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STRUCTURE AND THERMAL PROPERTIES OF POLYMERIC COPPER(II) COMPLEXES WITH UNSATURATED CARBOXYLIC BRIDGES

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ABSTRACT

Unsaturated copper(II) carboxylates with aniline as the axial ligand $Cu_2(acryl)_4an_2$, $Cu(crot)_4an_2$ and $Cu(dmacryl)_4an_2$ are the molecular antiferromagnetics. Thermogravimetric investigations in the range 0 - 1000^{0}C revealed the decomposition of these compounds to be the multistage process. Thermal decomposition mechanism confirmed the structure postulated for these adducts, where two out of four carboxylic groups function as the bridge bidentate ligands (Cu-O-C-O-Cu) and the remaning two carboxylic groups form the monoatomic Cu-O-Cu type bridges between the copper atoms.

INTRODUCTION

Unsaturated copper(II) carboxylates with aniline as an axial ligand $Cu_2(acryl)_4an_2$, $Cu_2(crot)_4an_2$ and $Cu_2(dmacryl)_4an_2$ (where acryl = acrylate, crot = crotonate, dmacryl = 3.3'-dimethylacrylate anions, an = aniline) are identical to that of copper(II)propionate with toluidine $Cu(C_2H_5COO)_2\,p\text{-}CH_3\text{-}C_6H_4NH_2$ [1]. This compound crystallizes in the $P\bar{1}$ spacial group with the following lattice constants. a = 12.466(7), b = 12.183(6), c = 11.598(6) Å and α = 116.03, β = 91.79(3) and γ = 73.82(2)^0. Crystal structure of the copper propionate with toluidine is build from the monodimensional, polimeric chains. The shortest distance between chains is equal 3.47 Å.

Each of the two crystallographically independent copper atoms: Cu(1), Cu(2) is bound in the distorted square pyramidal configuration, with four oxygen atoms of the carboxyl group and the nitrogen atom from the toluidine molecule. Two out of four independent carboxyl group function as bidendate ligands, bridging Cu(1) with Cu(2) in the syn, configuration, like in the typical dimers (Cu-O-C-O-Cu).

Two remaning carboxyl groups form the monoatomic, centrosymetric Cu-O-Cu bridges between the copper atoms. The Cu(1) - Cu(2) distance is equal 3.197(4) Å and exceed the Cu-Cu distance observed for copper(II) acetate (2.61 Å) [2] and $Cu_2(crot)_4quin_2$ (2.66 Å) [3].

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EXPERIMENTAL

Thermal stability of the synthetized copper(II) unsaturated carboxylates was examined thermogravimetrically on the Paulik-Paulik Derivatograph Q-1500 D using aluminium oxide as a standard. DTG, DTA and TG curves have been recorded up to 1000^0C, by using heating rates of 2.5 and 5^0C/min and samples about 200 mg , the examination were carried out in the platinium sample holder in the air.

RESULTS AND DISCUSSION

The aniline adducts of unsaturated copper(II) carboxylates are thermally relatively stable. Thermal decomposition of these compounds is the multi-stage process.

The subsequent detachment of the axial ligands and of the bridge groups was observed. CuO was the final product.

The derivatogram for $Cu_2(acryl)_4an_2$ is shown in the Fig. 1. The TG curve for that complex indicates, that it is stable at temperature up to 80^0C, when begins the slow decomposition to CuO, as to the final product formed at 480^0C. The TG curve shows three bendings at 112, 160 and 296^0C. They correspond to the presence of three intermediate decomposition products: $Cu_2(acryl)_4an$, $Cu_2(acryl)_4$ and $Cu_2(acryl)_2$. The most probable thermal decomposition scheme is here:

$$Cu_2(acryl)_4an_2 \xrightarrow{80-112^0C} Cu_2(acryl)_4an$$

$$Cu_2(acryl)_4an \xrightarrow{112-160^0C} Cu_2(acryl)_4$$

$$Cu_2(acryl)_4 \xrightarrow{160-296^0C} Cu_2(acryl)_2$$

$$Cu_2(acryl)_2 \xrightarrow{296-480^0C} CuO$$

The DTA curve for the complex presents one exothermic maximum in the range 112 - 160^0C, corresponding to the stepwise loss of the two aniline molecules and one broad maximum with a centre about 380^0C , with two peaks at 312 and 440^0C, corresponding to decomposition reaction of acrylane with simultaneous formation of CuO .

