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MÖSSBAUER SPECTROSCOPIC STUDIES OF THERMAL DECOMPOSITION OF SUBSTITUTED PENTACYANOFERRATE(II) COMPLEXES

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Abstract

The thermal behaviour of substituted pentacyanoferrates(II) of the type $Na_3[Fe(CN_5)L]\cdot xH_2O$, where *L*=*n*-, *sec*-, *tert*- or *iso*-butylamine, *di-iso*-butylamine or *tri-n*-butylamine, was investigated with the aid of Mössbauer spectroscopy, XRD and TG-DTG-DTA. The Mössbauer spectra of these complexes exhibit a quadrupole doublet with ΔE_Q=0.70–0.83 mm s^{-1} at room temperature. The isomer shift, δ=0.00±0.03 mm s^{-1} suggests that the iron atom is in the +2 low-spin state. The complexes start to decompose at 50°C, yielding a residual mass of 5.8 –21.3% in the temperature range 900–950°C. The Mössbauer spectra recorded after heating at 150 and 300°C exhibit an asymmetric doublet, suggesting partial decomposition. The Mössbauer spectra at higher temperature are complex. At different stages of the thermal process, the presence of α-Fe_2O_3, γ-Fe_2O_3, α-Fe, Fe_3C and Fe_3O_4 was demonstrated.

Keywords: iron complex, Mössbauer spectroscopy, pentacyanoferrate(II), thermal decomposition

Introduction

Extensive Mössbauer spectroscopic studies of substituted pentacyanoferrate(II) complexes of the type $[Fe(CN)_5L^n]^{(3-n)-}$ (where *L*=H_2O, NH_3, NO^+or RNH_2) have been carried out [1–5]. Earlier, we investigated several alkyl and arylamine-substituted pentacyanoferrate(II) complexes [6, 7]. Monaghan and Fanning [3] rationalized the linear correlation of the Mössbauer parameters on the basis of the σ–π interactions of the ligands. Thermal decomposition studies of the simple complex cyanide suggested cyanogen release with the evolution of nitrogen and the formation of metal carbides [8–10]. Brar and Varma [11] studied the thermal decomposition products of sodium pentacyanoferrate(II) by us-

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ing Mössbauer spectroscopy. Sileo *et al.* [12] investigated the thermal behaviour of pentacyanoligandferrate(II) complexes with *L*=pyrazine or pyridine and proposed water release and the final formation of metal carbide. Recently, Araujo *et al.* [13] reported on spectroscopic and substitution kinetic studies of complexes of pentacyanoferrate(II) with sulphur heterocyclic ligands.

In the present communication, we report the synthesis of substituted pentacyanoferrate(II) complexes $Na_3[Fe(CN)_5L]\cdot xH_2O$, where *L*=*n*-butylamine (N-Bu), *sec*-butylamine (*sec*-Bu), *tert*-butylamine (*tert*-Bu), *iso*-butylamine (i-Bu), *di-iso*-butylamine (*di-iso*-Bu), *di-sec*-butylamine (*di*-s-Bu) or *tri-n*-butylamine (*tri-n*-Bu). The complexes have been characterized by elemental analysis, infrared spectroscopy, Mössbauer spectroscopy and XRD. An attempt has been made to identify intermediates and final products of the thermal decomposition by employing TG, DTG, DTA, XRD and Mössbauer spectroscopy.

Experimental

All reagents used were of AR, GR or high-purity grade. The complexes were prepared by modifying the procedure adopted by Monaghan and Fanning [3] and Altabef *et al.* [14] as follows:

(1) Preparation of *n*-, *sec*-, *tert*- and *iso*-butylamine-substituted pentacyanoferrate(II): 3 g sodium pentacyanonitrosylferrate(II) and 2 g sodium acetate were dissolved in 20 ml ethanol–water (1:1) and the resulting solution was mixed with an ice-cold solution of amine (20–25 ml) in absolute ethanol. The solution was continuously stirred for 3–4 h and additional amine was added until a negative test for sodium pentacyanonitrosylferrate(II) was obtained. The precipitate was obtained by adding cold absolute alcohol. The complexes were filtered off and dried in vacuo over $CaCl_2$.

(2) Preparation of *di-iso*-, *di-sec*- and *tri-n*-butylamine-substituted pentacyanoferrate(II): A solution containing 0.47 g hydroxylamine hydrochloride and 0.54 g NaOH in 20 ml water was prepared. Then, 10 ml of the respective amine was added. The mixture was kept in ice for 1 h and was then added dropwise to an ice-cold solution of 2 g sodium pentacyanonitrosylferrate(II) in 20 ml water. In each case, an oily layer separated after the addition of cold alcohol. The complexes were forced to solidify by thorough washing with absolute ethanol and then drying for 24 h over conc. H_2SO_4 in a desiccator.

The complexes were characterized by elemental analysis (C, H and N). The contents of water molecules were adjusted according to the molecular formula.

