Journal of Thermal Analysis, Vol. 42 (1994) 443-459

THERMAL LATENT COORDINATION COMPOUNDS

The thermal degradation of imidazole and pyrazole adducts of metal acetates

M. Döring, W. Ludwig and H. Görls[*]

University, Institute of Inorganic and Analytical Chemistry, Jena
[*]Max Planck Society, Working Group on 'CO$_2$ Chemistry', Jena, Germany

Abstract

The thermal behaviour of complexes of the type M(HIm)$_2$ac$_2$ (*HIm* = imidazole, *ac* = acetate, *M* = Co, Ni, Cu) is different. Comparable to the thermal degradation of Ni(acac)$_2$(HIm)$_2$ [10] the Ni(HIm)$_2$ac$_2$ loss acetic acid by formation of Ni(Im)$_2$. All nitrogen ligands are splitt off from the copper complex by formation of stable basic copper acetate. The cobalt compound eliminated acetic acid partially while acetate and imidazolate bridging species are obtained.

The thermal behaviour of the acetate complexes of pyrazole and the bulky 3,5-dimethylpyrazole is quite similar. In a first step pyrazoliumacetate is removed.

The crystal structure of Ni(HPz)$_4$ac$_2$ is determined by X-ray diffraction: monocline, space group C 2/c.

The water molecule represents the centre of two N–H···O–H···O-bridges. The system of H-bridges in the compound relieves the proton transfer, indicated by the elimination of pyrazolium acetate.

Keywords: crystal structure, imidazole and pyrazole acetate compounds, TG-DTG-DTA

Introduction

Metal carboxylates containing heterocycles and especially copper(II) complexes have been studied in an extensive way because of their interesting magnetic and spectroscopic behaviour [1]. Moreover, the imidazole addition compounds of copper and cobalt carboxylates may form biochemical models for copper proteins or carboxy peptidases respectively [2] and they are also important in the field of pharmacology [3].

The interest that we show for metal carboxylates with such coordinated heterocycles as imidazoles and pyrazoles, which have a trapped atom that is similar

0368–4466/94/ $ 4.00

John Wiley & Sons, Limited
Chichester

to both pyridine and pyrrole, is due to the fact that these compounds are latent accelerators for epoxy resins. Imidazole (HIm) and pyrazole (HPz) and their derivatives are efficient accelerators for the homopolymerization of epoxy resins [4]. But dative bond blocks the heterocycle in such a way that it is possible to achieve a good distribution of the latent accelerator in the resin. After this, a raise in temperature allows to set free the desired amount of heterocycles. An optimum setup of the polymer can be obtained in this way. This is decisive for the material properties of the products. In addition to this, modern technology can be used without any problem in order to process epoxy resins. This includes prepreg processes and unitary systems [5].

The first investigations made by us have shown that the thermal degradations of the imidazole 1,3-diketonates of cobalt, nickel and copper are topochemical reactions and that the process of these reactions largely depends on chelate anions (e.g. on acetylacetonate or benzoylacetonate) and on the crystal structure marked by these anions [6]. In addition to this, we were able to show that the thermal decomposition within the substance goes on in a way similar to the degradation process in protic solvents or in epoxy resins themselves. Then, we directed our attention to the thermal behaviour of the heterocyclic addition compounds of the metal acetates of cobalt, nickel and copper. Investigations with regard to polymer chemistry have shown rather quickly that the accelerating action and thus the thermal degradation are metal specific in this case.

Experimental

The preparation of complex compounds has been done according to the following reference guidelines: I [7, 8], II [9], IIIb [10], VII [7, 11], VIII [12], IX [13], XI [14a]. Compound IIIa has been obtained in an analytically pure way in the form of light-blue crystals by the dissolution of equimolar amounts of Ia and IIa in ethanol and subsequent concentration. All newly prepared compounds present correct data of analysis.

The thermobalance designed by this Institute and the DTA measurement setup have been described in earlier papers [6a, 15].

The determination of crystallographic structure and the collection of data for VIIIa was done on a blue and irregular crystal with the help of an Enraf-Nonions CAD4 diffractometer using MoK_α radiation (λ = 71.069 pm, graphite monochromator) at room temperature. An X-ray intensity of up to $\Theta_{max} = 27°$ has been measured by means of ω-2Θ scanning. Correction according to Lorentz and correction of polarization was carried out [16]. No absorption correction was done. Patterson synthesis (SHELXS-86 [17]) has yielded the position of the heavy atom and of most non-hydrogen atoms. The remaining non-hydrogen atoms have been established by means of differential Fourier syncally according to the full matric LSQ process [16]. Hydrogen atoms have been localized using differential Fourier synthesis and they have been included in the improvement in an isotropic way. The final *R*-value has converged at 0.033 (R_W = 0.042).

Results and discussion

The thermal degradation of metal acetate imidazole addition compounds $M(HIm)_x ac_2$

The acetates of cobalt, nickel and copper each form the binary addition compounds of $M(HIm)_2ac_2$ I [19]. The complex compounds of $M(HIm)_6ac_2$ II are known of cobalt and nickel in addition to this. In these complexes, six imidazole molecules surround the central atom in an octahedral way [9]. The structure of the tetraimidazole addition compound $Cu(HIm)_4ac_2$ IIIb has been established as well [10]. A marked hydrogen bond system appears in all these complex compounds.

The acetate acts as a single-count chelate ligand in the tetrahedral complex $Co(HIm)_2ac_2$ Ic [7] and as a binary chelate ligand in $Ni(HIm)_2ac_2$ Ia (μ_{eff} = 3.1 B.M.), which obviously has an octahedral form. The acetato ligand is in a central position in the copper complex of $Cu(HIm)_2ac_2$ Ib [8]. Both of the oxygen atoms enter into reciprocal action with the central atom in this case as well. The (4+2)-coordination which characterizes copper is taken into account by differing Cu–O distances (i.e. Cu–O = 129.1 or 279.9 pm respectively). The hydrogen bond system is analogous in all cases [7, 8] and it is comparable to the respective system of the corresponding acetyl acetate complexes $Ni(acac)_2(HIm)_2$ IVa or to $Co(acac)_2(HIm)_2$ IVb [6b] respectively (intermolecular hydrogen bridges between imidazole and acetato- or acetylacetonato ligands).

