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Thermal investigation and structural characterisation of some Cd-picoline-iodides prepared from solution

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Abstract

Some solid CdI_2–picoline complexes were studied by derivatographic and X-ray powder diffraction techniques.

The structural and thermal observations of $Cd(\gamma\text{-pic})_4I_2$ resemble those of the corresponding chlorides and bromides. However, $Cd(\alpha\text{-pic})_2I_2$ and $Cd(\beta\text{-pic})_2I_2$ are different from their lighter analogues.

On the basis of the earlier measurements and of observed and calculated true densities we predict the existence and properties of some complexes not yet prepared.

INTRODUCTION

In previous work we have reported on the solid complexes of different transition metal–picoline halides [1–3], especially those which include cadmium [4–7]. This contribution deals with the same type of measurements on some of the heavier members of the series, i.e. the iodides.

EXPERIMENTAL

In the preparation of the picoline complexes of cadmium iodides, the type and amount of solvent were as used in the literature [8–10]. The cadmium iodide : picoline ratio was in each case 1:5, and the procedure was as described.

The cadmium content of the complexes was determined by complexometric titration.

The thermal properties were measured on a MOM-OD2 Derivatograph (sample weight, 100 mg; $\beta = 5°C\ min^{-1}$, in a platinum crucible under static air atmosphere).

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TABLE 1

Preparation and characterisation of Cd-picoline-iodides

Compound	Method [a]	Yield (%)	Cd content (mg g^{-1})	n	pK_a^{25} [b]
Cd(α-pic)$_2$I$_2$	A	39.8	312	2.0	5.94
	B	74.4	320	2.0	
	C	66.6	304	2.0	
	D	60.4	265	2.0	
Cd(β-pic)$_2$I$_2$	A	92.5	270	2.0	5.52
	B	100.0	309	2.0	
	C	67.0	316	2.0	
	D	58.9	304	2.0	
Cd(γ-pic)$_4$I$_2$	A	57.0	175	4.0	6.03
	B	88.1	198	4.0	
	C	67.7	185	4.0	
	D	52.8	203	4.0	

[a] Method A: reaction of dry CdCl$_2$ in excess of picoline; methods B, C and D, reaction of concentrated aq. CdCl$_2$ solution in water, ethanol or acetone respectively. Cd:picoline ratio, 1:5 in all cases.

[b] Measured at 25°C.

Powder samples were analysed in a Guinier–Hagg focusing camera with Cu Kα_1 radiation and photographic recording. The film strips were measured with an automatic reader [11] with respect to relative intensity and geometrical position. By a trial-and-error indexing program [12], the powder diffraction characteristics were further evaluated.

RESULTS

The methods of preparation, percentage yields and the number of picolines, both as measured by titration and as calculated on the basis of the TG curve, are listed in Table 1.

All the complexes prepared are sparingly soluble in water or other common solvents, but can be recrystallised from dimethylformamide or dimethylsulphoxide.

The number of ligands were 2, 2 and 4 in the cases of α-, β- and γ-picoline respectively. No effect on the complexation was observed caused by the reaction media.

The coordination number depends on the nature of the ligand (represented by the pK_a values in Table 1). The steric hindrance decreases according to α- > β- > γ-picoline and the solubilities of the compounds formed in the appropriate reaction media were in the order α- $\approx$ γ- < β-complexes.

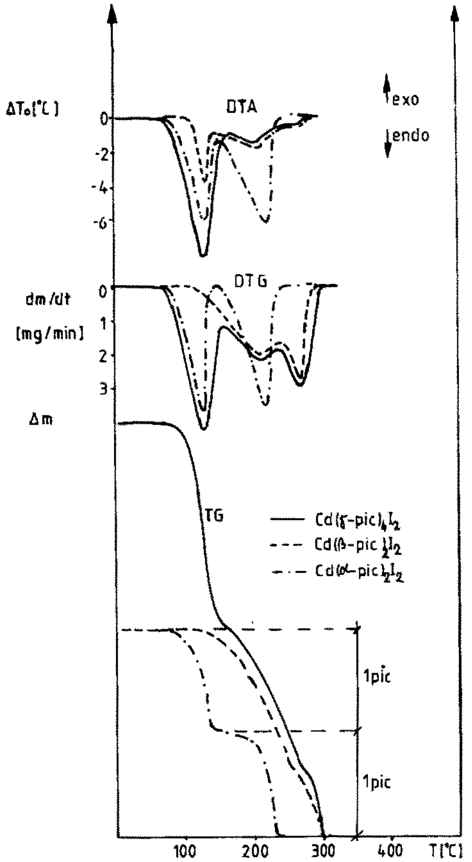

Fig. 1. Thermal decomposition of cadmium-picoline-iodides. $Cd(\alpha\text{-pic})_2I_2$, (·–·–·); $Cd(\beta\text{-pic})_2I_2$, (- - - - - -); $Cd(\gamma\text{-pic})_4I_2$, (———).

In Fig. 1 the thermoanalytical curves of the complexes are presented and data from the thermoanalytical measurements are listed in Table 2.

