After Effects of the Cobalt-57–Iron-57 Electron-capture Reaction in Hexacyanocobaltate(III) Complexes

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Isomorphous hexacyanocobaltate(III) complexes with the bivalent metal cations Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} have been labelled with ^{57}Co and used as Mössbauer sources. Whilst the spectrum of the complex $Fe_3[^{57}Co(CN)_6]_2$ can be resolved into a single line corresponding to the ion $Fe^{II}(CN)_6{}^{4-}$ and a doublet, those of all the other sources result in two doublets, of which one corresponds to the ion $Fe^{III}(CN)_6{}^{3-}$. The extra doublet in these spectra shows that the ^{57}Co–^{57}Fe electron-capture reaction gives rise to the formation of a new ^{57}Fe labelled species, tentatively identified as a pentacyanide ion. The relative yield of the new species decreases with increasing ionization energy for the divalent cation. This can be understood by assuming that the observed chemical effects are due to Auger cascades followed by Coulomb fragmentation; if, however, the charge relaxation is sufficiently rapid, such fragmentation may be prevented.

MÖSSBAUER emission spectra of ^{57}Fe formed by electron-capture decay of ^{57}Co in cobalt complexes sometimes show that the excited ^{57}Fe must be present in a chemical form different from that of the parent ^{57}Co.[1,2] Electron-capture decay normally releases an Auger cascade which may lead to the loss of several electrons; [3] it is therefore not surprising that in Co^{II} complexes some Fe^{III} is formed, although its method of stabilization in the lattice is still discussed. In some cobalt complexes, however, the chemical effects are more drastic than a mere change in the state of oxidation. In order to explain such observations three mechanisms have been proposed: [1,2] (*a*) radiolysis by Auger electrons of the parent complex [4] or of species in its immediate neighbourhood; [5] (*b*) Coulomb fragmentation of the charged molecule; [6] and (*c*) molecular excitation leading to dissociation, caused by the emission and/or recapture of electrons. As demonstrated by time-dependent Mössbauer spectroscopy (*e.g.*, ref. 7), all such processes are probably complete before the 14 keV quantum is emitted, *i.e.* well within 10^{-7} s.

Our previous experiments [8,9] suggested that in hexacyanocobaltate(III) complexes a decoupling of a CN ligand takes place, but they did not indicate the actual mechanism. In order to test the above theories in this system it was decided to compare the chemical effects of the ^{57}Co–^{57}Fe electron-capture reaction in a series of closely related salts. As such the most suitable appeared to be hexacyanocobaltate(III) complexes of the divalent metal ions Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} which precipitate readily [10] and form isomorphous crystals [11,12] that are also isomorphous with the corresponding hexacyanoferrate(III) complexes.[13-16] The unit cell is cubic (a = 10—10·6 Å) with divalent cations and $Co(CN)_6{}^{3-}$ ions arranged in a NaCl structure; charge balance is obtained with cations inside some of the octants. The composition is generally believed to be $M_3[Y(CN)_6]_2$, but in case of nickel the complex $KNi[Co(CN)_6]$ has also been reported.[17] Various amounts of H_2O in the lattice have been reported, and it is probably of zeolitic nature.[18] When Fe^{2+} is precipitated with $Fe^{III}(CN)_6{}^{3-}$ a redox reaction takes place, so that the precipitate contains Fe^{3+} and $Fe^{II}(CN)_6{}^{3-}$ ions; similar reactions cannot be excluded for other iron hexacyanide complexes, but apparently do not occur with hexacyanocobaltate(III) complexes.[15,19]

EXPERIMENTAL

Preparations.—Absorbers. The complexes $M_3[Fe(CN)_6]_2$ (M = Mn, Co, Ni, Cu, Zu, or Cd) were prepared by precipitation of the divalent cations with the ion $Fe(CN)_6{}^{3-}$. The pentacyanide complexes $Na_2[Fe(CN)_5H_2O]$ and $Na_3[Fe(CN)_5H_2O],7H_2O$, had been prepared previously.[8] For $K_4[Fe(CN)_6],3H_2O$ a commercial reagent (AnalaR) was used. Aliquot portions (100 mg cm^{-2}) of the compounds were used for the absorbers.

