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CHARACTERIZATION OF $[Ni(Py)_4]Br_2$ AND ITS THERMAL DECOMPOSITION

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The stepwise thermal decomposition of $[Ni(Py)_4]Br_2$ was studied by means of a derivatograph. By the introduction of a larger halide atom than Cl the degradation mechanism became simpler. The solid intermediates and the starting material was also analysed with X-ray powder diffraction methods and the unit-cell dimensions were calculated.

In a previous work [1] we have investigated a large group of solid Me-pyridin-halide-complexes. We carefully studied the thermal decomposition and the solid intermediates formed of the Ni-pyridin-chloride system [2]. In order to observe the influence of a larger halide atom than chloride we prepared and studied the stepwise degradation properties of the bromide analogue. The starting material and the intermediary compositions which were obtained with the freezing-out technique were further analysed with XRD-powder methods.

Experimental

The intermediates can not be prepared from solution. Their isolation is possible only by means of derivatograph freezing at the appropriate minima

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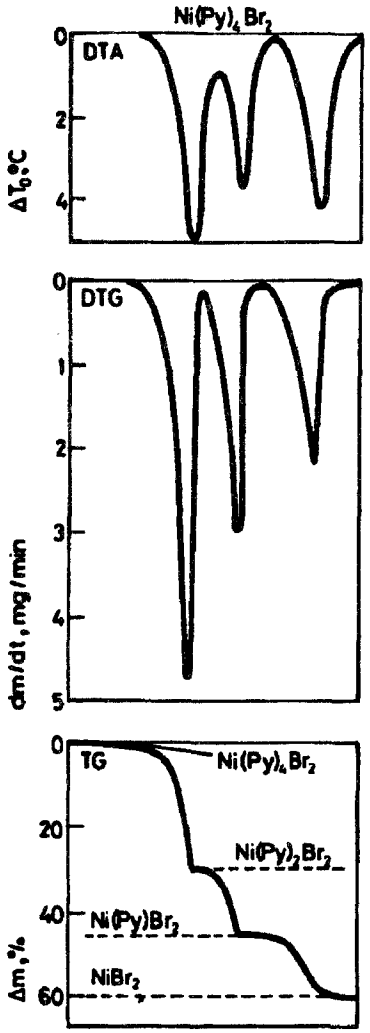

Fig. 1 Thermal curves of Ni(Py)4Br2

temperature values 160 and 220°, respectively, registered by the DTG-curve, when the oven was lifted up. The structure of the different intermediates were then analysed with X-ray powder diffraction techniques in a Guiner-Häg focusing camera with photograhic recording and with $CuK_{\alpha 1}$, radiation. Potassium chloride (a = 6.2930Å) was added as an internal standard. In order to avoid reactions with humid air the specimens were covered with

Mylar foil. The intensity distribution on the film strips were measured with an automatic film scanner [3].

The thermal analysis techniques were the same as in Ref. 2.

Table 1

Composition	$Ni(Py)_4Br_2$	$Ni(Py)_2Br_2$	$Ni(Py)Br_2$	$NiBr_2$
a Å	15.92	36.00	17.88	3.71
b Å	15.92	3.79	7.32	3.71
c Å	18.16	17.12	12.31	18.3
	-	88.72	101.0	
Volume, $Å^3$	4603	2335	1582	218.1
D_x, g/cm^3	1.54	2.14	2.50	4.98
D_{obs},	-	-	-	5.10
Z	8	8	8	3

Results

In Fig. 1 the characteristic decomposition is presented. From this curve we can see the breakdown in three steps *viz.*

1. $Ni(Py)_4Br_s$ (s) → $Ni(Py)_2Br_2$ (s) + 2 Py (s)
2. $Ni(Py)_2Br_2$ (s) → $Ni(Py)_1Br_2$ (s) + 1 Py (g)
3. $Ni(Py)_1Br_2$ (s) → $NiBr_2$ (s) + 1 Py (g)

All steps were endothermic according to the DTA-measurements.

