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THERMOANALYTICAL INVESTIGATION OF CADMIUM PICOLINE HALIDES

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ABSTRACT

The thermal behaviour of cadmium halide complexes formed with picoline was studied by derivatograph. The thermal decomposition takes place stepwise. The degradation process consists of four steps, all of which give well-defined intermediates of stoichiometric composition. The polynuclear structure must be attributed to the intermediates with ligand number 2/3 belonging to the very last decomposition step. This compound was prepared by means of derivatograph freezing in the thermal decomposition at the appropriate temperature. Its structure was analysed by X-ray powder diffraction.

INTRODUCTION

It is well known, that transition metal halides form complex compounds of different ligand numbers with bases containing nitrogen. The transition metal picoline halides have proved to be suitable models for thermoanalytical investigation /1/. In our previous works we studied the thermal properties of a number of cadmium chloride picoline complexes /2/. The constant oxidation number of the central metal atom makes sure the composition of the intermediates, and the measurement reproducibility, respectively.

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EXPERIMENTAL

The preparation of the complexes is based on the reaction:

$$MX_2 + nL \longrightarrow ML_nX_2$$

where M is cadmium, L is a picoline (α, β and γ picoline, respectively) and X is a halide (Cl, Br, I). The metal halide was dissolved and added to the picoline in a molar ratio of 1:5. The applied solvents were: water, ethanol, acetone or even picoline. The reaction mixture was refluxed for an hour. After cooling the solid phase was filtered off, dried in vacuum.

The thermoanalytical investigations were carried out with a MOM-G 425 derivatograph and the structure investigations by means of X-ray powder diffraction techniques in a Guinier-Hägg focusing camera with photographic recording and CuK_{α_1} radiation. Potassium chloride (a = 6,2930 Å) was added as an internal standard.

RESULTS AND DISCUSSION

For the preparation of cadmium halide picoline complexes we used four different reaction media and applied the same reaction parameters. The intention was to examine the solvent influence on the quality of the products. It was established, that the reaction medium was a determining factor for the ligand number of the complex compounds.

The question was whether or not the products with the same ligand number formed in different reaction media had the same crystalline structure.

The X-ray investigations proved in the case of $Cd(\gamma\text{-pic})_4Cl_2$, that the solvent applied as reaction medium had no effect on the structure of complex compounds with identical ligand members.

The crystalline structure of $Cd(\gamma\text{-pic})_2Cl_2$ and $Cd(\beta\text{-pic})_2Cl_2$ were identical independent of the different quality of the ligands, or of the preparation methods, i.e. whether the compounds were prepared in solvents or whether they were the products of the thermal decomposition.

All the well defined products formed during the thermal decomposition process were investigated by D-ray analysis.

Without reviewing the details of the appropriate calculations we found a relationship between the measured and calculated density data and the molaryolume and molarweight values, respectively (Fig. 1). The appropriate values of the complexes with ligand numbers 4, 2 and 1 resulted in a linear relationship.

In the case of intermediates with ligand number two-third, this point shifted off the straight line and another straight line can be seen between this one and the appropriate value of cadmium chloride.

In the case of preparation of the β and γ-picoline complexes we could only get the products with ligand number two although the reaction media were changed. The α-picoline complex was characterized by ligand number one or sometimes this value was greater than one. It indicated the existence of a mixture consisting of complex compounds with ligand numbers one and two.

The cadmium picoline bromide complexes decomposed stepwise like the cadmium picoline chloride compounds.

$$Cd(pic)_2Br_2 \rightarrow Cd(pic)_1Br_2 \rightarrow Cd(pic)_{2/3}Br_2 \rightarrow CdBr_2$$

