Journal of Thermal Analysis, Vol. 36 (1990) 7-15

THERMAL DECOMPOSITION OF BIS(DIMETHYLGLYOXIMATE) IRON(II) COMPLEXES CONTAINING AXIAL N-HETEROCYCLIC LIGANDS

H. E. Toma and *L. A. Morino*

INSTITUTO DE QUIMICA, UNIVERSIDADE DE SAO PAULO, CAIXA POSTAL 20780, SAO PAULO, SP, BRAZIL

(Received January 30, 1989)

A systematic TG and DTG study of the thermal decomposition of a series of bis(dimethylglyoximate)iron(II) complexes containing axial N-heterocyclic ligands is reported. The decomposition reaction is very exothermic, coinciding with the loss of the axial ligands. The average temperatures of decomposition correlate linearly with the basicity properties of the axial ligands.

In this work we report a systematic study of the thermal decomposition of bis(dimethylglyoximate)iron(II) complexes containing imidazole, pyridine or pyrazine derivatives in the the axial position. These complexes are interesting examples of coordination compounds which mimic biologically important heme groups in their ability to bind carbon monoxide reversibly [1-4].The axial ligands in these macrocyclic complexes are highly important, influencing their redox and kinetic properties and their affinity for unsaturated bases in solution [5-7]. The role of the N-heterocyclic ligands in the thermal behaviour of the iron(II)-dioximate complexes is discussed in this paper.

Experimental

The complexes $[Fe(Hdmg)_2L_2]$ were synthesized from iron(II) acetate and the corresponding ligands /Aldrich/ by the method of Pang and Stynes [3].The results of elemental analysis are given in Table 1. The following

John Wiley & Sons Limited, Chichester
Akadémiai Kiadó, Budapest

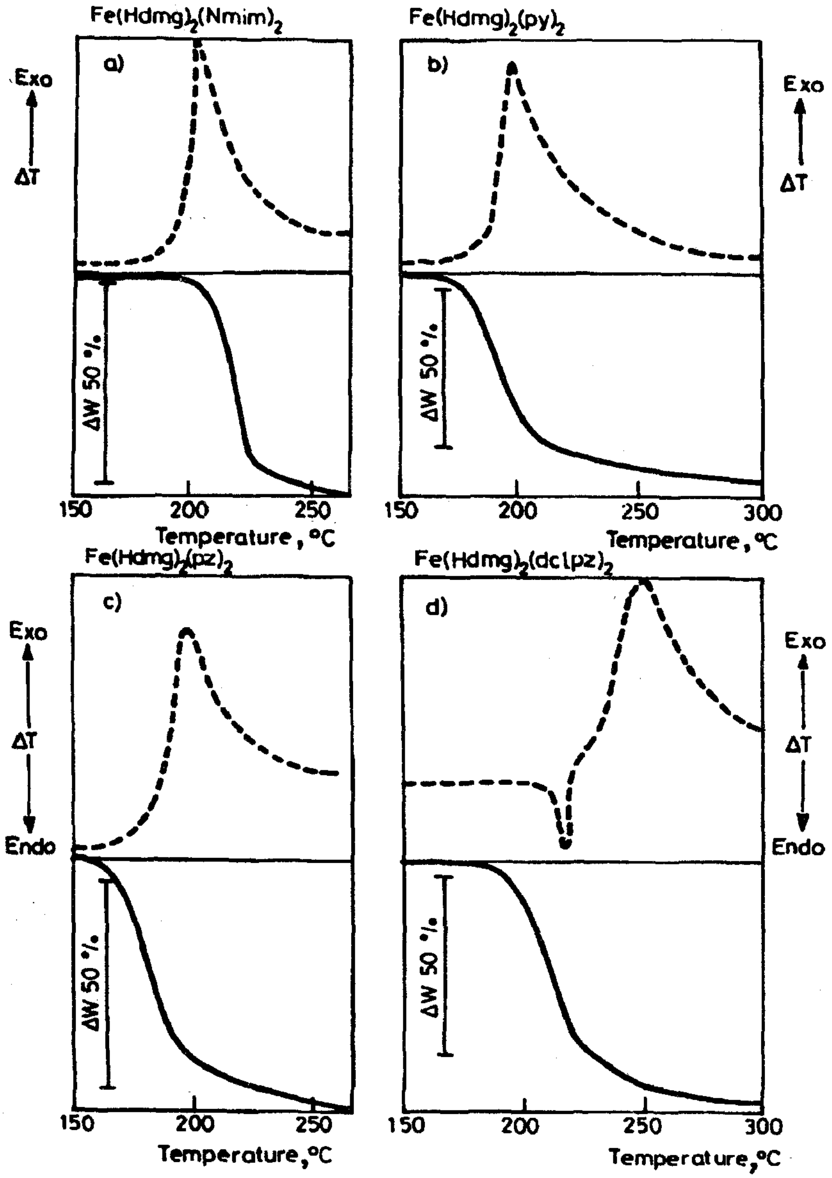

Fig.1 Typical TG and DTA curves of complexes [Fe(Hdmg)$_2$L$_2$]

