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CHARACTERIZATION OF $[Ni(py)_4]Cl_2$ AND ITS THERMAL DECOMPOSITION

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The stepwise thermal decomposition of $[Ni(py)_4]Cl_2$ was studied by means of a derivatograph. The stepwise mode of thermal decomposition allowed the preparation of new complexes. X-ray powder diffraction and IR methods were used to study the structures of the decomposition intermediates. $[Ni(py)_4]Cl_2$ was applied as a model substance. The decompositions of a great number of complex compounds of similar type have been reported, but only a few of them have been investigated structurally by single-crystal X-ray diffraction techniques due to the difficulty of obtaining large single-crystals.

In a previous paper we studied the thermal decomposition of $[Ni(py)_4]Cl_2$ [1]. This complex was found to decompose in several steps and transitory intermediates with various stoichiometric compositions were formed. The stepwise thermal decomposition showed the possibility of preparing the individual decomposition products by means of derivatograph freezing, and hence the degradation mechanism and products of this complex family can be studied.

Experimental

In [1] the IR spectra were reported. The starting complex loses two pyridine ligands in the first decomposition step (Fig. 1), and in the next step one molecule of pyridine leaves. In the third step only "1/3" of a molecule of pyridine is released and a solid complex of formula $[Ni(py)_{2/3}]Cl_2$ remains. Finally, this polynuclear compound decomposes and $NiCl_2$ is obtained as end-product.

The stepwise thermal decomposition can be described by the following equations:

$$[Ni(py)_4]Cl_2 \rightarrow [Ni(py)_2]Cl_2 + 2\ py \quad (1)$$

$$[Ni(py)_2]Cl_2 \rightarrow [Ni(py)]Cl_2 + 1\ py \quad (2)$$

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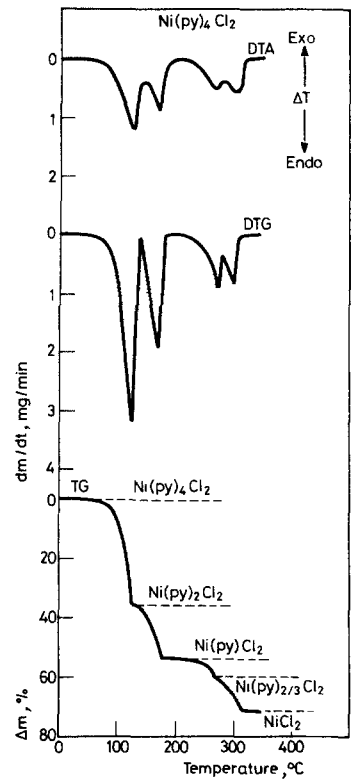

Fig. 1 Thermoanalytical curves of $Ni(py)_4Cl_2$

$$[Ni(py)]Cl_2 \rightarrow [Ni(py)_{2/3}]Cl_2 + 1/3\ py \quad (3)$$

$$[Ni(py)_{2/3}]Cl_2 \rightarrow NiCl_2 + 2/3\ py \quad (4)$$

The decomposition curves exhibit similar shapes in air and in nitrogen atmospheres.

The degradation steps we observed (Eqs 3 and 4) are not in accordance with the experience of some authors [2–4], but they are similar to the findings of others [5, 6].

$[Ni(py)_4]Cl_2$ was prepared by the Reitzenstein method [7] from anhydrous $NiCl_2$, which was dissolved in dry pyridine. The solution was refluxed for 1–2 hours and the crystalline complex was obtained on cooling.

The intermediates can not be prepared from solution. Their isolation is possible only by means of derivatograph freezing at the appropriate minima temperatures of 140, 200, 280°, respectively, registered by the DTG curve, when the oven was lifted up. The structures of the different intermediates were then analysed by means of X-ray powder diffraction techniques in a Guinier–Hägg focusing camera with

