THERMAL ANALYSIS OF METAL COMPLEXES, III[+]

INVESTIGATION OF THE THERMAL DECOMPOSITION OF PYRIDINE HALIDE (PSEUDOHALIDE) MIXED COMPLEXES AND OF THEIR DECOMPOSITION PRODUCTS

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On the basis of the thermal investigation of $Mpy_n X_z$ mixed complexes (where $M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; py = pyridine; or α-, β- and γ-picoline; $X = Cl^-$, Br^-, I^-, OCN^-, SCN^-, NO_3^-, SO_4^{2-}; and $n = 2, 3, 4, 6$; $z = 1, 2$), factors influencing the stability of the metal-pyridine-N bond have been determined.

On the basis of the measured magnetic susceptibilities the symmetry of the coordination sphere of the central atom has been established in the intermediate products formed by the thermal decomposition of cobalt(II) complexes.

With metal complexes the thermal decomposition of which begins with the splitting of a coordinate bond, the decomposition temperature can be used for the characterization of the strength of this bond [1]. The thermal decomposition of metal complexes containing pyridine ligands begins with the liberation of pyridine, i.e. with the splitting of the metal-pyridine-nitrogen bond. Therefore, an investigation of the thermal decomposition of complexes of this type may furnish information on the factors influencing the strength of this bond. With this end in view, the derivatograms of the complexes listed in Tables 1 and 2 were recorded under identical experimental conditions. Several of these complexes had already been examined earlier by this method but the results of various authors are often inconsistent [2—12]. Comparative data could be obtained only by determining the thermal behaviour of the whole series again under identical conditions. For a better understanding of the thermal decomposition processes, some of their intermediate products were also isolated. The probable structure of these products has been interpreted on the basis of their i.r. spectra and magnetic susceptibility.

Experimental

The complexes were prepared by methods described in the literature [13—17].
The metal content of the complexes was determined by complexometry, their halide or pseudohalide content by argentometry. The pyridine content of the

[+] Previous paper of the series: G. Liptay, K. Burger, E. Papp Molnár, Sz. Szebeni, F. Ruff: J. Inorg. Nucl. Chem. 31 (1969) 2359.

mixed complexes was calculated from the TG curves. The complexes were also identified on the basis of their infrared spectra.

The derivatograms were recorded on a Paulik—Paulik—Erdey Model GYEM derivatograph, in air, at a heating rate of 3°/min.

The weight of the samples investigated was about 200 mg. The intermediate products of the thermal decomposition were prepared as described in one of our earlier papers [2].

Results and discussion

Peak temperatures characteristic of the thermal decomposition of the mixed complexes investigated are summarized in Tables 1 and 2. It is to be seen that the thermal decomposition of complexes of analogous composition can proceed in different ways according to equations (1) to (7).
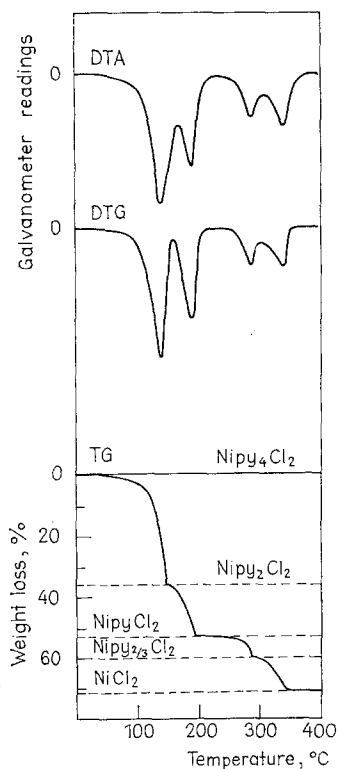