In this context, it is not surprising that IVa and Ia show a similar thermal behaviour (Eqs (1) and (2)). But thermally induced proton migration from imidazole to the acetate in Ia does not comprise one step as in the case of IVa but two steps. The amount of acetic acid split off allows the conclusion that there is a multinuclear mechanism (Fig. 1)*.

$$\underset{\textbf{IVa}}{Ni(acac)_2(HIm)_2} \xrightarrow[260^{\circ}C]{-\,2\ Hacac} \underset{\textbf{V}}{NiIm_2} \qquad (1)$$

---

* Equations (1) through (14) show the Δm values [%] found without brackets and those obtained by calculation in brackets below the arrows. Temperature data refer to the initial temperature of DTG–curves, i. e. to the temperature of completed thermal degradation.

$$\underset{\textbf{Ia}}{\mathrm{Ni(HIm)_2ac_2}} \xrightarrow[180^\circ\mathrm{C}]{-\,0.75\ \mathrm{Hac}} \xrightarrow[250^\circ\mathrm{C}]{-\,1.25\ \mathrm{Hac}} \underset{\textbf{V}}{\mathrm{NiIm_2}} \qquad (2)$$

The formation of the polymer compound V [20] makes it also possible to understand the thermal degradation of compound $Ni(HIm)_6ac_2$ IIa (Eq. (3)) and of complex compound $Ni(HIm)_4ac_2$ IIIa (Eq. (4)). The latter can be obtained from Ia and IIa by means of ligand redistribution.

$$\underset{\textbf{IIa}}{\mathrm{Ni(HIm)_6ac_2}} \xrightarrow[\substack{22.0\ (21.9)\\ 190^\circ\mathrm{C}}]{-\,\mathrm{H_2Imac}} \text{"}\mathrm{Ni(HIm)_4(Im)ac}\text{"} \xrightarrow[\substack{45.0\ (45.1)\\ 270^\circ\mathrm{C}}]{\substack{-\,\mathrm{H_2Imac}\\ -\,2\ \mathrm{HIm}}} \underset{\textbf{V}}{\mathrm{NiIm_2}} \qquad (3)$$

$$\underset{\textbf{IIIa}}{\mathrm{Ni(HIm)_4ac_2}} \xrightarrow[\substack{28.5\ (28.5)\\ 185^\circ\mathrm{C}}]{-\,\mathrm{H_2Imac}} \xrightarrow[\substack{28.5\ (28.5)\\ 255^\circ\mathrm{C}}]{-\,\mathrm{H_2Imac}} \underset{\textbf{V}}{\mathrm{NiIm_2}} \qquad (4)$$

Equations (3) and (4) show that one mol each of imidazole and acetic acid is split off probably under the form of the H_2Imac 'imidazolium acetate' addition compound roughly at the same temperature in the first step during the thermal degradation of compounds IIa and IIIa. [The same applies to $H_2MeImac$ (Eqs (9) and (10)), H_2Me_2Pyac (Eq. (11)), and H_2Pzac (Eqs (12) and (13)).] A

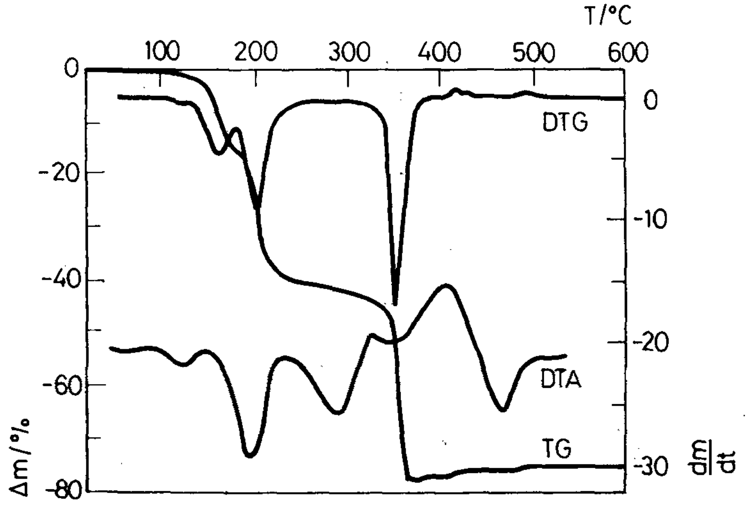

Fig. 1 Thermal degradation of $Ni(HIm)_2ac_2$ **Ia**

molecule of this salt is released once more in the second step and two more molecules of imidazole are set free in addition to this in order to preserve diimidazolate V in the case of compound IIa.

