer shell anions or molecules.

In addition to the structural investigation methods of metal complexes, like, for instance, spectroscopic methods, the results of which coinciding statements about the stability of these complex compounds, the thermochemical techniques, that means, calorimetry, thermogravimetry and differential scanning methods as DTA and DSC, represent valuable supplementary methods.

Liptay reports about the frequency of thermoanalytical investigations during the period 1975–1987 [6]. The compounds studied are most often inorganic compounds and coordination compounds are presented with more than 20%. The contributions in the Journal of Thermal Analysis in the last 5 years referred between 15–20% to coordination compounds.

Numerous complex compounds are of special interest in industry, medicine and biology, e.g., the electrical and thermochrome properties, antioxydation, vulcanization acceleration, protecting paintings and antibacterial properties.

Up to now a number of solid state reactions of coordination compounds (such as thermal isomerization, conformational changes, polymorphic transformations, thermal phase transitions, thermochromis) were studied and enter increasingly into the scientific basis of coordination chemistry [7, 8].

For a series of stability analyses, for instance, lewis-acid/lewis-base addition complexes, calorimetry is considered as the alternative method [9].

In the case of ion exchangers the effects of substituents at the ligands can be used for the selectivity of the formation of complexes and the stability of metal complexes.

Some of the hydrates of metal complexes have been convenient models for studying the kinetics of topochemical processes of thermal dissociation especially in the case of dehydration.

In the past two decades the development of catalysis was characterized by the wide application of metal complexes as catalysts. The catalytically active complexes must have at least one free position in their coordination spheres, and therefore, have often an energetically activated and therefore less advantageous arrangement of the ligands around the central ion.

Studies of complexes by means of thermal analysis have indicated, that there are thermal reactivities at which complexes lose volatile ligands connected with configurational changes.

Experimental

Materials

The preparation of the complex compounds described in part 1 and 2 takes place from the diketones and the heterocyclic compounds by [10] and [11].

The conversion of α, α -dipyridyl-cycloocta-1,5-diene-nickel(II) with glutaric anhydride in tetrahydrofuran yields the corresponding nickelacycle carboxylate [12].

By the synthesis of trimesityl aluminium as a substance for new synthetic reactions, a further conversion with aluminium chloride yields by comproporation to the intermediate products Almes_2Cl and AlmesCl_2 . Both compounds form adducts with tetrahydrofuran. The nickelchelates were prepared by conversion of the nickelsalts with the chelate ligands in an aqueous-alcoholic solution [13]. They are only available in the hydrated form.

Methods

Differential thermal analysis were carried out with an already described apparatus [14] and the following conditions were throughout applied: sample size 20 mg, heating rate $5 \text{ deg} \cdot \text{min}^{-1}$, and inert atmosphere.

The thermal decomposition was carried out on a photoelectric compensating thermobalance [15] with a sample size of 10 mg, heating rate of $10 \text{ deg} \cdot \text{min}^{-1}$ and sensitivity of $10 \text{ mg}/20 \text{ cm}$.

Results and discussion

The thermal degradation of Bisacetylacetonato-cobalt(II)-compounds with heterocyclic second ligands

Imidazole complexes may be useful in industry as catalytic agents in epoxy curing reactions [16]. For such applications the thermal stability of the complex could influence the curing mechanism of resin and subsequently its physical properties.

The results of the thermogravimetric analysis of the compounds described in chapters 1 and 2 are summarized in Table 1.

The two acetylacetonates and two of the isomers imidazol or pyrazol which formed innercomplexes of cobalt, decompose, as shown in Fig. 1. In a first step of reaction the elimination of acetylaceton takes place by simultaneous protontransfer from the heterocyclic compound to the diketonate. As intermediates originate the Bis-imidazolato-or Bis-pyrazolato-cobalt(II)-compounds, which decompose completely at higher temperatures forming the corresponding diheterocyclic compounds and metallic cobalt. By consideration of the structure of the Bis-acetylacetonato-cobalt(II)-diimidazol, shown in Fig. 2, only the protontransfer is comprehensible, while the splitting of the chelate ligands cannot be simply explained.