Sources. ^{57}Co labelled hexacyanocobaltate(III) complexes of Mn, Fe, Co, Ni, Cu, Zn, and Cd were prepared as follows. The ion $^{57}Co(CN)_6{}^{3-}$ was first prepared from carrier free $^{57}CoCl_2$ (International Chemical and Nuclear Corporation), which was heated under reflux for 24 h in a solution containing a large excess of KCN. These two preparations were checked by radioelectrophoresis [8,9] in order to ensure that all the ^{57}Co was complexed to the hexacyanide and not to the intermediate pentacyanide ion. Commercial

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$K_3Co(CN)_6$ (AnalaR) was then added, the mixture was filtered, and the excess of KCN was removed by reprecipitation and washing with ethanol. The solution of the ion $^{57}Co(CN)_6{}^{3-}$ was divided in portions containing about 1 mCi ^{57}Co. One of the above metal cations was added to each portion after neutralization or acidification with the acid[10] which gave the best precipitation conditions for the relevant cation. The mixtures were heated on a steam bath for *ca.* 0·5 h to facilitate coagulation, and then centrifuged. Finally the precipitates were washed a few times with water, dried overnight *in vacuo*, and powdered. The source materials thus prepared were mounted in aluminium holders and covered with a 1 mm thick lucite lid. The source thicknesses were all less than *ca.* 100 mg cm^{-2}.

Determination of the Stoicheiometry of the Precipitates.—A modified[20] Job's method, which can determine the stoicheiometry of precipitates, was applied to the hexacyano-ferrate(III) and -cobaltate(III) complexes. Since these complexes form colloids, the accuracy of the method is modest but the results were consistent with the general formula $M_3[Y(CN)_6]_2$ (Y = Fe, M = Mn, Co, Ni, Cu, Zn, or Cd; Y = Co, M = Mn, Fe, Co, Cu, Zn, or Cd). The complex $Fe_3[Fe(CN)_6]_2$ was not prepared since it does not contain the ion $Fe(CN)_6{}^{3-}$. In the case of precipitation of Ni^{2+} with the ion $Co(CN)_6{}^{3-}$ significant discrepancies were observed, therefore inactive material, prepared in the same way as the source material, was analysed (Alfred Bernhardts Mikroanalytisches Laboratorium) (Found: Co, 18·65; Ni, 18·95. Calc. for $KNi[Co(CN)_6]$: Co, 18·85; Ni, 18·75%). On the basis of these results and information obtained from the literature, we conclude that the nickel salt differs from the other hexacyanocobaltate(III) complexes in having the charge balance made up with K^+ ions; *i.e.* its structure is similar to that of soluble Prussian blue.[19]

Mössbauer Measurements.—Details of the recording of the Mössbauer spectra and their resolution by least-squares fitting in Lorentzian lines have been described in previous publications (refs. 8 and 9 and refs. therein). The hexacyano-ferrate(II) and -ferrate(III) complexes used for identification were measured as absorbers at -125 °C against a Pd(^{57}Co) source at room temperature (*ca.* 25 °C). The hexacyanocobaltate(III) sources were measured at -125 °C or at room temperature against absorbers at room temperature; two absorbers were used: 310 stainless steel (1 mg ^{57}Fe/cm^2, >85% enriched; Nuclear Science and Engineering Corporation) and $K_4[Fe(CN)_6],3H_2O$ (1 mg ^{57}Fe/cm^2, 91% enriched; New England Nuclear Corporation, NENC). In addition some spectra were recorded with a resonance detector,[21] where a 310 stainless-steel absorber (1 mg ^{57}Fe/cm^2, 91% enriched; NENC) was placed inside a flat proportional counter. In such a system Mössbauer absorption is registered *via* the subsequent emission of conversion electrons in the decay of excited ^{57}Fe. The effective absorber thickness is determined by the range of conversion electrons and is thus only of the order of 1000 Å; therefore the linewidths are smaller than those obtained when the stainless-steel absorber is used in a conventional set-up. These measurements were made only with the sources at room temperature.