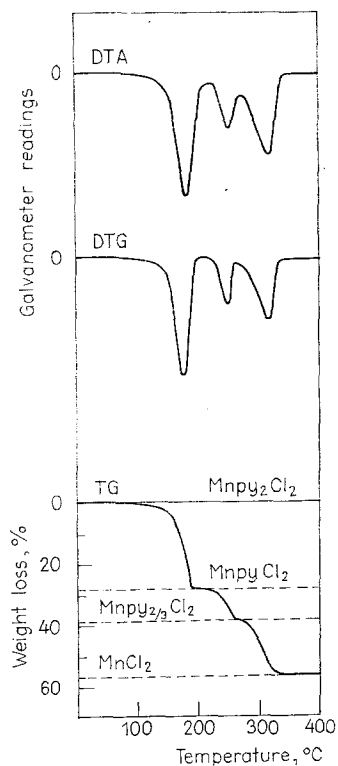Fig. 1. The derivatogram (TG, DTG and DTA curves) of Ni(py)$_4$Cl$_2$
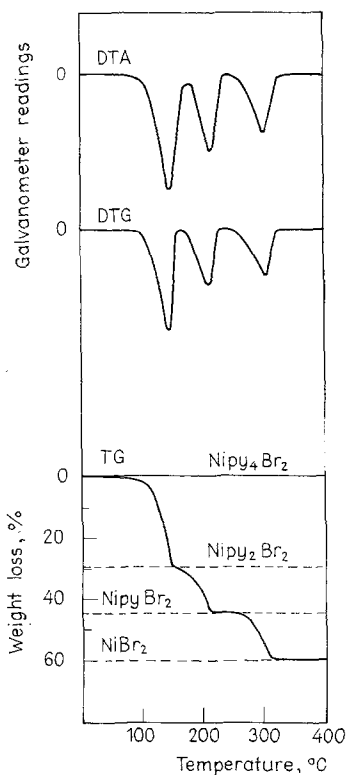
Fig. 2. The derivatogram (TG, DTG and DTA curves) of Mn(py)$_2$Cl$_2$

$$M(py)_4X_2 = M(py)_2X_2 + 2\,py \tag{1}$$

$$M(py)_2X_2 = MX_2 + 2\,py \tag{2}$$

$$M(py)_2X_2 = M(py)X_2 + py \tag{3}$$

$$M(py)X_2 = M(py)_{2/3}X_2 + 1/3\,py \tag{4}$$

$$M(py)_{2/3}X_2 = MX_2 + 2/3\,py \tag{5}$$

$$M(py)X_2 = MX_2 + py \tag{6}$$

$$M(py)_6X_2 = M(py)_4X_2 + 2\,py \tag{7}$$
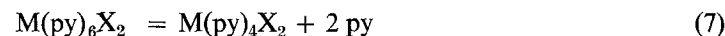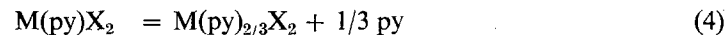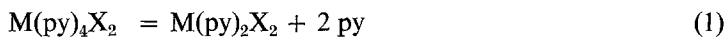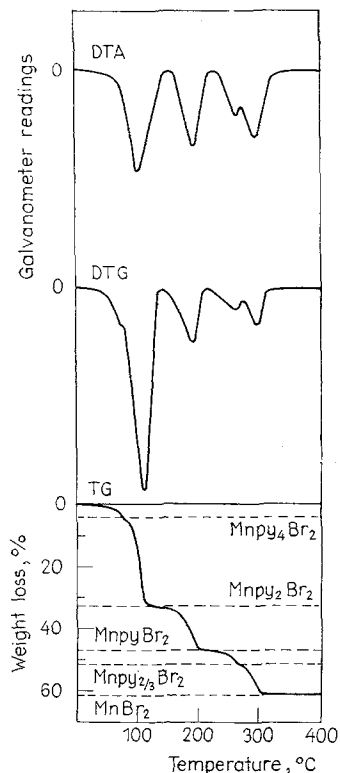

Fig. 3. The derivatogram (TG, DTG and DTA curves) of Ni(py)$_4$Br$_2$

Fig. 4. The derivatogram (TG, DTG and DTA curves) of Mn(py)$_4$Br$_2$. (The sample contains also a small amount of adsorbed pyridine.)

The first process in the thermal decomposition of the Ni(II) and Co(II) M(py)$_4$Cl$_2$ complexes proceeds according to Eq. (1), while 1 mole of py is liberated in the second decomposition process as in Eq. (3) The splitting off of the last pyridine ligand occurs, according to the observations of Majumdar et al. [3], Beech et al. [4], Allan et al. [5] and Brown et al. [6], in a single step as described by Eq. (6), however our investigations proved the liberation to be a two-step process, accord-