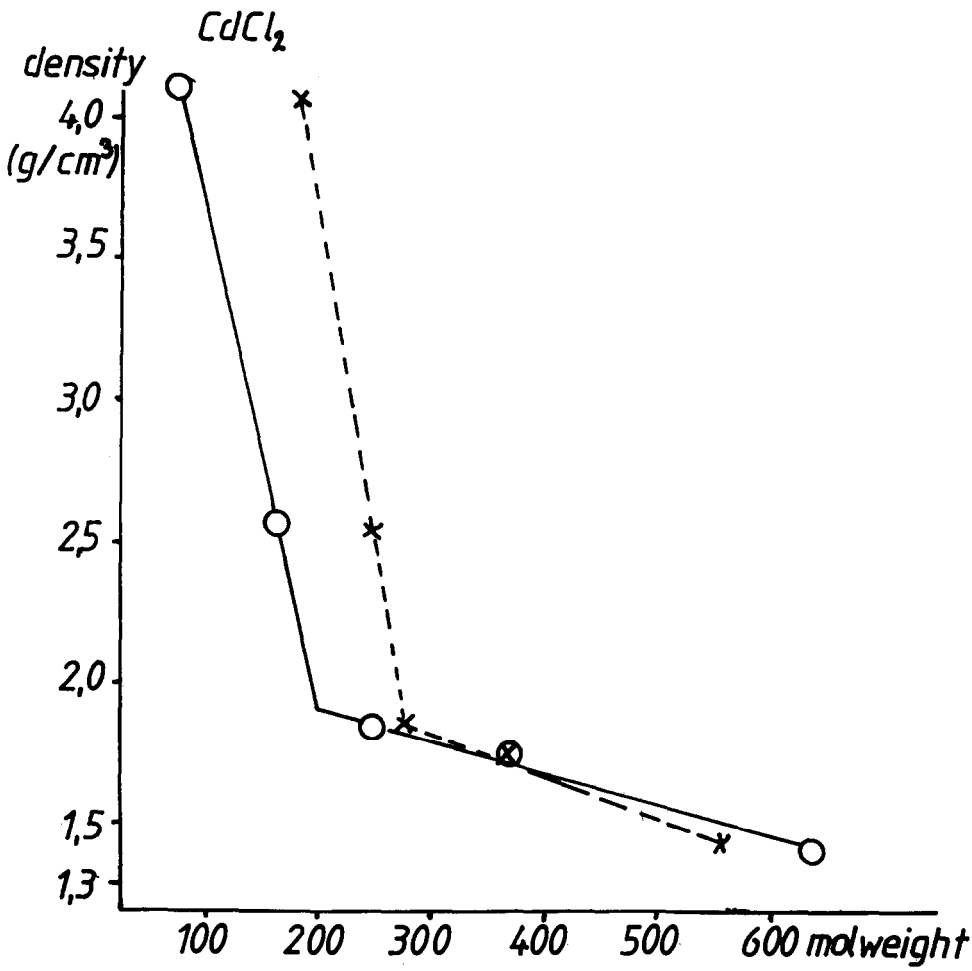
The decomposition temperature of the first step was identical with that measured in the case of $Cd(pic)_2Cl_2$, but the other step temperatures were generally 10-30 °C lower. It indicated a weaker bond between central atom and ligands, which is due to the larger bromine atom.
volume of bromine.

In the case of cadmium picoline iodide we established that the solvents applied in the preparation process had no influence on the ligand number. It only depended on the picoline isomer. This value was in the case of α and β picoline two and of γ picoline four. It is probably due to steric reasons.

The thermal decomposition of cadmium picoline iodide complexes differed from the two other complex types. Namely, in the decomposition of cadmium α-picoline iodide with ligand number two, one ligand molecule was left and the complex with ligand number 2/3 did not occur.

The thermal decomposition of iodine β and γ complexes with ligand numbers 4 and 2 was also different from the degradation process of the identical β and γ derivatives.

Fig. 1. Density in g/cm^3 (observed and calculated) plotted versus molar volumes (O) and molar weights (X) of Cd-chloride-complexes including also pure $CdCl_2$ for comparison (arbitrary units)



The decomposition of the compounds with ligand number 2 took place in molten phase (see Fig. 2 DTA curve had an endothermic peak, which indicated the melting of the product). The intermediate had a ligand number 1/2 (see Fig. 2 second step of the TG-curve).

In the case of $Cd(\gamma\text{-pic})_4I_2$ left the first two picolines from solid phase - in the same way with the identical bromine and chloride complexes - and after this process the product melted and a compound with ligand number 1/2 occurred.