The coordination polymer Bis-imidazolato-cobalt(II) shows a significantly higher thermal stability than the corresponding Bis-pyrazolato-compound.

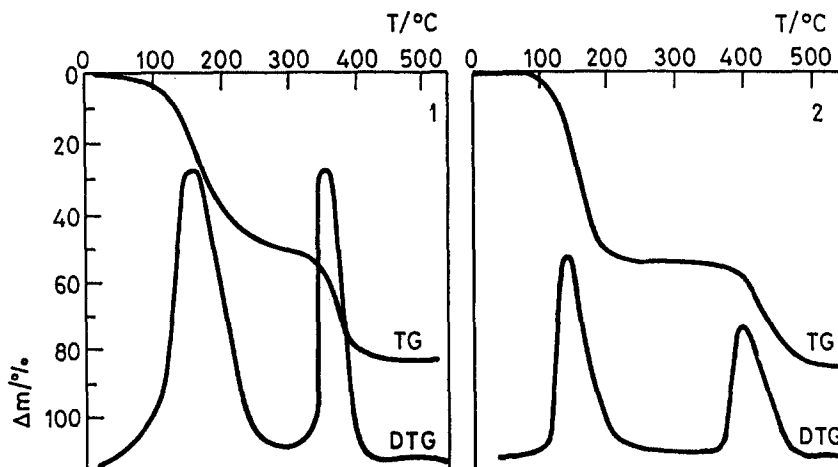


Fig. 1 TG-DTG curves of $\text{Co}(\text{acac})_2(\text{HIm})_2$ and $\text{Co}(\text{acac})_2$ and $(\text{Hpyra})_2$

Table 1 Thermogravimetric data of the studied complexes ((a) = $\Delta m_{theor.}$, (b) = $\Delta m_{exp.}$)

Co(acac) ₂ (Hpyra) ₂									
(a)	50.9%	- 2 acac-H	49.5%	Co(ba) ₂ (Hpyra) ₂	(a)	26.2%	25.3%	- 2 pyra	
	34.1%	- 2 pyra	30.2%		(b)	31.2%	28.5%	- ba	
						31.2%	27.0%	- ba	
Co(acac) ₂ (HIm) ₂									
(a)	50.9%	- 2 acac-H	52.5%	Co(ba) ₂ (HIm) ₂	(a)	17.2%	18.3%	- HIm, MeOH	
	34.1%	- 2 Im	32.5%		(b)	33.3%	31.2%	- ba-H, MeOH	
Co(acac) ₂ (ac-Im) ₂									
(a)	29.8%	- acac-ac	30.0%	Co(ba) ₂ (ac-Im) ₂	(a)	11.3%	12.5%	- HIm	
	23.1%	- ac-Im	20.2%		(b)	18.3%	18.5%	- ac-Im	
						17.0%	16.5%	- 1.2 ba-ac	
Co(acac) ₂ (cet-Im) ₂									
(a)	2 × 26.1%	- cet-Im	26.0%	Co(ba) ₂ (cet-Im) ₂	(a)	21.2%	22.0%	- cet-Im	
		- cet-Im	25.2%		(b)	35.1%	33.2%	- ba-cet	
Co(acac) ₂ (H ₂ OIm) ₂									
(a)	17.2%	- 1/2 acac-H	16.5%	Co(ba) ₂ (H ₂ OIm) ₂	(a)	7.5%	7.5%	- 1/2 H ₂ OIm	
	35.2%	- 1.5 acac-H, 0.5 H ₂ OIm	34.0%		(b)	44.3%	47.0%	- 1.5 ba-H	
	36.0%	- 1.5 H ₂ OIm	28.0%			32.0%	28.0%	- 1.5 ba-H, 1.5 H ₂ OIm, C ₂ H ₂	
Co(acac) ₂ (H ₂ SIm) ₂									
(a)	15.0%	- 3 MeOH	14.5%	Co(ba) ₂ (H ₂ SIm) ₂	(a)	13.9%	12.5%	- 1/2 ba-H	
	54.1%	- 2 acac, H ₂ SIm	55.0%		(b)	41.7%	44.0%	- 1.5 ba-H	
						21.6%	22.0%	- H ₂ SIm, C ₂ H ₂	

The coordination compounds formed from the imidazol derivatives of cyclic urea- or thiourea show, as obvious in Fig. 3, a course of reaction of the thermal degradation, which also follows a proton transfer.

