Thermochimica Acta, 145 (1989) 281–289
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND SPECTROSCOPIC CHARACTERIZATION OF Mn(II), Fe(II) AND Fe(III) DIPHENYLCARBAZONATE COMPLEXES

M.F.R. FOUDA, R.S. AMIN and M. HASSANEIN

Inorganic Chemistry Department, National Research Centre, Dokki, Cairo (Egypt)

(Received 14 October 1988)

ABSTRACT

Mn(II), Fe(II) and Fe(III) diphenylcarbazonate complexes with 3-oxo-1,5-diphenylformazan (Ph–N=N–CO–NH–NHPh, abbreviated as H_2DCO) as ligand were synthesized by shaking the buffered aqueous metal salts with solutions of diphenylcarbazone in benzene for sufficient time, and then evaporating off the solvent to obtain the solid product. The molecular structures of the complexes were elucidated from the results of chemical analysis and infrared (IR) spectra. The vibrational bands revealed that both the Mn(II) and Fe(III) complexes are ketonic in nature, whereas the Fe(II) complex is an enolic one. The electronic absorption bands show that the metal ions are hexacoordinated to the ligand molecules. The thermogravimetric and differential thermogravimetric curves of the complexes showed several thermal decomposition steps ending with Fe_4N, and $Fe_{10}N$ at temperatures above 550 °C.

INTRODUCTION

Diphenylcarbazone (H_2DCO) has been the subject of several investigations due to its diverse applications in many fields where it is used as a catalyst [1] and as a highly sensitive microanalytical reagent for the determination of traces of metals, especially transition elements [2].

Although a large number of metal diphenylcarbazonates have been reported, no study has been made of their molecular structure, or their thermal behaviour over a relatively wide range of temperatures. The present study is a continuation of our previous work on Ni(II) and Co(III) diphenylcarbazonates [3]. In this paper we describe the synthesis, the characterization, by infrared (IR) spectroscopy and electronic absorption spectroscopy, and the thermal behaviour of Mn(II), Fe(II) and Fe(III) diphenylcarbazonate complexes.

EXPERIMENTAL

Chemicals

All the chemicals used in this study were of AnalaR grade.

Purification of diphenylcarbazone

Diphenylcarbazone (H_2DCO) was purified using the method reported by Krumholz and Krumholz [4].

Preparation of chelates

Bis- and tris-diphenylcarbazonate complexes of Mn(II), Fe(II) and Fe(III) were prepared by shaking an aqueous solution of the appropriate metal salt (ca. 10^{-5} M) buffered at pH $\simeq$ 7.5, 4.0 and 2.5 respectively with a stoichiometric quantity of diphenylcarbazone in benzene (ca. 2 or 3×10^{-5} M) for about 15 min. The organic layer was separated and the bulk of the solvent distilled off under mild reduced pressure at 40 °C. The residual complexes were washed several times with water and benzene to remove unreacted metal salts and ligand, respectively.

Analysis of complexes

The complexes were dried under vacuum and the results of their analysis are given in Table 1.

The IR spectra of the solid complexes were recorded on a Perkin-Elmer 577 spectrophotometer (KBr-disc method), and the electronic-absorption spectra were recorded on an automatic Shimadzu 240 spectrophotometer using MgO as reference. The TG and DTG curves were measured using a Netzsch apparatus (F.R.G.) at a heating rate of 5 °C min^{-1} in static air.

IR spectra

The presence of sharp and strong ketonic ($>$C=O) bands at 1705 and 1710 cm^{-1} in the spectra of the Mn(II) and Fe(II) complexes, respectively, but with a small shift to higher frequencies in comparison to that of the ligand at 1700 cm^{-1}, is taken as evidence that the ketonic groups are coordinated to both Mn(II) and Fe(III) ions in the *cis* position (Fig. 1). On other hand, the presence of the [N(I)HCO] stretching vibration at ca. 3180–3190 cm^{-1} and 1645–1670 cm^{-1} (very weak shoulder) indicates that

