Pak. j. sci. ind. res., vol. 37, nos. 6-7, June-July 1994

DETERMINATION OF THERMODYNAMIC PARAMETERS FOR THE DECOMPOSITION OF SOME METAL CHELATES OF SUBSTITUTED HYDRAZOPYRAZOLONES

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(Received April 1, 1993; revised November 18, 1993)

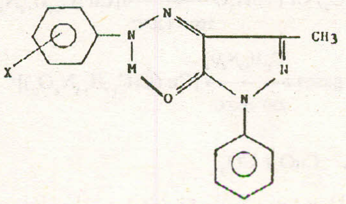
The relative thermodynamic parameters of a series of metal derivatives of hydrazopyrazolone dyes containing meta -OH, -COOH, and -OCH_3 groups have been determined by TGA, DTG and differential thermal analysis (DTA). The effects of substitutent on the hydrazo-moiety of the ligand on the stability of the complexes are discussed. The affinity of different ligands for complexation with metal ions M^{n+} [$M=UO_2^{2+}$, Fe^{3+}, Cu^{2+} and Hg^{2+}] reaches its highest value with metahydroxyphenylhydrazopyrazolone. The relative order of thermal stability is : $UO_2^{2+} > Fe^{3+} > Cu^{2+} > Hg^{2+}$. The data were correlated and the results were used to explain the stabilization of such chelates by dative π-bonding between M^{n+} and the ligand.

Key words: Thermodynamic parameters, Metal chelates, Hydrazopyrazolones.

Introduction

The coordination selectivity of some substituted 5-pyrazolone dye chelates with lanthanides, actinides and transition metal ions has recently been reported [1-5]. As part of our programme for the synthesis and characterization of solid complexes [6] of UO_2(II), Fe(III), Cu(II) and Hg(II) derived from hydrazopyrazolone ligands, we presently report on the determination of thermodynamic parameters for decomposition of these complexes.

From the foregoing results [1-6] the structure of the complexes under investigation is given in Scheme (1).



x = *m*-OH-[I], *m*-COOH-[II] or *m*-OCH_3-[III]

M = UO_2^{2+}, Fe^{3+}, Cu^{2+} or Hg^{2+}

Scheme 1.

Experimental

Substituted 5-pyrazolone dyes [4] (I-III) were prepared by coupling 1-phenyl-3-methyl-5-pyrazolone [7] in sodium acetate with diazonium salt of the corresponding amine. The crude products were recrystallized from acetic acid.

The solid complexes were prepared [6] in 1:1 metal to ligand ratio [except for the Hg^{2+}-ligand[I] complex where a 1:2 metal : ligand ratio was prepared]. The preparations were performed by the addition of an aqueous solution of the metal to the respective ligands dissolved in 75% (v/v) dioxane-water solvent. The mixture was heated to 60° with stirring for about 2 hrs. and was left to stand overnight. The collected solid complexes were washed with double distilled water followed by alcohol, then dried in air and stored in a vacuum dessicator. The elemental analysis is given in Table 1.

The thermal stabilities of the solid complexes were studied by using TGA, DTG and DTA techniques. The measurements were made with an OD-102 Paulik - Paulik- Erdey derivatograph (MOM, Hungary) with sensitivities TG=100 mg., DTG=1/5 and DTA=1/5. The samples were heated in platinum crucibles in static air atmosphere at a heating rate of 5 deg. min^{-1} upto 600°, using Al_2O_3 as a reference compound. All reagents used in this work were of A.R. grade (Merck or BDH).

Calculations. The basis for calculation was the Arrhenius equation:

$$\frac{dm}{dt} = A \cdot C^x \exp^{(-E_a/RT)} \qquad \text{.................................(1)}$$

$\frac{dm}{dt}$, C^x and T were read from the thermal curves,

where $\frac{dm}{dt}$ = distance between DTG curve and base line, mm,

m = mass loss, mg

A = frequency factor

C = extent of change given by Eq. (2):

$$C = \frac{\Delta m_x - \Delta m}{\Delta m_x} \qquad \text{...(2)}$$

[8]

where Δm_x = maximum loss during the given change, mg.

It was assumed from the calculation that the decomposition processes satisfy the Arrhenius equation i.e. there are definite values of A, E_a and x. In addition, it was assumed that the increase in the reaction rate depends mainly on physical processes (desorption, evaporation, etc.).