Physical measurements

Mössbauer spectra were recorded on a transducer-driven Mössbauer spectrometer (ELSCINT) in constant acceleration mode at room temperature. A ~185 MBq $^{57}Co(Rh)$ source was used. The spectrometer was calibrated by using enriched iron foil. All isomer shift values were referred to metallic iron. The spectra were fitted with Lorentzian lines. Mössbauer spectra of thermal decomposition products were recorded after heating the complexes at different temperatures in a N_2 atmosphere in a tube furnace for 2 h, followed by quenching to room temperature.

Infrared spectra in KBr medium were recorded on an FTIR (HITACHI Nicolet) spectrophotometer. Thermogravimetric (TG-DTG-DTA) studies were carried out in a N_2 atmosphere, using a Seiko Instrument Inc.SSC/5200 at a heating rate of 10°C min^{-1}. XRD of the decomposition products were recorded by using a MAC Science MXP-18 automated diffractometer with CuK_α radiation.

Results and discussion

All the complexes are coloured solids that are stable under normal atmospheric conditions. Analytical data, electronic spectral bands and characteristic IR frequencies due to $\nu(C\equiv N)$, $\delta(Fe-CN)$ and $\nu(Fe-C)$ are listed in Table 1. The Mössbauer spectra of all the complexes exhibit a well-resolved quadrupole doublet at room temperature. Typical Mössbauer spectra of the *n*-Bu, *iso*-Bu, *tert*-Bu, *di-iso*-Bu and *tri-n*-Bu-substituted pentacyanoferrate(II) complexes at room temperature and after heating at different temperatures are shown in Figs 1, 2, 3, 4 and 5 respectively. Mössbauer parameters at room temperature and different temperatures are listed in Table 2. Also given in Table 2 are the percentages of iron species formed during decomposition. TG, DTG and DTA plots of the *n*-Bu, *iso*-Bu, *tert*-Bu, *di-iso*-Bu and *tri-n*-butylamine-substituted pentacyanoferrates(II) are shown in Figs 6 and 7. Their respective thermogravimetric data are listed in Table 3.

When one of the cyano ligands in $[Fe(CN)_6]^{4-}$ is replaced by a neutral ligand to give $[Fe(CN)_5L]^{3-}$, the octahedral geometry remains unaffected, but the symmetry is lowered from O_h to approximately C_{4v}. Even though the electronic configuration will be t_{2g}^{6}, it will be further split into d_{yz}, d_{xz} and d_{xy} (also called e and b_2) [3, 6]. All the complexes are expected to be diamagnetic. All amines are essentially σ-donors. The five CN ligand, however, have vacant $\Pi^{*}_{2\,\beta,2p_z}$ orbitals available for bonding, while no such orbital is available in the amine. X-ray structure determination of sodium pentacyanonitrosylferrate(II) has shown that the sixth ligand (NO^+) and the trans CN^- are approximately collinear with the central Fe atom, which is slightly displaced in the direction of the NO^+ ligand from the plane of the four CN^- ligands [15, 16].

Electronic spectra

The electronic spectra of spin-paired octahedral complexes are characterized by transitions from a singlet ground state ($^1A_{1g}$) to one-electron excited states $^1T_{1g}$ and $^1T_{2g}$. Since the t_{2g} orbitals are filled, lower energy transitions are not possible. The reflectance spectra of all the complexes exhibit two bands, an in-

Table 1 Analytical, electronic spectral bands and IR frequencies of substituted pentacyanoferrates(II)

Complex	Found (calc.) %			Electronic spectral bands/cm^{-1}		IR frequencies/cm^{-1}		
	C	H	N			ν(CN)	δ(Fe–CN)	ν(Fe–C)
$Na_3[Fe(CN)_5((n\text{-}C_4H_9NH_2)]\cdot 2H_2O$	30.59 (29.75)	3.75 (3.85)	23.07 (23.14)	20000	25000	2045s	575s	430m
$Na_3[Fe(CN)_5(i\text{-}C_4H_9NH_2)]\cdot 3H_2O$	28.07 (28.34)	3.49 (4.19)	21.92 (22.04)	20410	25000	2051s, 2025w	575s	425w
$Na_3[Fe(CN)_5(s\text{-}C_4H_9NH_2)]\cdot 3H_2O$	29.21 (28.34)	4.98 (4.19)	21.21 (22.04)	20000	24300	2054s	565s	430w
$Na_3[Fe(CN)_5(t\text{-}C_4H_9NH_2)]\cdot 3H_2O$	29.16 (28.34)	4.22 (4.19)	22.95 (22.04)	20410	25640	2175s, 2145m, 2060m, 1940w	570s	415m
$Na_3[Fe(CN)_5\{(i\text{-}C_4H_9)_2NH\}]\cdot 2H_2O$	37.90 (37.23)	5.82 (5.25)	19.42 (20.04)	20000	25000	2046s, 2015m	570s	430w
$Na_3[Fe(CN)_5\{(s\text{-}C_4H_9)_2NH\}]\cdot 3H_2O$	34.65 (35.68)	5.63 (5.49)	20.88 (19.21)	20000	24390	2045s 2015m	570m	430s
$Na_3[Fe(CN)_5\{(n\text{-}C_4H_9)_3N\}]\cdot 4H_2O$	39.45 (39.82)	6.41 (6.83)	16.41 (16.39)	19920	23890	2045s 2015m	570m	435w

