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THERMOLYSIS OF COMPLEX CYANIDES, XX. THERMAL DECOMPOSITION OF $Zn[Fe(CN)_5NO]\cdot 3H_2O$ AND IDENTIFICATION OF THE PRODUCTS OF DECOMPOSITION

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The thermal decomposition of $Zn[Fe(CN)_5NO]$ was studied by thermal analysis, IR and Mössbauer spectroscopy. The experimental results showed that the decomposition starts with cyanogen formation, giving a tetracoordinated cyano-nitrosyl intermediate. The NO ligand elimination is followed by a structural rearrangement to $Fe[Zn(CN)_4]$.

It was previously observed that some of the mixed ligand nitrosyl complexes decompose in exothermic reactions. The dinitrogen content of the gases evolved suggested that the exothermic effect was a consequence of a redox reaction between the NO ligand and the other part of the complexes [1–6]. However, the exothermic peaks in the DTA curve of $Zn[Fe(CH)_5NO]$ can not be interpreted in terms of an intramolecular redox reaction of the NO ligand, for stoichiometric nitrogen monoxide is found in the gases evolved. To elucidate the reasons for the exothermic effects, the decomposition processes of $Zn[Fe(CN)_5NO]\cdot 3H_2O$ have been investigated by different methods (IR and Mössbauer spectroscopy).

Results of thermal and spectroscopic investigations

The water of the pale brick-red $Zn[Fe(CN)_5NO]\cdot 3H_2O$ is lost in a strong endothermic step at 160° (Fig. 1)*. The decomposition of the anhydrous complex

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* According to Brennan et al. [7], the complex has only two moles of crystal water, which are evolved at 94°. The great difference between the temperature data is due to the fact that Brennan et al. give the temperature of the starting point of the process, while the DTA peak temperature relating to the highest decomposition rate is given in our paper, as reported in [8].

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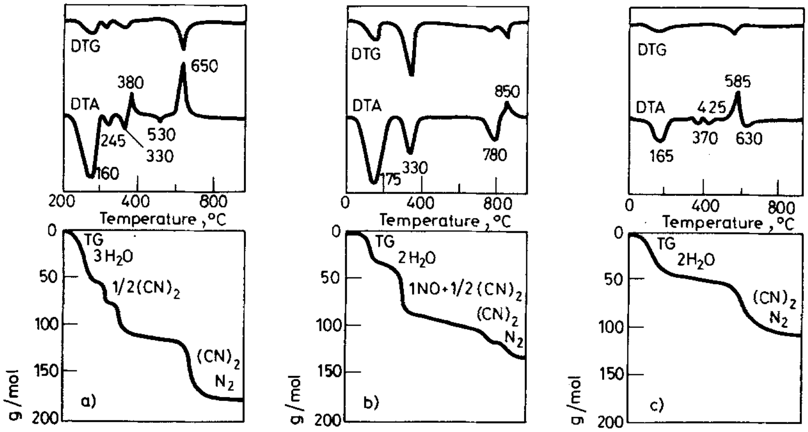

Fig. 1 TG, DTG and DTA curves of $Zn[Fe(CN)_5NO]\cdot 3H_2O$ (a), $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ (b) and $Fe[Zn(CN)_4]\cdot 2H_2O$ (c)

Table 1 Thermal and stoichiometric data on the thermolysis of $Zn[Fe(CN)_5NO]\cdot 3H_2O$

Decomposition temperature, °C	m_{found}, $g\cdot mol^{-1}$	Decomposition products, mol^{-1}	$m_{\text{theoretical}}$, $g\cdot mol^{-1}$	DTA peak
160	55.4	$3\,H_2O$	54.0	strong, wide, endo
245	25.9	$1/2\,(CN)_2$	26.0	moderate, flat, endo
330	29.8	1 NO	30.0	moderate, sharp, endo
380	—	structural	—	strong, sharp, exo
530	—	rearrangements	—	weak, sharp, endo
650	54.2	$1/3\,(CN)_2+$ $+4/3\,N_2$	54.6	very strong, sharp, exo

proceeds via the elimination of half a mole of cyanogen and the nitrogen monoxide in two steps (245 and 330°). It can be seen in Fig. 1b that dehydration of the sodium compound occurs at higher temperature (175°). The cyanogen and the nitrogen monoxide evolve in one step (330°). This is in accordance with the higher stability of the strict ionic structure of the alkali metal complex, as expected. (According to the data in Table 2, ν_{CN} and ν_{NO} for the zinc compound are larger than those for the sodium complex, which is a consequence of the appreciably covalent nature of $Zn[Fe(CN)_5NO]$).

The small difference between the molecular masses of the CN and NO group means that the leaving order of the two components can not be determined exactly from the TG curve alone.