ing to Eqs (4) and (5) (Fig. 1). Our results are in agreement with those of Bowman and Rogers [7], Murgulescu et al. [8] and Segal and Vasile [9]. These latter authors also elucidated the kinetics of the decomposition [10]. In the decomposition of the Mn(II), Cd(II) and Cu(II) $M(py)_2Cl_2$ complexes, Beech et al. [4, 11] found, similarly to us, that a fraction of the pyridine is liberated (Fig. 2). However, these findings differ from those of Bowman et al. [7].
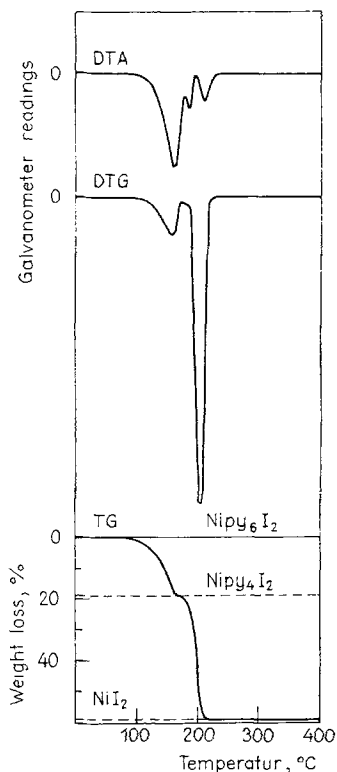
Fig. 5. The derivatogram (TG, DTG and DTA curves) of $Ni(py)_6I_2$
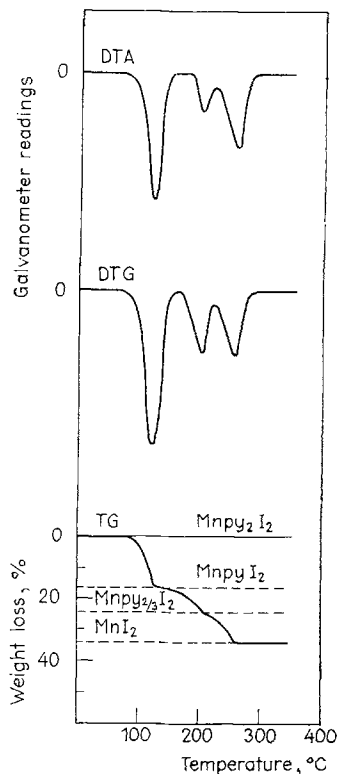
Fig. 6. The derivatogram (TG, DTG and DTA curves) of $Mn(py)_2I_2$

In the thermal decomposition of nickel and cobalt bromide mixed complexes, we found the liberation of pyridine to occur always according to Eqs (1), (3) and (6) (Fig. 3). Our results are in contrast with the experimental findings of Majumdar et al. [3], according to which the Ni complex containing 4 pyridines is converted directly into the intermediate product $Ni(py)Br_2$, and finally into NiOBr. Neither do our investigations support the results of Knyazeva et al. [12] who found that the liberation of the last mole of pyridine occurs in two steps, each of 0.5 mole. On the other hand, our results support the investigations of Allan et al. [5], proving that the last pyridine molecule leaves in a single step.

In the thermal decomposition of the $Mn(py)_4Br_2$ mixed complex, which (according to our knowledge) was first investigated by us, the last pyridine ligand leaves as in Eqs (4) and (5) (Fig. 4).

In the thermal decomposition of $Ni(py)_6I_2$ (Fig. 5), first a complex containing 4 pyridines was found formed as in Eq. (7). In our investigations concerning the further decomposition of the tetra-derivative, neither the product of Beech et al. [4] containing two pyridines, nor that of Majumdar et al. [3] containing one pyridine could be detected; the four pyridine ligands are released in one step. The decomposition of the analogous cobalt complex begins with the liberation of two pyridines according to Eq. (7), while further decomposition proceeds according to Eqs (1), (3) and (6).

In the decomposition of the $Mn(py)_2I_2$ complex (Fig. 6), the liberation of the last pyridine proceeds in two separate steps according to Eqs (4) and (5), with the formation of a polynuclear intermediate product.

In the decomposition of $Cd(py)_6I_2$, after the liberation of the two pyridine ligands bound in the outer coordination sphere, the remaining four pyridines are liberated in four steps each involving 1 mole of pyridine. In the case of the analogous copper complex, 2, 2, 1 and 1 moles of pyridine were successively liberated during the decomposition. These decomposition steps are not in agreement with the results of Beech et al. [11], who, though examining dipyridine derivatives, found that the liberation of the last pyridine takes place in two steps, according to Eqs (4) and (5).

