Aftereffects of the ^{57}Co(EC)^{57}Fe-Reaction in Some Cobalt and Iron Complexes

By **K. E. Siekierska, J. Fenger,* and J. Olsen,** Chemistry and Reactor Physics Departments, Danish Atomic Energy Commission Research Establishment Risø, Roskilde, Denmark

Mössbauer emission spectra of iron and cobalt complexes, doped or labelled with ^{57}Co, demonstrate that the ^{57}Co(EC)^{57}Fe reaction can have significant chemical effects, although the probability of displacement of the nascent ^{57}Fe is very low. Measurements on specifically ^{57}Co-labelled [Co(bipy)$_3$][Co(CN)$_6$],2H$_2$O failed to show transfer of ^{57}Fe from one complex to the other.

MÖSSBAUER emission spectra of ^{57}Fe formed by EC-decay of ^{57}Co in cobalt compounds often contain resonances which are different from those of the corresponding iron compounds.[1] Since the EC-process can release an Auger cascade, Fe^{3+} may readily be formed from Co^{2+}; further it has been shown [2] that in hydrated cobaltous compounds Fe^{3+} can be stabilized *via* radiolysis of water by the Auger electrons. The appearance of resonances corresponding to Fe^{II} species

---

[1] H. H. Wickman and G. K. Wertheim, in 'Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York and London, 1968, p. 604.

[2] G. K. Wertheim and D. N. E. Buchanan, *Chem. Phys. Letters*, 1969, **3**, 87.

in Co^{III} compounds is more difficult to explain. Hazony and Herber[3] have suggested that the changes in the emission spectra could reflect a redistribution of electrons caused by the internal pressure which an iron ion will experience in the lattice of a cobalt compound. As $^{57}Fe^{II}$ resonances have later been observed in ^{57}Co-doped Fe^{III} complexes[4,5] this hypothesis cannot be generally accepted. It seems more reasonable to assume that the emitted Auger electrons can cause radiolysis of the parent complex[4-6] but it has not been established whether this involves a displacement of the ^{57}Fe from the ^{57}Co site. In our studies on soluble Prussian Blue[6] it has been shown that ^{57}Fe born in a hexacyanide complex may be stabilized in a different chemical form; the computer analyses of the data, however, did not permit a decision as to whether ^{57}Fe was stabilized as Fe^{3+}, giving a single line, or as a pentacyanide with one of the doublet lines hidden under the ferrous cyanide line. Probably formation of Fe^{3+} would require an atomic displacement, whereas formation of a pentacyanide would not. In other systems it has not been agreed upon whether there are observable chemical effects of the $^{57}Co(EC)^{57}Fe$ reaction or not; thus Mathur[7] has reported formation of Fe^{2+} in $[^{57}Co(bipy)_3](ClO_4)_3,3H_2O$, whereas Nath *et al.*[8] have not detected new species.

In the present report these ambiguities are discussed on the basis of comparisons between the Mössbauer spectra of iron and cobalt compounds containing $^{57}Co(CN)_6^{3-}$ or $^{57}Co(bipy)_3^{3+}$. In an attempt to check whether an exchange of central atoms could be induced between the two complexes, some measurements were performed on a specifically ^{57}Co-labelled double complex, $[Co(bipy)_3][Co(CN)_6],xH_2O$ (*x ca.* 2).

EXPERIMENTAL

Preparation and Analyses of the Double Complex.—$Co(bipy)_3(ClO_4)_3$ was prepared as described by Burstal and Nyholm.[9] $K_3Co(CN)_6$ was prepared as described by Bigelow.[10] Finally light yellow microcrystals were precipitated by mixing warm solutions of the above components. The crystals were dried *in vacuo* and analysed by the Alfred Bernhardts Mikroanalytisches Laboratorium (Found: C, 55·5; H, 3·7; N, 21·5; O, 4·1; $[Co(bipy)_3][Co(CN)_6],2H_2O$ requires C, 55·5; H, 3·6; N, 21·6; O, 4·1%). Further samples of the complex separately labelled with ^{60}Co in each complex ion were prepared and analysed by radio-electrophoresis; no cobalt exchange between the two complexes was observed.