RESULTS

Absorber Measurements.—The absorption spectra of the complexes $Mn_3[Fe(CN)_6]_2$, $Ni_3[Fe(CN)_6]_2$, $Cu_3[Fe(CN)_6]_2$, $Zn_3[Fe(CN)_6]_2$, $Cd_3[Fe(CN)_6]_2$, $Na_2[Fe(CN)_5H_2O]$, and $Na_3[Fe(CN)_5H_2O],7H_2O$ were all fitted to doublets for the relevant iron anion, and the spectrum of $K_4[Fe(CN)_6],3H_2O$ contained a single line for the ion $Fe(CN)_6{}^{4-}$. The spectrum of the complex $Co_3[Fe(CN)_6]_2$, however, could only be accounted for with a doublet for the ion $Fe(CN)_6{}^{3-}$ and a single line presumably for $Fe(CN)_6{}^{4-}$. Since the relative intensity of the single line varied with the preparation, it is assumed that the absorbers are not pure, probably because some hexacyanoferrate(III) ions were reduced during the preparation; this question was not investigated further.

Results pertinent to the present investigation are summarized in Table 1; a typical spectrum {that of the complex $Cd_3[Fe(CN)_6]_2$} is shown in Figure 1. The isomer shifts in the Table are corrected to refer to stainless steel and are transformed to a hypothetical source experiment by change of sign; for comparison some published data are also included. In a few cases our results differ more from the previously published values than is justified by the quoted uncertainties but, in view of larger uncertainties in the source spectra, these discrepancies do not affect the identification of the species present.

Source Measurements.—Emission spectra of the $Fe_2[^{57}Co(CN)_6]_3$ source were resolved into a single line and a doublet, but possibly the spectra are more complex since χ^2 tests indicated that not all fits were quite satisfactory. The spectra of all the other sources were resolved into two doublets. With a $K_4[Fe(CN)_6],3H_2O$ absorber the observed linewidths were about 0·1 mm s^{-1} smaller than with a stainless-steel absorber, but at the same time the intensities were halved owing to the lower f factor (recoil-free fraction) of this complex.[22] A similar reduction in linewidth was obtained if a stainless-steel absorber was used in the resonance detector.[21] Spectra recorded at -125 and 25 °C showed only small differences in isomer shifts and quadrupole splittings, but there was a factor of 1·7 between the line intensities (θ_D *ca.* 200 K); this is in agreement with previously observed temperature effects for absorbers.[22] The relative intensities of the lines were not significantly different for spectra recorded at -125 and 25 °C. Small effects may, however, have been overlooked, since the room-temperature measurements were not very accurate; this question will be investigated further.

Since all the spectra were composed of broad lines (2Γ *ca.* 1 mm s^{-1}), the reduction in linewidth did not compensate for the reduction in line intensity, and therefore the most accurate spectra were obtained with sources at -125 °C measured against a stainless-steel absorber in a conventional set-up. Results of these measurements are listed in Table 2. A typical emission spectrum {that of the complex $Cd_3[^{57}Co(CN)_6]_2$} is shown in Figure 2. In all the computer fits doublet lines were constrained to have equal intensity and width, but otherwise all parameters were freely variable. It can be seen that the lines overlap, therefore the fitted parameters are strongly interdependent and the accuracy of the subsequently calculated isomer shifts, quadrupole splittings, and relative intensities was not well determined. Comparisons between results of duplicate measurements and between results of measurements with the two absorbers suggest, however, that the uncertainties of the results presented in Table 1 are as

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TABLE 1

Results of absorber measurements. Absorber temperature, −125 °C; source temperature, 25 °C