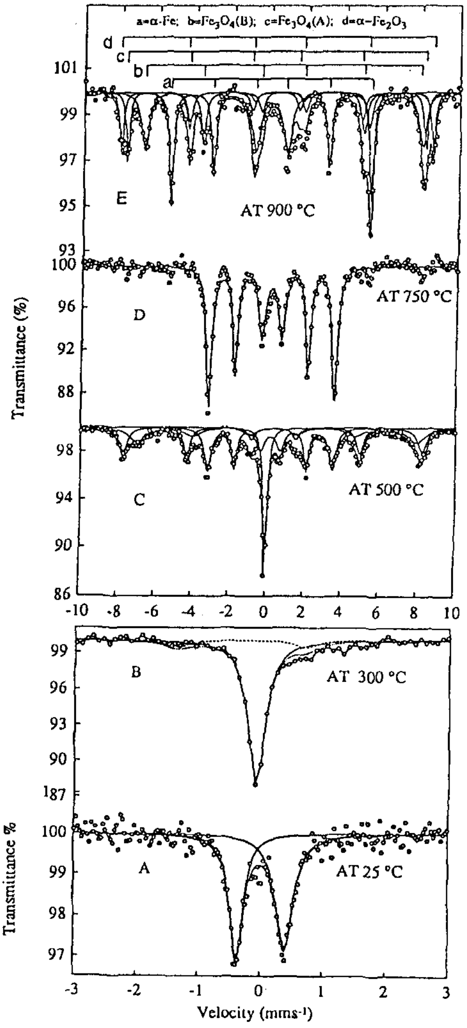

Fig. 1 Mössbauer spectra of *n*-butylamine-substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 300°C, (C) 500°C, (D) 750°C and (E) 950°C for 2 h

tense band at 25000 cm^{-1} and a weak shoulder at 20000 cm^{-1}, corresponding to the transitions $^1A_{1g}\rightarrow{}^1A_2$ and $^1A_1\rightarrow E(2)$, respectively. Toma *et al.* [17] have reported a band due to $^1A_1\rightarrow E(1)$ in pentacyanoferrate(II) complexes. It is expected that the band position of the transition $^1A_{1g}\rightarrow{}^1A_2$ is hardly affected by the variation in the axial amine ligand, whereas the other transition, $^1A_{1g}\rightarrow E(2)$, may vary with the nature of the ligand. Araujo *et al.* [18] have proposed a linear correlation between the Mössbauer isomer shift and the tetragonal distortion caused by the ligand *L*.

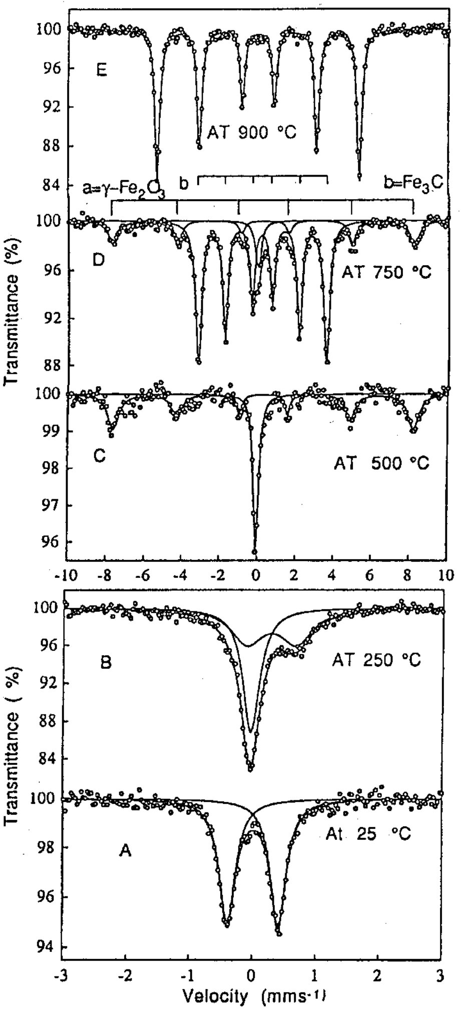

Fig. 2 Mössbauer spectra of *iso*-butylamine-substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 250°C, (C) 500°C, (D) 750°C and (E) 900°C for 2 h

Infrared spectra

Various vibrational modes were assigned by comparison with those for other substituted pentacyanoferrate(II) complexes [19–22]. The most intense band due to ν(C≡N) was observed in the range 2175–2045 cm^{-1}. Earlier, three modes have been observed for ν(*C*≡N) of some *di-* and *tri*-alkylamine-substituted pentacyanoferrate(II) complexes [4]. In the present work, we have observed two bands at ~2045 and 2015 cm^{-1} for ν(C≡N) in all substituted complexes except