nomenclature is employed in this work: Hdmg = diacetyldioximate anion, L = nmin (N-methylimidazole), pmepy (4-methylpyridine), py (pyridine), pcnpy (4-cyanopyridine), pz (pyrazine), dclpz (2,6-dichloropyrazine) or dmez (2,6-dimethylpyrazine).

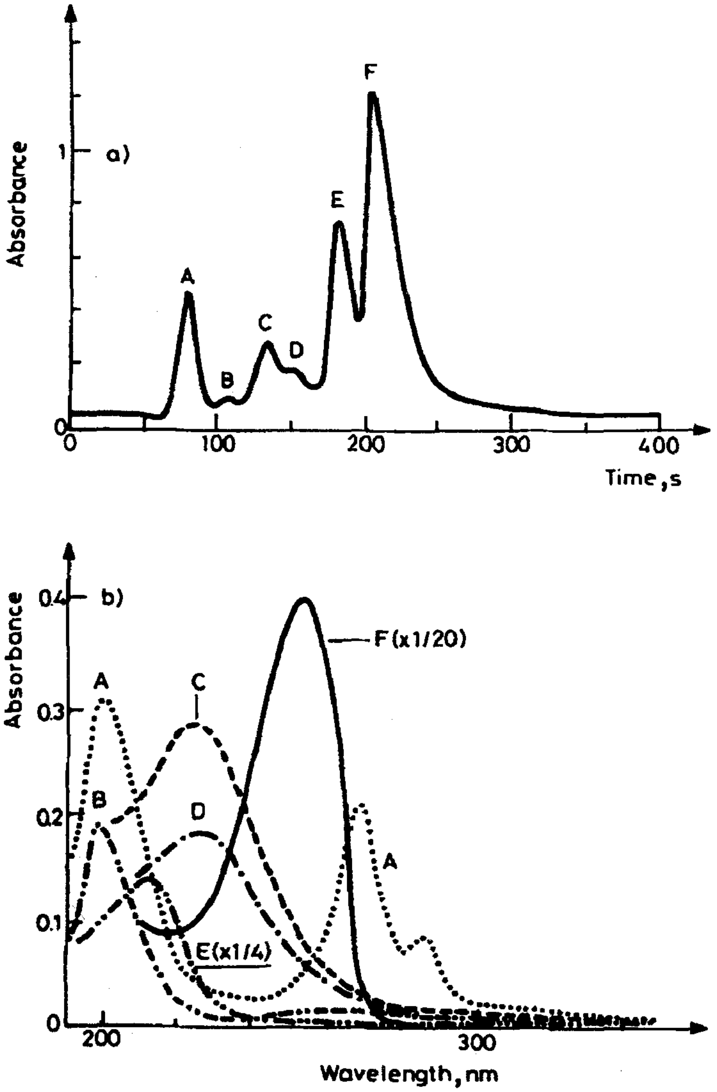

Fig. 2 (A) Chromatogram and (B) electronic spectra of the volatile products resulting from pyrolysis of the complex [Fe(Hdmg)$_2$(py)$_2$] at 250 °C. (Merck Lichrocart RP-18 column, 5 μm; mobile phase = methanol/water (60/40); flow rate =0.6 ml/min.)

The electronic spectra of the complexes in the visible and UV region were recorded on a Cary 17 or a Hewlett-Packard 8451-A diode-array spectophotometer. The samples were dissolved in $CHCl_3$, in the presence of a ten-fold excess of the axial ligands, under an argon atmosphere. The pK_a values of the N-heterocyclic ligands were determined spectrophotometrically, in aqueous solution, at 25°.