For this reason, the IR spectra of the solid residue obtained by heating the compound to 245° and 330°, respectively, were recorded and compared with the IR spectrum of the undecomposed complex. Besides ν_{CN} for the original compound, another band of similar intensity appeared at lower frequency, but ν_{NO} was unchanged in the spectrum of the sample heated to 245° (Table 2). The large shift in ν_{CN}, which is expected due to the reduction of the central atom (cyanogen formation), is partially compensated by the increase in wavenumber as a consequence of the coordination number decrease. (The compensation is nearly complete for the NO ligand, which has a considerably higher sensitivity for $d\pi-p\pi$ back-donation.) The IR spectrum of the intermediate formed at 330° reveals ν_{CN} only at the lower wavenumber and does not show ν_{NO}. This means that the elimination of CN precedes that of the NO ligand. This assumption is supported by the Mössbauer spectroscopic investigation (Fig. 2), which gives other information on the structure of the intermediate.

Table 2 IR and Mössbauer spectroscopic data on $Na_2[Fe(CN)_5NO]\cdot 2H_2O$* and $Zn[Fe(CN)_5NO]\cdot 3H_2O$

Compound	δ_1	ΔE_Q	δ_2	ν_{CN}	ν_{NO}
		mm s^{-1}		cm^{-1}	
$Na_2[Fe(CN)_5NO]\cdot 2H_2O$	−0.62	1.70	—	*2150*	
				(2160, 2165)	*1945*
				2180	
$Zn[Fe(CN)_5NO]\cdot 3H_2O$	−0.64	1.91	—	*2195*	*1960*
Sample heated to:					
245°	−0.62	1.87	−0.45	2100, 2195	1955
330°	—	—	−0.46	2100	—

* The Mössbauer parameters in [9] were measured at liquid nitrogen temperature.

If the Mössbauer spectra of $Zn[Fe(CN)_5NO]\cdot 3H_2O$ and its solid residue heated to 245° are compared, a new absorption band can be observed. Since the isomer shift (δ_1) and the quadrupole splitting (ΔE_Q) of the original doublet are practically unchanged, it can be concluded that a proportion of the central atoms maintain their hexacoordinated position, but the chemical environment of the others is different from the primary one. (On the basis of peak areas, the mole ratios of the two iron complexes are considered to be equivalent.)

The data suggest that instead of the pentacoordinated compound expected from the results of the investigation by Schmidt and coworkers in solution [10], a "tetracoordinated" complex is formed during cyanogen production:

$$\mathrm{Zn[Fe(CN)_5NO]} \xrightarrow[\text{endo}]{245^\circ} 1/2\,\mathrm{Zn[Fe(CN)_5NO]} + \\ + 1/2\,\mathrm{Zn[Fe(CN)_3NO]} + 1/2\,\mathrm{(CN)_2} \qquad (1)$$

The decrease in the coordination number of the product is confirmed by the values of the isomer shifts (Fig. 2). The relation of the isomer shifts ($\delta_2 > \delta_1$) indicates the lower electron density at the iron nucleus (higher δ_2) in the compound formed in reaction (1), which is a consequence of the higher shielding effect of the *d* electron density, increased by the elimination of CN ligands.

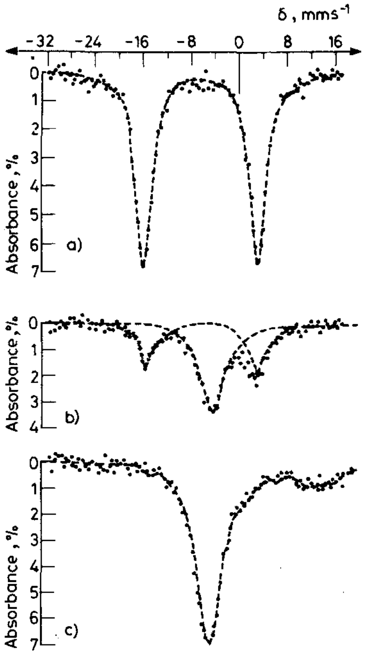

Fig. 2 Mössbauer spectra of $\mathrm{Zn[Fe(CN)_5NO]\cdot 3H_2O}$ (a) and its solid thermal residues at 245° (b) and at 330° (c)

The Mössbauer spectrum of the sample heated to 330° shows only a single absorption band and the isomer shift is almost identical to δ_2 in the former spectrum (Fig. 2). This indicates that the complex produced by NO loss at 380° contains only one type of iron(II):

$$1/2\,\mathrm{Zn[Fe(CN)_5NO]} + \\ + 1/2\,\mathrm{Zn[Fe(CN)_3NO]} \xrightarrow[\text{endo}]{330^\circ} \mathrm{Zn[Fe(CN)_4]} + \mathrm{NO} \qquad (2)$$