Preparation of the Sources.—Sources of $[^{57}Co(bipy)_3](ClO_4)_3$, $K_3{}^{57}Co(CN)_6$, $[^{57}Co(bipy)_3][Co(CN)_6],2H_2O$, and $[Co(bipy)_3][^{57}Co(CN)_6],2H_2O$ were prepared as described above, using $^{57}CoCl_2$. Sources of $[Fe(^{57}Co)(bipy)_3](ClO_4)_3$ were prepared in two steps; first carrier-free $^{57}Co^{2+}$ was oxidized in the presence of bipyridyl, then $Fe(bipy)_3SO_4$ was added, and the mixture was treated with Cl_2 to oxidize the iron complex. Finally sources of ^{57}Co-doped iron hexacyanides: $K_3[Fe(^{57}Co)(CN)_6]$ and $K_4[Fe(^{57}Co)(CN)_6],3H_2O$ were prepared by refluxing carrier-free $^{57}CoCl_2$ in a KCN solution[6] and adding commercial $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$. The excess of KCN was removed by reprecipitation and washing with ethanol. The final precipitation and (or) drying of the source material was performed in a small aluminium suction funnel (i.d. 1 cm) which also served as support during the subsequent Mössbauer measurements. The weight of the source material was 20—30 mg corresponding to less than 40 mg/cm². The preparations were checked by radio-electrophoretic analysis[6]—first of ^{60}Co-labelled material and later of actual Mössbauer sources. This was especially important in the case of $^{57}Co(CN)_6^{3-}$, where the intermediate pentacyanide might survive, and this very species is subsequently observed in the emission spectra. The ^{57}Co-*labelled cobalt* compounds did not contain any dectectable (< *ca.* 2%) ^{57}Co in a chemical form other than that intended.

TABLE 1

Results of Mössbauer source measurements. All velocities refer to a stainless-steel absorber. The identifications are based on comparisons with the transformed data from absorption spectra, shown in Table 2

Source	Assumed ^{57}Fe-Species	Yield/%	δ/mm s⁻¹	Δ/mm s⁻¹	2Γ/mm s⁻¹
$[Fe(^{57}Co)(bipy)_3](ClO_4)_3$	Fe^{2+}	13 ± 4	−1·26 ± 0·03	2·39 ± 0·04	1·0 ± 0·2
	$Fe(bipy)_3^{2+}$	7 ± 2	−0·41 ± 0·05	0·31 ± 0·08	1·0 ± 0·5
	$Fe(bipy)_3^{3+}$	80 ± 4	−0·19 ± 0·03	1·83 ± 0·04	0·77 ± 0·03
$[^{57}Co(bipy)_3](ClO_4)_3$	Fe^{2+}	10 ± 4	−1·60 ± 0·03	1·79 ± 0·0	1·3 ± 0·2
	$Fe(bipy)_3^{2+}$	30 ± 4	−0·41 ± 0·05	0·31 ± 0·08	2·0 ± 0·5
	$Fe(bipy)_3^{3+}$	60 ± 4	−0·18 ± 0·03	1·79 ± 0·03	0·65 ± 0·03
$[^{57}Co(bipy)_3][Co(CN)_6],2H_2O$	$Fe(bipy)_3^{2+}$	24 ± 3	−0·40 ± 0·03	0·31 ± 0·03	0·62 ± 0·03
	$Fe(bipy)_3^{3+}$	76 ± 3	−0·17 ± 0·03	1·78 ± 0·03	0·76 ± 0·03
$K^3[Fe(^{57}Co)(CN)_6]$	‘ $Fe^{III}(CN)_5$’	80 ± 3	−0·29 ± 0·05	1·82 ± 0·07	1·8 ± 0·2
	$Fe(CN)_6^{3-}$	20 ± 3	0·16 ± 0·05	0·45 ± 0·07	1·3 ± 0·6
$K_3[^{57}Co(CN)_6]$	‘ $Fe^{III}(CN)_5$’	80 ± 3	−0·25 ± 0·03	1·82 ± 0·05	1·72 ± 0·02
	$Fe(CN)_6^{3-}$	20 ± 3	0·17 ± 0·03	0·12 ± 0·04	0·89 ± 0·02
$[Co(bipy)_3][^{57}Co(CN)_6],2H_2O$	‘ $Fe^{III}(CN)_5$’	72 ± 4	−0·53 ± 0·08	2·16 ± 0·10	2·2 ± 0·5
	$Fe(CN)_6^{3-}$	28 ± 4	0·05 ± 0·02	0·68 ± 0·04	0·8 ± 0·1
$K_4[Fe(^{57}Co)(CN)_6],3H_2O$ (at room temperature)	‘ $Fe^{II}(CN)_5$’	82 ± 4	−0·19 ± 0·03	1·09 ± 0·05	1·66 ± 0·08
	$Fe(CN)_6^{4-}$	18 ± 4	0·02 ± 0·01	—	0·67 ± 0·04

---

[3] Y. Hazony and R. H. Herber, *J. Inorg. Nuclear Chem.*, 1969, **31**, 321.