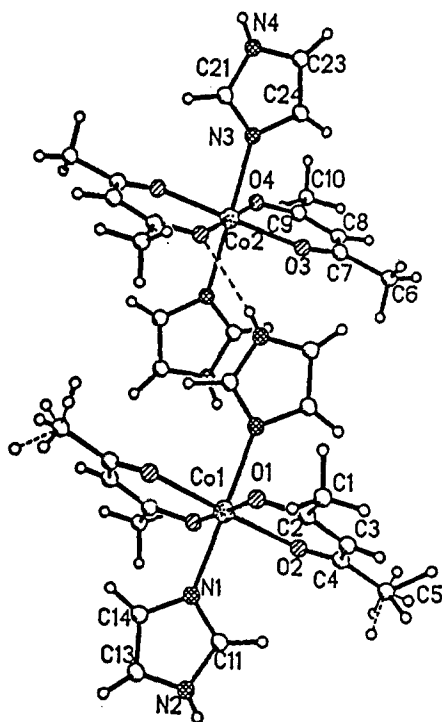


Fig. 2 Structure of the Bis-acetylacetonato-cobalt(II)-diimidazol

At the complex compound with 2-imidazolidin-on, in the progress of a first step of the reaction, the splitting of half a mole of acetylacetonate takes place, followed by the further thermal elimination of the residual chelate-ligands and half a mole of the heterocyclic part. In the case of the cobalt(II)-complex with 2-imidazolidin-thiol, at first the additionally bound methanol decomposes thermally in two steps. At higher temperature a mixture of acetylacetonate and cyclic thione originates.

For further investigations of thermal exchange reactions with second ligands nitrogen substituted imidazoles have been used.

Whereas at the cobalt(II)-compound with the N-carbethoxyimidazole the heterocyclic part decomposes unchanged in two steps. The thermal elimination of the complex with N-acetylimidazole first takes place at the acetylated

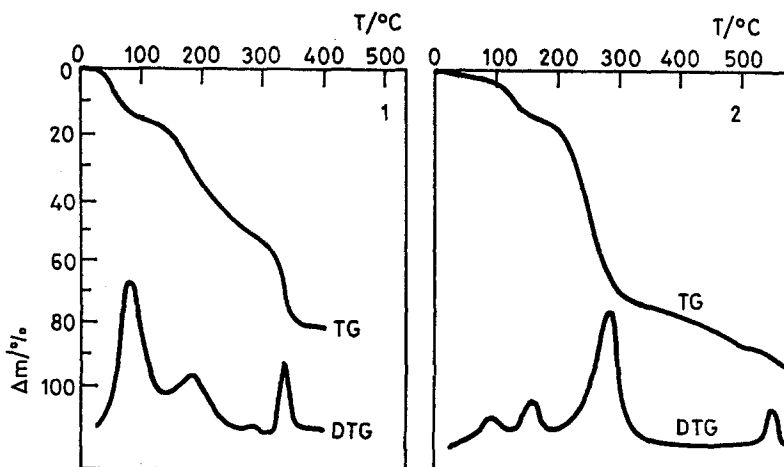


Fig. 3 TG-DTG curves of $\text{Co}(\text{acac})_2(\text{H}_2\text{OIm})_2$ and $\text{Co}(\text{acac})_2(\text{H}_2\text{SIm})_2$

acetylacetonate followed by the unchanged heterocyclic compound. In this case a thermally induced shifting of an acetyl group may be initiated (Fig. 4).