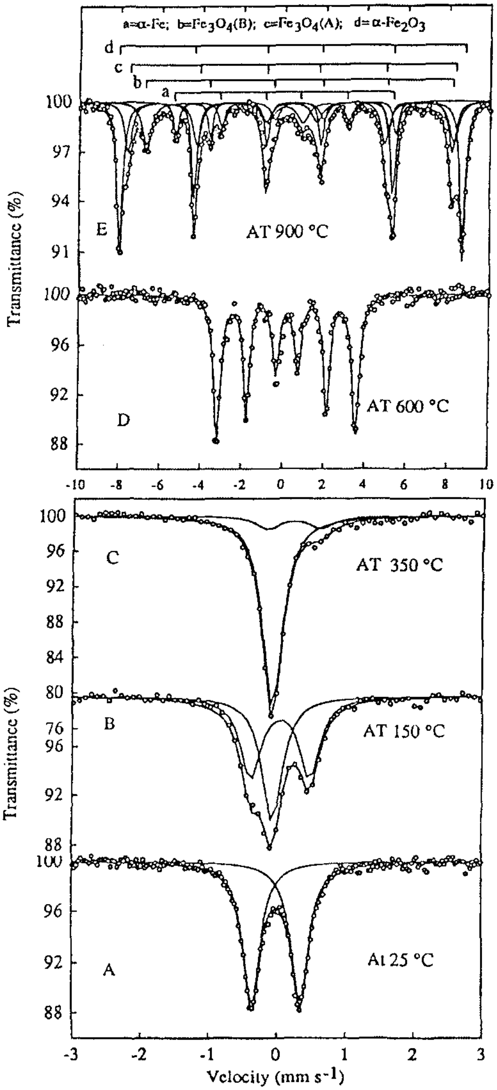

Fig. 3 Mössbauer spectra of *tert*-butylamine-substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 150oC, (C) 350°C, (D) 600°C and (E) 900°C for 2 h

the *tert*-butylamine-substituted complex, where four bands were observed at 2175, 2145, 2060 and 1490 cm^{-1}. Three of these bands are at frequencies higher or lower by 100 cm^{-1} as compared with the normal ν(C≡N) mode observed at 2040 cm^{-1}, suggesting some difference in bonding characteristics in this complex. Another characteristic mode of medium intensity, due to δ(Fe –CN), is ob-

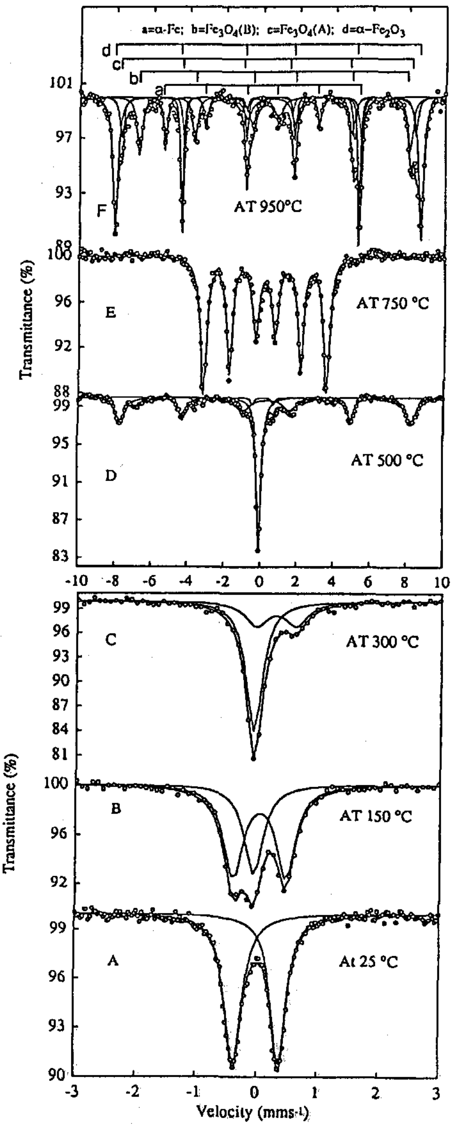

Fig. 4 Mössbauer spectra of *di-iso*-butylamine-substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 150°C, (C) 300°C, (D) 500°C and (E) 750°C and (F) 950°C for 2 h

served at ~560±5 cm^{-1}. A very weak band in the range 495–415 cm^{-1} has been assigned to ν(Fe–C), in accordance with the assignments of Fluck *et al.* [21]. The stretching mode Fe–N could not be assigned, as this is expected to be observed at ~250 cm^{-1}. An intense weak broad peak in the region 3575 –3445 cm^{-1} arose