[4] J. Fenger, K. E. Siekierska, and A. G. Maddock, *J. Chem. Soc.* (*A*), 1970, 1456.

[5] H. Sano, K. Sato, and H. Iwagami, *Bull. Chem. Soc. Japan*, 1971, **44**, 2570.

[6] J. Fenger, A. G. Maddock, and K. E. Siekierska, *J. Chem. Soc.* (*A*), 1970, 3255.

[7] P. K. Mathur, *Indian J. Chem.*, 1969, **7**, 183.

[8] A. Nath, R. D. Argarwal, and P. K. Mathur, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 161.

[9] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 1952, 3570.

[10] J. H. Bigelow, *Inorg. Synth.*, 1946, **2**, 225.

The checks of the ^{57}Co-*doped iron* compounds were less conclusive since the ^{57}Co migrated partly with the iron species; a further complication arose from the gradual reduction of trisbipyridyl ferric ion during electrophoresis. However, the ^{57}Co was complexed by the same procedures as for the 'Co' and 'Fe' sources, and their emission spectra were nearly identical (*cf.* Table 1).

Mössbauer Measurements.—The spectra shown were recorded with the sources at −125 °C *versus* an absorber of stainless steel containing 1 mg/cm^2 ^{57}Fe; room temperature measurements gave nearly the same spectra, but with lower absorptions; with one exception they are not presented. The velocity scan of the spectrometer was calibrated with (1) a hyperfine spectrum of a soft iron foil measured *versus* a Pd(^{57}Co) source, and (2) a measurement of the isomer shift between the Pd(^{57}Co) source and the stainless-steel absorber. All spectra were analysed with the programme described previously.[11] Published absorber spectra of possible iron species are used for identification; they are first referred to a stainless-steel source using an ^{57}Fe isomer shift scale for sources,[12] and then transformed to a hypothetical source experiment by change of sign of the isomer shift. The spectra used for identification had been recorded at various temperatures; since, however, our source spectra showed only a small temperature dependence—and very broad lines—a correction for temperature shifts [13] was found unnecessary. The transformed data from absorption spectra are shown in Table 2.

TABLE 2

Published results of absorber measurements. The isomer shifts (δ) are converted to refer to stainless steel and transformed to a hypothetical source experiment

Absorber	^{57}Fe-Species	Ref.	δ/mm s^{-1}	Δ/mm s^{-1}	2Γ/mm s^{-1}
Ferrous salts	Fe^{2+}	13	∼−1·4	1·7 – 3·6	
$Fe(bipy)_3(ClO_4)_2$	$Fe(bipy)_3^{2+}$	*a*	−0·42 ± 0·01	0·39 ± 0·02	
$[Fe(bipy)_3]_3[Fe(CN)_6]_2$	$Fe(bipy)_3^{2+}$	15	−0·39 ± 0·02	0·40 ± 0·06	0·26 ± 0·03
$Fe(bipy)_3(ClO_4)_3$	$Fe(bipy)_3^{3+}$	*a*	−0·16 ± 0·01	1·76 ± 0·02	
$Na_3[Fe(CN)_5H_2O],7H_2O$	$Fe(CN)_5H_2O^{3-}$	6	−0·12 ± 0·01	0·73 ± 0·01	0·43 ± 0·03
$Na_2[Fe(CN)_5H_2O]$	$Fe(CN)_5H_2O^{2-}$	6	0·01 ± 0·02	1·91 ± 0·02	0·42 ± 0·03
$K_4Fe(CN)_6,3H_2O$	$Fe(CN)_6^{4-}$	6	−0·08 ± 0·02	—	0·46 ± 0·03
$K_3Fe(CN)_6$	$Fe(CN)_6^{3-}$	6	0·00 ± 0·02	0·30 ± 0·03	0·44 ± 0·05
$[Fe(bipy)_3]_3[Fe(CN)_6]_2$	$Fe(CN)_6^{3-}$	16	0·00 ± 0·03	0·56 ± 0·06	0·36 ± 0·06

[a] R. L. Collins, R. Pettit, and W. A. Baker, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1001.