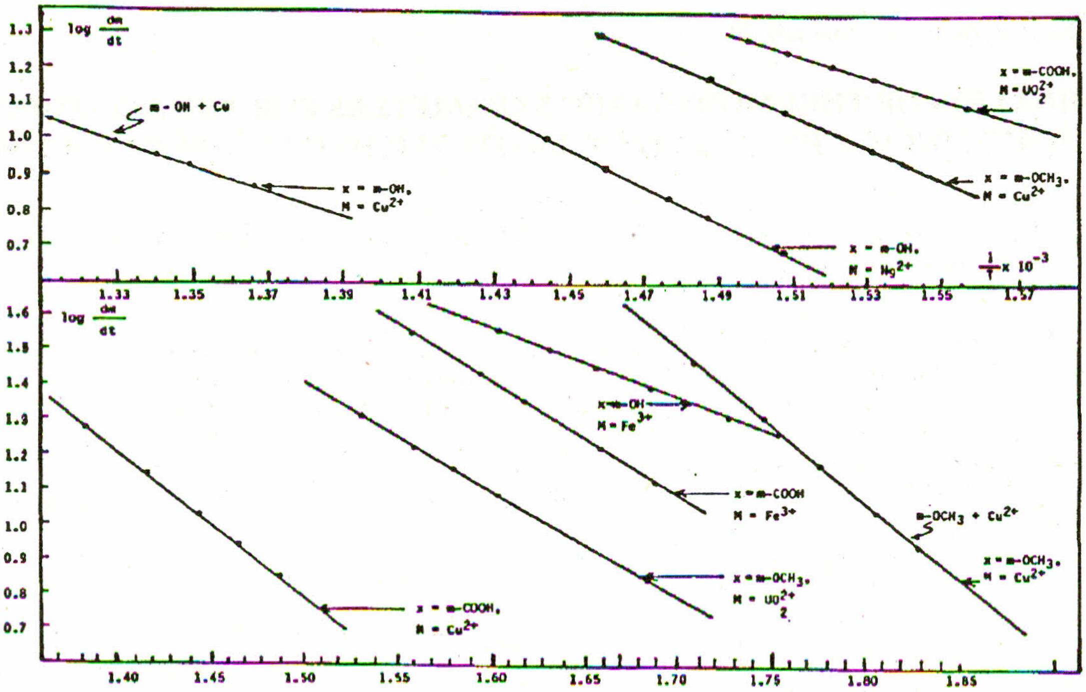


Fig. 1. Graphic determination of the kinetic parameters for the final stage of metal complexes of 1-phenyl-3-methyl-4-(x-phenylhydrazo)-5-pyrazolone ligands (substitutent (x) and the metal used in chelation as shown on the plot).

The activation energy was calculated from Eq. (3).

$$E_a = 2.303\ R\ \tan\alpha_1 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)\ [8]$$

where R = Universal gas constant; tan α_1 = directional coefficient

$$\log\frac{dm}{dt} = f\left(\frac{1}{T}\right) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$\log\frac{dm}{dt} + \frac{1}{T}\tan\ \alpha_f = \tan\ \alpha_2 \log C + a_2 \ \ldots\ldots\ldots\ldots \quad (5)\ [8]$$

The pre-exponential factor log A is the value intercepting the straight line Eq. (5) on the y axis. The graphical relationships in Eq.(4) are illustrated in Fig. 1. The parameters of these equations and the scatter of the results were calculated by the linear regression method [9].

The activation enthalpy $\Delta H^{\neq}$ was calculated from $\Delta H^{\neq} = E_a\text{-}RT$, while the activation entropy $\Delta S^{\neq}$ was obtained from $\Delta S^{\neq} = R[1n(Ah/kT)\text{-}1]$, where k is the Blotzman constant, and h, the Planck constant. The activation free energy $\Delta G^{\neq}$ was calculated by the relation $\Delta G^{\neq} = \Delta H' - T\,\Delta S^{\neq}$. The results are given in Tables 2,3 and 4. An example for the calculations of thermodynamic parameters is given in Table 5.