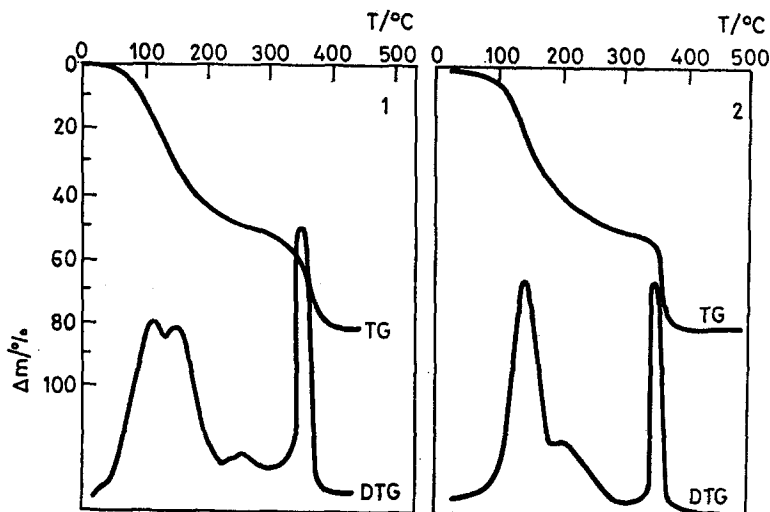


Fig. 4 TG-DTG curves of $\text{Co}(\text{acac})_2(\text{cet-Im})_2$ and $\text{Co}(\text{acac})_2(\text{ac-Im})_2$

Thermal stability of Bis-benzoylacetonato-cobalt(II)-complexes with heterocyclic second ligands

As earlier described [17] aromatically substituted 1,3-diketones show principally another course of the thermal degradation. As shown in Fig. 5, for

the complex compounds with the imidazole and with the pyrazole, the previously described reactionstriplett appears in the course of the thermal decomposition at 330° and 350°C respectively. This starts with the decomposition of imidazole or pyrazole and with the elimination of the first acetylacetonone. In a following smaller limited temperature range till 450° or 400°C respectively, the second mole of diketone decomposes, besides residual cobaltoxid. For the compound with pyrazol as second ligand a significantly lower thermal stability was visible.

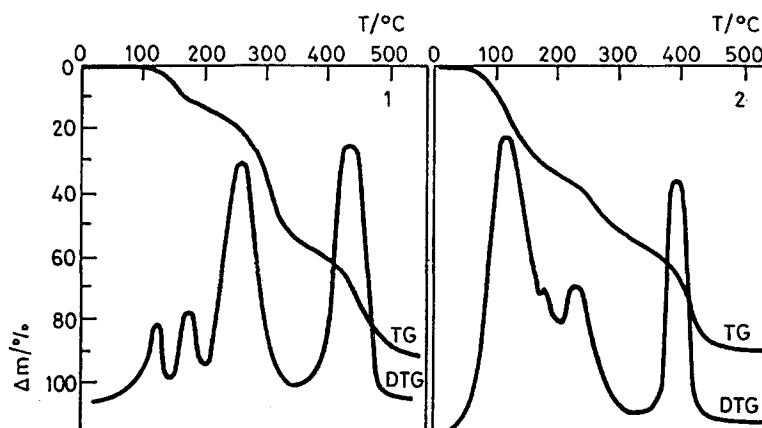


Fig. 5 TG-DTG curves of $\text{Co}(\text{ba})_2(\text{HIm})_2$ and $\text{Co}(\text{ba})_2(\text{Hypra})_2$