TG and DTA measurements were carried out with Shimadzu TG 20 and DTA 203 instruments, at a heating rate of 5 deg/min, under a flow of nitrogen (100 ml/min). For analytical purposes, the pyrolysis was carried out in a tubular oven, under a flow of nitrogen, at a heating rate of 20 deg/min. After passing through a glass wool filter, the flow of nitrogen carrying the volatile species was bubbled into a series of washers containing HPLC grade methanol. The products were analysed by using a Merck Lichrocart RP-18 column, with an HPLC instrument (CG model 480), equipped with visible-UV diode-array detection.

Results and discussion

The complexes $[Fe(Hdmg)_2L_2]$ are stable solids, soluble in $CHCl_3$, yielding violet, red or brown solutions, depending on the nature of L. The electronic spectra exhibit a strong absorption band in the range 470-550 nm, ascribed to a metal-to-equatorial ligand charge-transfer (MECT) transition [8, 10]. A vibronic shoulder is observed at lower wavelengths.

Table 1 Analytical data on the complexes $[Fe(Hdmg)_2L_2]$

L in complex	Mol. weight of complex	Found (Calcd.),% C	H	N
nmin	450.3	42.94(42.68)	6.01(5.82)	24.86(24.89)
pmepy	472.3	49.96(50.86)	5.98(5.98)	16.97(17.79)
py	444.3	48.62(48.66)	5.43(5.45)	19.10(18.92)
pcnpy	494.3	48.37(48.60)	4.55(4.49)	22.81(22.67)
pz	446.2	42.80(43.07)	4.93(4.97)	25.55(25.11)
dmepz	502.4	47.83(47.82)	6.00(6.02)	22.55(22.31)
dclpz	584.0	33.88(32.91)	3.33(3.11)	20.47(19.19)

The pyridine and pyrazine derivatives exhibit an additional band in the visible region. This band is strongly sensitive to the substituents on the aromatic ring, and has been ascribed to a metal-to-axial ligand chargetransfer (MACT) transition [8, 10].

In some cases, the MECT and MACT bands were superimposed, and were resolved by means of Gaussian analysis. The spectral data for the complexes [Fe(Hdmg)$_2$L$_2$] are given in Table 2.

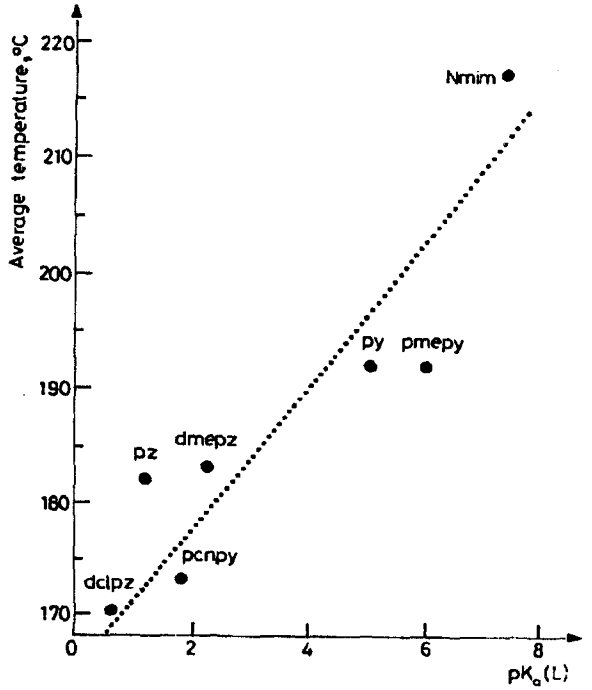

Fig. 3 Correlation of the average temperature of decomposition of the complexes [Fe(Hdmg)$_2$L$_2$] with the pK$_a$ values of the axial ligands

Typical TG and DTA curves of the complexes [Fe(Hdmg)$_2$L$_2$] can be seen in Fig. 1. In general, the decomposition reaction proceeded rapidly within the temperature range 140-220°, with a large exothermic effect. Similar behaviour has recently been reported [11] for the complexes [Co(Hdmg)$_2$XY] (X, Y = Cl^-, Br^-, I^-, NO_2^-, N_3^-, NCS^-, $NCSe^-$, CN^- and H_2O). Stoichiometric calculations (Table 2) showed the weight loss to correspond approximately to the elimination of the 2 molecules of L, plus an additional value consistent with a molecular weight of 51 ± 5 daltons. HPLC analyses of the volatile material allowed the detection of six components, as illustrated in Fig. 2. The axial ligand (peak F) was readiliy identified by its UV absorption spectrum as the major species, corresponding to 2 mol L per mol [Fe(Hdmg)$_2$L$_2$]. The formation of diacetyl (peak B) was evidenced by its characteristic smell, and by its absorption band at 206 nm, corresponding approximately to 0.3 mol per mol complex. The spectrum corresponding to peak E coincides with the absorption spectrum of dimethylfurazan (λ_{max} = 210 nm, Stadler Catalog 7673 UV). This heterocyclic molecule is usually obtained by the dehydration of dimethylglyoxime [12]. In our case, the thermal decomposition of one mol [Fe(Hdmg)$_2$L$_2$] yielded 0.1 mol dimethylfurazan.