TABLE 1

Results of the microanalysis of the complexes studied

Complex	C (%)		N (%)		H (%)		Metal (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$Mn(HDCO)_2$	58.82	58.49	20.75	20.99	4.32	4.16	10.52	10.30
$Fe(HDCO)_2$	59.10	58.17	20.79	20.88	4.30	4.13	10.70	10.41
$Fe(HDCO)_3$	62.55	60.26	21.19	21.63	4.78	4.28	7.30	7.19

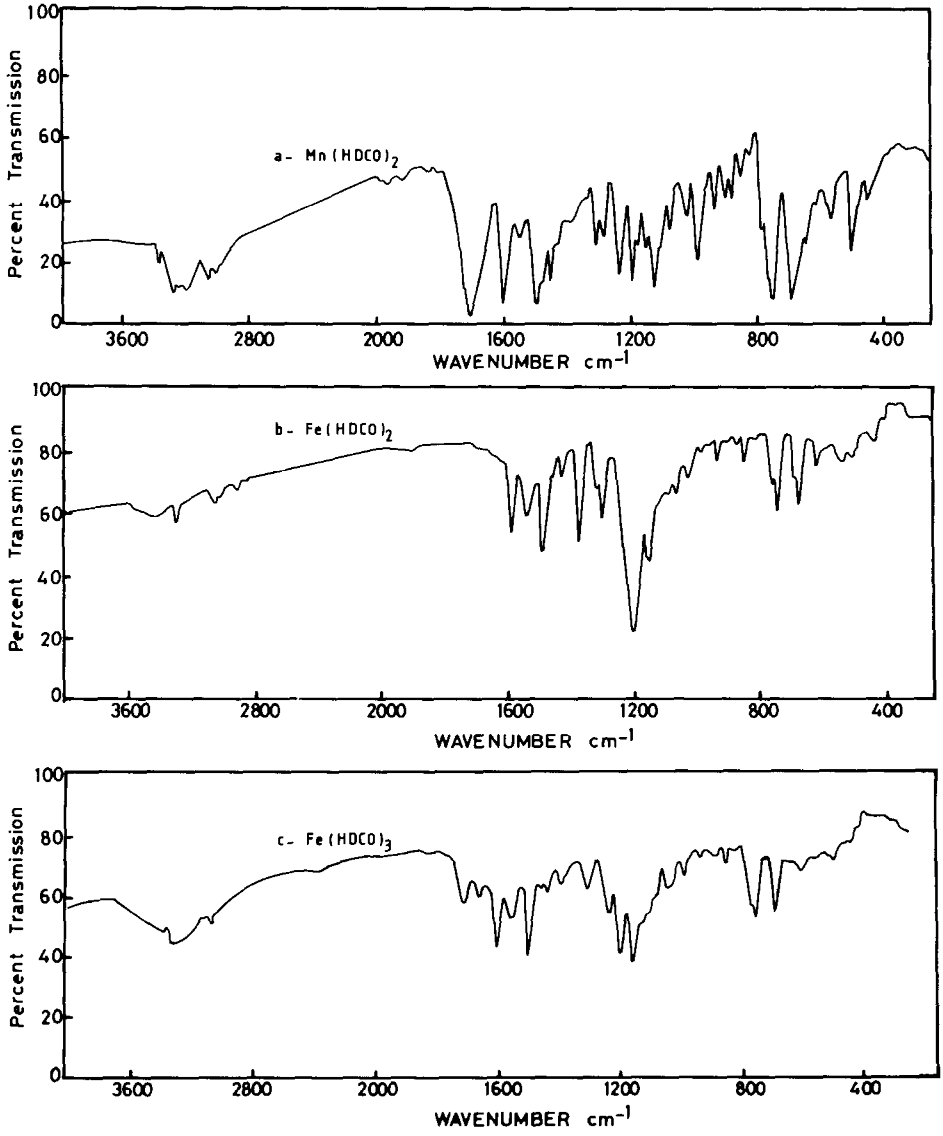


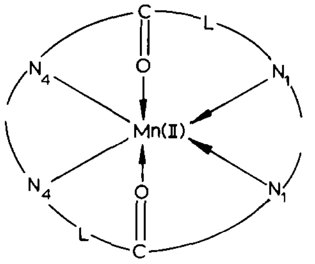
Fig. 1. IR vibrational spectra of the (a) Mn(II), (b) Fe(II), and (c) Fe(III) diphenylcarbazonate complexes.

