SOME ASPECTS OF THE PREPARATION, CHARACTERIZATION AND THERMAL DECOMPOSITION OF ANISALDEHYDE GIRARD T COMPLEXES OF SOME TRANSITION ELEMENTS

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Anisaldehyde Girard T complexes of Mn(II), Fe(III), Co(II) and Cu(II) with the general formula [MCl₂(AGT)₂]Cl₂ or [MCl₂(AGT)]Cl, where (AGT) = anisaldehyde carbohydrazone methyltrimethylammonium cation, H₃C—O—C₆H₄—CH = N–NHCOCH₂N⁺(CH₃)₃ and M = Mn(II), Co(II), Fe(III) or Cu(II) were prepared. Elemental analysis, electrical conductance and IR spectra showed that the ligand coordinates with the studied metals in keto form through the azomethine and carbonyl groups. The molar conductances, electronic spectra and magnetic moments of the solid complexes were determined. The processes of thermal decomposition of these complexes were studied. From the analysis of the thermal decomposition curves obtained, the corresponding kinetic parameters n, Eₐ and log A were evaluated by two different methods and the effects of the central metal ions on the stabilities of the complexes are discussed.

This paper is a continuation of our investigations on complexes of Girard reagents and their hydrazone derivatives with transition metals [1–4].

The aim of the present work was the preparation, isolation and characterization of anisaldehyde Girard T complexes of Mn(II), Fe(III), Co(II) and Cu(II). The kinetic parameters n, Eₐ and log A, which are the order of the decomposition reaction, the activation energy and the pre-exponential factor, respectively, were calculated from the TG and DTG curves.

Experimental

The ligand and metal complexes were prepared according to the general method described previously [1]. The elemental analyses were performed in
the Microanalytical Unit, Cairo University. IR (Nujol) and electronic spectra (DMF) of solid complexes were recorded on Unicam SP 2000 Infracord and SP 1800 spectrophotometers. Conductance values of 10^{-3} M solutions in DMF at 25^\circ were measured with an M.C.3 (England) bridge. NMR measurements were carried out on a Varian (U.S.A) instrument. Magnetic moments were determined by the Gouy method at the Physics Department, Faculty of Science, Alexandria, and corrected for the diamagnetism of the component atoms by using the Pascal constants [5].

The thermal decompositions were carried out with a standard thermoanalyzer TG–DTG–DTA (1600^\circ) GDTA 16, Seteram, Lyon, France. The specimens were placed in a standard platinum crucible. The sample weight taken was 14–35 mg, and the heating rate was 5.5 deg/min.

**Determination of the kinetic parameters**

1. Coats and Redfern method [6]:

   This method was proposed for determination of the order of reaction (n) on the basis of thermogravimetric data based on a plot of
   \[
   -\log \frac{1-(1-\alpha)^{1-n}}{T^3(1-n)} = A \text{ vs. } \frac{1}{T} \cdot 10^3
   \]
   where \(\alpha\) is the degree of thermal decomposition of the sample, calculated from the TG curve by means of the formula
   \[
   \alpha = \frac{W_0 - W}{W_0 - W_k},
   \]
   in which \(W_0, W_k\) and \(W\) are the initial weight, the final weight and the weight of the sample at temperature \(T, K\), and \(n\) is the reaction order. A number of such relationships are plotted for a number of assumed values of \(n\). The correct value of \(n\) for a given thermal decomposition reaction yields a straight line. Figure 1 shows the plots of the above relationship. The activation energy is calculated from the equation
   \[
   E = 2.303 R \cdot S
   \]
   where \(S\) is the slope of the straight line found in the previous plot, and \(R\) is the gas constant.

2. Chatterjee method [7]

   This method is based on the general equation for the rate of a heterogenous kinetic reaction, \(V\):
   \[
   V = -\frac{dm}{dt} = km^n
   \]