Table 1

Composition	$NiPy_4Cl_2$	$NiPy_4Cl_2$	$NiPy_2Cl_2$	$NiPy_2Cl_2$	$NiPyCl_2$	$NiPyCl_2$	$NiPy_{2/3}Cl_2$	$NiCl_2$
Reference	This work	[10]	This work	[13]	This work	[15]	This work	[16]
Unit a Å	15.82±2	15.9±.05	34.29±2	17.0	17.24±1	17.21	12.75±1	3.42
Cell b Å	15.82±2	15.9±.05	3.690±1	8.57	7.291±2	8.45	8.96±1	3.42
Dim-c Å	17.08±2	17.0±.05	17.12±1	3.86	12.10±1	21.46	9.600±4	17.75
Tension Å			88.70°	91.45°	99.7°		113.2°	60°
Volume Å^3	4275	4298	2166	562	1499	3121	1005	180
z	8	8	8	2	8	16	8	3
Density obs.	1.41	—	1.82	—	—	1.89±2	2.35	3.55
(X-ray) calc.	1.39	1.38	1.77	1.70	1.86	1.78	2.41	3.59

photographic recording and with CuK_{α_1} radiation. Potassium chloride (a = 6.2930 Å) was added as an internal standard. In order to avoid reactions with humid air, the specimens were covered with Mylar foil. The intensity distributions on the film strips were measured with an automatic film scanner [8]. The results thus obtained were evaluated with a trial-and-error indexing program [9].

Results

$NiPy_4Cl_2$

By single-crystal methods it was confirmed that the starting material has tetragonal symmetry; the dimensions found are given in Table 1, and part of the X-ray diffraction powder pattern is presented in Table 2.

The crystal structure was solved by single-crystal techniques [10].

Table 2 $NiPy_4Cl_2$. X-ray diffraction powder pattern refined by least square techniques

d, Å	F/I_{obs}	h k l
7.907	493	2 0 0
6.778	411	1 1 2
6.527	28	2 1 1
5.868	16	2 0 2
5.592	82	2 2 0
4.435	258	2 1 3
4.317	155	3 1 2
4.266	10	0 0 4
3.955	66	4 0 0
3.859	21	4 0 1
3.757	12	2 0 4
3.588	36	4 0 2
3.477	211	3 2 3
3.251	36	4 0 3
3.180	7	4 1 3
3.004	8	4 2 3
2.794	7	4 4 0
2.760	19	1 1 6
2.724	9	5 1 3
2.697	43	3 2 5
2.570	14	6 1 1
2.553	6	4 1 5
2.340	80	4 4 4
2.308	19	2 1 7
2.263	12	3 3 6
2.177	8	6 4 1

$NiPy_2Cl_2$

By using the cell dimensions of α-$CoPy_2Cl_2$ [11], a better correspondence was obtained than by indexing with the smaller cell of $CuPy_2Cl_2$ [11–13]. The dimensions of the Co compound have been determined by single-crystal techniques, but the crystals obtained in this study were not large enough for further investigation. The indexed powder pattern is given in Table 3.

Table 3 $NiPy_2Cl_2$. X-ray diffraction powder characteristics

d, Å	I/I_{obs}	h k l
8.532	415	4 0 0
7.706	600	$\bar{4}$ 0 1
6.080	76	4 0 2
4.767	162	6 0 2
4.198	27	2 0 4
3.864	37	4 0 4
3.844	29	8 0 2
3.542	33	$\bar{2}$ 1 1
3.528	16	2 1 1
3.453	33	1 0 5
3.386	46	4 1 0
3.280	120	7 0 4
3.112	12	$\bar{3}$ 0 5
3.053	19	$\bar{6}$ 1 1
2.885	35	1 0 6
2.803	11	3 0 6
2.691	16	8 0 5
2.638	26	13 0 0
2.600	21	$\bar{5}$ 1 4
2.578	17	$\bar{9}$ 0 5
2.493	39	$\bar{10}$ 1 1
2.449	9	$\bar{10}$ 0 5
2.391	45	8 0 6
2.346	10	8 1 4
2.333	13	$\bar{11}$ 0 5
2.185	6	12 1 2
2.182	6	$\bar{8}$ 1 5
2.174	18	0 0 8

Table 4 $NiPyCl_2$. X-ray diffraction powder diffraction lines

d_{obs}, Å	I/I_{obs}	h k l
10.63	250	$\bar{1}$ 0 1
8.48	440	2 0 0
7.54	29	$\bar{2}$ 0 1
6.00	221	$\bar{1}$ 1 1
5.34	27	1 0 2
4.30	31	$\bar{2}$ 1 2
4.25	10	4 0 0
3.77	27	$\bar{4}$ 0 2
3.45	62	$\bar{1}$ 2 1
3.10	32	$\bar{3}$ 1 1
3.06	122	3 2 0
2.76	8	0 1 4
2.65	70	$\bar{2}$ 2 3
2.63	66	4 2 1
2.52	65	$\bar{6}$ 0 3
2.33	58	$\bar{1}$ 2 4
2.04	14	$\bar{3}$ 1 5
2.03	14	$\bar{8}$ 1 2
2.00	13	$\bar{3}$ 3 3
1.99	31	0 0 6
1.77	24	$\bar{2}$ 4 1
1.75	7	2 4 1
1.74	12	3 3 4
1.73	18	$\bar{9}$ 0 4
1.70	10	10 0 0
1.69	17	$\bar{3}$ 3 5
1.45	15	0 4 5
1.41	7	3 5 0