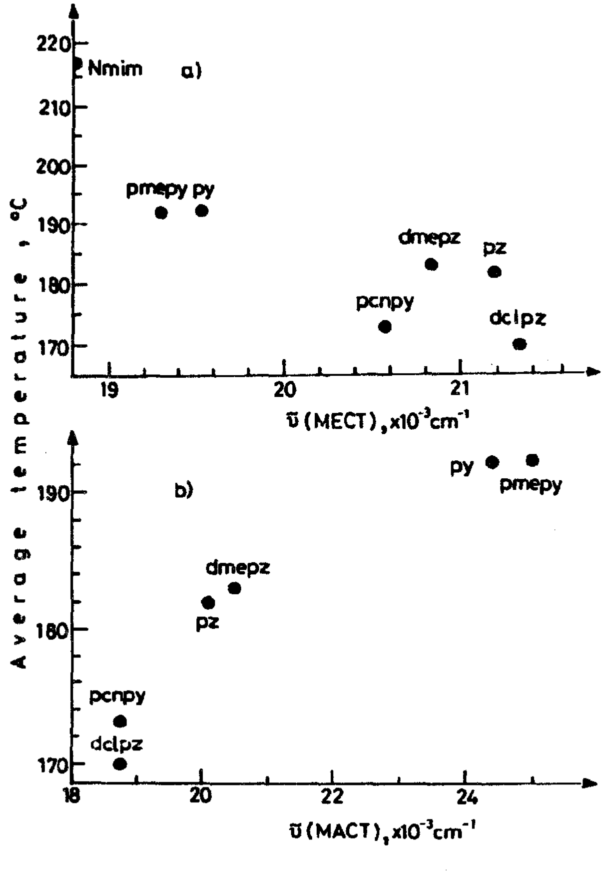

Fig. 4 Plots of the average temperature of decomposition of the complexes [Fe(Hdmg)$_2$L$_2$] versus the wavenumbers of the MECT (A) and MACT (B) bands

The remaining products represent less than 10% of the mixture, corresponding to diacetylmonoxime (peak D) and dimethylglyoxime (peak C). Peak A was observed independently of the nature of the axial ligand. The absorption spectrum is similar to those of aromatic N-heterocyclic compounds, such as the substituted pyrazines. These species can result from the condensation of unsaturated oxime and carbonyl products, but the identification requires further work on a preparative scale. HPLC analyses showed that the loss in the case of the N-methylimidazole complex, the exothermic peak coincided with the beginning of the decomposition reaction (Fig. 1.A.). In the majority of the cases, however, the exothermic peak occurred at the end of the decomposition reaction (Fig. 1.B-C), and was nearly the same (around 205 $\pm 5^{\circ}$) in the series of complexes the axial ligands starts before or at the beginning of the exothermic reaction. In fact, in the case of the dichloropyrazine complex (Fig. 1.D), a small endothermic peak was observed to precede the exothermic reaction.

The loss of the ligands seems to yield the unstable species [Fe(Hdmg$_2$L$_2$], containing iron(II) ions in an incomplete coordination environment. On the other hand, at high temperatures the oxime group can be reduced by the iron(II) ion, yielding volatile species such as dinitrogen and diacetyl, with a great expansion of volume.

Table 2 Thermal and spectroscopic data on the [Fe(Hdmg)$_2$L$_2$] complexes

L in	T_i-T_f,	T_{av},	ΔW(%)	T_{peak},	$10^{-3}\bar{\nu}$	
complex	°C	°C	°C	°C	MECT cm^{-1}	MACT cm^{-1}
nmim	209-225	217	47.7	209(exo)	18.80	-
pmepy	179-205	192	50.2	205(exo)	19.31	25.00
py	179-205	192	54.3	198(exo)	19.53	24.39
dmepz	167-201	184	56.5	200(exo)	20.83	20.49
pz	167-197	182	52.3	201(exo)	21.19	20.08
pcnpy	138-208	173	53.2	205(exo)	20.58	18.76
dclpz	136-205	170	58.8	164(endo) 205(exo)	21.32	18.76

*T_i and T_f are the initial and final temperatures of decomposition; $T_{av} = (T_i + T_f)/2$; ΔW = weight loss from T_i to T_f; $\bar{\nu}$(MECT, MACT) = optical energies of the charge-transfer bands.