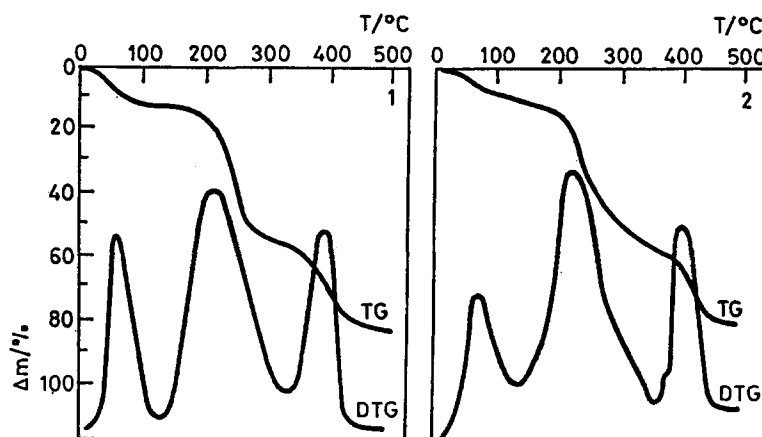


Fig. 6 TG-DTG curves of $\text{Co}(\text{ba})_2(\text{H}_2\text{SIm})_2$ and $\text{Co}(\text{ba})_2(\text{H}_2\text{OIm})_2$

In the case of the derivatives of cyclic urea or thiourea the thermal decomposition starts either with the heterocyclic part or with the chelate ligands depending on of either the attachment is through oxygen or sulfur respectively (Fig. 6).

Analogous to the acetylacetonates the thermal degradation starts with the elimination of half a heterocyclic ligand at the cobalt-(II)-complex with imidazolidin, followed by the degradation of the residual heterocyclic and the diketone. In the case of the decomposition of the heterocyclic part by releasing of ethin, the formation of a nickel-urea-species must be supposed.

The second ligand, 2-imidazolidin-thion is obviously more strongly fixed by the sulfur to the central atom than to the benzoylacetone. The thermal degradation begins with the removal of half a chelate ligand in a first significantly separated step followed by the releasing of the residual 1,5-chelateligands. Now the elimination of the heterocyclic ligands starts first with the degradation of unchanged heterocyclic part followed by the releasing of ethin and formation of a nickel-thiourea-species as residue.

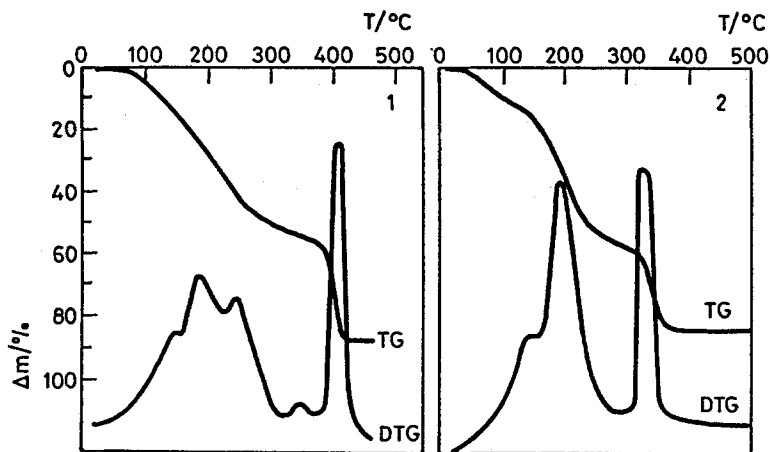


Fig. 7 TG-DTG curves of $\text{Co}(\text{ba})_2(\text{ac-Im})_2$ and $\text{Co}(\text{ba})_2(\text{cet-Im})_2$

At the nitrogen substituted imidazole derivatives as second ligands also a different behaviour opposite to the acetylacetonato-complexes is shown in Fig. 7. In the case of the N-acetylimidazole in a first step one imidazole decomposes by shifting of the acetyl group to the diketone. Then follows the degradation of the second N-acetylimidazole and the acetylated diketone.

At extremely lower thermal stability, the fixed carbethoxyimidazol has been observed. Already above 50°C the elimination of the heterocyclic part starts and above 150°C that of the first chelate ligand.

Thermally induced β -hydridelimination

Nickelacycles are of special interest for carbon-carbon-coupling reactions in the synthetic chemistry.

