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 $[MCl_2(AGT)_2]Cl_2$ or $[MCl_2(AGT)]Cl$, where (AGT) = anisaldehyde carbohydrazone methyltrimethylammonium cation, $H_3C-O-C_6H_4-CH=N-NHCOCH_2N^+-(CH_3)_3$ 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, E_a 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, E_a 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 $25°$ 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 ($1600°$) 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 $-\log \dfrac{1-(1-\alpha)^{1-n}}{T^3(1-n)} = A$ *vs.* $\dfrac{1}{T} \cdot 10^3$ where α is the degree of thermal decomposition of the sample, calculated from the TG curve by means of the formula $\alpha = \dfrac{W_0 - W}{W_0 - W_k}$, 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:

$$V = -\frac{dm}{dt} = k\,m^n \tag{1}$$

where k, m, t and n are the rate constant of the reaction, the active weight of the reacting material, the time elapsed from the start of the experiment and the order of the reaction. Substituting k from the Arrhenius equation into Eq. (1) gives

$$\log V = \log A + n \log m - \frac{E_a}{2.303R},$$

where A, E_a and T are the pre-exponential factor, the activation energy and the absolute temperature, respectively.
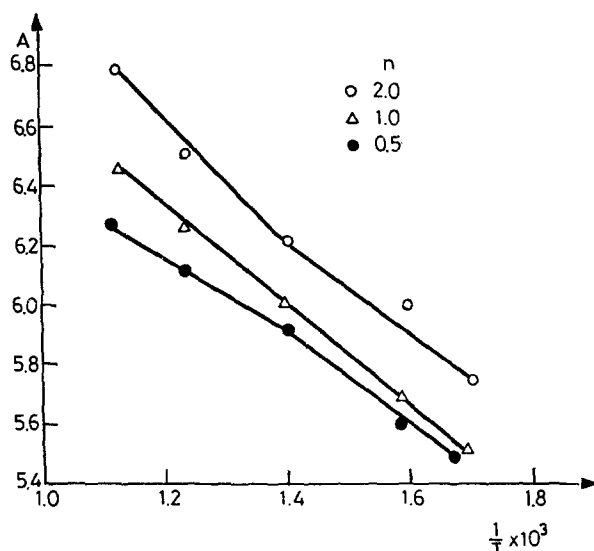

Fig.1 Graphical determination of the order of reaction. For $n = 1$: $A = -\log[-\log(1-\alpha)/T^2]$; for $n = 0.5$, 2: $A = -\log[1-(1-\alpha)^{1-n}/T^3(1-n)]$;

Results and discussion

I. Proof of metal complex structures

The studied metal ions form two types of complexes with anisaldehyde Girard T as ligand: 1:1 metal:ligand complexes in the cases of Fe(III) and Cu(II), and 1:2 metal:ligand complexes in the cases of Mn(II) and Co(II). The stoichiometries of the isolated complexes, together with some analytical and physical data, are given in Table 1. All the isolated metal complexes are

Table 1 Analytical and physical data for ligand and its complexes

Compound	Calculated (found), %					Colour and shape	M.p., °C	Λ_m^*
	C	H	Cl	N	M			
$[C_{13}H_{20}N_3O_2]Cl$	54.7	7.0	12.4	14.7	–	white crystals	215	50
	(54.7)	(6.8)	(12.2)	(14.5)	–			
$[Cu(C_{13}H_{20}N_3O_2)Cl_2]Cl$	37.2	4.8	25.3	10.0	–	faint green crystals	195	48
	(37.2)	(4.7)	(25.1)	(9.8)	–			
$[Co(C_{13}H_{20}N_3O_2)_2Cl_2]Cl_2$	44.5	5.6	20.2	12.0	8.4	Deep blue crystals	205	99
	(44.5)	(5.6)	(20.2)	(11.5)	(9.0)			
$[Mn(C_{13}H_{20}N_3O_2)_2Cl_2]Cl_2$	44.8	5.8	20.3	12.1	7.9	white crystals	210	98
	(44.7)	(5.8)	(20.3)	(11.9)	(8.0)			
$[Fe(C_{13}H_{20}N_3O_2)Cl_3]Cl$	34.9	4.5	31.7	9.4	12.5	shiny brown crystals	185	51
	(34.9)	(4.8)	(31.5)	(9.2)	(12.6)			

Λ_m^* ohm^{-1} cm^2 mol^{-1}

partially soluble in most common organic solvents, but readily soluble in DMF and DMSO. The ligand (AGT)Cl is a 1:1 electrolyte at 25° in DMF, with a molar conductance $\Lambda_m = 50\,ohm^{-1} \cdot cm^2 \cdot mol^{-1}$ [8]. The bi– and monoligand complexes are 1:2 and 1:1 electrolytes, respectively. Their aqueous solutions give immediate precipitates with sodium tetraphenyl-borate, which is known to yield precipitates with large cations [9]. The precipitates could be decomposed by nitric acid, and subsequent treatment with $AgNO_3$ solution gave a precipitate of silver halide, which indicates the presence of halide in the complex cations, as suggested by the formulae of the isolated complexes (Table 1).