$NiPyCl_2$

This composition has been studied and indexed with powder methods by Murgulescu and Segal [14, 15]. In comparison with their data, our findings reveal a smaller monoclinic cell, with the dimensions presented in Table 1. Our results were again obtained from calculations with trial-and-error programs. The indexed powder diffraction characteristics are given in Table 4.

$NiPy_{2/3}Cl_2$

This sample was assigned its composition on the basis of thermogravimetric measurements. With the same trial-and-error indexing program as before, a monoclinic cell was obtained (Table 1); the complete powder pattern is to be found in Table 5.

Table 5 $NiPy_{2/3}Cl_2$. X-ray diffraction powder pattern

d, Å	I/I_{obs}	h k l
8.961	310	0 1 0
6.113	131	$\bar{2}$ 0 1
5.859	18	2 0 0
4.465	16	$\bar{2}$ 0 2
4.402	9	0 0 2
3.672	8	1 0 2
3.389	18	1 1 2
3.078	10	$\bar{3}$ 2 1
2.935	17	0 0 3
2.893	47	$\bar{1}$ 3 0
2.685	9	$\bar{4}$ 1 2, $\bar{2}$ 3 1
2.660	6	2 3 0
2.615	10	1 0 3
2.508	67	1 1 3
2.336	38	$\bar{1}$ 0 4
2.233	8	$\bar{4}$ 0 4
1.795	8	5 0 2
1.772	9	0 3 4
1.765	15	6 0 1
1.731	10	6 1 1

Discussion

In this work we used powder diffraction data on materials with crystals too small to be handled by normal crystal techniques.

A great number of compositions of similar type are known in the literature, but

with a few exceptions such compounds have been obtained in large crystal dimensions, i.e. single-crystal structures are rare.

By indexing the X-ray powder patterns with the method used in Ref. [9], it was possible to obtain cell dimensions, symmetries and hence calculated densities for the whole series of compositions. Table 1 contains the observed data and some earlier data for comparison.

In Fig. 2 the densities are plotted versus molar volume and molar weight (arbitrary units).

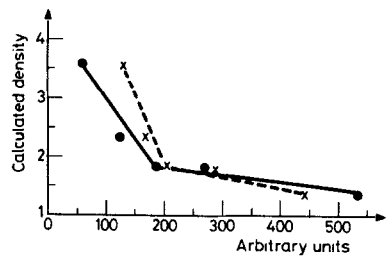

Fig. 2 Density change of the complex compound with different ligands is plotted *vs.* proper molar volume in arbitrary units, respectively

It was found that the number of formal units per cell was eight, with the exception of pure $NiCl_2$ (with hexagonal symmetry), which had three.

The above new basic structural results stemmed from an attempt to use X-ray diffraction data to explain the structural changes involved in the decomposition steps.

Our results so far suggest that the three-dimensional metal skeleton undergoes very small changes during the thermal degradation. This is in agreement with the small enthalpy changes recorded.

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Zusammenfassung — Die schrittweise thermische Zersetzung von $[Ni(py)_4]Cl_2$ wurde mit einem Derivatographen untersucht. Diese Methode ermöglicht die Darstellung neuer Komplexverbindungen. Zur Untersuchung der Struktur der intermediären Zersetzungsprodukte wurden ebenfalls XPD und IR-Spektroskopie angewandt. $[Ni(py)_4]Cl_2$ wurde als Modellsubstanz gewählt. Eine große Zahl ähnlicher Komplexverbindungen ist bekannt, aber nur von wenigen wurde die Kristallstruktur wegen der Schwierigkeiten, entsprechend große Einkristalle zu erhalten, durch Einkristall-Röntgendiffraktometrie bestimmt.

Резюме — С помощью дериватографа изучено ступенчатое термическое разложение комплекса $[Ni(py)_4]Cl_2$, что также представило возможность получения новых комплексных соединений. Для установления структуры образующихся соединений был использован порошковый рентгеноструктурный анализ и ИК спектроскопия. Исследовано большое число комплексных соединений подобного типа, но только для некоторых из них проведен рентгеноструктурный анализ их монокристаллов.