The thermal degradation of these compound takes place in three steps as shown in Fig. 8. The first relatively sharply limited region from 160–205 degrees yields a mass loss of 29% thus elimination the carboxycyclic system (th. 28.6%). By consideration of the DTA-curve in this temperature region the elimination starts by an endothermic reaction interrupted by a fast exothermic reaction.

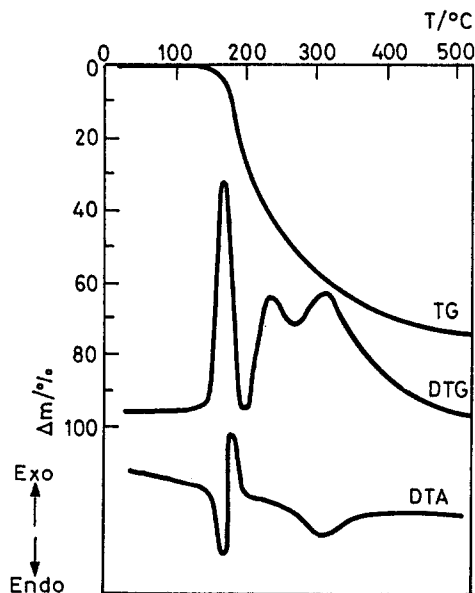
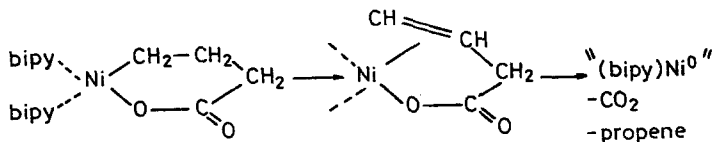


Fig. 8 Thermoanalytical curves of $(\text{bipy})\text{Ni}(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}\text{C}\text{O})$

Owing to the high mobility of the carboxycyclic system conformer compounds may be formed with nickel and hydrogen neighbouring. A nickel-hydrid species was found as the primary product. In the following reaction the hydrogenation takes place with a combined reductive coupling. This reaction sequence is reflected by the DTA-curve. Consequently carbondioxide and propene were found as decomposition products.

Basing on the results the mechanism of the decomposition can be summarized as

The remaining '(dipy)Ni⁰' is forming obviously a cluster which is subsequently modified by a further decomposition of half a dipyriddy. After the splitting of the residue dipyriddy elemental nickel remains as product.



The thermally induced reaction proceeds in a completely different course if the β -position is substituted or an oxygen atom is in this position of the cyclic system, as significantly shown in Fig. 9. This is because of the effect, that the preceding 'hydrid-phase' cannot build up.

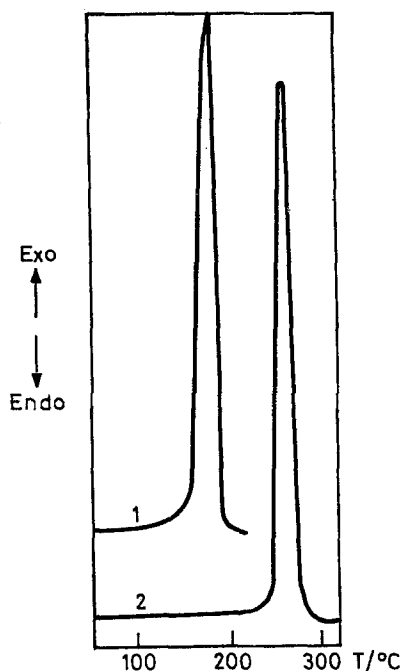




Fig. 9 DTA curves of (TMED)Ni  (1) and (bipy)Ni  (2)

Through the highest strain of the bond electrons by the oxygen in the β -position the neighbouring Ni-C bond undergoes a weakening and therefore the thermal splitting preferably starts at this position.

This knowledge on the thermal stability and the thermally induced progress of the reaction allows now systematic reactions in solution at higher temperatures for the synthesis of new final products.

Thermal behaviour of mesityl aluminium compounds

A comparative study of the thermal behaviour between trimesityl aluminium and similar three valency transition metal compounds have been undertaken in earlier investigations [18].