The IR spectrum of the ligand exhibits a strong band at 1685 cm^{-1}, as-signed to $\nu(C = O)$. The band at 1615 cm^{-1} is attributed to the azomethine $\nu(C = N)$. In the IR spectra of the studied complexes, $\nu(C = N)$ was shifted to lower frequency by 5–20 cm^{-1}, whereas $\nu(C = O)$ was nearly unaffected on chelation or was raised by 5–30 cm^{-1} probably due to an increase in bond order [10] or to the prevention of intramolecular hydrogen-bonding in the ligand between the adjacent -NH and C = O groups, which was not compen-sated for by the lowering in $\nu(C = O)$ as a result of coordination. Conse-quently, the ligand may function as a bidentate one in keto form through the azomethine and carbonyl groups. A similar situation exists in the case of anisaldehyde Girard P complexes [2]. Moreover, the NMR spectrum of the ligand in DMSO shows a signal at 12.6 ppm downfield from TMS (tetramethylsilane). This confirms that enolization does not occur from N–H to the adjacent C = O. On the basis of elemental analyses, IR and NMR spectra and conductivity measurements, the structure of the biligand com-plexes of Co(II) and Mn(II) may be represented by (I):


(I)

$y = C_6H_4 \cdot OCH_3$ $M = Co(II), Mn(II)$ $Me = CH_3$
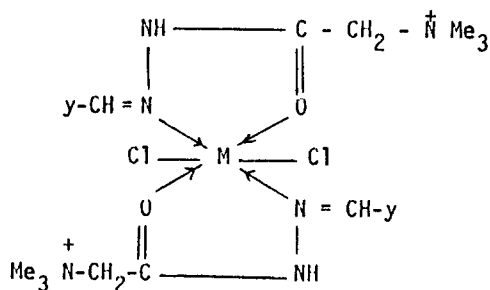
The magnetic moment of 4.6–4.5 B.M. (Table 2) for [Co(AGT)$_2$Cl$_2$]Cl$_2$ agrees with the reported value [5]. The electronic bands observed at 14706 cm^{-1} due to the $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) spin-allowed transition further support the proposed octahedral arrangement [11]. The structures of the monoligand complexes of Cu(II) and Fe(III) may be represented by (II) and (III):

Cl ——————— N ═ CH – y
  ╲   ╱   ╲
   ╲ Cu ╱   NH
  ╱   ╲   ╱   +
Cl ——————— O ═ C — CH$_2$-N Me$_3$
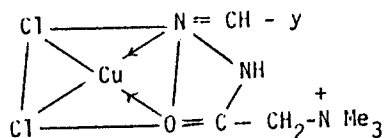
(II)

The magnetic moments of the Cu(II) halide complexes (Table 2) support this square planar structure. Moreover, the complex shows two broad bands at 13793 and 12579 cm^{-1}, in agreement with those reported previously [9].

                           Cl
                            |
y - CH ═ N ——————— Cl
       NH   ╲   ╱ Fe ╱
            ╲ ╱   ╱
Me$_3$N-CH$_2$-C═O ——————— Cl
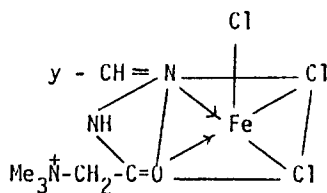
(III)

The band observed at 15152 cm^{-1} and the magnetic moment value of 5.4 B.M. (Table 2) confirm such a structure for Fe(III).

II. A study of the thermal decomposition of these complexes

In order to characterize the TG curves obtained, the kinetic parameters n, A and E_a of the thermal decomposition processes were derived. Two methods were used: the Coats-Redfern [6] and Chatterjee [7] methods. Table 3 gives the kinetic parameters evaluated by means of these methods.