Absorber	^{57}Fe Species	Ref.	δ mm s^{-1}	Δ mm s^{-1}	2Γ mm s^{-1}
$Mn_3[Fe(CN)_6]$	$Fe^{III}(CN)_6^{3-}$		0·03 ± 0·02	0·59 ± 0·03	0·44 ± 0·03
		a, b	0·04 ± 0·02	0·66 ± 0·02	
$Co_3[Fe(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$		0·02 ± 0·02	0·67 ± 0·02	0·43 ± 0·04
		15 [c]	0·02 ± 0·01	0·81 ± 0·02	
		a, b	0·07 ± 0·02	0·75 ± 0·02	
$Ni_3[Fe(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$		0·00 ± 0·02	0·68 ± 0·02	0·61 ± 0·03
$Cu_3[Fe(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$		0·01 ± 0·02	0·64 ± 0·02	0·44 ± 0·02
		a, b	−0·07 ± 0·02	0·62 ± 0·02	
		c, d	0·015 ± 0·006	0·754 ± 0·005	
$Zn_3[Fe(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$		0·01 ± 0·02	0·46 ± 0·03	0·52 ± 0·03
		a, b	0·01 ± 0·02	0·44 ± 0·04	
$Cd_3[Fe(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$		0·01 ± 0·02	0·67 ± 0·03	0·46 ± 0·03
$K_4[Fe(CN)_6],3H_2O$	$Fe^{II}(CN)_6^{4-}$		−0·04 ± 0·01	Not detected	0·33 ± 0·03
		22	−0·10 ± 0·01		
$Na_2[Fe(CN)_5H_2O]$	$Fe^{III}(CN)_5H_2O^{2-}$		−0·05 ± 0·01	2·06 ± 0·01	0·52 ± 0·02
		c, e	−0·04 ± 0·02	1·82 ± 0·05	
		8	−0·03 ± 0·05	1·91 ± 0·02	
$Na_3[Fe(CN)_5H_2O],7H_2O$	$Fe^{II}(CN)_5H_2O^{3-}$		−0·16 ± 0·01	0·78 ± 0·01	0·34 ± 0·02
		c, e	−0·18 ± 0·05	0·80 ± 0·05	
		8	−0·16 ± 0·01	0·73 ± 0·01	

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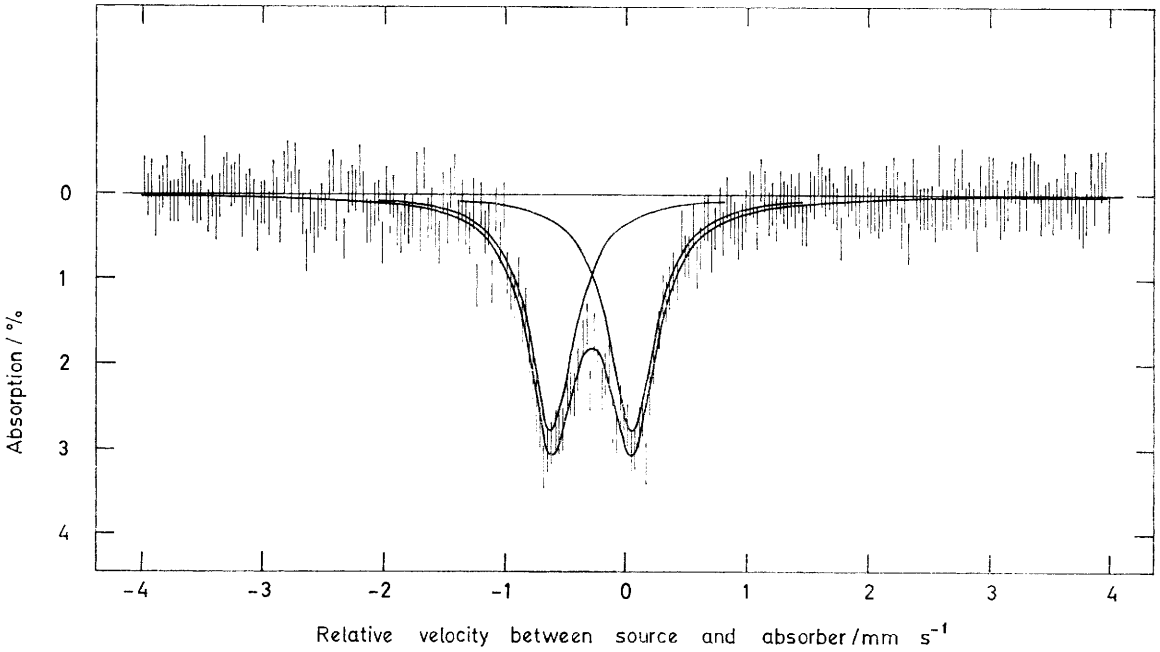

FIGURE 1 Mössbauer absorption spectrum of the complex $Cd_3[Fe(CN)_6]_2$ showing a single doublet for the ion $Fe(CN)_6^{3-}$: source Pd(^{57}Co)

follows: ±0·05 mm s^{-1} for δ, Δ, and 2Γ for species assumed to be hexacyanide ions; ±0·08 mm s^{-1} for δ and Δ, and ±0·2 mm s^{-1} for 2Γ for the assumed pentacyanide ions. Relative intensities are estimated to be correct to within ±3% of the total intensity.