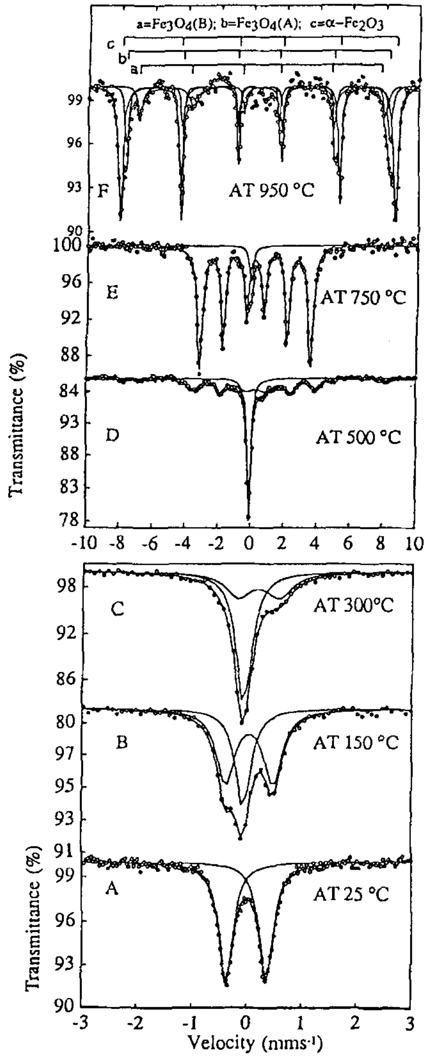

Fig. 5 Mössbauer spectra of *tri-n*-butylamine-substituted pentacyanoferrate(II) complex at (A) room temperature and after heating at (B) 150°C, (C) 300°C, (D) 500°C and (E) 750°C and (F) 950°C for 2 h

mainly from weakly bonded water molecules in the lattice. The exact assignment of various bands in this region was not possible, due to several overtones and combinations of bending vibrations. Similarly, a sharp to medium band at ~1600 cm^{-1} has been assigned to a bending mode of H_2O. It may be noted that ν(C≡N), ν(Fe–C) and δ(Fe–CN) remain unaffected by the substitution on the butylamine isomers in pentacyanoferrate(II) complexes.

Mössbauer parameters

The room-temperature Mössbauer spectra of all the complexes exhibit a well-resolved quadrupole doublet with ΔE_Q=0.70–0.83 mm s^{-1}. The data in Table 2 reveal that the δ values for all the complexes are in the narrow range 0.00±0.03 mm s^{-1} with respect to α-Fe. These are well within the typical range for the iron(II) low-spin state in octahedral geometry [23]. The δ values for all the substituted pentacyanoferrate(II) complexes are nearly the same, suggesting

Table 2 Mössbauer parameters for substituted pentacyanoferrate(II) and its thermal decomposition products

Complex* L	T/ °C	δ**/ mm s^{-1}	ΔE_Q**/ mm s^{-1}	H_{eff}**/ kOe	Possible products	% of iron species
n-$C_4H_9NH_2$	25	0.02	0.77	–	–	
	300	0.20	1.10	–	–	
		–0.02	–	–	–	
	500	0.30	0.05	496	Fe_3O_4(A)	25
		–0.42	–0.15	464	Fe_3O_4(B)	24
		0.16	0.01	207	Fe_3C	35
		–0.07	–	–	–	16
	750	0.19	0.00	209	Fe_3C	100
	950	0.36	0.13	517	α–Fe_2O_3	16
		0.00	0.02	331	α–Fe	43
		0.26	0.02	494	Fe_3O_4(A)	16
		0.65	0.02	460	Fe_3O_4(B)	25
i-$C_4H_9NH_2$	25	0.01	0.80	–	–	
	300	0.53	2.17	–	–	
		–0.05	–	–	–	
	500	0.30	0.02	492	γ–Fe_2O_3	65
		–0.06	–	–	–	35
	750	0.31	0.08	494	γ–Fe_2O_3	19
		0.18	0.01	207	Fe_3C	75
		–0.03	–	–	–	6
	900	0.00	–	331	α–Fe	100
s-$C_4H_9NH_2$	25	0.03	0.80	–	–	
	300	0.00	1.35	–	–	
		–0.01	–	–		
	500	0.30	0.04	493	Fe_3O_4(A)	40
		0.47	0.25	441	Fe_3O_4(B)	13
		0.19	0.04	210	Fe_3C	23
		–0.06	–	–	–	24
	750	0.19	0.01	208	Fe_3C	81
		–0.02	0.02	332	α–Fe	12
		–0.04	–	–	–	7
	950	0.37	0.13	518	α–Fe_2O_3	43
		0.04	0.03	333	α–Fe	23
		0.32	0.01	495	Fe_3O_4(A)	18
		0.61	0.05	463	Fe_3O_4(B)	16

Table 2 Continued

Complex* L	T/ °C	δ**/ mm s^{-1}	ΔE_Q**/ mm s^{-1}	H_{eff}**/ kOe	Possible products	% of iron species
(i-$C_4H_9)_2NH$	25	–0.01	0.74	–	–	
	150	0.03	0.86	–	–	
		–0.06	–	–	–	
	300	0.28	0.66	–	–	
		–0.07	–	–	–	
	500	0.29	0.05	495	γ–Fe_2O_3	57
		0.04	0.12	206	Fe_3C	7
		–0.06	–	–	–	37
	750	0.19	0.01	209	Fe_3C	100
	950	0.37	0.12	520	α–Fe_2O_3	41
		0.03	0.04	333	α–Fe	18
		0.36	0.04	500	Fe_3O_4(A)	14
		0.64	0.08	460	Fe_3O_4(B)	27
(n-$C_4H_9)_3N$	25	0.00	0.74	–	–	
	150	0.05	0.87	–	–	
		–0.06	–	–	–	
	300	0.21	0.75	–	–	
		–0.06	–	–	–	
	500	0.28	0.06	228	Fe_3C	61
		–0.07		–	–	39
	750	0.19	0.01	209	Fe_3C	95
		–0.06		–	–	5
	950	0.37	0.13	518	α–Fe_2O_3	55
		0.32	0.01	496	Fe_3O_4(A)	24
		0.61	0.05	463	Fe_3O_4(B)	21