Results and Discussion

The TG, DTG and DTA curves for metal chelates of 1-phenyl-3-methyl-4(x-phenylhydrazo)-5-pyrazolone ligands [x = 3-OH, 3-COOH and 3-OCH_3] are shown in Fig. 2. Analysis of the thermal decomposition data of these complexes (Table 6), suggested the following decomposition stages [6] (taking Cu^{2+} -3-OCH_3-PhHP complex as an example):

$$[Cu(C_{17}H_{15}N_4O_2)\ Cl\ ].3H_3O \xrightarrow[100-120^{\circ}C]{-3H_2O} [Cu\ (C_{17}H_{15}N_4O_2)\ Cl]$$

$$CuCO_3 + C + gases \xleftrightarrow[230\text{–}460^{\circ}C]{-C_{17}H_{15}N_4O_2} [Cu\ (C(C_{17}H_{15}N_4O_2)]^+ \xleftarrow[180\text{–}230^{\circ}C]{-Cl}$$

$$\xrightarrow[460^{\circ}C]{\text{more than}} CuO + CO_2$$

For complexes containing mercury, Hg(II) began to sublime [10] within the temperature range 210-240°. The organic part of the chelate gradually burned away and the crucible was empty within the temperature range 410-550°. The decomposition of the organic part of the complex was an endothermic reaction leaving carbon as a residue. The combustion of the carbon residue to volatile carbon dioxide was an exothermic reaction [8].

The kinetic stability of the metal-oxygen and metal-nitrogen bonds (oxygen and nitrogen atoms are the sites of chelation of our ligands under investigation) were expected to vary with the basicity of the ligands. However, inspite of pK_a values (the protonation constant values of the ligands are 23.89, 18.00 and 11.10 for 3-OH- 3-COOH and 3-OCH_3

derivatives respectively) [4] varying in a wide range, the activation free energy $\Delta G^{\neq}$ changed in a narrow range as seen from Tables 2,3 and 4. In the present complexes the hydroxy derivative of the hydrazopyrazolone ligand was expected to be more stable than the carboxy and methoxy derivatives which was interpreted by taking into account a significant contribution of metal - ligand π - back-bonding to the bond stability.

The complexation is increased by increasing the electron density at the chelation sites. The basicity of the *m*-hydroxy derivative of the hydrazopyrazolone ligand is greater than that

TABLE 1. DATA OF ELEMENTAL ANALYSIS FOR UO_2^{2+}, Fe^{3+}, Cu^{2+} AND Hg^{2+} COMPLEXES WITH HYDRAZO-LIGANDS DERIVED FROM 1-PHENYL-3-METHYL-5-PYRAZOLONE.

Complex	Colour	% C [a]	% H [a]	% N [a]	% Cl [a]	% M [a]
LIGAND (I)						
$[UO_2LNO_3 . 4H_2O]$	Red	26.90	3.30	10.28	–	33.77
		(27.54)	(3.01)	(10.04)	–	(34.15)
$[FeLCl_2 . H_2O]$	Green red	44.40	3.71	13.10	15.80	13.01
		(43.95)	(3.43)	(12.81)	(16.02)	(12.78)
$[CuLCl . 2 H_2O]$	Dark red	46.18	3.87	13.25	8.41	15.83
		(46.83)	(3.66)	(13.66)	(8.66)	(15.49)
$[HgL_2 . 4H_2O]$[b]	Light red	44.31	4.21	13.21	–	23.25
		(44.72)	(3.95)	(13.04)	–	(23.36)
LIGAND (II)						
$[UO_2LNO_3] . H_2O$	Orange	30.95	2.60	10.85	–	33.22
		(30.40)	(2.23)	(10.43)	–	(33.68)
$[FeLCl_2 . H_2O]$	Orange	44.20	3.50	11.90	14.77	12.21
		(43.88)	(3.23)	(12.05)	(15.06)	(12.01)
$[CuLCl . H_2O]$	Red	46.15	3.16	12.24	7.85	14.80
		(46.57)	(3.42)	(12.78)	(8.10)	(14.49)
$[HgLCl . 2H_2O]$	Orange	34.90	3.04	10.81	6.13	34.47
		(34.39)	(2.86)	(9.44)	(5.98)	(33.82)
LIGAND (III)						
$[UO_2LNO_3 . 2H_2O]$	Orange	29.71	3.23	9.98	–	34.78
		(30.22)	(2.81)	(10.27)	–	(35.26)
$[FeLCl_2 . H_2O]$	Green yellow	45.81	4.01	12.20	15.29	11.96
		(45.25)	(3.77)	(12.42)	(15.53)	(12.39)
$[CuLCl] . 3 H_2O$	Red	45.03	4.47	12.50	7.70	13.31
		(44.35)	(4.56)	(12.17)	(7.72)	(13.80)
$[HgLCl]. H_2O$	Orange	36.87	3.25	10.46	6.52	35.20
		(36.49)	(3.04)	(10.02)	(6.35)	(35.88)

(a) % Found (% Calculated); (b) Molar Ratio 2 : 1 (Ligand : Metal).