DISCUSSION

Comparison between pairs of corresponding absorption and emission spectra (*e.g.* Figures 1 and 2) demonstrates clearly that not all ^{57}Fe formed by the ^{57}Co–^{57}Fe electron-capture process is present in the form of the ion $Fe(CN)_6^{3-}$ placed in regular lattice positions. As shown in Table 2, all the source spectra {with the exception of that of the complex $Fe_2[^{57}Co(CN)_6]_3$} were resolved into two doublets, one with a quadrupole splitting of 0·5—0·8 and the other 1·6—2·0 mm s^{-1}. By means of the absorber spectra (Table 1), the more narrow doublet is readily ascribed to the ion $Fe(CN)_6^{3-}$. The identification of the other doublet, which must represent a new chemical species, is more difficult. Since the isomer shift and quadrupole splitting of the iron cyano-complexes depend on the nature of the cations in the lattice, exact calculations of the parameters for possible species are precluded; however, on the basis of a comparison with absorber spectra (Table 1), we assume that the new species is the ion $Fe^{III}(CN)_5^{2-}$. It must be admitted that its isomer shift (δ) is smaller than that expected for the aquopentacyanide ion, $Fe^{III}(CN)_5H_2O^{2-}$; in source experiments, this corresponds to a lower *s*-electron density at the ^{57}Fe nucleus, and consequently to a higher degree of 3*d* shielding.[23] In a previous publication,[9] describing similar observations with the complex $K_3{}^{57}Co(CN)_6$, we argued that this result is unexpected since H_2O probably donates electrons to 3*d* levels, and that therefore the ion $Fe^{III}(CN)_5H_2O^{2-}$ would have more 3*d* shielding than that of $Fe^{III}(CN)_5^{2-}$. However, if π-bonding to the H_2O ligand occurs there may be less 3*d* shielding in the former. The quadrupole splitting (Δ) is smaller for the new species than for the ion $Fe^{III}(CN)_5H_2O^{2-}$, and this is consistent with the explanation of the difference in isomer shift, since the anisotropy may be lower in $Fe^{III}(CN)_5^{2-}$. It has also been pointed out [24] that in absorber spectra of analogous substituted pentacyanide ions a larger value of δ corresponds to a smaller Δ.

TABLE 2

Results of source measurements. Source temperature, −125 °C; absorber temperature 25 °C

Source	Assumed ^{57}Fe sepcies	Yield %	$\frac{\delta}{\text{mm s}^{-1}}$	$\frac{\Delta}{\text{mm s}^{-1}}$	$\frac{2\Gamma}{\text{mm s}^{-1}}$	Ionization energy for $M^{2+} \rightarrow M^{3+} + e^-$ $\frac{I_3}{\text{eV}}$
$Mn_3[^{57}Co(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$	69	0·00	0·47	0·98	33·69
	$Fe^{III}(CN)_5^{2-}$	31	−0·11	1·68	1·06	
$Fe_3[^{57}Co(CN)_6]_2$	$Fe^{II}(CN)_6^{4-}$	75	0·02		0·86	30·64
	$Fe^{II}(CN)_5^{3-}$	25	−0·23	1·22	1·29	
$Co_3[^{57}Co(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$	90	−0·01	0·63	1·18	33·49
	$Fe^{III}(CN)_5^{2-}$	10	−0·21	1·94	0·94	
$KNi[^{57}Co(CN)_6]$	$Fe^{III}(CN)_6^{3-}$	57	0·04	0·83	0·93	36·16
	$Fe^{III}(CN)_5^{2-}$	43	−0·11	1·97	1·33	
$Cu_3[^{57}Co(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$	49	0·05	0·72	0·81	36·83
	$Fe^{III}(CN)_5^{2-}$	51	−0·09	1·78	1·50	
$Zn_3[^{57}Co(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$	35	0·08	0·61	0·84	39·70
	$Fe^{III}(CN)_5^{2-}$	65	−0·10	1·64	1·81	
$Cd_3[^{57}Co(CN)_6]_2$	$Fe^{III}(CN)_6^{3-}$	24	0·14	0·63	0·89	44·5
	$Fe^{III}(CN)_5^{2-}$	76	−0·14	1·78	1·73	