The combination of Almes_2Cl and AlmesCl_2 refers to a fourfold coordinated aluminium. As distinctly shown in Fig. 10, the trimesityl aluminium

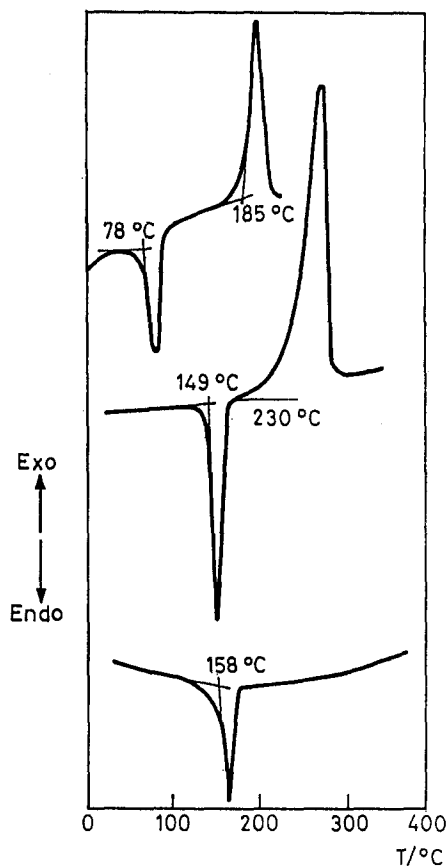


Fig. 10 DTA curves of Almes_3 , Almes_2Cl and AlmesCl_2

shows, in spite of its monomer state, up to 300°C no decomposition appears. With decreasing amounts of mesityl groups and increasing content of halogen respectively, a significant decreasing of the thermal stability of these compounds was visible.

The dimesityl aluminium chloride-tetrahydrofuran shows with at 149°C unlike the trimesityl aluminium, a previous evolution of tetrahydrofuran connected with melting. A more distinct difference takes place here in contrary to trimesityl aluminium showed by the decomposition at 230°C due to separation of mesitylene. In this case the mass loss amounts nearly 50%, corresponding to the decomposition of tetrahydrofuran and one mole mesitylene. Besides only less amounts of dimesityl were found.

Mesityl aluminium dichloride-tetrahydrofuran already melts at 78°C, below this temperature removal of the tetrahydrofuran and short after that the beginning of the decomposition by formation of hydrogen chloride and with a high decomposition rate at 185°C.

This remarkable gradation of the thermal elimination of the mesitylene at these intermediates allows the expectations, that in spite of the increasing grade of the covalent of the aluminium-mesitylene bond with increasing content of chlorine, in consequence of loss of polar parts of the bond, this previous elimination has been enabled.

Thermal properties of nickelchelates of alkylsubstituted chinolin-8-ols

Hydroxychinolins and its derivatives have long been used as potential antimicrobiological agents and drugs [19]. As shown in Fig. 11 the dehydration starts just above room temperature in some cases. Therefore all samples were desiccated for 24 hours at 30 degrees.

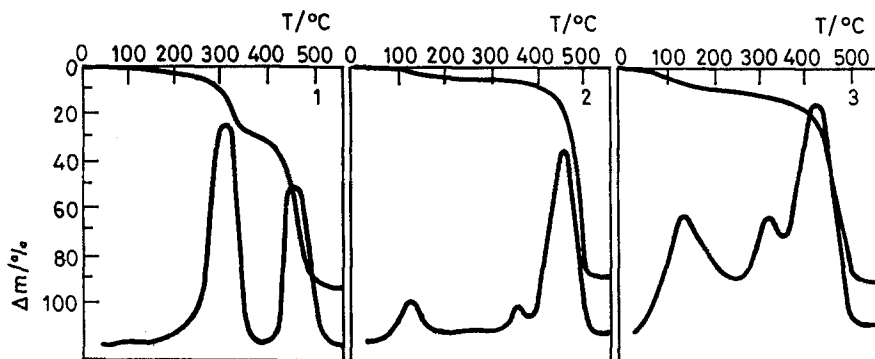


Fig. 11 TG-DTG curves of Ni-complexes with 7-methylchinolin-8-ol·0.5H₂O (1), 7-n-propylchinolin-8-ol·H₂O (2) and 2,7-dimethylchinolin-8-ol·2H₂O (3)