TABLE 2. KINETIC PARAMETERS OF THE FINAL STAGE OF DECOMPOSITION OF METAL CHELATES OF 1-PHENYL-3-METHYL -4 (3-HYDROXY PHENYLHYDRAZO)-5-PYRAZOLONE LIGANDS.

Complex	E_a $kJmol^{-1}$	Log A S^{-1}	$\Delta H^{\neq}$ (623K) $kJmol^{-1}$	$\Delta S^{\neq}$ (623K) $JK^{-1}mol^{-1}$	$\Delta G^{\neq}$ (623K) $kJmol^{-1}$
$[UO_2 (3\text{-}OH\text{-}PhHP)(NO_3) . 4H_2O]$	40.2	4.87	35.02	-166.08	138.5
$[Fe (3\text{-}OH\text{-}PhHP) Cl_2 . H_2O]$	41.5	5.04	36.30	-162.90	137.8
$[Cu(3\text{-}OH\text{-}PhHP) Cl] H_2O]$	72.6	5.96	67.4	-139.80	154.5
$[Hg(3\text{-}OH\text{-}PhHP)_2 . 4H_2O]$	95.8	8.23	90.5	-101.90	154.0

E_a, Activation energy; A, Frequency factor; $\Delta H^{\neq}$ Activation enthalpy; $\Delta S^{\neq}$ Activation entropy; $\Delta G^{\neq}$ Activation free energy.

TABLE 3. KINETIC PARAMETERS OF THE FINAL STAGE OF DECOMPOSITION OF METAL CHELATES OF 1-PHENYL-3-METHYL-4 (3-CARBOXY PHENYLHYDRAZO)-5-PYRAZOLONE LIGANDS.

Complex	E_a kJmol^{-1}	Log A S^{-1}	ΔH$^{\neq}$ (623K) kJmol^{-1}	ΔS$^{\neq}$ (623K) JK^{-1}mol^{-1}	ΔG$^{\neq}$ (623K) kJmol^{-1}
$[UO_2(3\text{-}COOH\text{-}PhHP)(NO_3) . H_2O]$	56.5	5.72	51.3	-149.7	144.6
$[Fe(3\text{-}COOH\text{-}PhHP)Cl_2 . H_2O]$	61.3	6.55	56.1	-134.1	139.6
$[Cu(3\text{-}COOH\text{-}PhHP)Cl. H_2O]$	80.9	7.12	75.7	-123.1	152.4
$[Hg(3\text{-}COOH\text{-}PhHP)Cl . 2 H_2O]$	134.5	10.18	129.3	-64.6	169.6

E_a , Activation energy; A, Frequency factor; ΔH$^{\neq}$ Activatioiin enthalpy; ΔS$^{\neq}$ Activation entropy; ΔG$^{\neq}$ Activation free energy.

TABLE 4. KINETIC PARAMETERS OF THE FINAL STAGE OF DECOMPOSITION OF METAL CHELATES OF 1-PHENYL-3-METHYL -4 (3-METHOXY PHENYLHYDRAZO)-5-PYRAZOLONE LIGANDS.

Complex	E_a kJmol^{-1}	Log A S^{-1}	ΔH$^{\neq}$ (623K) kJmol^{-1}	ΔS$^{\neq}$ (623K) JK^{-1}mol^{-1}	ΔG$^{\neq}$ (623K) kJmol^{-1}
$[UO_2(3\text{-}OCH_3\text{-}PhHP)(NO_3) . 2 H_2O]$	61.3	6.22	56.1	-140.3	143.5
$[Fe(3\text{-}OCH_3\text{-}PhHP)Cl_2] H_2O]$	84.2	7.74	79.0	-11.2	148.3
$[Cu(3\text{-}OCH_3\text{-}PhHP)Cl] . 3H_2O]$	87.2	9.26	82.0	-82.2	133.2
$[Hg(3\text{-}OCH_3\text{-}PhHP)Cl] . H_2O]$	154.1	12.14	148.9	-27.0	165.7

E_a , Activation energy; A, Frequency factor; ΔH$^{\neq}$ Activation enthalpy; ΔS$^{\neq}$ Activation entropy; ΔG$^{\neq}$ Activation freee energy.