The linewidths observed in source spectra recorded with a stainless-steel absorber cannot be compared directly with the linewidths observed in corresponding absorber spectra recorded with a Pd(^{57}Co) or Pt(^{57}Co) source. These sources are reported to have a linewidth of 0·20—0·22 mm s^{-1}, whereas a stainless-steel source has a linewidth of 0·32—0·37 mm s^{-1};[14] further, in absorber spectra recorded with a Pd(^{57}Co) source, the linewidth of stainless steel is 0·5—0·6 mm s^{-1}, whereas values down to 0·3 mm s^{-1} have been reported for $K_4Fe(CN)_6,3H_2O$.[13] From these data we estimate that the lines in our source spectra may, *ceteris paribus*, be 0·1—0·3 mm broader than in the absorber spectra which are used for identification.

RESULTS

All the recorded spectra were composed of several resonances. In some cases various combinations of resonances were used as initial estimates in the computer fit in order to find a satisfactory resolution. The best combinations and the resulting fits are presented in Table 1. The tolerances are estimates from repeated measurements (not from individual fits). The indicated identifications will be discussed below. All data refer to measurements at −125 °C except for $K_4Fe(^{57}Co)(CN)_6,3H_2O$ where the data for room temperature are shown. Spectra recorded with the cobalt complexes are shown in Figures 1 and 2.

DISCUSSION

The resonance lines observed in our source experiments are significantly broader than in the corresponding absorber experiments—even when the above-discussed contribution to the linewidth from the stainless-steel absorber is taken into account; this is informative since it indicates some damage to the crystal lattice, but it makes identification of the species difficult. Furthermore the isomer shifts of some iron complexes differ very little, and both isomer shifts and quadrupole splittings are influenced by neighbouring ions in the lattice; these effects are particularly pronounced for cyanides.[6,15]

The spectra of $[Fe(^{57}Co)(bipy)_3](ClO_4)_3$ and $[^{57}Co(bipy)_3](ClO_4)_3$ are similar, therefore neither pressure effects nor faulty doping are important factors. The calculated product distribution is different from that reported by Mathur [7] showing formation of $^{57}Fe(bipy)_3^{2+}$; we believe, however, that a more accurate resolution of Mathur's spectra could yield a result similar to ours. In the spectra of $[^{57}Co(bipy)_3][Co(CN)_6],2H_2O$ only resonances corresponding to $^{57}Fe(bipy)_3^{2+}$ and $^{57}Fe(bipy)_3^{3+}$ were resolved. The photoreduction of $^{57}Fe(bipy)_3^{3+}$ has been studied in detail in solution [16] and also observed in the solid. Possibly electronic excitation caused by the emission of Auger electrons could have a similar effect. It is worth noting that the yield of

---

[11] A. J. Stone, H. J. Aagaard, and J. Fenger, Risö-M-1348 (Feb. 1970) (A Danish version of: G. M. Bancroft, A. G. Maddock, W. K. Ong, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

[12] A. H. Muir, K. J. Ando, and H. M. Coogan, 'Mössbauer Effect Data Index, 1958—1965,' Interscience, New York, 1966, p. 26.

[13] E. Fluck, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 433.

[14] The Radiochemical Centre, Amersham, 'Mössbauer Sources,' Technical bulletin 70/2.

[15] B. V. Borshagovskii, V. I. Goldanskii, G. B. Seifer, and R. A. Stukau, *Bull. Acad. Sci. U.S.S.R. Div. Chem. Sci.*, 1968, 1623.

[16] V. Balzani and V. Carassit, 'Photochemistry of Coordination Compounds,' Academic Press, London, 1970.

^{57}Fe(bipy)$_3{}^{2+}$ (*ca.* 7%) is significantly lower in the [Fe(^{57}Co)(bipy)$_3$](ClO$_4$)$_3$ source than in the two ' Co ' sources (24—30%), where the matrix ions are not readily reduced.

The sources K$_3$Fe(^{57}Co)(CN)$_6$ and K$_3{}^{57}$Co(CN)$_6$ likewise show similar spectra. One doublet with a relative yield of about 20% is ascribed to ^{57}Fe(CN)$_6{}^{3-}$, although however, the observed lower isomer shift corresponds to a *lower* *s*-electron density. In order to explain the isomer shift we therefore assume that the pentacyanide species sits in a distorted region of the lattice; this is in agreement with the line broadening observed (2Γ *ca.* 1·8 mm s^{-1}).