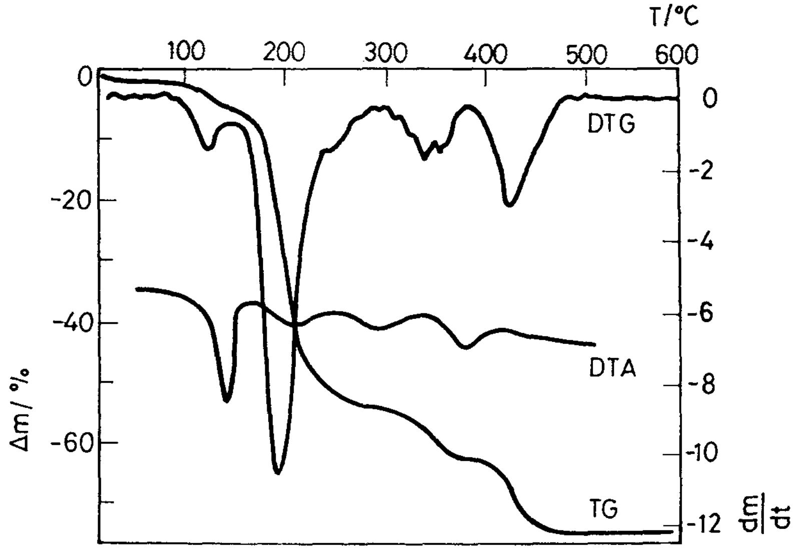

Fig. 2 Thermal degradation of $\mathrm{Cu(HIm)_2ac_2}$ **Ib**

The thermal behaviour of complexes $\mathrm{Cu(HIm)_2ac_2}$ Ib (Fig. 2) and $\mathrm{Cu(HIm)_4ac_2}$ IIIb has quite a different outlook. Both compounds split off all constituents containing nitrogen during a first step (Eqs (5) and (6)) and form an alkaline and extremely stable copper acetate with the composition of $\mathrm{Cu(OH)_2{\cdot}3Cuac_2}$. The formation of hydroxo groups might be explained by the formation of N-acetylimidazole [$\mathrm{Im{-}C(O)CH_3}$]. No detection was made to find $\mathrm{Im{-}C(O)CH_3}$ in gaseous decomposition products. Air humidity might transfer the compound into imidazole and acetic acid. As it is known of verdigris, alkaline copper acetate transforms into mixed copper oxide acetates while splitting of acetic acid [21]. The following transformation is done releasing acetic anhydride in analogy to copper(II) acetate at increased temperatures.

$$\underset{\textbf{Ib}}{2\mathrm{Cu(HIm)_2ac_2}} \xrightarrow[\substack{49.4\ (49.8)\\ 290^\circ\mathrm{C}}]{\substack{-3\ \mathrm{HIm}\\ -\text{"Im–C(O)CH}_3\text{"}}} 1/2\mathrm{Cu(OH)_2{\cdot}3Cuac_2} \xrightarrow[\substack{9.1\ (9.4)\\ 390^\circ\mathrm{C}}]{-\mathrm{Hac}} \mathrm{CuO{\cdot}Cuac_2} \qquad (5)$$

$$\underset{\textbf{IIIb}}{2\mathrm{Cu(HIm)_4ac_2}} \xrightarrow[\substack{64.5\ (64.6)\\ 285^\circ\mathrm{C}}]{\substack{-7\ \mathrm{HIm}\\ -\text{"Im–C(O)CH}_3\text{"}}} 1/2\mathrm{Cu(OH)_2{\cdot}3Cuac_2} \xrightarrow[\substack{6.5\ (6.6)\\ 385^\circ\mathrm{C}}]{-\mathrm{Hac}} \mathrm{CuO{\cdot}Cuac_2} \qquad (6)$$

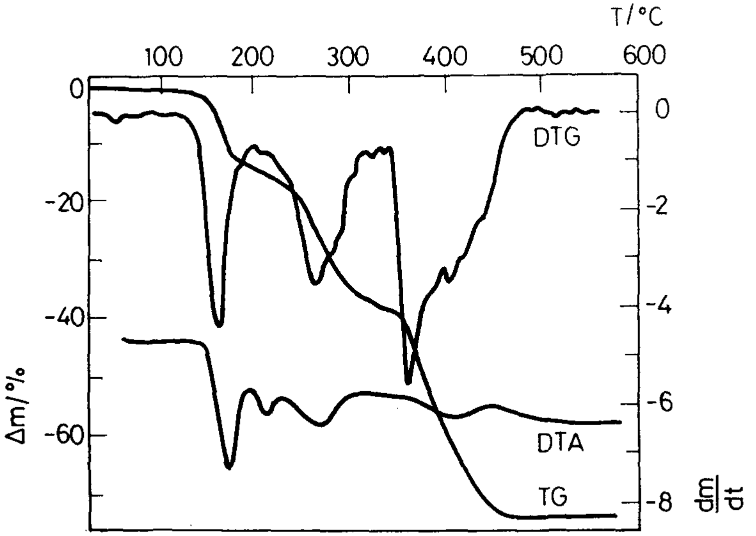

Fig. 3 Thermal degradation of $\mathrm{Co(HIm)_2ac_2}$ Ic

Ib shows a characteristic difference to $\mathrm{Cu(acac)_2(HIm)_2}$ with regard to thermal degradation. In the latter case, acetylacetone is eliminated in the first step in analogy to IVa [6a]. Complex compound $\mathrm{Co(HIm)_2ac_2}$ Ic also shows a specific behaviour during thermal degradation (Fig. 3). One mol of acetic acid is split off for every two mols of cobalt complex in a first step. This leads to a blue cobalt complex IV which has a tetrahedral coordination. VI is insoluble in all known solvents and it is very accessible in a preparative way. Two molecules of imidazole as well as one molecule of imidazolium acetate are split off for every dimer unit at a temperature in a range of more than 150°C in a second degradation step (Eq. (7)).

$$\begin{array}{ccccc} 2\mathrm{Co(HIm)_2ac_2} & \xrightarrow[9.3\ (9.6)]{-\mathrm{Hac}} & \mathrm{Co_2(HIm)_3(Im)ac_3} & \xrightarrow[30.8\ (31.3)]{\substack{-\mathrm{HIm}\\ -\mathrm{H_2Imac}}} & 2\text{"Co(Im)ac"} \\ \mathbf{Ic} & 175^{\circ}\mathrm{C} & \mathbf{VI} & 330^{\circ}\mathrm{C} & \end{array} \qquad (7)$$

The 'imidazolato-cobalt(II) acetate' coordination polymer obtainable in this way decomposes into cobalt(II) oxide at a temperature up to 460°C. N-acetyl imidazole should be eliminated formally in this process. But the wide peak in the DTG diagram (Fig. 3) shows that this process is by far more complex.

Thermal behaviour is accompanied by the oxidation of the central atom in the case of complex $\mathrm{Co(HIm)_6ac_2}$ IIb surrounded by 6 molecules of imidazole in an octahedral way. This feature is encountered often for cobalt(II) complexes in a nitrogen rich environment and it is also found for compound $\text{Co(HPz)}_4\text{ac}_2$ VIIIc (section 3) which contains pyrazole. An imidazolato-cobalt(III) oxide is the decomposition product which remains at a temperature of between 350 and 400°C (24.3%).