* Complex: $Na_3[Fe(CN)_5L]$

**Errors in δ and ΔE_Q values are ±0.02 mm s^{-1} and for H_{eff} it is ± kOe;

δ=Isomer shift, ΔE_Q=Quadrupole spliting

that the variation in the butylamine ligand does not have a significant effect on the s-electron density at the Fe nucleus. For the *di-sec-*, *di-iso-* and *tri-n-*butylamine-substituted pentacyanoferrate(II) complexes, the δ values are identical, which suggest that the basic character of the amine does not affect the δ-donor property of bulky amine ligands.

Since the six $3d$ electrons form a closed shell (t_{2g}^6), no quadrupole splitting is expected due to the valence shell electronic configuration. However, substitution with the butylamine ligands causes a distortion of the octahedral geometry. Hence, ΔE_Q is a direct measure of the distortion due to the ligand contribution, although a small electronic contribution may also be expected due to the further lifting of degeneracy in the t_{2g} level, as suggested by Manoharan and Gray [24] for sodium pentacyanonitrosylferrate(II). All the ΔE_Q values fall in the narrow range 0.70–0.83 mm s^{-1}. The average quadrupole splitting for all the complexes is 0.76 mm s^{-1}. All ΔE_Q values are <1 mm s^{-1}, which is comparable to those for primary and secondary amine-substituted pentacyanoferrate(II) complexes [2–4]. It is postulated that, since the alkylamines are only σ-bonded, the d_π orbitals of iron remain distributed among the five CN^- ligands only. Hence, the nature of the alkylamine isomer does not cause any change in the ΔE_Q values.

Thermal decomposition studies

Mössbauer spectroscopy is a good tool for examining the various iron species formed during the decomposition of an iron complex. It is possible to distinguish not only between Fe^{2+} and Fe^{3+} species, but also between their modes of coordination (tetrahedral or octahedral). The parameters used are the isomer shift, quadrupole splitting and hyperfine field. By means of these parameters, earlier researchers [9–11] were able to identify the different iron species in iron complexes. Several workers [9–12] were able to identify the different iron species in iron complexes. Several workers [9–12] have studied the thermal decomposition behaviour of substituted pentacyanoferrate(II) complexes. Ganguli and Bhattacharya [25] concluded that Prussian blue exhibits semiconducting behaviour in the temperature range 30–150°C, with three different stages of hydration. Inoue *et al.* [26] recently reported on the thermal decomposition of Prussian blue

Table 3 Thermogravimetric data for substituted pentacyanoferrates(II) $Na_3[Fe(CN)_5L]\cdot xH_2O$ complexes

Complex *L*	DTG peak/ °C	Decomposition process	$T_{\mathrm{Constant\ Wt}}$/ °C	Final mass/%
n-$(CH_2)_4NH_2$	180, 485, 930	fast, slow, fast three stages	945	21.2
i-$(CH_3)_2CHCH_2NH_2$	188, 485, 905	fast, slow, fast three stages	940	15.9
s-$CH_3CH_2CH(CH_3)NH_2$	75, 325, 530, 905	fast, slow, slow, fast four stages	940	21.3
t-$(CH_3)_3C$-NH_2	120, 325, 470, 860	fast, slow, slow, fast four stages	895	21.0
(*n*-$C_4H_9)_2NH$	55, 120, 500, 905	fast, slow, slow, fast four stages	970	17.4
(*i*-$C_4H_9)_2NH$	80, 130 575, 915	fast, slow, slow, fast four stages	950	5.8
(*s*-$C_4H_9)_2NH$	65, 125, 560, 910	fast, slow, slow, fast four stages	960	17.7
(*n*-$C_4H_9)_3N$	65, 130, 585, 890	fast, fast, slow, fast four stages	950	18.8
(*i*-$C_4H_9)_3N$	60, 115, 600, 905	fast, fast, slow, fast four stages	940	6.1

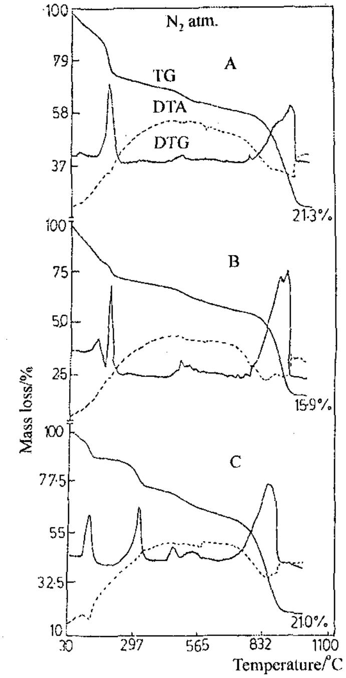

Fig. 6 Typical TG, DTG and DTA plots of (A) *n*-butylamine, (B) *iso*-butylamine and (C) *tert*-butylamine-substituted pentacyanoferrate(II) complexes