The spectrum of K$_4$Fe(^{57}Co)(CN)$_6$,3H$_2$O is analogous to that of the other hexacyanides, but the doublet attributed to pentacyanide has a smaller quadrupole splitting. It cannot be guaranteed that the ^{57}Co is incorporated in a regular lattice position; probably it is incorporated as Co(CN)$_6{}^{3-}$, whereas the lattice contains Fe(CN)$_6{}^{4-}$ and does not offer charge compensation as in the case of Prussian Blue[6] where nearby Fe^{3+} may be reduced to Fe^{2+}. Nevertheless, the doublet in ferrous cyanide has the same parameters

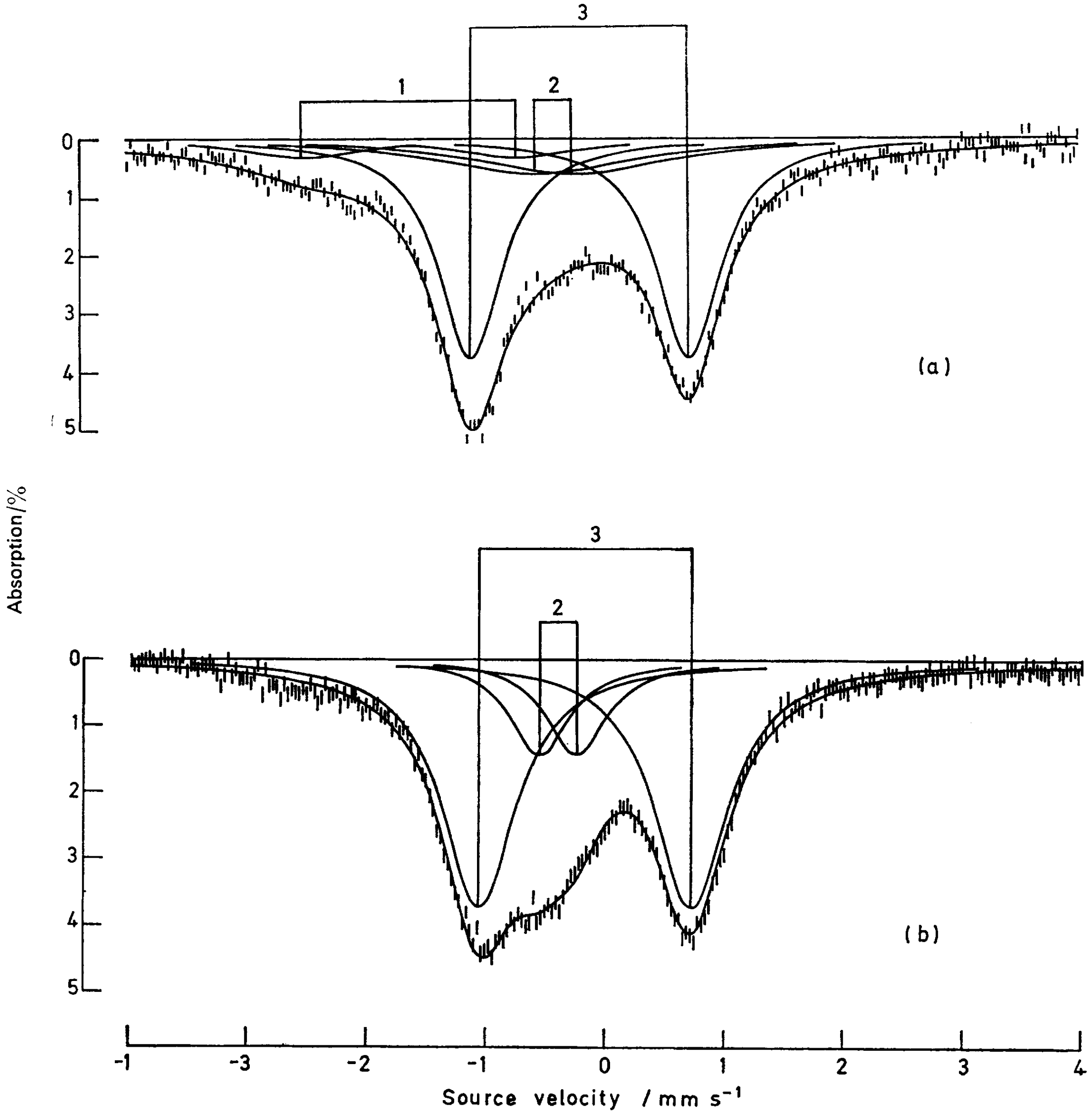

FIGURE 1 Mössbauer spectra of (a) ^{57}Co(bipy)$_3$(ClO$_4$)$_3$ and (b) ^{57}Co(bipy)$_3$Co(CN)$_6$,2HO. The resonances form doublets which are identified with the data shown in Table 1 and ascribed to: 1, Fe^{2+}; 2, Fe(bipy)$_3{}^{2+}$; 3, Fe(bipy)$_3{}^{3+}$

it is not significantly different from a ^{57}Fe(CN)$_6{}^{4-}$ singlet in the case of the ' Co ' source. Another doublet (yield *ca.* 80%) has a quadrupole splitting similar to that observed in Na$_2$[Fe^{III}(CN)$_5$H$_2$O],7H$_2$O,[6] but a lower isomer shift. In the Fe^{III}(CN)$_5$H$_2$O^{2-} complex H$_2$O probably donates electrons to 3*d* orbitals; a pentacyanide without an H$_2$O ligand should therefore have less 3*d*-shielding and consequently *higher* *s*-electron density on the ^{57}Fe-nucleus. In a source experiment, as the doublet that could explain the asymmetry of the Prussian Blue spectra (*cf.* Introduction); we therefore conclude that iron pentacyanide is actually formed in Prussian Blue.

The spectrum of $[Co(bipy)_3][^{57}Co(CN)_6],2H_2O$ contains two doublets with larger splittings than in the simple hexacyanides. One of the doublets corresponds to a doublet observed in $[Fe(bipy)_3]_3[Fe(CN)_6]_2$ (at room temperature) and is ascribed to $Fe(CN)_6^{3-}$.[17] The other doublet could be a ferripentacyanide.