Coordination compounds of the type 1,2 $\text{M(HMeIm)}_2\text{ac}_2$ (VII) will be formed only if imidazole is replaced by the more bulky 2-methyl imidazole (HMeIm). Heterocycles substituted with methyl show very much the same behaviour towards the corresponding metal halogenides [22].

The thermal behaviour of copper compound VIIb (Eq. (8)) and of cobalt compound VIIc (Eq. (9)) corresponds to those of imidazole complexes Ib and Ic (Eqs (5) and (7)).

$$\underset{\textbf{VIIb}}{2\text{Cu(HMeIm)}_2\text{ac}_2}\ \underset{310^\circ\text{C}}{\xrightarrow[53.4(53.0)]{\substack{-3\ \text{HMeIm}\\ -\text{MeIm–C(O)CH}_3}}}\ 1/2\text{Cu(OH)}_2\cdot 3\text{Cuac}_2\ \underset{360^\circ\text{C}}{\xrightarrow[8.1\ (8.7)]{-\text{Hac}}}\ \text{CuO}\cdot\text{Cuac}_2 \qquad (8)$$

$$\underset{\textbf{VIIbc}}{2\text{Co(HMeIm)}_2\text{ac}_2}\ \underset{140^\circ\text{C}}{\xrightarrow[8.3(8.8)]{-\text{Hac}}}\ \text{Co}_2\text{(HMeIm)}_3\text{(MeIm)ac}_3\ \underset{340^\circ\text{C}}{\xrightarrow[32.5(32.8)]{\substack{-\text{HMeIm}\\ -\text{H}_2\text{MeImac}}}}\ 2\text{"Co(MeIm)ac"} \qquad (9)$$

But the structural analysis of VIIb has shown a cis-arrangement of ligands [11] in contrast to trans-$\text{Cu(HIm)}_2\text{ac}_2$ Ib [8]. Equations (5) and (8) show that both present the same thermal splitting pattern. This leads to the conclusion that the elimination process is controlled by thermodynamics.

The thermal behaviour of $\text{Ni(HMeIm)}_2\text{ac}_2$ VIIa (Eq. 10) appears to be very much different in comparison with Ia (Eq. 1).

$$\underset{\textbf{VIIa}}{\text{Ni(HMeIm)}_2\text{ac}_2}\ \underset{310^\circ\text{C}}{\xrightarrow[41.2(41.6)]{-\text{H}_2\text{MeImac}}}\ \text{"Ni(MeIm)ac"}\ \underset{360^\circ\text{C}}{\xrightarrow[37.5(37.0)]{-\text{MeIm–C(O)CH}_3}}\ \text{NiO} \qquad (10)$$

The reasons leading to the different thermal behaviour of $\text{Ni(HMeIm)}_2\text{ac}_2$ (VIIa) and $\text{Ni(HIm)}_2\text{ac}_2$ (Ia) are not of a trivial nature. It might be due to differences in the hydrogen bonding system which might allow thermally induced proton migration to proceed only from a single 2-methyl imidazole ligand to a single acetato ligand in the case of VIIa.

The thermal decomposition of metal acetate pyrazole addition compounds $M(HPz)_xac_2$

The $M(HPz)_4ac_2$ 1,4 complexes of nickel VIIIa, copper VIIIb and cobalt VIIIc are the only ones known for pyrazole (HPz) [12] while the 1,2 complexes of $Ni(HMe_2Pz)_2ac_2$ IXa $Cu(HMe_2Pz)_2ac_2$ IXb [13], and $Co(HMe_2Pz)_3ac_2$ IXc can be prepared with the help of the more bulky 3,5-dimethyl pyrazole (HMe_2Pz).

The compounds belonging to the IX type and nickel complex VIIa show a comparable thermal behaviour. '3,5-dimethyl pyrazolium acetate' is eliminated in every first stage of decomposition (Eq. (11)).

$$\underset{\textbf{IX}}{M(HMe_2Pz)_2ac_2} \xrightarrow[1)]{-H_2Me_2Pzac} \text{"}M(Me_2Pz)ac\text{"} \xrightarrow{-Me_2Pz\text{-}C(O)CH_3} MO \qquad (11)$$

IXa: 1) 43.0 (42.3); 230°C
IXb: 1) 41.5 (41.8); 190°C
IXc: $Co(HMe_2Pz)_3\ ac_2$: 1) 34.0 (33.5); 190°C

In addition, the separation of N-acetyl-3,5-dimethyl pyrazole [Me_2Pz-$C(O)CH_3$] allows the conservation of the metal oxides. Stoichiometry suggests the additional decomposition of 1 mol of HMe_2Pz only in the case of cobalt compound IXc.