Factors affecting the strength of the
metal-pyridine-N bond

The temperatures of the thermal decomposition peaks in Tables 1 and 2 show that the thermal stability of complexes of analogous composition increases in general along the series $Mn < Co < Ni < Cu$, which corresponds to the order of stability of the high-spin transition metal complexes.

The effect of the anions is less unidirectional. Thus, e.g. in the case of the cadmium complexes, the temperature of the liberation of the first pyridine increases along the series Cl^-, Br^-, SCN^-. On the other hand, in the case of the copper complexes it decreases in the previous order of the ligands. For the nickel and cobalt complexes, the thermal stability of the bromide and chloride complexes is about the same, while that of the thiocyanate complexes is higher.

This apparent contradiction is indicative of the fact that the effect of the halide or pseudohalide ions on the strength of the metal-pyridine-N bond can be traced back to several, but at least two, opposing actions. For these ligands, electron density decreases in the order Cl^-, Br^-, SCN^-, while their polarizability increases in the same order. Thus, with central metal ions of stronger polarizing effect (e.g. Cu), the polarization of the ligands will be the dominating factor. The stronger the linkage of the polarizable anion to the metal, the more diminished will be the effective charge on the metal, and hence its affinity for pyridine.

Table 1

The temperatures of the thermal decomposition peaks of pyridine halide (pseudohalide) mixed complexes

Complex	°C	Complex	°C	Complex	°C	Complex	°C
$Nipy_4Cl_2$	140	$Nipy_4Br_2$	140	$Nipy_6I_2$	155	$Nipy_4(SCN)_2$	175
$Nipy_2Cl_2$	190	$Nipy_2Br_2$	210	$Nipy_4I_2$	200	$Nipy_2(SCN)_2$	270
$NipyCl_2$	290	$NipyBr_2$	300				
$Nipy_{2/3}Cl_2$	340						
$Copy_4Cl_2$	115	$Copy_4Br_2$	120	$Copy_6I_2$	100	$Copy_4(SCN)_2$	165
$Copy_2Cl_2$	200	$Copy_2Br_2$ melt	215	$Copy_4I_2$	125	$Copy_3(SCN)_2$	195
$CopyCl_2$	250	$CopyBr_2$	345	$Copy_2I_2$ melt	200	$Copy_2(SCN)_2$	260
$Copy_{2/3}Cl_2$	330			$CopyI_2$	270	$Copy(SCN)_2$	350
$Mnpy_2Cl_2$	180	$Mnpy_4Br_2$	115	$Mnpy_2I_2$	120	$Mnpy_4(SCN)_2$	125
$MnpyCl_2$	255	$Mnpy_2Br_2$	195	$MnpyI_2$	200	$Mnpy_2(SCN)_2$	225
$Mnpy_{2/3}Cl_2$	315	$MnpyBr_2$	265	$Mnpy_{2/3}I_2$	255		
		$Mnpy_{2/3}Br_2$ y	300				
$Znpy_2Cl_2$ melt	210	$Znpy_2Br_2$ melt	155	$Znpy_2I_2$	95	$Znpy_2(SCN)_2$	265
				$ZnpyI_2$	120		
$Cdpy_2Cl_2$	160	$Cdpy_2Br_2$	170	$Cdpy_6I_2$	110	$Cdpy_2(SCN)_2$	240
$CdpyCl_2$	240	$CdpyBr_2$	225	$Cdpy_4I_2$	150	$Cdpy(SCN)_2$	300
$Cdpy_{2/3}Cl_2$	300	$Cdpy_{2/3}Br_2$	260	$Cdpy_3I_2$	160		
				$Cdpy_2I_2$ protracted			
				$CdpyI_2$	245		
$Cupy_2Cl_2$	235	$Cupy_2Br_2$	230	$Cupy_6I_2$	115	$Cupy_2(SCN)_2$	190
$CupyCl_2$	265	$CupyBr_2$	260	$Cupy_4I_2$	135		
					150		
$Cupy_{2/3}Cl_2$	275	$Cupy_{2/3}Br_2$	270	$Cupy_2I_2$	190		
				$CupyI_2$	210		

In the case of the rigid, less polarizable ions, such as for example cadmium (having a closed spheric symmetrical d^{10} electron shell), the polarizability of the anions plays no, or only a minor, role, so that they will diminish in the order of their original increasing negativity ($SCN^- < Br^- < Cl^-$) the effective charge on the central atom, and consequently its affinity for pyridine.

