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THERMAL BEHAVIOUR OF COMPLEXES BETWEEN DI-2-PYRIDYLDICHALCOGENIDES AND 3d TRANSITION METALS.I.STUDY ON DICHLORO[BIS(2-PYRIDYL)DISULFIDE]MERCURY (II).

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ABSTRACT

The synthesis in the solid state between $HgCl_2$ and bis(2-pyridyl) disulfide has been performed on heating the reactants directly in a DSC and in a TA apparatus.The ΔH value associated with the formation of the complex has been evaluated.The polymerization degree of the complex obtained by solid-solid interaction seems different of that obtained from ethanolic solution.

INTRODUCTION

The coordination of organic disulfides with transition metal ions is very interesting because of the role that the complexes so obtained have in the biochemical processes.

On continuing our studies on chemical species(compounds or ions) to which is due to environmental pollution,in this work we studied the synthesis,in the solid state,of dichloro[bis(2-pyridyl)disulfide]mercury (II).In this way it is possible to evaluate thermodynamic parameters not affected by the solvent presence and to make suitable comparisons between the compound obtained by solid-solid interaction and that obtained in solution.

EXPERIMENTAL

Materials:$HgCl_2$ (C.ERBA RP) and bis(2-pyridyl)disulfide (Aldrich) were used without any further purification.The dichloro[bis(2-pyridyl)disulfide]mercury (II) was prepared from ethanolic solution as reported in literature (1).

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DSC,TG and DTG measurements:DSC,TG and DTG measurements were performed as reported in our previous papers (2).
Syntheses in the solid state:solid-solid interactions were performed by introducing finely powdered stoichiometric (1:1) mixtures of $HgCl_2$ and bis(2-pyridyl)disulfide into the pan of the DSC or into the crucible of the thermoanalyzer and heating successively.

RESULTS

DSC measurements

The DSC curves of both $HgCl_2$ and bis(2-pyridyl)disulfide were preliminarly obtained to compare their thermal behaviour with both those of the stoichiometric (1:1) mixture and the complex.

In the DSC curve of $HgCl_2$ no thermal effect is observed in the temperature range 30-270°C,when the product melts.

The DSC curve of the ligand shows an endothermic peak at 58.7°C, due to melting of the compound (ΔH_m= 21.4 KJ $mole^{-1}$).After this temperature only exothermic decomposition is observed at 250°C.

The 1:1 complex prepared in solution as reported in the experimental shows only one endothermic peak (ΔH_m= 47.7 KJ $mole^{-1}$),due to melting,in the temperature range 140-170°C,and successively decomposes.

The 1:1 stoichiometric mixture of $HgCl_2$ and ligand exhibits two endothermic effects at 58.7°C and 140-170°C.After this temperature an exothermic decomposition is observed.The ΔH values associated with these thermal effects were calculated:the obtained values were less endothermic than those associated with the corresponding peaks of ligand and complex.

TG and DTG measurements

The thermogravimetric curves of $HgCl_2$ and bis(2-pyridyl)disulfide were previously performed in the temperature range 50-450°C:both reactants completely decompose in a single step.

TG and DTG measurements were also performed,in the temperature range 50-450°C,on both products obtained from ethanolic solution

and 1:1 stoichiometric mixture,in order to compare the thermal behaviour of the differently obtained products.

A different behaviour was observed:the stoichiometric mixture decomposes after 170°C in a single irregular step,with a weight loss of 95%;the TG and DTG curves of the complex,on the contrary,show that the product obtained from ethanolic solution decomposes in three consecutive unseparable steps,the initial decomposition temperature being the same of mixture;the comprehensive weight loss is 88%.

DISCUSSION

The obtained qualitative and quantitative DSC results indicate that $HgCl_2$ and bis(2-pyridyl)disulfide partially react (76.1%) to form dichloro[bis(2-pyridyl)disulfide]mercury (II)in the melted ligand (at 58.7°C) and that the formed product melts at 140-170°C and successively decomposes.Utilizing the obtained enthalpic values,we also calculated the ΔH associated with the formation of the complex in the melted phase (ΔH_f= 5.9 KJ $mole^{-1}$).

Furthermore,on considering the polymeric structure of the complex (1),we think,on the basis of the TG and DTG results,that the different thermal behaviour of the complex obtained in the melted phase and that obtained in solution can be explained by a different polymerization degree.

REFERENCES

1 M.M.Kadooka,E.Hilti,L.G.Warner and K.Seff,Inorg.Chem.,15 (1976) 1186
2 L.Abate,A.Chisari,R.Maggiore and G.Siracusa,J.Therm.Anal.,27 (1983) 139.