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EMISSION MÖSSBAUER SPECTROSCOPY OF ^{57}Co-LABELLED MERCURY(II), TETRAALKYLAMMONIUM AND COBALT(II) CRYPTATE SALTS OF TETRATHIOCYANATOCOBALTATE(II)

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Based on the comparison of emission Mössbauer spectra of tetraalkylammonium and cobalt(II) cryptate salts of tetrathiocyanatocobaltate(II) at 78 K, it has been concluded that the cryptate is stable against the local radiolysis initiated by EC-decay and that it accomodates the transient ^{57}Fe(III) species before the restoration of ^{57}Fe(II) state.

A number of emission Mössbauer spectroscopic studies have been carried out in order to clarify the behavior of decaying atoms produced in the nuclear transformations, especially in the EC-decay of ^{57}Co[1-7)] and in the nuclear isomeric transition of ^{119m}Sn.[8-11)] In the case of ^{57}Co-labelled compounds, the following Auger ionization cascade will produce highly-charged ^{57}Fe ions which lead to a formation of metastable species. The concentration of the metastable or the unstable species is usually too low to be detected by ordinary physicochemical techniques. However, emission Mössbauer spectroscopy allows the observation of the species, provided that the mean lifetime of the newly-formed species is longer or of the same order compared with the first excited level of ^{57}Fe nucleus. The highly-charged states are rapidly neutralized through an electron transfer mechanism from ligand molecules or neighbouring atoms. It has been reported that the chemical states of decaying ^{57}Fe atoms found by means of Mössbauer spectroscopy are iron(III) or iron(II), depending upon the chemical environments of the decaying atoms. The purpose of the present work is to elucidate the significance of the chemical properties of species surrounding the decaying atoms.

^{57}Co-labelled mercury(II), tetramethylammonium, and tetraethylammonium tetrathiocyanatocobaltate(II), $Hg[Co(NCS)_4]$, $[N(CH_3)_4]_2[Co(NCS)_4]$, and $[N(C_2H_5)_4]_2[Co(NCS)_4]$, were prepared by using aqueous solutions of cobalt(II) salts including ca. 1 mCi ^{57}Co according to the literature.[12)] Tetraethylammonium tetrathiocyanatoferrate(II), $[N(C_2H_5)_4]_2[Fe(NCS)_4]$, was also prepared by following a similar procedure.[13)]

^{57}Co-labelled cryptate compound, $[Co(C_{16}H_{32}N_2O_5)][Co(NCS)_4]$, was prepared by following the method reported in the literature.[14)]

The purity of the labelled compounds was checked by comparing the data of elementary analysis obtained in the cold run for each compound.

Emission Mössbauer spectra of ^{57}Co-labelled compounds were determined at 78 and 4.2 K by using an ^{57}Fe-enriched stainless-steel absorber moving at 295 K in a constant acceleration mode.

Typical emission Mössbauer spectra of ^{57}Co-labelled compounds at 78 K are shown in Fig. 1 together with the absorption spectrum of $[N(C_2H_5)_4]_2[Fe(NCS)_4]$ for the sake of comparison. It is known that $[N(C_2H_5)_4]_2[Co(NCS)_4]$ has the same crystal structure as $[N(C_2H_5)_4][Fe(NCS)_4]$,[13,15] although ^{57}Co-labelled $[N(C_2H_5)_4][Co(NCS)_4]$ shows two sets of quadrupole doublets in the emission spectrum. One of the two doublets is assigned to $[^{57}Fe(NCS)_4]^{2-}$ species based on the values of isomer shift and quadrupole splitting obtained in the absorption spectrum of $[N(C_2H_5)_4]_2[Fe(NCS)_4]$. Another component has a quadrupole splitting similar to that of $[Fe(NCS)_4]^{2-}$ species but somewhat smaller isomer shift. Tominaga et al, reported that thermal decomposition of dithiocyanatotetrapyridineiron(II), $[Fe(Py)_4(NCS)_2]$, produced two kinds of iron(II) species based on the Mössbauer spectroscopic studies, which showed two kinds of quadrupole-split components.[16] One of them was assigned to sulfur-coordinated iron(II) thiocyanate species. By analogy to their conclusion, it may be reasonable to assume the possibility that some of the decaying atoms sit at the interstitial sites where the produced ^{57}Fe atoms can be coordinated, even particularly, with sulfur atoms of thiocyanate anions after the EC-decay process, while the other ^{57}Fe atoms remain at the original sites coordinated with nitrogen atoms of thiocyanate anions.