The solid residues after pyrolysis at 250° were black, and exhibited the approximate composition C, 26; N, 14; and H, 3%. They were slightly soluble in water, but dissolved in the presence of hydrochloric acid, e.g. 0.1 M, to yield solutions containing iron(III) species. The composition of the solid, however, depends on the final temperature. A variable composition, $Fe_2O_x[dmg]_{3-x}$, can be suggested, where x increases with the temperature, approaching 3 at 400°.

Therefore, the decomposition of the complexes $[Fe(Hdmg)_2L_2]$ is consistent with the equation $2[Fe(Hdmg)_2L_2] \rightarrow 4\ L + Fe_2O_x(dmg)_{3-x} +$ dec.prod.(A-E) involving the loss and vaporization of the axial ligands L (endothermic processes), and a redox reaction between the iron(II) center and the oxime ligand (exothermic process), responsible for the carbonyl products (B, D). The loss of dimethylglyoxime and the formation of dimethylfurazan occur in secondary steps, below 250°.

For comparison purposes, one can define an average temperature, $T_A = (T_i + T_f)/2$, where T_i is the temperature at the beginning of the decomposition reaction and T_f is the temperature of completion of the exothermic reaction, as indicated in Fig. 1.A. The average temperature are linearly correlated with the pK_a values of the axial ligands, as shown in Fig. 3. This means that the σ-bond strength of the axial ligands makes an important contribution to the thermal stability of the complexes $[Fe(Hdmg)_2L_2]$.

The contribution of π-back-bonding depends on the competing effects involving the axial and equatorial ligands in the complex. As the σ-donor properties of L increase, the π-back-bonding interactions in the axial position decrease and the energies of the MACT bands are shifted to higher levels. On the other hand, the π-back-bonding interactions involving the iron(II)-dioxime chromophore increase, lowering the energy of the MECT bands. As a consequence, the thermal stability, expressed by T_A, displays a direct correlation with the energies of the MACT bands, and an inverse correlation with respect to the MECT bands (Fig. 4.).

The investigation of the thermal behaviour of the complexes $[Fe(Hdmg_2L_2]$ was restricted to the cases involving volatile ligands. Anomalous behaviour is excepted for the complexes containing less volatile axial ligands, such as 4,4'-bipyridylethylene (m.p. 190°), or ligands susceptible to decomposition below 250°.

References

1 B. J. Jillot and R. J. P. Williams, J. Chem. Soc., (1958) 462
2 L. Vaska and T. Yamaji, J. Am. Chem. Soc., 93 (1971) 6673.
3 I. W. Pang and D. V. Stynes, Inorg. Chem., 16 (1977) 590.
4 D. V. Stynes and X. Chen, Inorg. Chem. 26 (1987) 3145.
5 H. E. Toma and L. A. Morino, Talanta, 31 (1984) 224.
6 H. E. Toma and A. C. Silva, Can. J. Chem., 64 (1986) 1280.
7 X. Chen and D. V. Stynes, Inorg. Chem., 25 (1985) 1173.
8 N. Sanders and P. Day, J. Chem. Soc. (A), (1969) 2303.
9 Y. Yamano, I. Masuda and K. Shinra, Bull. Chem. Soc. Japan, 44 (1971) 1581.
10 H. E. Toma, L. A. Morino and P. S. Santos, Inorg. Chim. Acta, 108 (1985) 125.
11 C. Varhelyi, J. Zsako, G. Liptay and Z. Finta, J. Thermal Anal. 32 (1987) 785.
12 T. L. Gilchrist, Heterocyclic Chemistry, Pitman Publishing Co, London, 1985, p. 255.

Zusammenfassung - Es wird eine systematische TG- und DTA-Untersuchung der thermischen Zersetzung einer Reihe von Bis(dimethylglyoximat)-Komplexe von Eisen(II) mit axialem N-heterocyclischen Liganden beschrieben. Die Zersetzungsreaktion ist sehr exotherm, was mit dem Verlust der axialen Liganden zusammenfällt. Die durchschnittliche Zersetzungstemperatur ist den Basizitäts eigenschaften der axialen Liganden proportional.