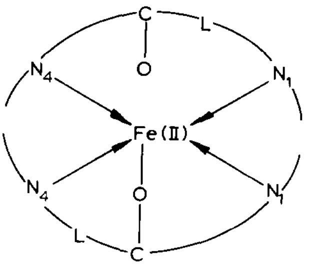
complexation occurs through the formation of Mn–N(4) covalent bonds.

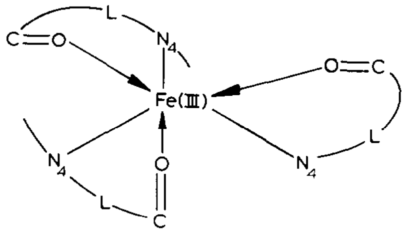
Comparison of IR spectra of the Fe(II) complex with those of the Mn(II) and Fe(III) complexes shows the following dissimilarities: (a) the absence of ($>$C=O) at 1700 cm^{-1}; (b) the presence of the ($>$C=N) stretching vibration at 1590 cm^{-1}, and (c) the absence of (NHCO) stretching vibrations at 3190 and 1645–1670 cm^{-1} (very weak shoulder). These findings support the enolic nature of the Fe(II) complex, involving the formation of covalent

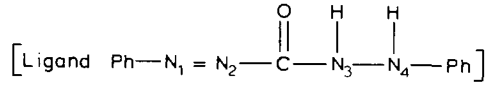
Fe(II)–O bonds and Fe(II) → N coordination bonds. The three complexes exhibit a number of very weak peaks in the region 650–250 cm^{-1}. However, their assignments are difficult because the ligand also reveals a series of bands in the same range.

Based on the IR spectroscopy results and the hypothesis which states that the low-spin tetrahedral complexes of ions of the first transition series with d^5 and d^6 configurations would be scarce or unknown, Mn(II), Fe(II) and Fe(III) diphenylcarbazonate complexes are assumed to possess octahedral geometry around their metal ions [5]. The molecular formula of these complexes may be suggested to be as follows









$$\left[\text{Ligand}\quad Ph—N_1=N_2—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{\overset{\displaystyle H}{|}}{N_3}—\overset{\overset{\displaystyle H}{|}}{N_4}—Ph\right]$$

Electronic absorption spectra

Based on many results which state that Mn(II) and Fe(III) ions form high-spin d^5 complexes with most ligands, except those with cyanide and phenanthroline ligands [6–9], it is assumed that diphenylcarbazonate complexes of both ions have high-spin electronic configurations. The assignments of various d–d transitions of them in the visible and ultraviolet (UV) regions are clarified in Table 2.

Similarly, the EA spectrum of the Fe(II) complex (Fig. 2) shows, in general, the features of an octahedrally high-spin ferrous complex with a symmetry lower than O_h. It exhibits a strong peak at 18180 cm^{-1}, which may be assigned to the $^5T_{2g} \rightarrow {}^5E_g$ transition, in addition to a well-dis-

TABLE 2

The electronic absorption spectra of Mn(II) and Fe(III) diphenylcarbazonate complexes (cm^{-1})

Complex	d–d band	Transition
$Mn(HDCO)_2$	18180 sh	$^6A_1 \rightarrow {}^4T_1(G)$
	21050 sp	$^6A_1 \rightarrow {}^4T_2(G)$
$Fe(HDCO)_3$	14280 br	$^6A_1 \rightarrow {}^4T_1(G)$
	19800 sp	$^6A_1 \rightarrow {}^4T_1(G)$
	25640–28570 sh	Charge transfer

br, broad; sp, sharp; sh, shoulder.

tinguished shoulder at ca. 28570 cm^{-1} which may be assigned to the $^5T_{2g} \rightarrow {}^3T_{1g}$ and $^5T_{2g} \rightarrow {}^3T_{2g}$ transitions [10] and/or charge transfer.