The decomposition of $Cd(\alpha\text{-pic})_2I_2$ is a two-step process, which takes place in the solid phase, i.e. not in a melt. In the case of $Cd(\gamma\text{-pic})_4I_2$ (after releasing the first two ligands) and $Cd(\beta\text{-pic})_2I_2$, the decomposition takes place in the molten phase. The DTG peaks for the iodides are shifted to lower temperatures compared with those of their chloride and bromide analogue [4,5]. The mechanism of the thermal decomposition is somewhat different from the corresponding $CdCl_2$ and $CdBr_2$ complexes, but the increasing order of the thermal stability is the same as previously observed for $\alpha < \beta < \gamma$-picoline complexes [4].

According to the previously reported freezing-out technique [6], very little structural information is obtained for the iodides. However, samples recrystallized from solutions are worth testing the same way as before [2]. The unit cell data thus obtained are collected in Table 3.

TABLE 2

Thermal investigations of Cd-picoline-iodides

Compound	Step N°	DTG peak temp. (°C)	Melting point (°C)	Eqn. N°
Cd(α-pic)$_2$I$_2$	1	120–125	–	(5)
	2	225–230	–	(6)
Cd(β-pic)$_2$I$_2$	1	–	130	(2)
	2	130–135	–	(3)
	3	200–202	–	(4)
Cd(γ-pic)$_4$I$_2$	1	120–130	–	(1)
	2	–	100	(2)
	3	200–205	–	(3)
	4	260–280	–	(4)
Decomposition scheme of Cd-picoline-iodides				
$Cd(L_4)I_{2(s)}$		$Cd(L_2)I_{2(s)} + 2L_{(9)}$		(1)
$Cd(L_2)I_{2(s)}$		$Cd(L_2)I_{2(l)}$		(2)
$Cd(L_2)I_{2(l)}$		$Cd(L_x)I_{2(l)} + (2-x)L_{(9)}$		(3)
$Cd(L_x)I_{2(l)}$		$CdI_{2(s)} + xL_{(9)}$		(4)
$Cd(L_2)I_{2(s)}$		$Cd(L_1)I_{2(s)} + L_{(9)}$		(5)
$Cd(L_1)I_{2(s)}$		$CdI_{2(s)} + L_{(9)}$		(6)

Cd(γ-pic)$_4$I$_2$ exhibits tetragonal symmetry. This compound has structural resemblances to the corresponding chloride and bromide, but with the expected larger cell dimensions [6,7].

X-ray powder diffraction data of Cd(α-pic)$_2$I$_2$ and Cd(β-pic)$_2$I$_2$ look very similar, indicating structural identity with triclinic symmetry. These complexes are somewhat different from the corresponding chlorides and

TABLE 3

Symmetry and cell dimensions of Cd-picoline-iodides

Compounds	Cd(α-pic)$_2$I$_2$	Cd(β-pic)$_2$I$_2$	Cd(γ-pic)$_4$I$_2$
Symmetry	Triclinic	Triclinic	Tetragonal
a (Å)	8.296	8.513	16.61
b (Å)	16.51	17.37	16.61
c (Å)	23.88	15.26	18.21
α (deg)	125.2	75.8	–
β (deg)	103.5	96.7	–
γ (deg)	63.9	36.6	–
V (Å^3)	2397	1174	5024
Z	6	3	8
D (g cm^{-3})	2.30	2.34	1.95

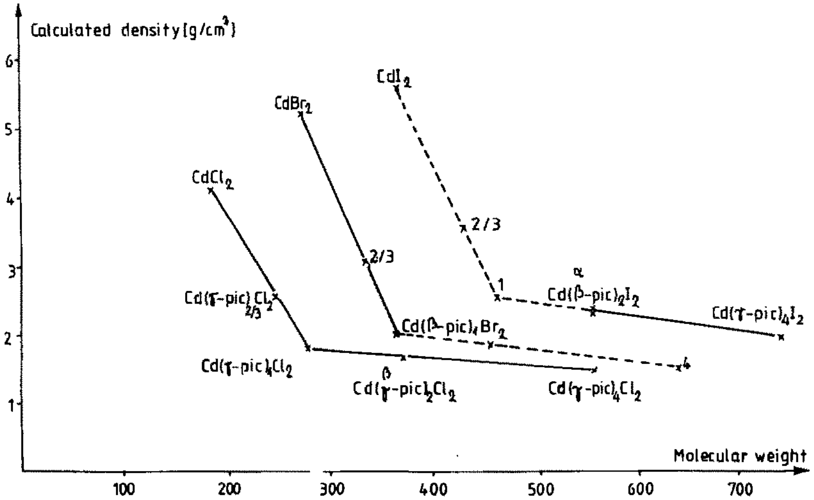

Fig. 2. Calculated density vs. molecular weight in the Cd-picoline-iodide system.

bromides, which is also in agreement with the thermal properties of the complexes.

By plotting the values of the calculated densities thus obtained vs. molar weight (see Fig. 2) we are able to predict the densities of the complexes containing fewer picoline members. This prediction is based on the previously observed properties of the chloride and bromide analogues [13].

In the diagram there is a linear relationship between the density and the molecular weight except for the 2/3-complexes and the final products which are the pure Cd halides. The most probable reason why these compounds do not fit to the straight line [4] is due to the polymeric structure realised by halide bridges [14]. In the case of chloride complexes we have all the data of the series [6]. On the basis of the structural resemblance to the corresponding bromides and iodides we postulate the densities of some complexes not yet prepared (broken lines in Fig. 2).

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