With metal ions occupying a medium position with respect to polarizability, these two actions can occur simultaneously. The thermal stability of the complexes containing the strongly polarizable thiocyanate ligand is the highest in the case of each of these metals, while the relatively smaller difference in the polarizabilities of the chloride and bromide ions becomes effective only insofar as it can just compensate the effect of the difference in their negativities.

On comparing the decomposition temperatures of SCN^- and OCN^- (the thermal decomposition of the latter will be discussed later), it can be established that the stability of the cyanate complexes is always lower than that of the thiocyanate complexes.

It is difficult to fit the data of the iodide complexes into the preceding series, because the structure of these complexes differs from those of the analogous com-

plexes on account of the greater space requirement of the iodide ion. For example, the nickel(II), cobalt(II), cadmium(II) and copper(II) complexes contain six pyridine ligands. On the basis of the peak temperatures of the liberation of the first pyridine, it is to be assumed that in the nickel complex all six pyridines are bound in the inner coordination sphere and the iodide ions are in the outer coordination sphere. However, in the cobalt, copper and cadmium complexes, the two pyridines removed at a temperature of about 100° are most probably attached in the outer coordination sphere. Zinc and manganese form dipyridino complexes. However, their thermal decomposition takes a different course so that comparison is not justified. Neither can the decomposition temperatures of those complexes which melt before the loss of pyridine (e.g. zinc complexes) be compared. The different surface conditions and specific heat of the melt change the course of thermal decomposition.

For comparison, the derivatograms of a few pyridine nitrate and sulphate mixed complexes were also recorded (Table 2).

Table 2

The temperatures of the thermal decomposition peaks of some mixed complexes

Complex	°C	Complex	°C	Complex	°C
$Nipy_6(NO_3)_2$	125	$Nipy_3SO_4 \cdot H_2O$	175		
$Nipy_3(NO_3)_2$	165	$NiSO_4 \cdot H_2O$	380		
$Nipy_2(NO_3)_2$	300				
$Copy_6(NO_3)_2$	110	$Copy_3SO_4 \cdot H_2O$	150		
$Copy_3(NO_3)_2$	160	$CopySO_4 \cdot H_2O$	190		
$Copy_2(NO_3)_2$	258	$CoSO_4 \cdot H_2O$	320		
$Co(\alpha\text{-pic})_2Cl_2$	160	$Co(\beta\text{-pic})_4Cl_2$	130	$Co(\gamma\text{-pic})_4Cl_2$	150
		$Co(\beta\text{-pic})_2Cl_2$	230	$Co(\gamma\text{-pic})_2Cl_2$	280
			290		
		$Co(\beta\text{-pic})Cl_2$	340	$Co(\gamma\text{-pic})Cl_2$	300
				$Co(\gamma\text{-pic})_{2/3}Cl_2$	340

py = pyridine
pic = picoline

It may be concluded from the course of the thermal decomposition and the decomposition temperatures of the $Ni(py)_6(NO_3)_2$ and the analogous cobalt complex (in the first step 3 pyridines are liberated simultaneously) that in these complexes all six pyridines are arranged in the inner coordination sphere.

For the verification of this conclusion, the i.r. spectra of the complexes were recorded. The spectra exhibited bands characteristic of nitrate in weak ionic bonding proving that the nitrate is in the outer coordination sphere of the metal.

On comparing the decomposition temperatures of the nitrate complexes with those of the corresponding iodide complexes, it may be seen that in the $Co(py)_6I_2$ complex, in contrast to the analogous nitrate complex, two pyridines are in the outer coordination sphere, while the pyridine ligands of $Ni(py)_6I_2$, as in the case of the nitrate complex, are bound in the inner sphere. The considerably higher stability of the iodide-containing complex as compared to the nitrate complex can be explained by the fact that in the case of $Ni(py)_6I_2$ pyridine is also linked by hydrogen bonds to the strongly negative iodide. This phenomenon does not occur with the nitrate complex as a result of the smaller negativity of NO_3^-.