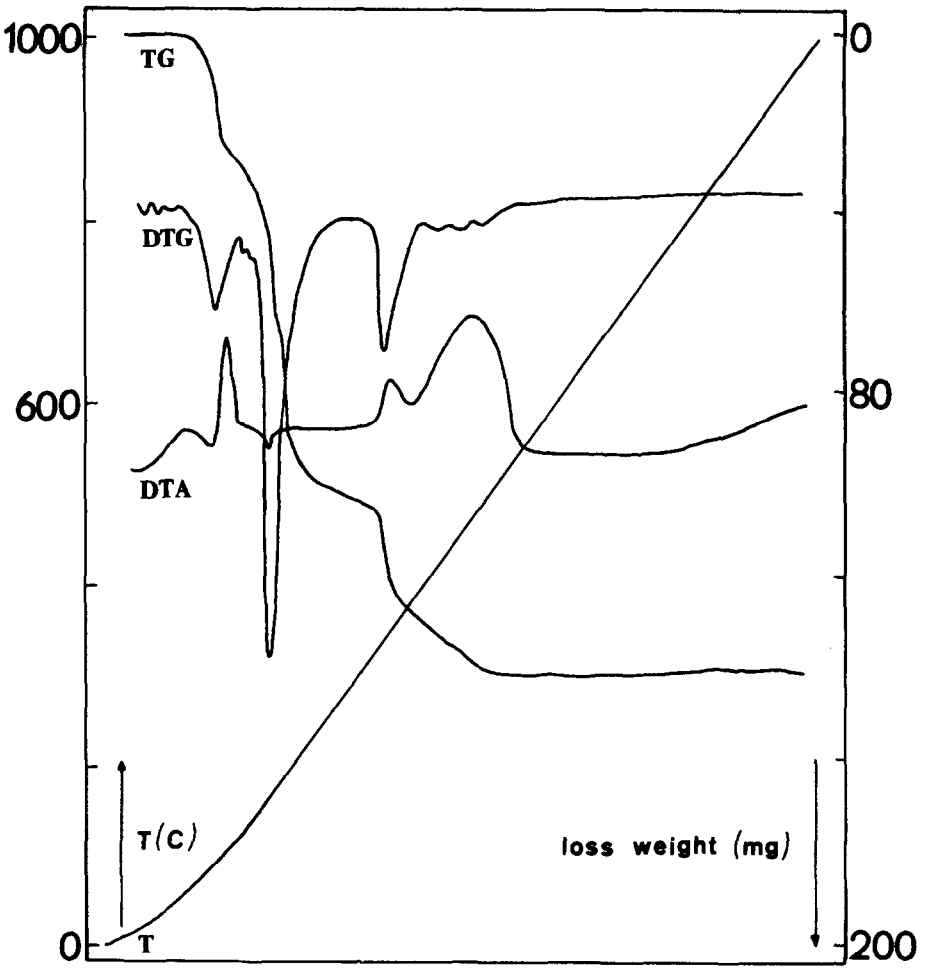

Figure 1. Thermolysis curve of $Cu_2(acryl)_4an_2$.

Thermal decomposition process for $Cu_2(crot)_4an_2$ and $Cu_2(dmacryl)_4an_2$ is analogous. Here we have observed the evident loss of the amine ligands, followed by the simultaneous loss of two carboxyl groups, and finally, the simultaneous loss of two acid groups.

This fact suggests the existence of two different Cu-Cu bondings via carboxyl bridges.

Thermogravimetric results confirmed the structure of the aniline adducts of the unsaturated copper(II) carboxylates, where two carboxyl group bound the copper ions in a different way than the other two.

REFERENCES

1 P.B.W. Yawney, J.A. Moreland, R.J. Doedens, J. Am. Chem. Soc. 95 (1973) 1164
2 P.de Meester, S.R. Flechter, A.C. Skapski, J. Chem. Soc. Dalton Trans (1973) 2575
3 M. Bukowska-Strzyżewska, J. Skoweranda, E. Heyduk, J. Mroziński, Inorg. Chim. Acta 73 (1983) 207