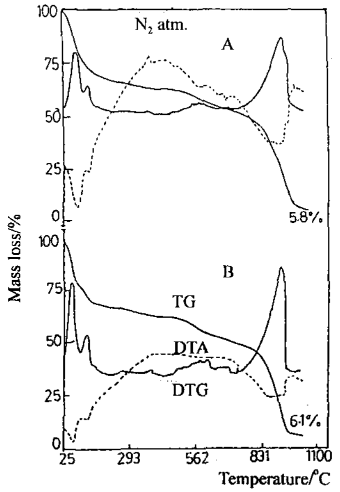

Fig. 7 Typical TG, DTG and DTA plots of (A) *di-iso*-butylamine and (B) *tri-n*-butylamine-substituted pentacyanoferrate(II) complexes

and identified various products by Mössbauer spectroscopy. Robinett and Collins [27] suggested that the cyanide ligands in Prussian Blue readily rotate on pyrolysis above 300°C to yield ferrous ferricyanide with intermediate iron sites.

TG, DTG and DTA curves of substituted pentacyanoferrate(II) complexes are shown in Figs 6 and 7. The data in Table 3 suggest that all the complexes start to decompose at 50°C and yield the final stable product with 5.8–21.2% residual mass at 900–950°C. In all cases, multistage decomposition occurs, as evidenced by the number of DTG peaks (Figs 6 and 7). The thermal decomposition behaviour of the various butylamine, dibutylamine and tributylamine-substituted pentacyanoferrate(II) complexes may be divided into three groups:

Monobutylamine (isomers of butylamine)-substituted pentacyanoferrates(II)

The TG, DTG and DTA curves of *n*-Bu, *iso*-Bu and *tert*-butylamine-substituted pentacyanoferrates(II) reveal multistage decomposition. In the first stage, fast decomposition occurs at around 100°C. It later slows down, passing through different stages and ultimately yielding the stable end-product at 900–950°C. For the *n*-Bu and *iso*-Bu-substituted complexes, two sharp DTG peaks appear at 180 and 930°C. In the case of the *tert*-Bu-substituted complex, a four-stage decomposition occurs (Fig. 6C). In the first stage, water molecules are lost and in the later stages ligand and cyanogen gas may be released [12]. There is also a possibility that some interaction may proceed in the reaction vessel at higher temperature, as proposed by Sileo *et al.* [12]. Since these thermograms were recorded in N_2 atmosphere, the only possibility is participation of the C atoms of the amine ligand, leading to the further evolution of $(CN)_2$ gas rather than simple ligand release.

The Mössbauer spectrum of the *tert*-butylamine-substituted pentacyanoferrate(II) complex heated at 150°C for 2 h exhibits an asymmetric doublet (Fig. 3B), which may be further resolved into a quadrupole doublet (ΔE_Q= 0.85 mm s^{-1} and δ=0.05 mm s^{-1}) and a singlet with δ=–0.06 mm s^{-1}. On further heating at 250–350°C, all these complexes afford an asymmetric doublet and singlet (Figs 1B, 2B and 3C). In all these complexes, both ΔE_Q and δ values are higher than those at room temperature. This may correspond to Fe(III) and Fe(II) both being in a low-spin state, presumably due to partial decomposition. In this process, water and ligand may be released [12]. The mass loss suggests the complete removal of the water molecules; this is supported by the infrared spectra, in which the intensity of the absorption band due to water decreases as compared to that for cyanide. The removal of the coordinated water changes the *s*-electron density at the iron nucleus. The dehydration of pentacyanoferrates(II) affects the crystal structure of the complexes without changing the octahedral geometry of the iron nucleus. The isomer shift of potassium hexacyanoferrate(II) trihydrate increases on dehydration [29]. A similar trend is observed in the present case.

When the *n*-Bu and *iso*-Bu-substituted complexes were heated at 500°C, drastic changes occurred in the Mössbauer spectra (Figs 1C and 2C), as 9 lines with a singlet were found. Computer fitting showed that around 49%, 35% and 16% of the iron corresponds to Fe_3O_4, Fe_3C and $Fe(CN)_2$ (Table 2). However, the Mössbauer spectrum is complex in the *n*-butylamine-substituted case and may be resolved into three set of sextets with H_{eff}=490, 464 and 207 kOe. These may correspond to the formation of mixed metal carbide phases along with Fe_3O_4 [30]. In the case the of *tert*-Bu-substituted complex at 600°C, the Mössbauer spectrum involves only a six-line pattern with δ=0.19 mm s^{-1} and H_{eff}= 209 kOe, suggesting the formation of Fe_3C. The XRD pattern pointed to the formation of Fe_3C.