Thermal analysis

Inspection of the TG and DTG curves of the three complexes under investigation (Fig. 3) shows that they have, in general, the same features of thermal decomposition as those, observed by us previously, of the ligands (H_2DCO), Co(III), $(HDCO)_3$ and $Ni(HDCO)_2 \cdot 2\ H_2DCO$ [3]. The complexes decomposed via several successive thermodynamically unstable intermediates over a wide range of temperatures. The molecular formulae of these intermediates can be deduced from the percentage weight losses estimated from the TG and DTG curves (Fig. 3, Table 3) at different temperature, as can be seen from the decomposition equations given below.

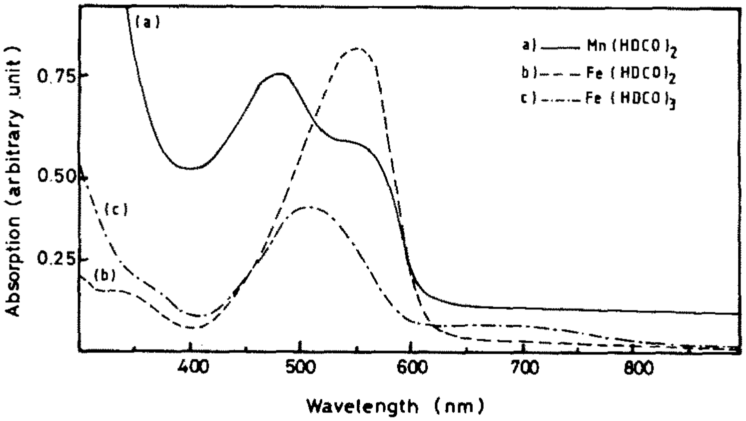


Fig. 2. Electronic absorption spectra of dilute solutions of the (a) Mn(II), (b) Fe(II) and (c) Fe(III) diphenylcarbazonate complexes in benzene.