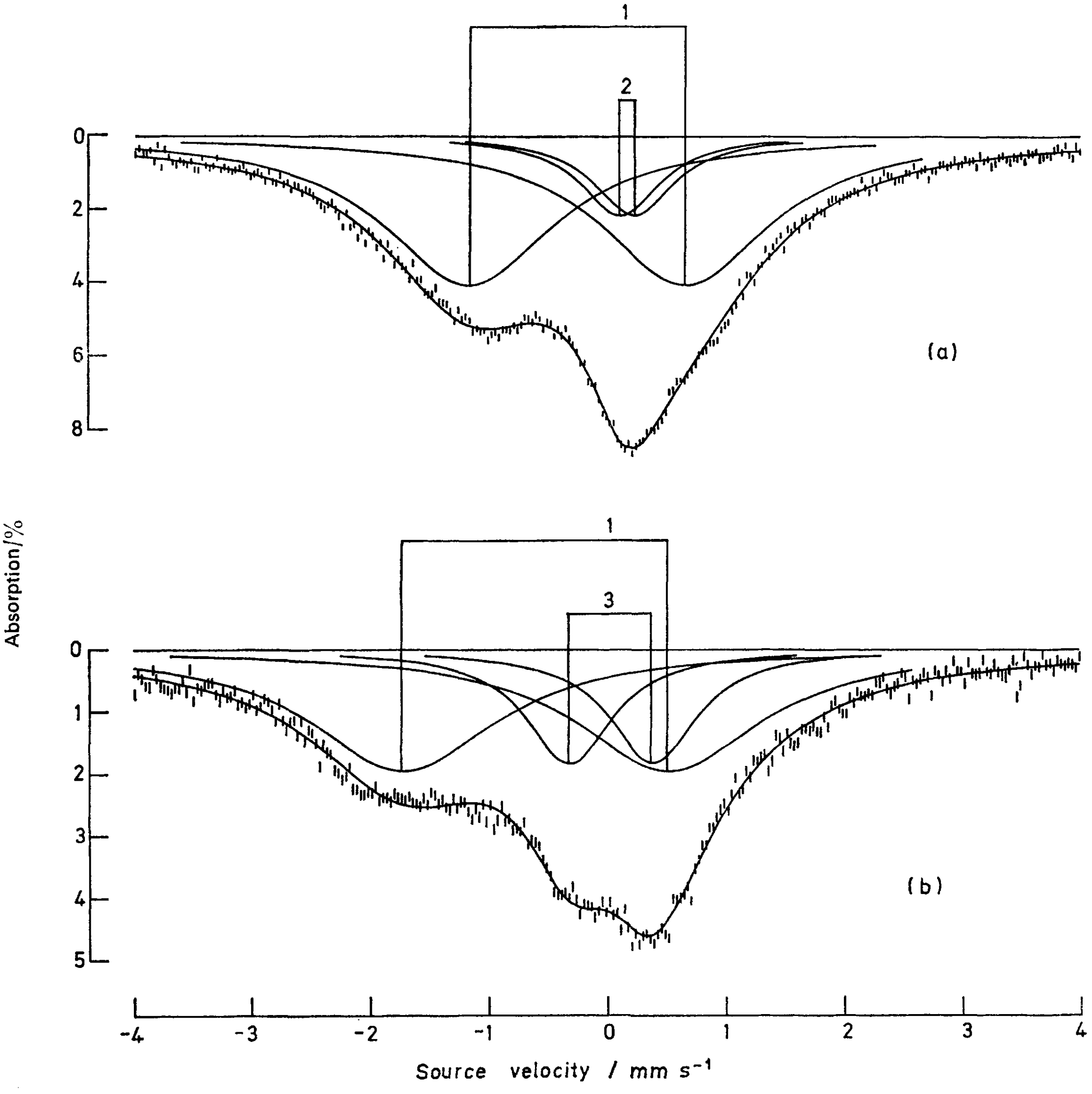

FIGURE 2 Mössbauer spectra of (a) $K_3{}^{57}Co(CN)_6$ and (b) $Co(bipy)_3{}^{57}Co(CN)_6,2H_2O$. The resonances form doublets which are identified with the data shown in Table 2 and ascribed to: 1, a ferripentacyanide; 2, $Fe(CN)_6^{4-}$ or $Fe(CN)_6^{3-}$; 3, $Fe(CN)_6^{3-}$

The spectra of the two specifically labelled cobalt double complexes are distinctly different; this excludes the possibility that the nuclear event produces a large disordered zone extending much beyond the vicinity of the affected ion. Moreover, as described above, the spectra can be accounted for with different resonances, although it cannot be excluded that the broad resonances detected in the $[Co(bipy)_3][^{57}Co(CN)_6],2H_2O$ source cover weaker resonances from $Fe^{III}(bipy)_3^{2+}$ or from mixed ligand complexes. We have therefore no evidence of an exchange of central atoms as a consequence of the EC-process; this is in agreement with our previous experiments with Prussian Blue.[6] None of our results, however, can determine whether the observed ^{57}Fe-labelled 'parent' species has avoided fragmentation owing to rapid electronic relaxation or has been reformed before the emission of the Mössbauer quantum.[18]