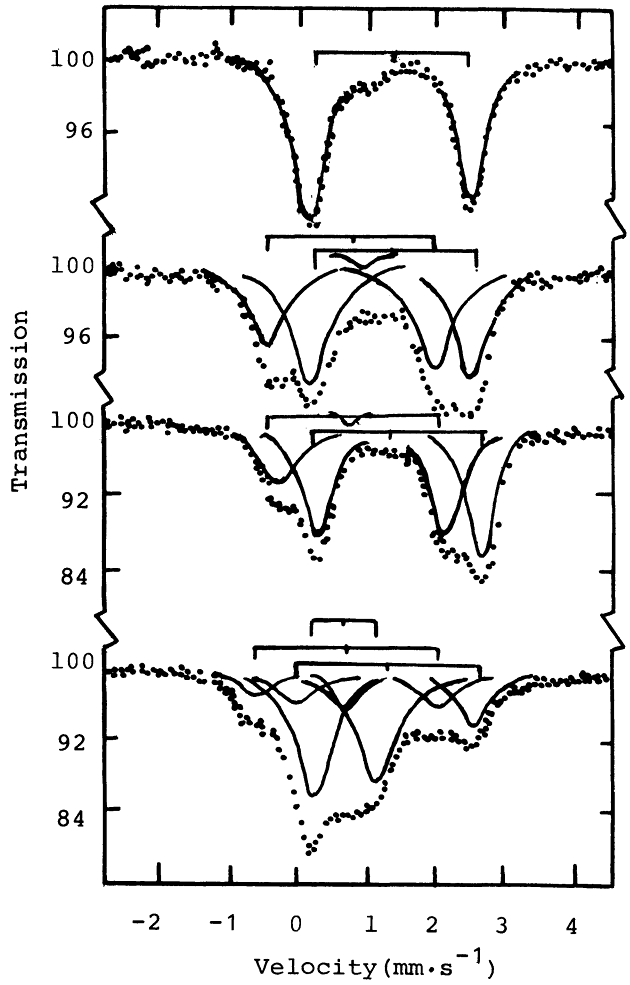

Fig. 1 (A) Absorption Mössbauer spectrum of $[N(C_2H_5)_4]_2[Fe(NCS)_4]$ and emission Mössbauer spectra of ^{57}Co-labelled (B) $[N(C_2H_5)_4]_2$-$[Co(NCS)_4]$, (C) $Hg[Co(NCS)_4]$, and (D) $[Co(C_{16}H_{32}N_2O_5)][Co(NCS)_4]$ at 78 K. Doublet I shows stable iron(II), doublet II a newly-formed iron(II) in $[Co(NCS)_4]^{2-}$, and doublet III newly-formed high-spin iron(III) in cryptate.

As seen in Fig. 1, there is a negligible amount of line component assigned to $^{57}Fe(III)$ species in the emission spectra of $[N(C_2H_5)_4]_2[^{57}Co(NCS)_4]$ and $Hg[^{57}Co(NCS)_4]$. By contrast there is found, in the emission spectrum of $[^{57}Co(C_{16}H_{32}N_2O_5)][^{57}Co(NCS)_4]$, a large amount of $^{57}Fe(III)$ species including a magnetic hyperfine relaxation component, in addition to the component assigned to $[^{57}Fe(NCS)_4]^{2-}$ species, although very few ^{57}Co-labelled cobalt(II) compounds show magnetic hyperfine structure in their emission spectra above at 78 K. In order to confirm the assignment, emission Mössbauer spectra of $[N(C_2H_5)_4]_2[^{57}Co(NCS)_4]$ and $[^{57}Co(C_{16}H_{32}N_2O_5)][^{57}Co(NCS)_4]$ were measured at 4.2 K over a wider Doppler velocity range. As shown in Fig. 2, $[^{57}Co(C_{16}H_{32}N_2O_5)][^{57}Co(NCS)_4]$ has a large contribution of magnetic hyperfine component which is unambiguously assigned to

Table 1. Mössbauer spectroscopic data for ^{57}Co-labelled tetrathiocyanatocobaltate(II) at 78 K