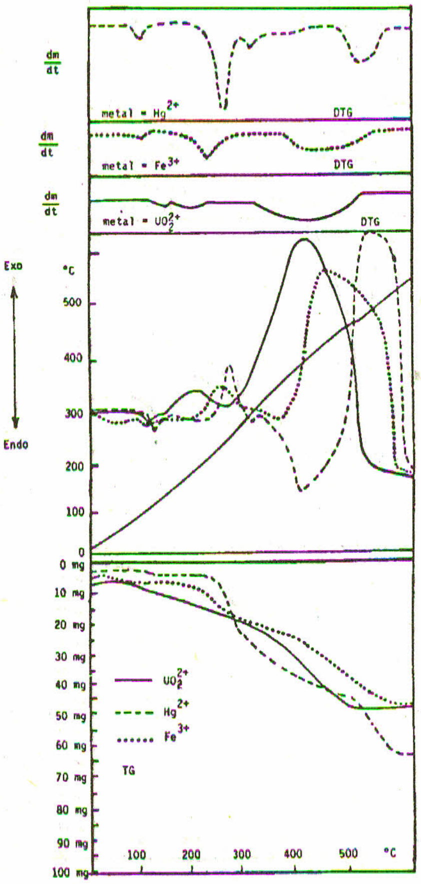


Fig. 2. TG, DTG, DTA curves of metal complexes of 1-phenyl-3-methyl-4-(3-methyoxyphenylhydrazo)-5-pyrazolone ligand (metal used in chelation as shown on plot).

TABLE 5. CALCULATION OF THE THERMODYNAMIC PARAMETERS OF Fe^{3+}-1-PHENYL-3-METHYL-4(3-OH-PHENYLHYDRAZO)-5-PYRAZOLOLONE LIGAND.

$\frac{dm}{dt}$ mm	T(K)	log $\frac{dm}{dt}$	$\frac{1}{T}.10^3$
20	578	1.301	1.730
26	593	1.415	1.686
28	603	1.447	1.658
30	613	1.477	1.631
33	623	1.519	1.605

of the *m*-carboxy and *m*-methoxy. Thus the chelation sites of the *m*-hydroxy-derivative (carbonyl oxygen and the hydrazonitrogen) involved in coordination with the metal ions will have higher effective negative change than those of *m*-carboxy and *m*-methoxy. On the basis of the principle that the activation energy or enthalpy decreases as the attraction between two reagents increases [11], it could be deduced that in a given metal ion, the $H^{\#}$ for the decomposition of *m*-hydroxy would be less than *m*-carboxy- and *m*-methoxyhydrazopyrazolone ligands as seen from Tables 2-4. Thus, the thermal stability of the complexes depends on the nature of the substituent on the phenylhydrazo moiety. As a result, it is expected that a more basic ligand should form more stable complexes.

A rough order of thermal stability for the complexes was $UO_2^{2+} > Fe^{3+} > Cu^{2+} > Hg^{2+}$.

TABLE 6. THERMOGRAVIMETRIC ANALYSIS OF SOME SOLID COMPLEXES OF 1-PHENYL-3-METHYL-4-(X-PHENYLHYDRAZO)-5-PYRAZOLONE LIGANDS.

