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THERMAL AND STRUCTURAL RELATIONSHIPS WITHIN THE Cd-PICOLINE-CHLORIDE FAMILY INCLUDING THE α, β AND γ-TYPES

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Thermal and structural properties of complexes of $CdCl_2$ with picolines were studies. The structures of tetra-γ- and tetra-β-picoline as well as di-γ- and di-β-picoline complexes were found to be identical and their thermal decomposition paths were analogous. New polynuclear complexes which could not be obtained from solution have been prepared through thermal decomposition. Their symmetry and cell dimensions were determined.

The transition element halogenides with pyridine and picoline give solid complexes which exhibit a step-wise thermal decomposition character [1]. As a model system we choosed Cd-picoline-halogenides because the central metal-atoms does not oxidize and the intermediate solid products can be easily obtained and further analysed [2, 3]. In this work we have prepared the starting materials in different ways and have investigated all solid compositions with respect to structural properties.

Experimental

In this investigation we were interested if different ways to prepare the starting materials could change the chemical/physical behaviour of the degradation profile. We prepared the solid Cd-picoline-halide complexes in four different ways [2] *viz*

A) excess of picoline as solvent
B) in water solution
C) in etanol (96%) solution
D) in aceton solution

The thermal characteristics were registered in a Derivatograph, MOM Budapest Model OD–2 [4].

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In previous works [2, 3] we have discovered that the intermediates could be prepared only by the freezing-out technique during decomposition of the solid substances. This preparation method usually reveals polycrystalline compounds with small crystals which were carefully investigated by single crystal techniques. The different powder intermediates were thus analysed by means of a Guiner–Hägg focusing camera with Cu–K_{α_1}-radiation and photographic recording. As an internal standard potassium chloride (a = 6.2930 Å) was always added. In order to avoid the interaction of moist air, the specimens were covered with foil.

The film strips were measured with an automatic reader [5] with respect to relative intensity and geometrical position. By a trial- and -error indexing program [6], the powder diffraction characteristics were further evaluated.

The starting material was obtained with crystals large enough to be investigated by Weissenberg-techniques which gave symmetry and cell-dimensions and the most probable space group.

Results

Starting material I

Previously we reported that these types of compounds decompose in a step-wise manner according to a general description

$$Cd(pic)_4Cl_2 \rightarrow Cd(pic)_2Cl_2 \rightarrow Cd(pic)_1Cl_1 \rightarrow Cd(pic)_{2/3} \rightarrow CdCl_2$$

We have analysed all the starting substances prepared in different ways as well as the solid intermediates obtained. It was thus observed that materials with four ligands i.e. α, β and γ were structural identical in spite of the chemical pre-history.

$Cd(\gamma\text{-pic})_4Cl_2$ exhibits a tetragonal symmetry with cell-dimensions

$$a = b = 11.01 \pm 1 \text{ Å}$$

$$c = 10.51 \pm 1 \text{ Å}$$

derived from single-crystal Weissenberg data and refined from powder data (Table 1).

$Cd(\gamma\text{-pic})_4Cl_2$ has been found to be a rather unstable compound even at room temperature. This phenomenon made this investigation very difficult until it was observed and taken into account. So far a pure crystalline phase of Cd has not been obtained but with the help of single crystal data and differences in line quality Table 1 has been completed. All reflexions corresponding to the starting material are sharp whereas another group of lines have a slightly diffuse and broader appearance. That can be interpreted as resulting from very small and/or not to

Table 1 The first part of the characteristic and refined X-ray diffraction powder pattern of Cd(γ-pic)$_4$Cl$_2$ with indexing based on single crystal data

Relative intensity	*d*-spacing, Å	*hkl*
30	7.77_5	110
59	7.60_1	101
16	5.51_8	200
31	5.26_9	002
88	4.46_5	211
87	3.49_2	310
100	3.36_1	103
4	2.94_1	321
7	2.90_9	312
16	2.86_1	213
9	2.61_7	004
26	2.59_5	411
32	2.47_0	420

well ordered crystallites from a secondary face Cd(γ-pic)$_2$Cl$_2$, formed on the surfaces of the large solvent grown Cd(γ-pic)$_4$Cl$_2$.

From a variation in the intensity distribution between these two groups of characteristic lines it is also possible to register different ratio for the actual compounds.

Due to these reasons it is necessary to undertake measurements on young samples only.

Intermediary step with two ligands

We have observed that all solid complexes will two ligands exhibit the same structure, i.e. solvent grown or degradated are similar. In a late paper by Masuda et al. [7] the same phenomenon was registered. Table 2 presents the X-ray diffraction data calculated with respect to a most probable identity with the Zn-analog [8].

Intermediary steps with one ligand

Certain structural results concerning the α-picoline-halides will appear shortly [9].

From solution it is possible to crystallize the picoline only. The solid β- and γ-picolines with ligand number one—which are structurally identical with the α-product—can be obtained from a decomposed compounds by the freezing-out method. They are thus new compounds with a new structure.