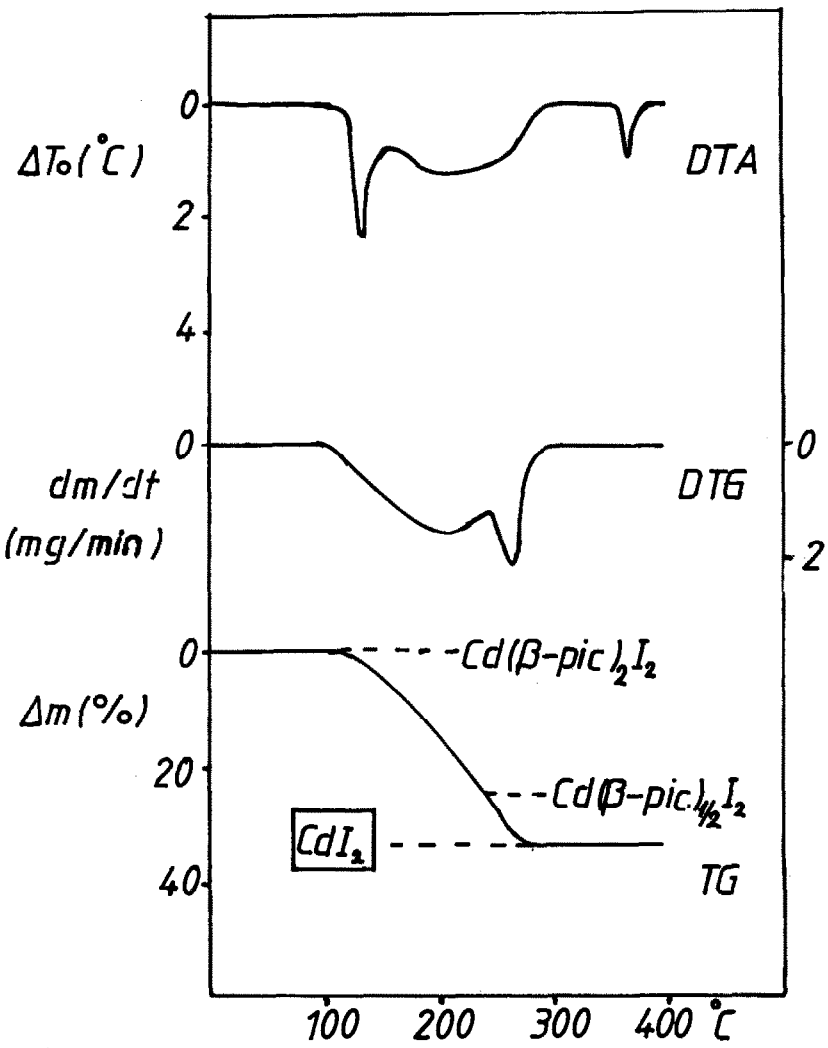
The cadmium α, β and γ ethylpyridin chloride compounds were also prepared and investigated. We established that in the case of α-ethylpyridine the compound had one ligand. The complexes with β-ethylpyridine and γ-ethylpyridine possessed ligand numbers two and four, respectively. The process of thermal decomposition was identical with that observed in the case of the picoline compounds. The decomposition peak temperatures of α and γ ethylpyridine complexes were lower values than these ones in the case of the identical α and γ picoline compounds. It might be in connection with the difference of the pK values of the ethylpyridines and picolines. In the case that the ligand was β ethylpyridine, the peak temperatures were identical with the peak temperature of the appropriate β picoline derivative, namely there was no basic strength difference between γ ethylpyridine and γ-picoline.

CONCLUSION

We established, that the cadmium α, β, γ picoline chloride, bromide and iodide decomposed stepwise and we got as an intermediate - in the most cases - a complex compound with ligand numbers 2/3 or 1/2 in the last but one decomposition process. We supposed, that these products may have had a polynuclear structure. It was investigated by far IR method.

Depending on the quality of the ligand and the type of halogenide, the ligand number changed. The quality of the halogenides exercised an influence on the decomposition process.

Fig. 2. Derivatogram of $Cd(\beta\text{-pic})_2I_2$ complex.



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