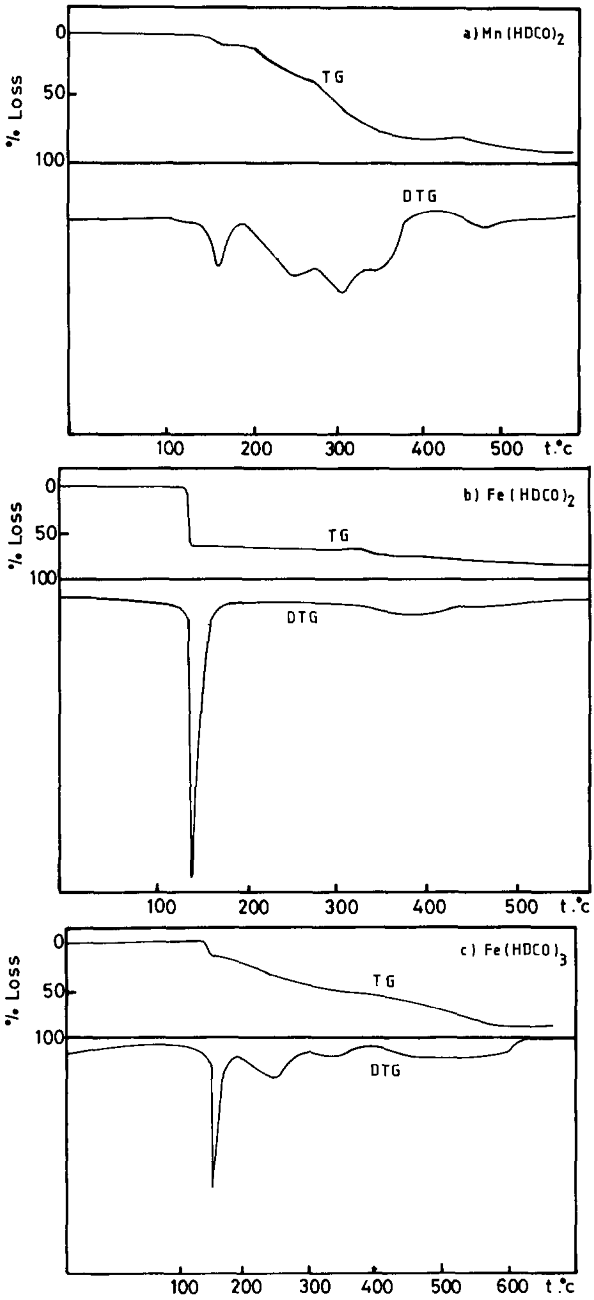


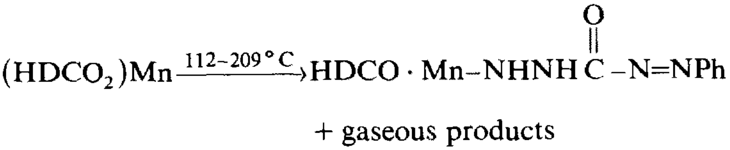
Fig. 3. TG and DTG curves of the (a) Mn(II), (b) Fe(II), and (c) Fe(III) diphenylcarbazonate complexes.

TABLE 3

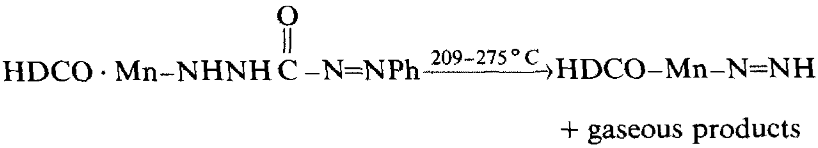
The TG and DTG data for Mn(II), Fe(II) and Fe(III) diphenylcarbazonates

Thermal step	$Mn(HDCO)_2$				$Fe(HDCO)_2$				$Fe(HDCO)_3$			
	Temp. range (°C)	DTG peak (°C)	Loss (%)		Temp. range (°C)	DTG peak (°C)	Loss (%)		Temp. range (°C)	DTG peak (°C)	Loss (%)	
			Calc.	Actual			Calc.	Actual			Calc.	Actual
1	112–209	160	14.45	14.20	95–187	149	64.78	65.00	92–197	156	28.98	27.82
2	219–275	248	39.41	40.08	322–452	400	84.37	83.75	197–318	244	51.66	50.43
3	276–332	348	64.36	66.68	452–550	–	88.97	90.00	318–381	343	58.87	58.26
4	332–427	343	78.61	81.68	–	–	–	–	381–634	broad	92.76	92.17
5	427–564	483	89.7	90.00	–	–	–	–	–	–	–	–

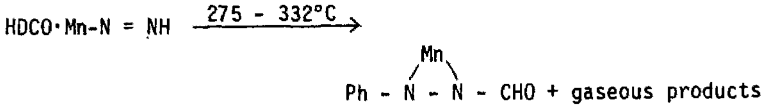
Manganous diphenyl carbazonate [Mn(HDCO)$_2$]



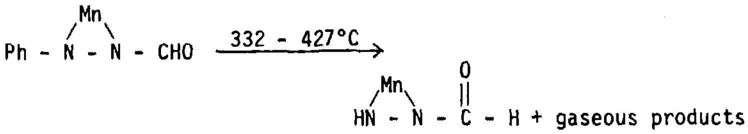
$$(HDCO_2)Mn \xrightarrow{112-209\,°C} HDCO\cdot Mn\text{-}NHNH\overset{\overset{O}{\|}}{C}\text{-}N{=}NPh + \text{gaseous products} \quad (1)$$



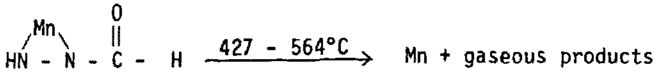
$$HDCO\cdot Mn\text{-}NHNH\overset{\overset{O}{\|}}{C}\text{-}N{=}NPh \xrightarrow{209-275\,°C} HDCO\text{-}Mn\text{-}N{=}NH + \text{gaseous products} \quad (2)$$



(3)

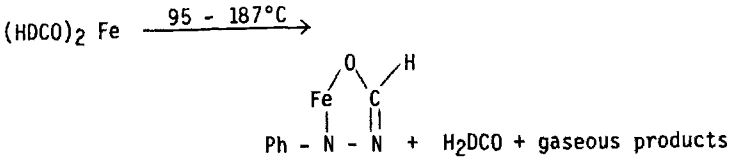


(4)