All our spectra can be qualitatively understood by assuming that the EC-process has chemical effects similar to radiolysis, but it remains to be explained why the product yields are influenced by other ions

---

[17] K. E. Siekierska and J. Fenger, Risö Report No. 240, 1971.

[18] *E.g.*, J. P. Adloff, AED-Conf.-1969-191-005.

present in the lattice. Especially, the low yield of pentacyanide in Prussian Blue—as compared with that in simple hexacyanides—is surprising; possibly, it is connected with the electron-accepting properties of ferric ions which have previously been shown to affect annealing reactions in solids.[19] This effect will be investigated further.

The chemical consequences of EC-processes are modest and thus entirely different from the consequences of (n, γ) recoil, which nearly always leads to complete fragmentation of the parent complex. Thus preliminary results of an investigation of an iron double complex, $[Fe(bipy)_3][Fe(CN)_6]$ [17,20] suggest that the fate of ^{59}Fe is the same when $^{58}Fe(n, \gamma)^{59}Fe$ reaction takes place in either of the two complexes.

We thank K. C. Nyvang Nielsen for skilful technical assistance.

[2/787 *Received*, *6th April*, 1972]

---

[19] S. Khorana and D. R. Wiles, *Radiochim. Acta*, 1969, **12**, 111.

[20] K. E. Siekierska and J. Fenger, 6th International Hot Atom Chemistry Symposium B.N.L. Sept. 1971, p. 104.