Table 2 The first part of the indexed X-ray powder pattern of $Cd(\gamma\text{-pic})_2Cl_2$

Relative intensity	*d*-spacing, Å	*hkl*
100	9.202	101
11	7.298	200
31	5.936	102
4	5.502	111
10	4.609	202
30	4.504	211
12	3.871	$30\bar{3}$
7	3.652	400
4	3.611	004
6	3.528	$41\bar{2}$
14	3.308	$41\bar{1}$, 302
2	3.254	402
12	3.228	410
4	3.183	$21\bar{4}$

By using the trial- and -error program with fixed constants for density and molecular weight we arrive at a proposed symmetry and cell dimensions given in Table 5. In Table 3 the characteristic X-ray pattern is presented.

Table 3 The characteristic and indexed powder pattern of the intermediary formed phase $Cd(\gamma\text{-pic})_1Cl_2$ (similar to the $Cd(\beta\text{-pic})_1Cl_2$)

Relative intensities	*d*-spacing, Å	*hkl*
60	10.42	001
35	9.51	110
100	8.78	101
8	5.49	120
3	5.21	002
6	5.10	021
2	4.41	202
2	4.00	320
5	3.85	410
6	3.78	122, 302
1	3.59	312
12	3.36	420
1	3.30	411
7	3.19	421
3	3.02	511
15	2.91	040

The intermediary step with 2/3 ligands

The β- and γ-compositions with a stoichiometry of 2/3-ligands according to TG-experiments have different X-ray character. As with the calculation concerning the previous step, we suggest a symmetry and cell-dimension in Table 5 so far for the γ-type. The indexed and refined powder pattern are given in Table 4.

Table 4 The indexed X-ray powder pattern of $Cd(\gamma.pic)_{2/3}Cl_2$

Relative intensity	*d*-spacing, Å	*hkl*
100	11.0	110
88	9.50	200
10	7.80	201
2	6.82	002
1	6.43	102
8	5.76	301
4	5.55	220
7	4.77	400
2	4.50	401
2	4.43	103
2	4.12	203
3	3.70	322
4	3.61	420
6	3.42	004
3	3.29	403
4	3.22	204

Conclusion

From these results we can so far conclude the following:

— The structure of the tetra-γ-picoline-complex is independent of solvent grown techniques, A or B.

— The structure of the tetra-β-picoline-complex is analogous to the corresponding tetra-γ-phase.

— All crystal structures with di- (β- or γ-) picoline-composition are identical and also independent of preparation method i.e. solvent grown (A, B, C and D) or thermal decomposition.

— The complex with 2/3-ligands is obtained by decomposition techniques only and the structures are different and new.

— The comprised structural data of the different solid phases, mainly obtained from X-ray powder diffraction calculations, are presented in Table 5.

Table 5 Symmetry and cell dimensions of the complexes

Cd(γ-pic)$_4$Cl$_2$ tetrahedral	Cd(γ-pic)$_2$Cl$_2$ monoclinic	Cd(γ-pic)$_1$Cl$_2$ orthorhombic,	Cd(γ-pic)$_{2/3}$Cl$_2$ hex.	CdCl$_2$ hex.	Symmetry
11.01	15.07	16.34	22.02	3.84	a, Å
11.01	6.89	11.65	22.03	3.84	b, Å
10.51	14.45	10.42	13.68	17.49	c, Å
	104.5		60	60	β°
1279	1455	1984	5746	223	volume, Å^3
2	4	8	36	3	Z (formule units)
	1.77 ($n=8$)		—	4.07	D_{obs}, g/cm^3
1.45	1.69	1.84	2.55	4.1	D_{calc}, g/cm^3
solvent	solvent + intermediary	intermediary	intermediary		method
640	364	248	160	74	volume/unit, Å^3
555.7	369.4	276.4	245.0	183.3	molecular weight
I 4/mmm (most probable)				R3m	space groups

— The values of the calculated densities, versus molecules volume or molecular weight [3] have all a straight line relation except for the 2/3-complex and the end product which is the pure Me-halide.

— The most probable reason why the 2/3-phase does not fit to the straight line [2] is due to a polymeric structure.

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Zusammenfassung – Es wurden die thermischen und strukturellen Eigenschaften von $CdCl_2$-Komplexen mit Pikolinen untersucht. Die Strukturen der tetra-γ- und tetra-β-, sowohl der di-γ- und di–β–Pikolinkomplexe wurden als gleich befunden, der Verlauf ihrer thermischen Zersetzung war ähnlich. Auf dem Wege der thermischen Zersetzung konnten neue polynukleare Polymerkomplexe hergestellt werden, was in Lösung nicht gelang. Es wurden deren Symmetrie und Zellabmaße ermittelt.

Резюме — Изучены термические и структурные свойства комплексов хлорида кадмия с пиколинами. Найдено, что строение комплексов тетра-γ- и β-пиколинов, а также комплексов ди-γ- и β-пиколинов является идентичным, наряду с аналогичными стадиями их термического разложения. Путем термического разложения получены новые многоядерные полимерные комплексы, ранее не полученные в растворах. Определена симметрия комплексов и размеры их кристаллических решеток.