Both transition metal atoms in the intermediate can form complexes with cyanide. Since the tetrahedral zinc complex is more stable than the planar $Fe(CN)_4^{2-}$, the exothermic effect observed at 380° (without weight loss on TG) (Fig. 1) is presumed to result from the following ligand exchange reaction:

$$Zn[Fe(CN)_4] \xrightarrow[\text{exo}]{380^\circ} Fe[Zn(CN)_4] \tag{3}$$

To confirm this assumption, $Fe[Zn(CN)_4]$ was prepared in solution and its IR spectra and thermal curves were recorded (Fig. 1c). The IR spectra of the solid residue of $Zn[Fe(CN)_5NO]$ heated to 400° and that of $Fe[Zn(CN)_4]$ are identical ($\nu_{CN} = 2100$ cm^{-1}). The exothermic effect does not appear in the DTA curve of the latter compound (see Figs 1a and 1c). According to the TG curve (Fig. 1a), the mass of the intermediate $Fe[Zn(CN)_4]$ does not change between 400 and 600°. The endothermic peak at 530° can therefore be interpreted as a consequence of decomposition of the complex to $Fe(CN)_2$ and $Zn(CN)_2$:

$$Fe[Zn(CN)_4] \xrightarrow[\text{endo}]{530^\circ} Fe(CN)_2 + Zn(CN)_2 \tag{4}$$

Fe_3C is formed in the final stage of the decomposition. This was verified (confirming the results of the X-ray diffraction measurement of Seifer [11]) by identification of the ferromagnetism of the solid residue [1]. However, Zn_3N_2 is formed on the decomposition of $Zn(CN)_2$; this was identified by evolving NH_3 as a product of the alkaline hydrolysis of the dark-gray final product.

These compounds (Fe_3C and Zn_3N_2) can be formed by two different reactions:

$$Fe(CN)_2,\ Zn(CN)_2 \begin{cases} \nearrow 1/3\,(Zn_3N_2 + Fe_3C) + 1/3\,C + 5/3\,(CN)_2 & (5) \\ \searrow 1/3\,(Zn_3N_2 + Fe_3C) + 11/3\,C + 5/3\,N_2 & (6) \end{cases}$$

Cyanogen is evolved in process (5), and dinitrogen in the second route. The mass changes expected are 86.7 g mol^{-1} and 46.7 g mol^{-1}, respectively, whereas the measured value is 54.2 g mol^{-1} (Table 1). This means that reactions (5) and (6) occur simultaneously with the following stoichiometry:

$$Fe(CN)_2,\ Zn(CN)_2 \xrightarrow[\text{exo}]{650^\circ} 1/3\,(Zn_3N_2 + Fe_3C) + \\ + 3C + 1/3\,(CN)_2 + 4/3\,N_2 \tag{7}$$

The mass loss calculated from Eq. (7) shows good agreement with the measured one (Table 1). The very strong exothermic effect at 650° supports the proposed mechanism, as the formation of Fe_3C and Zn_3N_2 and the decomposition of cyanogen are exothermic processes and their reaction heats overcompensate the endothermic effect of the primary decomposition of the metal cyanides.

Experimental

The complex $Zn[Fe(CN)_5NO] \cdot 3H_2O$ was prepared by mixing equivalent solutions of $Na_2[Fe(CN)_5NO]$ and $ZnSO_4$. The complex was precipitated as a pale brick-red powdery compound from the dilute solution. It was filtered off, washed with a mixture of water and ethanol (1 : 1) and dried in a desiccator.

To identify the complex and its decomposition products, spectroscopic investigations were carried out in KBr with a Zeiss UR–10 spectrophotometer and with a Mössbauer spectrometer using ^{57}Co diffused into Pt as a source [9] at room temperature. The iron and zinc contents were analyzed:

Zn: calc. 23.20%, found 23.1
Fe: calc. 19.84%, found 19.7

The thermal investigations were made on a MOM 3427/SK derivatograph.

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Zusammenfassung — Die thermische Zersetzung von $Zn[Fe(CN)_5NO]$ wurde derivatographisch und mittels IR- und Mössbauer-Spektroskopie untersucht. Die Zersetzung beginnt mit Dizyanentwicklung unter Bildung eines tetrakoordinierten Cyano-nitrosyl-Intermediärs. Der Eliminierung des NO-Liganden folgt eine zu $Fe[Zn(CN)_4]$ führende strukturelle Umordnung.

Резюме — Термическое разложение $Zn[Fe(CN)_5NO]$ было изучено дериватографическим методом, ИК спектроскопией и мёссбауэровской спектроскопией. Экспериментальные результаты показали, что процесс разложения начинается с образования дициана, давая тетракоординационное циано-нитрозил промежуточное соединение. Выделение лиганда NO сопровождается структурным превращением, приводящим к образованию $Fe[Zn(CN)_4]$.