The decomposition temperatures of the nickel and cobalt $M(py)_3SO_4 \cdot H_2O$ mixed complexes show that the pyridine ligands are situated in the inner coordination sphere. The i.r. spectra of these complexes also provided information on the mode of bonding of the sulphate. The spectrum exhibited four vibrational bands (430, 600, 960 and 1120 cm^{-1}) characteristic of sulfate bound as a monodentate ligand. Presumably, the one molecule of water of crystallization of the complex is also coordinated in the inner sphere. This seems to be indicated by the high decomposition temperature (above 300°) and by the relatively low OH stretching vibration (3100—3300 cm^{-1}). In accordance with the Irving—Williams stability series in the case of both the nitrate and the sulphate mixed complexes the stability of the nickel complexes is higher than that of the cobalt complexes.

By the investigation of the picolinocobalt chloride mixed complexes, we wished to determine the effect of the methyl substituent on the metal-donor-N bond. (Among the analogous Ni complexes, the β- and γ-picoline mixed complexes have already been investigated [5, 18].)

The temperatures of the decomposition peaks of the cobalt complexes showed that β- or γ-methyl groups increased the stability of the complex. The electron-repelling methyl group increases the electron density at the N-donor atom, and this increases the covalency of the metal-donor-N bond. Moreover, the decomposition temperatures show that the electron-repelling effect of the methyl group, as was to be expected on the basis of the Hammet σ values, is more operative from the γ-position than from the β-position.

The position of the substituent can also influence the composition and the stability of the complex on account of the different degrees of steric hindrance. This explains that the methyl group of α-picoline, adjacent to the N-donor atom, prevents the formation of the tetrapyridine derivative, and causes the lower decomposition temperature of $Co(\alpha\text{-pic})_2Cl_2$ than that of $Co(py)_2Cl_2$.

β-Picoline does form mixed complexes of composition $Co(\beta\text{-pic})_4Cl_2$ but the decomposition process is still different from that of the analogous pyridine complex. The methyl group of γ-picoline does not constitute a steric hindrance. The composition and the course of decomposition of this complex are completely similar to those of the analogous pyridine complex: the higher decomposition temperatures indicate simply the electron density increasing effect of the methyl group.

Gill et al. [19] in their investigation of the infrared spectra of pyridine mixed complexes found that the frequency of the pyridine bands in the metal complexes

depends only very slightly on the nature of the central metal atom. Only the frequencies of the γ C—C in-plane deformation vibration near 630 cm^{-1} and of the δ C—C out-of-plane deformation vibration in the 420—440 cm^{-1} region differed in the individual metal complexes. According to Gill et al. the energy of these vibrations increases with the decrease of the atomic radius of the central atom and with the consequent increase of its polarizing ability. We suggested that the difference in frequency of these pyridine bands is due to the change in the strength of the metal-pyridine-N coordinate bond. Therefore, in Tables 3, 4 and 5 the de-

Table 3

Temperatures of decomposition peaks and γC—C i.r. bands of M(py)$_2$Cl$_2$ mixed complexes

Complex	°C	γC—C, cm^{-1}
Mnpy$_2$Cl$_2$	180	627
Copy$_2$Cl$_2$	200	632
Cupy$_2$Cl$_2$	230	644
Znpy$_2$Cl$_2$	210	638
Cdpy$_2$Cl$_2$	160	626

Table 4

Temperatures of decomposition peaks and γC—C i.r. bands of mixed complexes containing different amounts of pyridine

Complex	°C	γC—C, cm^{-1}
Copy$_4$Cl$_2$	115	624
Copy$_2$Cl$_2$	200	632
CopyCl$_2$	250	637
Copy$_{2/3}$Cl$_2$	300	640
Copy$_4$Br$_2$	120	625
Copy$_2$Br$_2$	215	632
Cdpy$_2$Br$_2$	170	627
CdpyBr$_2$	260	638

Table 5

Temperatures of decomposition peaks and γC—C i.r. bands of Co(py)$_2$X$_2$ mixed complexes

Complex	°C	γC—C, cm^{-1}
Copy$_2$Cl$_2$	200	632
Copy$_2$Br$_2$	215	632
Cdpy$_2$Cl$_2$	160	626
Cdpy$_2$Br$_2$	170	627
Copy$_4$Cl$_2$	115	624
Copy$_4$Br$_2$	120	625

composition temperatures of the complexes are compared with the frequency of the γC—C vibration. It can be seen that in complexes of analogous composition but containing different metals (Table 3), and also in complexes containing the same metal but a different number of pyridine ligands (Table 4), the γC—C frequency increases with increasing thermal stability, i.e. with increasing covalence of the metal-nitrogen bond. The substitution of bromide for chloride in the mixed complexes (Table 5) produces in both the thermal decomposition temperatures and the infrared frequencies a change which though smaller shows the same trend.