At 750°C, the Mössbauer spectra of all the butylamine-substituted complexes, where two sextets appeared, corresponding to the formation of metal carbide Fe_3C with maghemite γ-Fe_2O_3 or α-Fe, except for the *n*-butylamine-substituted complex, where a sextet appeared, corresponding to the formation of metal carbide Fe_3C. The sextets due to Fe_3O_4 that are obtained at 500°C are missing in Fig. 1D, which indicates that the complexes undergo a change at 750°C.

Between 780 and 940°C, the TG curve reveals a large mass loss, in agreement with the inflection in the DTA curve, which indicates the beginning of an exothermic reaction with a maximum at ~940°C. After 900°C, the mass loss is constant indicating that stable end-products may be formed. In order to identify the end-products, the complexes were heated at 950°C. The Mössbauer spectra at 950°C (Figs 1E, 2E and 3F) were different from those at 750°C, which were complex. The complex spectrum may be resolved into three sextets with H_{eff}=520, 490, 460 and 330 kOe. These may correspond to the formation of α-Fe_2O_3, Fe_3O_4 (A and B) and α-Fe, except in the case of the *iso*-butylamine-substituted complex, where only α-Fe is formed, as demonstrated by only one sextet with H_{eff}=330 kOe. This is supported by the XRD pattern of the end-product in the case of *iso*-butylamine. The Mössbauer spectrum of one of the end-products is that of magnetite (Fe_3O_4), which is a spinel ferrite $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$. It has been reported that a fast electron transfer process take place between Fe^{2+} and Fe^{3+} at the octahedral sites at higher temperature. However, at lower temperature, the iron has discrete valence states and the material has an orthorhombic crystal structure. The temperature dependences of site A(Fe^{3+}) and site B (Fe^{2+}, Fe^{3+}) have been reported within the range 300–800 K [32].

Di-butyl-substituted pentacyanoferrate(II)

The *di-iso*-butylamine-substituted complex yields a similar δ-value (–0.002 mm s^{-1}) but a slightly smaller quadrupole splitting (ΔE_Q=0.74 mm s^{-1}) as compared to the *iso*-butylamine-substituted complex. This suggests varying distortion in octahedral geometry, which may be correlated with the σ-bonding the bulky subtituents. When the complex is heated at 150 and 300°C, its Mössbauer spectra exhibit an asymmetric doublet (Figs 4B and 4C), which may be resolved into a quadrupole doublet (ΔE_Q=0.86, 0.66 mm s^{-1} and δ=–0.06, –0.07 mm s^{-1}) and a single (δ=–0.06 and –0.07 mm s^{-1}). At 500°C, two sextets (Fig. 4D) with magnetic hyperfine splitting (H_{eff}=495 and 206 kOe) and a singlet (δ=0.06 mm s^{-1}) are observed, presumably due to the formation of maghemite γ-Fe_2O_3 [31], Fe_3C and $Fe(CN)_2$ [30]. On further heating at 750°C, a six-line pattern is observed, with a sextet due to the formation of Fe_3C (H_{eff}=209 kOe). At this temperature, the magnetic phase formed at 500°C has disappeared completely. In order to confirm the identity of the end-products, the *di-iso*-butylamine-substituted complex was heated at 950°C. The Mössbauer spectrum was very complex: it may be resolved into four sextets, with H_{eff}=520, 333, 500 and 460 kOe. These may correspond to the formation of α-Fe_2O_3, α-Fe, Fe_3O_4 (A) and Fe_3O_4 (B) respectively.

Tri-n-butylamine-substituted pentacyanoferrate(II)

When the *tri-n*-butylamine-substituted complex is heated at 150°C, it affords an asymmetric doublet (Fig. 5B), which can be resolved into a doublet with increased Mössbauer parameters and a singlet with a reduced δ value, suggesting partial decomposition. It seems that an iron state in a somewhat symmetric environment is formed. This is corroborated by the Mössbauer spectrum at 300°C exhibiting an asymmetric doublet that may be resolved into a doublet and a singlet. At 500°C, there is a six-line pattern with hyperfine splitting (H_{eff}=288 kOe) presumably due to the carbide phase Fe_xC, and a singlet with δ=–0.07 mm s^{-1}. Kraan and Niemantsverdriet [30] reported that the Fe_xC phase is always accompanied by iron metal and hence a higher value of the internal magnetic field. At 750°C, a well-defined sextet with H_{eff}=209 kOe suggests the formation of iron carbide. On further heating upto 950°C, the Mössbauer spectrum exhibits three sextets with H_{eff}=518, 496 and 463 kOe. This shows that the final product is mixture of haematite and magnetite.

Conclusions

The joint use of thermal techniques, Mössbauer spectroscopy and X-ray diffraction allowed us to study the thermal decomposition of alkylamine-substituted pentacyano-ferrates(II) in N_2 atmosphere from room temperature to 950°C. Three or four different stages have been found for these pentacyanoferrate(II) complexes: dehydration, ligand removal and oxidation-reduction. These studies suggest that the thermal decomposition involves first the release of water and ligand at 150 and 280–350°C, respectively. At 500°C, a mixture of metal carbide and magnetite is formed. On further heating at 750 and 950°C, the product is the mixed metal carbide and a mixture of ferrite, α-Fe and α-Fe_2O_3 with different particle sizes.

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