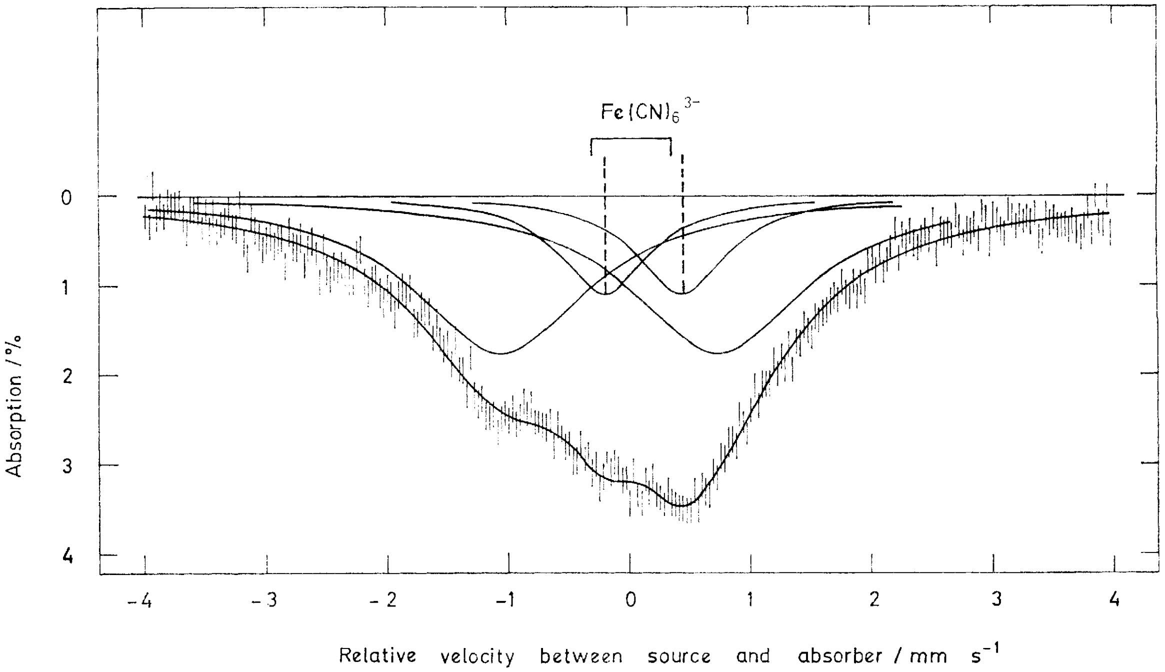

FIGURE 2 Mössbauer emission spectrum of the complex $Cd_3[^{57}Co(CN)_6]_2$ resolved in two doublets; absorber stainless steel (^{57}Fe). Transformed line positions from Figure 1 are indicated and show that one doublet arises from the ion $Fe(CN)_6^{3-}$

The spectrum of the $Fe_2[^{57}Co(CN)_6]_3$ source was resolved into a single line, ascribed to the ion $Fe(CN)_6^{4-}$, and a doublet with a splitting (*ca.* 1·2 mm s^{-1}) significantly smaller than that of the outer doublets observed with the other sources. This doublet, on the other hand, has parameters similar to those of a doublet observed in

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spectra of the ^{57}Co-doped complexes $KFe[Fe(CN)_6],H_2O$ [8] and $K_4Fe(CN)_6,3H_2O$,[9] and we assume that it may arise from the ion $Fe^{II}(CN)_5{}^{3-}$. As indicated in the Experimental section, the presence of minor amounts of other species cannot be excluded; *e.g.*, these may be the iron(III) cyanide ions found in all the other sources. Granting the above species identifications, we conclude (*cf.* also refs. 8 and 9) that the ^{57}Co–^{57}Fe electron-capture process can cause the decoupling of a CN ligand.

The stainless-steel absorber used in the source measurements had a bigger linewidth than the Pd(^{57}Co) source used in the absorber measurements; even allowing for this, however, it is noted that the source resonances, especially those attributed to the ion $Fe^{III}(CN)_5{}^{2-}$, are broader than expected. The consequences of the ^{57}Co–^{57}Fe electron-capture process may therefore also involve some damage to the surrounding lattice. On the other hand, our previous experiments with a specifically ^{57}Co-labelled double complex [9] seem to indicate that the nascent ^{57}Fe does not leave the lattice site of the parent ^{57}Co.