Investigation of the thermal decomposition products

For the interpretation of the differences in the decomposition processes of analogous complexes (Eqs 1—7), the thermal decomposition products of the mixed complexes $Co(py)_4Cl_2$ and $Co(py)_4Br_2$ were prepared by the freezing of the decomposition processes at the corresponding temperatures. In the case of high-spin cobalt(II) complexes, their magnetic susceptibility (the degree of the orbital contribution) permits conclusions on the symmetry of the coordination sphere. Therefore, the magnetic susceptibilities of the tetrapyridino complexes and of their thermal decomposition products were determined at room temperature. The μ_{eff} values calculated from them are summarized in Table 6.

Table 6

Magnetic moments of the cobalt(II) complexes
(Spin-only value: 3.88 B.M.)

Complex	μ_{eff} B.M.	Stereochemistry
$Copy_4Cl_2$	4.72	distorted octahedral
$Copy_2Cl_2$	5.08	distorted octahedral
$CopyCl_2$	5.46	
$Copy_4Br_2$	4.76	distorted octahedral
$Copy_2Br_2$	4.40	tetrahedral

It is well known that with high-spin complexes of d^7 electron configuration, a considerably larger orbital moment contribution is to be expected in the case of octahedral symmetry than in that of tetrahedral symmetry. The data in Table 6 show unequivocally, therefore, that while the decomposition of the chloride mixed complex does not result in a tetrahedral coordination sphere, $Co(py)_2Br_2$, prepared by thermal decomposition of $Co(py)_4Br_2$, has a distorted tetrahedral symmetry. It is to be assumed that in the analogous chloride complex, chloride bridges lead to the distorted octahedral environment of the central cobalt(II) atom.

The different course of decomposition of the complexes is presumably due to the different bridge-forming abilities of the chloride and the bromide ligands.

Actually, in the case of polynuclear structures containing halide bridges, a step may also be produced on the thermal decomposition curve by the liberation of a fraction of the pyridine. The liberation of 1/3 molecule of pyridine, referred to 1 cobalt, is for example equivalent to the liberation of one pyridine from a trinuclear complex.

The thermal decomposition products prepared by us have also been characterized by their infrared spectra. It was established that these spectra, similarly to the magnetic data, were essentially the same as those of the complexes of analogous composition, prepared by Gill et al. by a synthetic method. Thus, the two methods yielded identical products.

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RÉSUMÉ — On a examiné des complexes du type Mpy_nX_z (où M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; py = pyridine, α-, β- et γ-piccoline; X = Cl^-, Br^-, I^-, OCN^-, SCN^-, NO_3^- SO_4^{2-}; n = 2, 3, 4, 6; z = 1, 2) dans le but de déterminer les facteurs ayant une influence sur la stabilité de la liaison métal-pyridine-N. Par mesure des susceptibilités magnétiques, on a pu établir dans la cas des complexes du Co^{2+} la sphère de coordination de l'atome central pour les phases intermédiaires produites par décomposition thermique.

ZUSAMMENFASSUNG — Aufgrund derivatographischer Untersuchungen von Mischkomplexen des Typs Mpy_nX_z (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}; py = Pyridin, α, β und γ Piccolin; X = Cl^-, Br^-, I^-, OCN^-, SCN^-, NO_3^- SO_4^{2-}; n = 2, 3, 4, 6; z = 1, 2) wurden die

die Stabilität der Metall-Pyridin-N Bindung beeinflussenden Faktoren geprüft. Durch Messung der magnetischen Suszeptibilitäten wurde die Symmetrie der Koordinationssphäre des Zentralatoms des bei der thermischen Zersetzung entstehenden Kobalt(II)-komplexes ermittelt.

Резюме — На основании исследований на дериватографе смешанных комплексов Mpy_nX_z (где $M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}$; py = пиридин, α, β и γ пиколин; $X = Cl^-$, $Br^-, I^-, OCN^-, SCN^-, NO_3^-, SO_4^{2-}$; $n = 2, 3, 4, 6$; $z = 1, 2$) определяли факторы, влияющие на стабильность связи металл-пиридин-N. На основании измерения магнитной восприимчивости установили симметрию координационной сферы центрального атома в переходных продуктах, образованных при термораспаде комплексов Co(II).