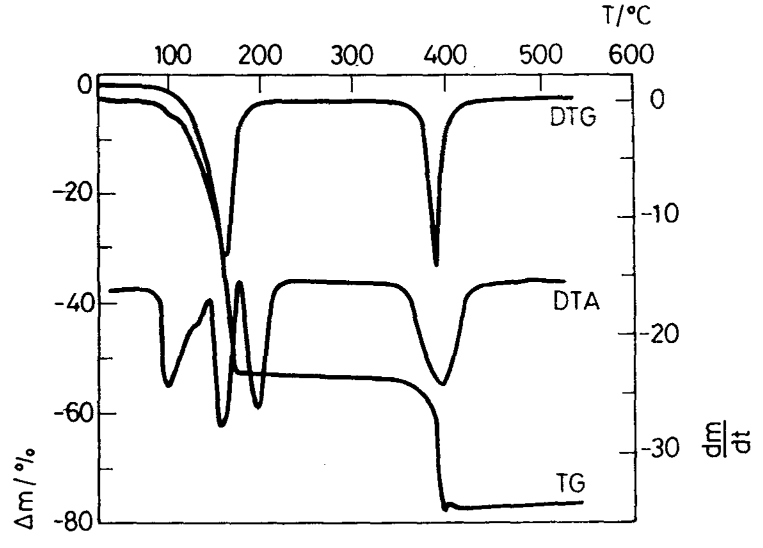

Fig. 4 Thermal degradation of $Ni(HPz)_4ac_2\ H_2O$ **VIIIa**

Compounds VIIIa and VIIIb present only small differences with regard to their thermal degradation (Fig. 4). Two clearly separated degradation stages have been found for VIIIa. They can be interpreted in accordance with Eq. (12). The first stage includes the separation of two molecules of pyrazolium acetate and of one water molecule. Several energetic processes can be assigned to this stage as it is expressed in the DTA curve (Fig. 4). Xa is very stable from a thermal point of view. (The thermochemical reaction can be used for the preparative obtention of binary pyrazolato nickel Xa [12]) and it only decomposes into metallic nickel above a temperature of 380°C. This is in analogy to imidazolate complex V [6a]. Complex Xb is also obtainable according to the acetate method [12]. But the release of pyrazolium acetate from VIIIb is characterized by a total of 3 individual steps at a temperature range above 150°C (Eq. (13)).

$$\underset{\textbf{VIIIa}}{\mathrm{Ni(HPz)_4ac_2(H_2O)}} \xrightarrow[\substack{57.6(57.0)\\ 180^\circ\mathrm{C}}]{\substack{-2\ \mathrm{H_2Pzac}\\ -\mathrm{H_2O}}} \underset{\textbf{Xa}}{\mathrm{Ni(Pz)_2}} \xrightarrow[\substack{29.2(29.8)\\ 410^\circ\mathrm{C}}]{-2\text{"Pz"}} \mathrm{Ni} \qquad (12)$$

$$\underset{\textbf{VIIIb}}{\mathrm{Cu(HPz)_4ac_2}} \xrightarrow[230^\circ\mathrm{C}]{} \xrightarrow[290^\circ\mathrm{C}]{-2\ \mathrm{H_2Pzac}} \xrightarrow[335^\circ\mathrm{C}]{} \underset{\textbf{Xb}}{\mathrm{Cu(Pz)_2}} \qquad (13)$$

A particular behaviour appears in the case of complex compound VIIIc. It is not astonishing that VIIIc (CoN_4O_2 chromophor) undergoes a process of oxidation in the course of thermal treatment if you take into account the fact that cobalt(III) compounds have a strong tendency for combining when the nitrogen content in the coordination sphere is high. The complex decomposes into pyrazolato-cobalt(III) oxide in a single stage at approximately 340°C (cf. the thermal degradation of IIc).

The structurally known complex compound $Ni(HPz)_4Cl_2$ XI [14] shows a characteristic difference to acetato complex VIIIa. All imidazole is eliminated thermally in 2 separate stages (Eq. (14)). The fact that the chloride ion presents an essentially weaker alkaline and in this way also a by far weaker proton acceptor in comparison to the acetate is especially important for this different behaviour.

$$\underset{\textbf{XI}}{\mathrm{Ni(HPz)_4Cl_2}} \xrightarrow[\substack{49.5(50.7)\\ 250^\circ\mathrm{C}}]{-3\ \mathrm{HPz}} \mathrm{Ni(HPz)Cl_2} \xrightarrow[\substack{16.8(16.9)\\ 355^\circ\mathrm{C}}]{-\mathrm{HPz}} \mathrm{NiCl_2} \qquad (14)$$

An X-ray structure analysis has been carried out for VIIIa in order show the structural differences which should be important for the characteristics of the thermal degradation processes.

The crystal structural analysis of complex Ni(HPz)$_4$ac$_2$·H$_2$O

Suitable crystals of the VIIIa compound have been obtained from a mix of ethanol and water. Tables 1 and 2 show crystal data and information on structure determination. The VIIIa complex is centrally symmetrical, while the nickel atom has an octahedral coordination geometry and is situated at the centre of symmetry (Fig. 5). For this reason, the opposite pyrazole rings are twisted by 180° with regard to one another. This is in analogy to the corresponding XI complex (Fig. 6) [14]. In addition to this, the pyrazole rings of complexes VIIIa and XI have quite comparable Ni–N distances and bonding lengths, cf. Fig. 6 and Table 3.

Table 1 Crystallographic dates VIIIa

Morphology of crystals	blue, irregular
Formula	$C_{16}H_{24}O_4N_8Ni\cdot H_2O$
Molweight	M_r = 467.1 g/mol
Crystal system	monoklin
Space group	C2/c (Nr. 15)
Lattice	
a	1214.7(2) pm
b	1440.7(1) pm
c	1207.3(1) pm
β	91.71(1)°
Volume of elementary cell	$V = 0.2111(1)$ nm^{-3}
Density (calc.)	$D_c = 1.47$ gcm^{-1}
Formula units	$Z = 4$
Absorption coefficient	$\mu = 9.6$ cm^{-1} (MoK$_\alpha$)
$\Theta_{max.}$	27°
Reflexes independence of symmetry	3648 (aus 3936)
observed reflexes with	2968
Quantity of improved parameters	178
R	0.033
R_w	0.042
Density of residual electrons	0.31 epm^{-3}

Table 2 Atomcoordinates $(\cdot 10^4)$ and parameter U $(\mathrm{pm}^2\cdot 10^{-1})$ for the äquivalente isotrope temperature factor $\exp(-8\pi^2 U \sin^2\theta / \lambda^2)$ for $Ni(Hpz)_4ac_2\cdot H_2O$ VIIIa

Atom	*x*	*y*	*z*	U_{eq}
Ni	2500	2500	0	29(4)
O(1)	3152(1)	1165(1)	26(1)	45(2)
O(2)	3554(1)	460(1)	–1541(1)	65(3)
O(3)	5000	796(1)	2500	47(3)
N(1)	4022(1)	2986(1)	608(1)	36(2)
N(2)	4787(1)	2430(1)	1179(1)	40(3)
N(3)	2972(1)	2828(1)	–1626(1)	35(2)
N(4)	3444(1)	2215(1)	–2301(1)	40(2)
C(1)	3414(1)	467(1)	–525(1)	37(3)
C(2)	3568(2)	–434(1)	110(2)	49(4)
C(3)	5702(1)	2897(1)	1368(1)	49(4)
C(4)	5535(2)	3796(1)	1070(2)	56(4)
C(5)	4485(2)	3819(1)	603(2)	50(4)
C(6)	3785(2)	2624(1)	–3224(1)	52(2)
C(7)	3520(2)	3539(1)	–3157(1)	53(4)
C(8)	3010(2)	3635(1)	–2158(1)	46(3)