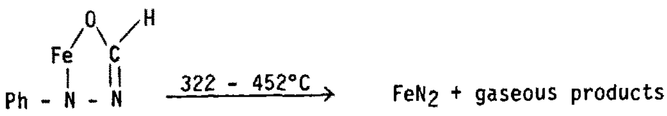


(5)

Ferrous diphenylcarbazonate [Fe(HDCO)$_2$]



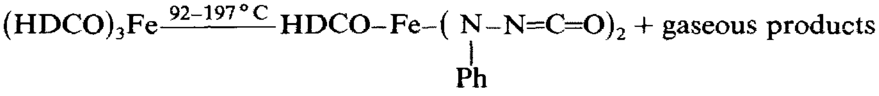
(6)



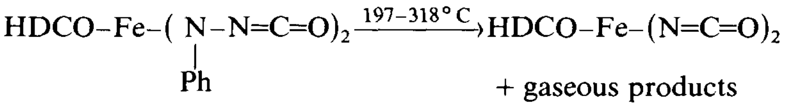
(7)

$$FeN_2 \xrightarrow{452-550\,°C} \tfrac{1}{4}Fe_4N + \text{gaseous products} \quad (8)$$

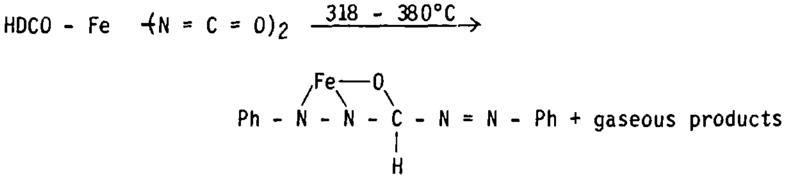
Ferric diphenylcarbazonate [Fe(HDCO)$_3$]



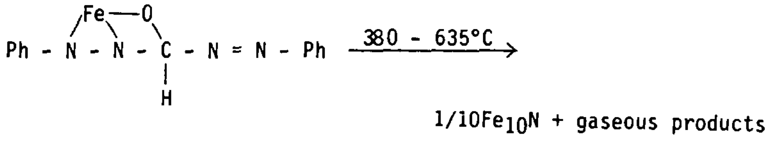
$$(HDCO)_3Fe \xrightarrow{92-197\,°C} HDCO\text{-}Fe\text{-}(\underset{\underset{Ph}{|}}{N}\text{-}N{=}C{=}O)_2 + \text{gaseous products} \quad (9)$$



$$\mathrm{HDCO{-}Fe{-}(\underset{Ph}{N}{-}N{=}C{=}O)_2 \xrightarrow{197-318\,°C} HDCO{-}Fe{-}(N{=}C{=}O)_2 + gaseous\ products} \qquad (10)$$



(11)



(12)

where it is known that the composition of the interstitial nitrides of iron varies considerably with temperature [11].

REFERENCES

1 H. Mimoun and C. Bocard, Fr. Demande 2175689; Chem. Abstr., 80 (1974) 145572.
2 S. Balt and E. van Dalen, Anal. Chim. Acta, 30 (1964) 434.
3 M.M. Hassanein, M.F.R. Fouda and R.S. Amin, Thermochim. Acta, 132 (1988) 265.
4 P. and E. Krumholz, Sitz. Ber. Akad. Wiss. Wien, 146(2B) (1937) 431.
5 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley-Interscience, London, 3rd edn., 1972, p. 566.
6 A.N. Speca, N.M. Karayanis and L.L. Pytlewski, Inorg. Chim. Acta, 9 (1974) 87.
7 A.N. Speca, N.M. Karayanis and L.L. Pytlewski, J. Inorg. Nucl. Chem., 36 (1974) 1227.
8 A.N. Speca, L.L. Pytlewski, C. Owens and N.M. Karayanis, J. Inorg. Nucl. Chem., 38 (1976) 1119.
9 P. Gutlich, Struct. Bond., 44 (1981) 85.
10 C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, London, 1962, p. 252.
11 A.F. Wells, Structural Inorganic Chemistry, Oxford University Press, London, 1975, p. 1058.