X —	Complex	Temp. range °C	%Loss in weight		Effect type	Assignment
			Calc.	Found		
3-OH	[UO$_2$ (x-PhHP) (NO$_3$) . 4H$_2$O]	170-210	10.33	10.84	Endo.	Loss of four coordinated H_2O
		235-260	19.23	19.87	Exo.	Loss of the NO_3 group
		330-340	36.59	37.42	Exo.	Loss of the organic part (HO- C_6H_4-N_2-)
		350-500	61.27	62.92	Exo.	Loss of the rest of the ligand (Phenylpyrazolone) and formation of metal oxide (UO_2)
3-COOH-	[UO$_2$ (x-PhHP) (NO$_3$) . H$_2$O]	100-110	2.68	2.80	Endo.	Loss of one water molecule
		260-310	11.92	12.00	Exo.	Loss of the NO_3 group
		330-430	34.13	34.79	Exo.	Loss of the organic part (COOH-C_6H_4-N_2-)
		450-560	59.76	61.18	Exo.	Loss of the rest of the ligand (Phenylpyrazolone) and formation of metal dioxide (UO_2)
3-OCH$_3$ -	[UO$_2$ (x-PhHP) (NO$_3$) . 2H$_2$O	105-130	5.33	4.82	Endo.	Loss of two water molecules
		210-260	14.52	14.14	Exo.	Loss of the NO_3 group
		280-470	59.99	57.98	Exo.	Decomposition of the complex and formation of metal oxide (UO_3)
3-OH-	[Hg (x-PhHP)$_2$. 4H$_2$O]*	190-210	8.38	8.41	Endo.	Loss of four coordinated H_2O
		230-360	91.61	91.53		Sublimation of Hg (II)
		360-410			Endo.	Decomposition of organic matter, leaving carbon black as a residue
		410-460	99.99	99.94	Exo.	Formation of volatile CO_2
3-COOH-	[Hg (x-PhHP)Cl . 2H$_2$O]	130-150	6.07	5.95	Endo.	Loss of two coordinated H_2O
		180-230	45.87	46.29	Exo.	Elimination of the chlorine atom
		240-300			Endo.	Sublimation of Hg (II)
		300-500	65.60	66.46	Endo.	Decomposition of the organic matter, leaving carbon black as a residue
		500-540	99.99	101.13	Exo.	Formation of volatile CO_2
3-OCH$_3$-	[Hg (x-PhHP)Cl] H$_2$O	115-130	3.22	3.20	Endo.	Loss of one water molecule
		185-200	45.45	44.93	Exo.	Elimination of chlorine atom
		210-290			Endo.	Sublimation of Hg (II).
		290-450	63.87	63.38	Endo.	Decomposition of the organic matter, leaving carbon as a residue
		450-550	9.99	100.11	Exo.	Formation of volatile CO_2
3-OH-	[Cu (x-PhHP)Cl] H$_2$O	80-110	4.39	4.32	Endo.	Loss of one water molecule
		180-205	13.05	12.52	Exo.	Elimination of chlorine atom
		205-310	42.56	41.00	Exo.	Loss of the organic part (HO-C_6H_4-N_2-)
		460-520	84.51	80.84	Exo.	Loss of the rest of the ligand (Phenylpyrazolone) and formation of CuO through $CuCo_3$.
3-COOH–	[Cu (x-PhHP)Cl . H$_2$O]	160-180	4.11	4.14	Endo.	Loss of one coordinated H_2O
		200-220	12.22	12.10	Exo.	Loss of one coordinated Cl
		230-360	46.24	46.19	Exo.	Loss of the organic part (COOH-C_6H_4-N_2-)
		400-540	85.51	83.42	Exo.	Loss of the rest of the ligand (Phenylpyrazolone) and formation of CuO through $CuCo_3$.

(Cont'd....)

(Table 6, continued...)

3-OCH_3-	[Cu (x-PhHP)Cl] . $3H_2O$	100-120	11.74	11.36	Endo.	Loss of three water molecules
		180-230	19.46	19.07	Exo.	Loss of one coordinated Cl
		230-460	86.20	84.77	Exo.	Decomposition of the complex and formation of metal oxide CuO
3-OH-	[Fe (x-PhHP)Cl_2] . H_2O	150-210	4.12	4.18	Endo.	Loss of one coordinated H_2O
		210-420	87.21	81.45	Exo.	Elimination of the chlorine atom, decomposition of the complex and formation of metal oxide Fe_2O_3
3-COOH-	[Fe (x-PhHP)Cl_2 . H_2O]	170-210	3.87	3.69	Endo.	Loss of one coordinated H_2O
		220-280	18.93	18.46	Exo.	Loss of two coordinated Cl
		310-480	87.98	83.32	Exo.	Decomposition of the complex and formation of Fe_2O_3
3-OCH_3-	[Fe (x-PhHP)Cl_2] H_2O	85-110	3.99	3.92	Endo.	Loss of one water molecule
		210-270	19.52	19.22	Exo.	Loss of two coordinated Cl
		350-540	87.61	83.55	Exo.	Decomposition of the complex and formation of Fe_2O_3

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[*] Metal : Ligand = 1 : 2.

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