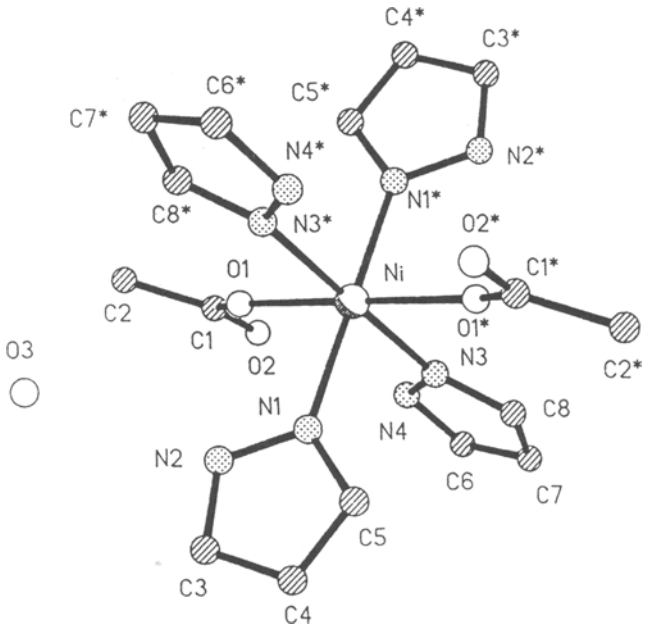

Fig. 5 Molecule structure of $Ni(HPz)_4ac_2\ H_2O$ with marking of the atoms [18]

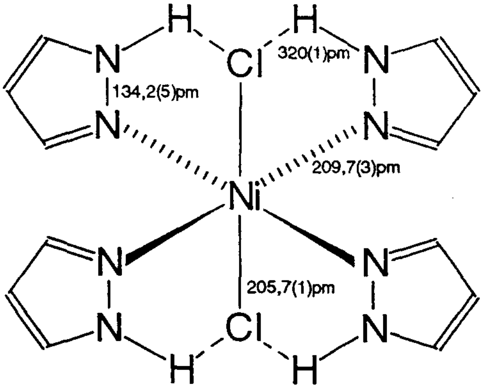

Fig. 6 Schematic representation of the molecule structure of Ni(HPz)$_4$Cl$_2$ [14]

Table 3 Selected bonding distances /pm/ and -angles /°/ of VIIIa with * marked atoms representing symmetry elements

Ni–O(1)	208.0(1)	N(2)–C(3)	133.7(3)
Ni–O(1)*	208.1(1)	N(3)–N(4)	134.2(2)
Ni–N(1)	208.9(1)	N(3)–C(8)	133.0(2)
Ni–N(1)*	208.9(1)	N(4)–C(6)	133.7(2)
Ni–N(3)	211.5(1)	C(1)–C(2)	151.6(2)
Ni–N(3)*	211.5(1)	C(3)–C(4)	135.7(3)
O(1)–C(1)	125.3(2)	C(4)–C(5)	138.0(3)
O(2)–C(1)	124.4(2)	C(6)–C(7)	136.0(3)
N(1)–N(2)	134.1(2)	C(7)–C(8)	137.9(3)
N(1)–C(5)	132.5(2)		

O(1)–Ni–O(1)*	180.0(0)	Ni–N(3)–N(4)	123.3(1)
O(1)–Ni–N(1)	88.4(1)	Ni–N(3)–C(8)	131.1(1)
O(1)–Ni–N(1)*	91.6(1)	N(4)–N(3)–C(8)	105.1(1)
O(1)–Ni–N(3)	96.2(1)	N(3)–N(4)–C(6)	111.4(2)
O(1)–Ni–N(3)*	83.8(1)	O(1)–C(1)–O(2)	125.1(2)
N(1)–Ni–N(1)*	180.0(1)	O(1)–C(1)–C(2)	116.7(2)
N(1)–Ni–N(3)	89.4(1)	O(2)–C(1)–C(2)	118.3(2)
N(1)–Ni–N(3)*	90.6(1)	N(2)–C(3)–C(4)	107.2(2)
Ni–O(1)–C(1)	146.9(1)	C(3)–C(4)–C(5)	105.1(2)
Ni–N(1)–N(2)	123.0(1)	N(1)–C(5)–C(4)	111.3(2)
Ni–N(1)–C(5)	132.3(1)	N(4)–C(6)–C(7)	107.3(2)
N(2)–N(1)–C(5)	104.7(1)	C(6)–C(7)–C(8)	105.3(2)
N(1)–N(2)–C(3)	111.7(2)	N(3)–C(8)–C(7)	110.9(2)

The essential difference between the two structures lies in their respective hydrogen bond systems. Intramolecular N–H···Cl hydrogen bridges (320 pm) appear in compound XI. In accordance with XI, coordination compound VIIIa presents a monoclinic lattice space group C2/c and also 4 formula units for every elementary cell. But one molecule of water is found for every formula unit in addition to this. It is fixed by means of intermolecular hydrogen bridges. In this way, a spatial hydrogen bond system is set up with the help of N–H···O–H···O (2) bridges (292.0 and 280.0 pm respectively). It includes the two acetate groups and 2 pyrazole groups each in the complex molecule (Fig. 7).

