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SOME STRUCTURAL AND THERMAL RELATIONSHIPS AMONG CADMIUM PICOLINE HALIDES

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Cadmium picoline halides, prepared from solution or by the "freezing out" technique are, compared with respect to their X-ray and thermal properties. Among the chlorides and bromides the similarities are obvious but the iodates are somewhat different.

From X-ray and thermoanalytical investigations it was established, that the solid complex compounds of $CdCl_2$ and $CdBr_2$ containing one α-picoline or two molecules of β-picoline, respectively – prepared from different solutions – exhibited isostructural properties. The complex compounds with the same ligands and ligand numbers of CdI_2 possessed however structures with other features.

In our previous works we systematically investigated the thermal properties of different complex compounds of $CdCl_2$ and $CdBr_2$ [1-3].

In this paper we report certain structural properties of these materials.

It was earlier established [1], that $CdCl_2$ formed a solid complex of ligand number two with β-picoline which decomposed stepwise according to the following equations:

$$Cd(\beta\text{-pic})_2Cl_2 \rightarrow Cd(\beta\text{-pic})_1Cl_2 + \beta\text{-pic}$$

$$Cd(\beta\text{-pic})_1Cl_2 \rightarrow Cd(\beta\text{-pic})_{2/3}Cl_2 + 1/3\,\beta\text{-pic}$$

$$Cd(\beta\text{-pic})_{2/3}Cl_2 \rightarrow CdCl_2^- + 2/3\beta\text{-pic}$$

This was reported at the fourth ESTAC conference in Jena August 1987 Masuda's coworker [4] achieved at the same results.

The cadmium picoline bromide complexes decompose also stepwise similar to the cadmium picoline chloride complexes, but the decomposition

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process takes place at lower temperatures as in the case of the identical cadmium chloride complexes [2].

One question is whether the similarity or the difference detected in the thermal decomposition could be clarified by the help of the data obtained from the structural measurements.

Experimental

The investigated complex compounds were prepared from water solution according to our previous works [1-3]. However certain corresponding samples were also obtained by the freezing-out technique also previously reported [3]. The thermal and X-ray measurements details are also the same as in reference [3].

Results and discussion

The X-ray powder diffraction data of $Cd(\alpha\text{-pic})_1Cl_2$ and $Cd(\alpha\text{-pic})_1Br_2$ look very similar indicating structural identity. By using a trial and error indexing program [5] it was possible to obtain and refine the cell parameters with orthorhombic symmetry. The results are collected in Table 1.

Table 1 The collected unit cell data for four Cd-picoline complexes

$Cd(\alpha\text{-pic})_1Cl_2$	$Cd(\alpha\text{-pic})_1Br_2$	$Cd(\beta\text{-pic})_2Cl_2$	$Cd(\beta\text{-pic})_1Br_2$	
orthorombic	orthorombic	monoclinic	monoclinic	
18.10	19.02	15.07	15.18	a in Å
12.32	13.13	6.89	6.97	b in Å
7.46	7.37	14.45	14.89	c in Å
		104.0	104.3	angle
1664	1841	1455	1527	Volume $Å^3$
8	8	4	4	z
max.2.32 min.2.07		1.77 (n=8)		D_{obs}
2.21	2.63	1.69	1.99	D_{calc}
solvent	solvent	solvent	solvent	Method

Concerning the $Cd(\gamma\text{-pic})_2Cl_2$ and $Cd(\gamma\text{-pic})_2Br_2$ indexing and refinement calculations were performed with the assumption of ismomorphic with the monoclinic $Zn(\gamma\text{-pic})_2Cl_2$ [6] and $Zn(\gamma\text{-pic})_2Br_2$-phase [7].

However it was not possible to obtain a complete structural identity. The monoclinic cell dimensions are analogous but the space group P $2_{1/c}$ is not relevant for the Cd complexes.

In Tables 2-4 and 5 the first parts of the indexed powder patterns of the corresponding materials are presented.

Table 2 The first point of the XRD patterns of Cd(α-pic)$_1$Cl$_2$

Relative intensity	d-spacing in Å-units	hkl
45	10.12	110
85	8.978	200
7	7.258	210
10	6.156	020
35	5.403	310
16	5.338	211
4	5.093	220
25	4.530	400
7	4.291	320
9	4.004	130
11	3.730	230, 002
27	3.654	420

Table 3 The first part of the characteristic XRD powder pattern of Cd(α-pic)$_1$Br$_2$ indexed with the assumption of structural similarity with Cd(α-pic)$_1$Cl$_2$

Relative intensity (max. 100)	d-spacing in Å-units	hkl
6	10.71	110
51	7.72	210
29	6.57	020
27	5.32	211
28	4.79	400
10	3.88	420
6	3.69	002
15	3.51	231
81	3.43	421
6	3.32	212
100	3.23	141

So far the similarities among the chlorides and the bromides are obvious. The situation becomes however quite different when the halogene atom is iodine, i.e. all properties change. In a coming publication we will report about the characterisation of the iodates.

Table 4 The first part of the indexed diffraction data of $Cd(\beta\text{-pic})_2Cl_2$

Relative intensity	d-spacing in Å-units	hkl
100	9.20	101
11	7.29	200
31	5.93	102
4	5.50	111
10	4.61	202
30	4.50	211
12	3.87	303
7	3.65	400
4	3.61	004
6	3.53	412

Table 5 The first part of the indexed X-ray powder pattern of $Cd(\beta\text{-pic})_2Br_2$

Relative intensity	d-spacing in Å-units	hkl
100	9.30	101
51	7.34	200
20	6.28	011
33	6.02	111
9	5.58	111
8	4.66	202
47	4.54	203
18	3.96	012
16	3.81	213, 104
30	3.68	400
14	3.61	004

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Zusammenfassung — Durch "Freezing out" Verfahren hergestellte oder mit Umkristallisierung erhaltene Kadmium-pikolin-halogenide sind mit röntgenographischen und thermishen Eigenschaften verglichen worden. Unter den Kloriden und Bromiden sind die Ähnlichkeiten offenbar, sind die Iodiden etwa verschieden.