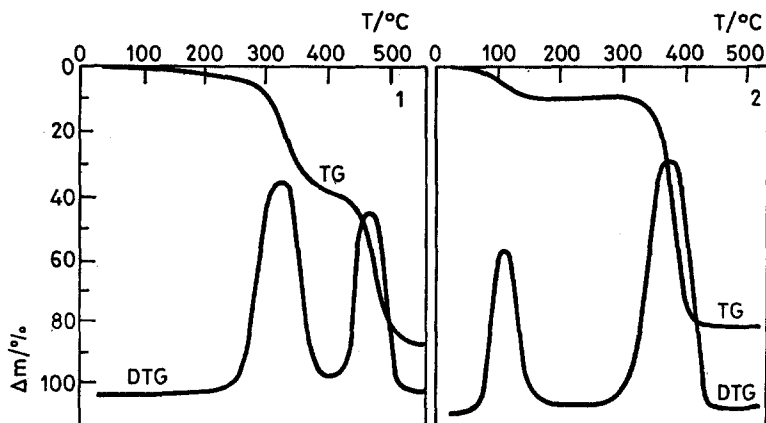


Fig. 12 TG-DTG curves of Ni-complexes with 7-methylchinolin-8-ol \cdot 0.5H₂O and 5-methylchinolin-8-ol \cdot H₂O

The decomposition curves show significant differences in the amount of bonded water. These variable amounts of water are important for the realization of definable tetrahedral structures of these complex compounds. The beginning dehydration of the 7-substituted species which is even starting at room temperature is obviously dependent on the chainlength and on the nature of the substituents. After the dehydration the further decomposition of the chelate ligands takes place in a stepless process, as shown in Fig. 11, for the case of the Bis-(chinolin-8-olato)nickel(II) and the 2-methyl, 5-methyl and long chain substituted ligands. In dependence on the chainlength the complex compounds with chelate ligands substituted in 7-position decompose, as shown in Fig. 12, in a two step process accompanied by a partial oxidation of the nickel. In the case of the 7-methylcompound both processes take place symmetrically. However, with increasing chainlength of the substituents a simultaneous modification of the chelate ligands turns out and both steps of the reaction appear no more equivalent.

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Zusammenfassung – Das Zersetzung Verhalten der Komplexverbindungen vom Typ CoD_2I_2 (D = acetylaceton, Benzoylaceton; I = Imidazol oder Derivate) erfolgt stufenweise. Im Falle von D = Acetylaceton erfolgt zuerst eine Eliminierung von Acetylaceton während bei D = Benzoylaceton zuerst ein Heteroligand eine Abspaltung erfährt.

Bei einer unsubstituierten β -Position von Nickelacyclen des Typs (bipy)Ni(CH₂CH₂CH₂COO) erfolgt eine thermisch induzierte β -Hydrideliminierung unter Ringspaltung und Freisetzung von CO₂.

Im Gegensatz zur hohen thermischen Stabilität des Trimesityl Aluminium erfahren die Zwischenverbindungen Almes₂Cl und AlmesCl₂ mit abnehmenden Mesityl- bzw. zunehmenden Chlorgehalt einen wesentlich früheren thermischen Zerfall. Bei zunehmenden Kovalenzgrad ist hier ein Einfluss der veränderten Polarisation anzunehmen.

Der thermische Abbau der prinzipiell wasserhaltig kristallisierenden Nickelchelate von alkyl-substituierten Chinolin-8-ol beginnt jeweils mit der Dehydratisierung. In Abhängigkeit von der Kettenlänge und der Position der Substitution am Chinolin schliesst sich der thermische Abbau der Chelatliganden ein- bzw. mehrstufig an.