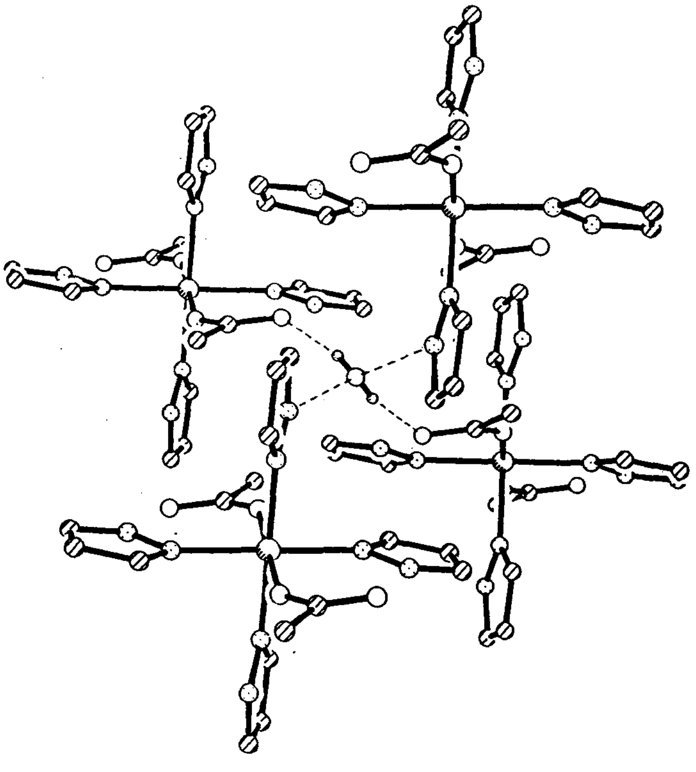

Fig. 7 Sight of $Ni(HPz)_4ac_2$ H_2O to illustrate the system of the H-bridges

This means that the replacement of chloride by acetate and the addition of one water molecule transform the intramolecular structure element N-H···Cl···H–N in the crystal lattice of XI into the intermolecular group N–H···O-H···O···C containing six atoms in the crystal lattice of VIIIa (Fig. 7). The thermochemical consequences of these different structural elements have been shown in section 3 (Eqs (12) and (14)) and they shall be discussed in the following part.

Discussion

The thermal degradation of pyrazole and of the 3,5-dimethyl pyrazole metal acetates VIII and IX is determined by kinetic factors to a large extent. This means that the process depends on reaction patterns which are set by the respective structural factors. This appears in a particularly characteristic way in the example of compound VIIIa (Eq. (12)). The water molecule acts as a mediator allowing several elimination processes (shown in Fig. 4) within a limited temperature interval. No proton transfer occurs in XI but pyrazole is split off (Eq. (14)). In contrast to this, a thermally induced proton transfer occurs from pyrazole to the acetato ligand in compound VIIIa. This finally leads to the elimination of pyrazolium acetate (Eq. (12)). The transfer of protons from the pyrazole molecules which do not have hydrogen bridges does not seem to present any problem either. The uncoordinated NH modules of the heterocycle in the crystal are arranged in such a way as to allow the formation of new hydrogen bridges (Fig. 7) and an additional transfer of protons after the separation of one molecule of pyrazolium acetate. For this reason, the same thermal degradation is observed when water is not available as a proton mediator. But is includes several individual steps and covers a temperature range that is by far larger (Eq. (13)).

The sublimation of the pyrazolium acetates seems to be favoured by their comparatively high volatility. It also presents the first reaction step in the decomposition of the acetate complexes with 3,5-dimethyl pyrazole (IX) (Eq. (11)). The intermediate products '$M(Me_2Pz)ac$' are obtained since these results only in complexes including 2 or respectively 3 coordinated heterocycles because of steric hindrance. These intermediates can decompose into metal oxide while formally eliminating N-acetyl-3,5-dimethyl pyrazole. The release of N-acetyl derivatives is mainly observed when only pyrazolate or imidazolate and acetate respectively are linked with the central atom at increased temperatures. This separation should be preceded by a nucleophilic attack on the acetate made by pyrazolate or imidazolate respectively. The electrophilic tendency of carbon in the acetate ligand increases as the negative charge is transferred more and more to the central atom. Two factors act in favour of an increased electrophilic tendency and they coincide especially in the 'M(Pz)ac' or 'M(Im)ac' compounds which have been partially decomposed by thermal processes. On the one hand, this is the binary function of the acetate (chelate or bridge) and, on the other hand, it is the small number of ligands on the central atom.

Topochemical factors determine the thermal degradation of the metal acetates containing imidazole and 2-methyl imidazole and belonging to types I, II, III and VII only to a limited extent. In spite of similar structures, we find different thermochemical reactions (Fig. 1 through 3) depending on the metal in compounds $M(HIm)_2ac_2$ Ia–Ic. The complexes of I form a space lattice by means of intermolecular hydrogen bridges [10, 8]. It is similar to the lattice of the corresponding acetylacetonate compounds IV [6b]. In this way, the analogous thermal behaviour of Ia and IV seems logical. Compounds IIa and IIIa contain more imidazole and their thermal degradation includes the separation of imidazolium acetate and imidazole by formation of V. This can also be explained since the acetate is fixed by means of several intermolecular N–H···O···C hydrogen bridges in both complex compounds [9, 10]. This allows a transfer of protons to the acetate or, respectively, by way of the acetate and thus the separation of imidazolium acetate within the solid body.

In a way different to the nickel compounds, the copper complexes Ib, IIIb and VIIb containing imidazole or methyl imidazole respectively, split off the heterocycles containing nitrogen and form alkaline copper acetates in a first stage although they have a different structural setup [7, 8, 11].

In contrast to this, the thermolysis of the copper complexes VIIIb and IXb containing pyrazole or dimethyl pyrazole respectively follow a different reaction process which is obviously determined by the special tendency to form products including pyrazolato ligands such as $Cu(Me_2Pz)ac$ or $Cu(Pz)_2$.