Debye–Waller factors for a series of inorganic salts were found by Kerler [22] to vary by a few per cent; further, in our sources the ^{57}Fe-labelled hexacyanide ions are presumably in less distorted surroundings than those of the pentacyanide ions. Therefore the relative intensities of the resonances, shown in Table 2, may not represent the true relative yields of the corresponding species. The ratios between the yields measured with different sources are, nevertheless, suitable to demonstrate general tendencies since they probably are in error by a common factor.

The formation of the ion $^{57}Fe(CN)_6{}^{3-}$ from $^{57}Co(CN)_6{}^{3-}$ presumably takes place in the following three steps: (*a*) the nuclear decay proper involving the capture of a K (or L) electron and the emission of a neutrino [this probably gives the ion $^{57}Fe(CN)_6{}^{3-}$ with a deep-lying electron vacancy]; (*b*) the subsequent Auger cascade, which may lead to the loss of up to seven electrons; [3] and (*c*) a charge relaxation to give the observed ion $^{57}Fe(CN)_6{}^{3-}$. The alternative formation of the new species, tentatively identified as pentacyanide ions, can hardly be a direct consequence of (*a*) which gives a recoil of only a few eV.[6] As stated in the Introduction, chemical effects may, however, be caused by the emitted electrons, by Coulomb repulsion inside the charged molecule (*b*), or by charge relaxation (*c*).

It is interesting to note that electron bombardment of the solid $K_3Co(CN)_6$ has been found to yield the ion $Co(CN)_5{}^{3-}$.[25] Moreover photolysis of hexacyano-complexes in solution [26] normally leads to formation of pentacyanide ions, although the actual mechanisms are still debated.[27] These observations could indicate that loss of a CN ligand subsequent to the electron-capture process is caused by an electronic excitation; but if this were so, it is difficult to imagine how the cation could influence the yield of the pentacyanide ion so drastically as has been observed. Alternatively, the cations could influence the charge relaxation by 'storing' the emitted electrons. Then there would be a correlation between product yields and the ionization energies of the reactions $M^+ \longrightarrow M^{2+} + e^-$, a measure of the electron affinity of the 2+ cations. Such a mechanism has been proposed in a study of the influence of cations on retention after (n,γ) reactions in bromate ions,[28] but it could not be applied to our data. If, however, the ratio between the yield of the pentacyanide and hexacyanide ions is plotted against the ionization energy [29] for the $M^{2+} \longrightarrow M^{3+} + e^-$ reaction (Table 2, Figure 3), a clear tendency is seen. Thus the probability of loss of a CN ligand increases with the energy required to remove electrons from the 2+ cations. We tentatively interpret this correlation by assuming that the fragmentation is caused by Coulomb repulsion and can be prevented if the missing electrons are supplied sufficiently rapidly from the surroundings. Since the $KNi[^{57}Co(CN)_6]$ source gave results that fit into this picture, the electron transfer may proceed essentially in the main cubic lattice.

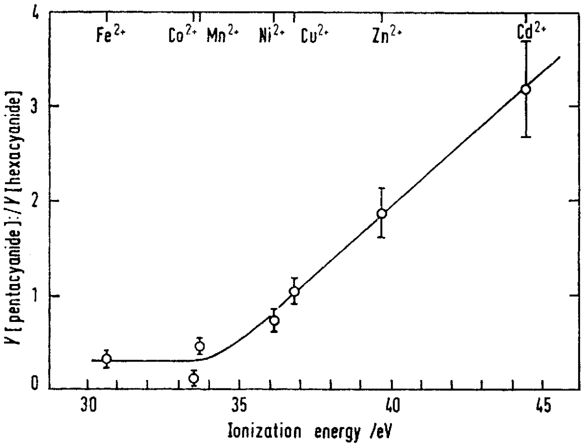

FIGURE 3 Ratio between the intensities of the resonances (Y) attributed to pentacyanide and to hexacyanide ions plotted against the third ionization energy (I_3) of the cation in the source. Error bars correspond to ±3% tolerances in the individual yields

The above interpretation is consistent with the observation of slightly different spectra for the $Fe_3[Co(CN)_6]_2$ source. Here substantial parts of the ^{57}Fe-labelled iron(III) cyano-complexes may capture an extra electron to form iron(II) cyano-complexes in analogy with redox reactions taking place on precipitation of Prussian blue from the ions Fe^{2+} and $Fe^{III}(CN)_6{}^{3-}$.

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