From the data in Table 3, it is clear that the order of the decomposition reaction for all the complexes is nearly one; this means that the decomposition reactions have the same mechanism. It is also obvious that the values of the activation energy of the metal hydrazone complexes as computed from the Coats-Redfern method are in good agreement with those obtained by

Table 2 Spectral and magnetic data of metal complexes

Complex	Magnetic moment, μ_{eff}, B.M.	Ligand field bands, cm^{-1}
[Cu(AGT)Cl$_2$]Cl	1.83	13793 (15); 12579 (14)
[Co(AGT)$_2$Cl$_2$]Cl$_2$	4.62	16393 (320); 14706 (525)
[Fe(AGT)Cl$_3$]Cl	5.4	15152 (50)

Molar extinction coefficient in parenthesis, ε, mol^{-1} l cm^{-1}

Chatterjee's method, and the activation energy varies in the sequence Mn(II) < Fe(III) > Co(II) > Cu(II) complex. This arrangement (except for Cu(II)) is in good agreement with the Irving-Williams series [12]. This difference in the activation energies may be due mainly to two factors: firstly, the variation in the effective electric field strength F^* of the central metal ion $F^* = \dfrac{Z^*}{r^2}$ where Z^* and r are the effective charge and radius of the cation, respectively, according to the following data [13]:

Ion	r	Z^*	F^*
Fe(III)	0.67	3.667	8.167
Cu(II)	0.72	3.433	6.627
Co(II)	0.78	3.104	5.106
Mn(II)	0.91	2.667	3.221

One may expect that, with the increase in F^*, the stabilities of the complexes increase in the sequence Fe(III) > Cu(II) > Co(II) > Mn(II): this means that the values of the activation energy for the thermal decomposition of the complexes increase in this direction. This arrangement is in good agreement with the sequence of thermal stabilities given in this work, except for the observed lower stability of the Cu complex, which may be attributed to the second factor, the covalent character of the bonds between the metal ion and the heteroatoms of the ligands (azomethine-nitrogen, and carbonyl-oxygen atoms), i.e. in this case the (N → Cu ← O) bonds. The higher electronegativity of the Cu(II) ion with respect to those of other metal ions present leads to a decrease in the covalent character of the (N → Cu ← O) bonds, and hence to decreases in the stability and activation energy of this complex.

Table 3 The results of the kinetic parameters of the thermal decomposition of the hydrazone complexes of Mn(II), Fe(III), Co(II) and Cu(II) by two different methods

Compound	$t_{1/2}$, min	*		**		
		n	E_a, kJ·mol^{-1}	n	E_a	$\log A$
[MnCl$_2$(C$_{13}$H$_{20}$N$_3$O$_2$)$_2$]Cl$_2$ stable up to = 74°C	66.7	1.00	211.42	1.02	205.94	12.57
[FeCl$_3$(C$_{13}$H$_{20}$N$_3$O$_2$)]Cl stable up to =142.1°C	67.7	1.00	245.28	1.15	241.01	12.43
[CoCl$_2$(C$_{13}$H$_{20}$N$_3$O$_2$)$_2$]Cl$_2$ stable up to = 98.2°C	69.7	1.00	233.24	1.15	229.48	13.37
[CuCl$_2$(C$_{13}$H$_{20}$N$_3$O$_2$)]Cl stable up to = 91.9°C	60.4	1.00	189.77	1.10	181.28	14.83

* by Coats-Redfern's method
** by Chatterjee's method

Table 1 shows that $\log A$ is inversely proportional to $t_{1/2}$. This is in good agreement with the collision theory [14], which means that an increase in A is accompanied by an increase in the number of collisions of the molecules. Such an effect leads to an increase in the reaction rate (decrease in $t_{1/2}$).

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Zusammenfassung — Es wurde die Herstellung und Isolierung von Anisaldehyd-G-T-Komplexen von Mn(II), Fe(III), Co(II) und Cu(II) der allgemeinen Formel [MCl2(AGT)2]Cl2 oder [MCl2(AGT)]Cl durchgeführt, wobei (AGT) = Anisaldehydcarbohydrazon-methyl-trimethyl-ammoniumkation $H_3C-O-C_6H_4-CH=N-NHCOCH_2N^+-(CH_3)_3$ und M = Mn(II), Co(II), oder Fe(III) und Cu(II). Elementaranalyse, elektrische Leitfähigkeit und IR-Spektren zeigten, daß der Ligand an den untersuchten Metallen in der Ketoform, über die Azomethin- und Carbonylgruppe koordiniert ist. Es wurden die molare Leitfähigkeit, Elektronenspektren und das magnetische Moment der festen Komplexe bestimmt. Der Vorgang der thermischen Zersetzung dieser Komplexe wurde untersucht. Durch Analyse der erhaltenen thermischen Zersetzungskurven wurden die entsprechenden kinetischen Parameter n, E_a und $\log A$ durch zwei verschiedene Methoden ermittelt und weiterhin der Einfluß des zentralen Metallions auf die Stabilität der Komplexe diskutiert.