Cobalt compound Ic eliminates acetic acid in a first step, thus forming a tetrahedral species VI which obviously seems to be bridged by acetate and imidazolate. The fact that no acetic acid but rather imidazole and imidazolium acetate are set free in the next decomposition stage of VI is due to the stability of these bridges. This is in agreement with the thermal degradation of $Co(ac)_2 \cdot 4H_2O$ which also splits off one molecule of acetic acid for every two molecules of cobalt acetate at approximately 130°C and forms a tetrahedral cobalt complex bridged by means of hydroxy and acetate groups [23]. The fact that it also appears in the decomposition pattern of VIIc (Eq. (9)) indicates the particular stability of the type of structure represented by VI. We would like to point out at this place that proton migration must always occur in the case of the thermal separation of acetic acid or imidazolium and pyrazolium acetate respectively. Imidazole and pyrazole act as a NH-acid species [6a] and acetate as an acceptor of protons. Proton acceptor strength is greater in single-count than in binary function. The transfer of protons from the heterocycle may fail to occur when the acetate has a strong binary linkage (bridge function as e.g. in compound VI).

The variation of central atom and nitrogen heterocycle has shown that the thermal behaviour of metal acetates containing imidazole and pyrazole presents great differences which are due to the relative domination of kinetic and thermodynamic factors. In this way, neutral compounds having the same stoichiometric composition can release either acetic acid or imidazole under similar thermal conditions, the latter being the predominant product. This makes it possible to achieve acid or alkaline thermal latence and it presents interesting aspects for application in polymerization accelerators.

* * *

We thank Mr. E. Uhlig, Prof. Dr. for his generous support and constant interest into the progress we made during this work. We also acknowledge the company Bakelite AG, Duisburg for having kindly supplied the chemical reagents.

References

1a R. J. Doedens, Prog. Inorg. Chem., 21 (1976) 209.
1b M. Melnik, Coord. Chem Rev., 36 (1981) 1.
1c M. Kato and Y. Muto, Coord. Chem. Rev., 92 (1988) 45.
2a R. Österberg, Coord. Chem Rev., 12 (1974) 309.
2b R. G. Bhirud and T. S. Srivastava, Inorg. Chem. Acta 173 (1990) 121.
2c A. Dobry-Duclaux and A. May, Bull. Soc. Chim. Biol., 52 (1970) 1447.
3 H. Tamura, H. Imai, J. Kuwahara and Y. Suguira, J. Am. Chem. Soc., 109 (1987) 6870.
4 M. Fedtke and V. Strehmel, Acta Polymer, 40 (1989) 997.
5 A. Böttcher, M. Döring, E. Uhlig, M. Fedtke, K. Dathe and B. Nestler, PCT-Patent 1991, WO 91/13925 vom 19.09.1991.
6a M. Döring, W. Ludwig, M. Meinert and E. Uhlig, Z. Anorg. Allg. Chem., 595 (1991) 45.
6 M. Döring, W. Ludwig, E. Uhlig. S. Wocadlo and U. Müller, Z. Anorg. Allg. Chem., 611 (1992) 61.
7 A. Gadet, Acta Crystallogr., B30 (1974) 349.
8 H. Å. Henriksson, Acta Crystallogr., B33 (1977) 1947.
9 A. Gadet, C. R. Acad. Sci. Paris, Sér., C 274 (1972) 263.
10 A. L. Abuhijleh and C. Woods, Inorg. Chim. Acta, 194 (1992) 9.
11 A. L. Abuhijleh, C. Woods and I. Y. Ahmed, Inorg. Chim. Acta, 190 (1991) 11.
12 S. Trofimenko, Chem. Rev., 72 (1972) 497.
13 M. Inoue M. Kishita and M. Kubo, Inorg. Chem., 4 (1965) 626.
14a C. W. Reimann, A. D. Mighell and F. A. Mauer, Acta Crystallogr., 23 (1967) 135.
14b C. W. Reimann, J. Chem. Soc., Chem. Comm., 1969 145.
15 W. Ludwig, J. Thermal Anal., 8 (1975) 75.
16 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, The Netherlands 1990.
17 G. M. Sheldrick, SHELXS, Programm zur Lösung von Kristallstrukturen, Göttingen 1980.
18 G. M. Sheldrick, SHELXTL/PC, Siemens Analytical X-ray Instruments, Inc., Madison WI 1992.
19 R. J. Sundberg, B. Martin, Chem. Rev., 74 (1974) 471.
20 W. Eilbeck, F. Holmes and S. Underhill, J. Chem Soc., A(1967) 757.
21 Gmelin's Handbuch der Anorganischen Chemie, 8. Auflage B60 2.Lfg. Verlag Chemie, Weinheim 1961, p. 697.
22 J. Reedijk, Recl. Trav. Chim. Pays-Bas, 91 (1972) 507.
23 S. J. Ashcroft and C. T. Mortimer, 'Thermochemistry of Transition Metal Complexes', Academic Press, New York 1970.

Zusammenfassung — Komplexverbindungen des Typs $M(HIm)_2ac_2$ (*HIm* = Imidazol, *ac* = Acetat, *M* = Co, Ni, Cu) zeigen ein differenziertes thermisches Verhalten. Der thermische Abbau der Nickelverbindung erfolgt analog dem $Ni(acac)_2(HIm)_2$ [10] unter Freisetzung von Essigsäure und Bildung von $Ni(Im)_2$. Der Kupferkomplex spaltet alle stickstoffhaltigen Liganden unter Ausbildung stabiler basischer Kupferacetate ab. Die Cobaltverbindung elininiert thermisch teilweise Essigsäure, sodaß stabile acetat- bzw. imidazolatverbrückte Species entstehen.

Die Pyrazol- bzw. die sterisch anspruchsvollen 3,5-Dimethylpyrazol-komplexe zeigen ein untereinander vergleichbares Verhalten, wobei in einem ersten Schritt jeweils Pyrazoliumacetat freigesetzt wird.

Die Kristalstruktur von $Ni(HPz)_4ac_2$ wurde durch Röntgenbeugung bestimmt: monoklin, Raumgruppe C2/c.

Die Verbindung besitzt ein ausgeprägtes Wasserstoffbrückensystem mit einem Wassermolekül als Zentrum zweier N–H···O–H···O-Brücken, wodurch der leichte Protonentransfer unter Abspaltung von Pyrazoliumacetat verständlich wird.