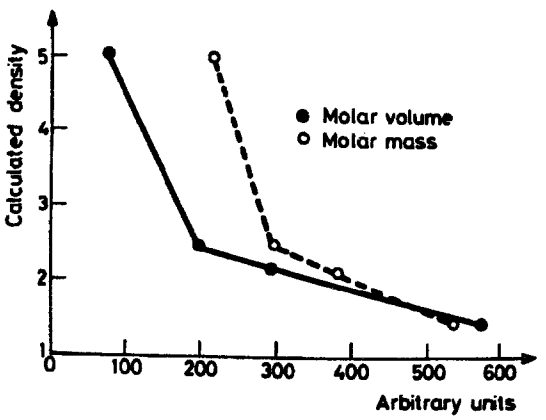

Fig. 2 Calculated density versus molare volume and weight

In this case we have no indication of a formation of the polynuclear intermediate complex with a 2/3 stoichiometry [2].

Table 2 The first part of the characteristic X-ray powder patterns for the Ni–Py–Br_2–complexes obtained by derivatograph freezing

Ni	$Ni(Py)_4Br_2$		$Ni(Py)_2Br_2$			$Ni(Py)_1Br_2$		
d, Å	I^*_{obs}	hkl	d, Å	I_{obs}	hkl	d, Å	I_{obs}	hkl
7.96	vst	200	8.95	st	200	10.85	m	$\bar{1}01$
7.84	st	102	7.71	vst	202	8.81	st	200
7.03	vst	112	6.30	vvw	402	7.78	st	$\bar{2}01$
5.59	m	220	6.16	vvw	402	6.24	m	$\bar{1}11$
5.28	m+	300	4.87	m	602	6.05	w	002
4.61	vw	213	4.25	vm	104	5.62	vw	110
4.31	m	321	4.14	w	204	5.41	vw	102
4.21	vm	114	3.95	st	802	4.39	vw	400

*st = strong; m = medium; w = weak; v = very

By assuming isostructural relationship among these compositions with the Cl-analogues the same symmetries but slightly larger cell parameters were used. In all cases it worked out well and the refined data are collected in Table 1.

In Fig. 2 the calculated densities versus molar volumes and molar weights are plotted. The curves show large resemblances to the corresponding data for the Cl-phases [2].

Due to experimental difficulties and time differences between preparation and measurements certain results are observed which may be interpreted as a solid-solid interaction between the intermediary compounds formed. The influence of the X-ray energy during the exposures should also be taken into account. Small non-isotropic variations of cell-parameteres as well as different ratii of the components in the mixtures are registered. This is also in agreement with other observations that by introducing a larger halogen atom a less stable compound is formed.

Discussion

With respect to the experimental difficulties observed for the solid bromide-complex is the characteristic first parts of the indexed X-ray powder pattern are presented in Table 2.

In this investigation the densities were not measured due to the uncertainty at dealing with pure single-phased materials. However, the comprised data presented in Fig. 2 show similarity to corresponding values, both observed and calculated, for the chloride analogues.

Reference

1 G. Liptay, K. Burger, É. Mocsári-Fülöp, and I. Porubszky, J. Thermal Anal., 2 (1970) 25.
2 G. Liptay, T. Wadsten and A. Borbély-Kuszmann, J. Thermal Anal., 31 (1986) 845.
3 C. P.-E. Werner, J. Phys. E. Sci. Instrum., 13 (1980).

Zusammenfassung - Mittels eines Derivatographen wurde die stufenweise thermische Zersetzung von $[Ni(Py)_4]Br_2$ untersucht. Mit Einbringung eines größeren Halogenidatomes als Cl gestaltet sich der Abbaumechanismus einfacherer. Feste Zwischenprodukte und Ausgangsmaterialien wurden ebenfalls mittels Röntgenpulverdiffraktionsmethoden untersucht und die Gitterzellenkonstanten berechnet.