Compound	Isomer shift*)	Quadrupole splitting	Line width**)		Intensity***)	
	δ/mm·s^{-1}	ΔE_Q/mm·s^{-1}	Γ_1/mm·s^{-1}	Γ_2/mm·s^{-1}	$10^2 I_1$	$10^2 I_2$
$[N(C_2H_5)_4]_2$-$[Fe(NCS)_4]$	1.32	2.30	0.54	0.52	9.58	8.15
$[N(C_2H_5)_4]_2$-$[^{57}Co(NCS)_4]$	1.33	2.32	0.69	0.62	6.79	6.39
	0.76	2.44	0.54	0.59	4.66	6.07
	0.98		0.43		0.86	
$[N(CH_3)_4]_2$-$[^{57}Co(NCS)_4]$	1.25	2.27	0.65	0.64	4.85	4.00
	0.87	1.96	0.58	0.61	3.43	2.70
	0.78		0.48		0.79	
$Hg[^{57}Co(NCS)_4]$	1.26	2.39	0.49	0.50	12.91	14.27
	0.78	2.46	0.59	0.57	7.13	11.88
	0.65		0.47		0.32	
$[^{57}Co(C_{16}H_{32}N_2$-$O_5)][^{57}Co(NCS)_4]$	1.23	2.63	0.62	0.50	4.01	5.92
	0.65	2.63	0.53	0.63	2.66	4.06
	0.63	0.85	0.65	0.76	14.22	11.75
	0.64		0.50****)		7.52****)	

*) Values of isomer shift were taken with respect to metallic iron.

**) Γ_1 shows a line width corresponding to a smaller Doppler velocity than Γ_2.

***) I_1 and I_2 represent the observed intensities, i.e., the relative difference between the counts in resonance and out of resonance.

****) Values are estimated only for the main peak of the magnetic hyperfine relaxation component by assuming a single Lorentzian shape as shown in Fig. 1.

^{57}Fe(III) species based on the value of internal magnetic field, whereas an almost negligible amount of magnetic hyperfine component is found in the spectrum of $[N(C_2H_5)_4]_2[^{57}Co(NCS)_4]$. The quadrupole split line component found in the emission spectra at 4.2 K is assigned to the same ^{57}Fe(II) species as those which are assumed in the spectra taken at 78 K. Besides the decreased resolution of spectrum due to the use of wide-scale Doppler velocity, the different temperature dependence of isomer shift in both the nitrogen-coordinated ^{57}Fe(II) species and the sulfur-coordinated ^{57}Fe(II) species will explain the fact that two resolved components are not observed in the spectrum at 4.2 K.

The comparison of $[^{57}Co(C_{16}H_{32}N_2O_5)]$-$[^{57}Co(NCS)_4]$ and $[N(C_2H_5)_4]_2[^{57}Co(NCS)_4]$ suggests that most ^{57}Fe(II) species are produced from thiocyanate anions, $[^{57}Co(NCS)_4]^{2-}$, and reside in the vicinity of

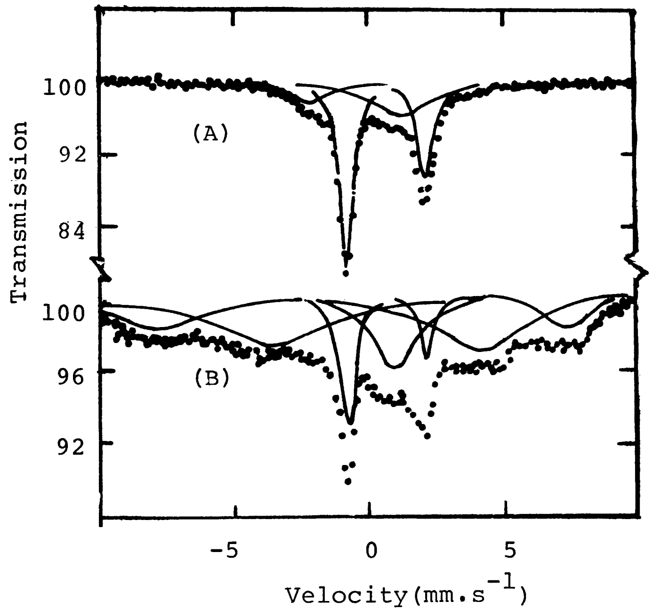

Fig. 2 Emission Mössbauer spectra of ^{57}Co-labelled (A) $[N(C_2H_5)_4]_2[Co(NCS)_4]$ and (B) $[Co(C_{16}H_{32}N_2O_5)][Co(NCS)_4]$ at 4.2 K.

thiocyanato ligands, and that ^{57}Fe(III) species found in the spectrum of [^{57}Co($C_{16}H_{32}N_2O_5$)][^{57}Co(NCS)$_4$] are mostly produced from [^{57}Co($C_{16}H_{32}N_2O_5$)]$^{2+}$ cations. It has been already demonstrated in a number of cobalt(III) coordination compounds that the fate of decaying atoms is determined by the local radiolytic process involving the species in the vicinity of the decaying atoms.3,5,6) The results obtained in the present work suggest that the cryptate structure is stable enough to isolate the transient ^{57}Fe(III) state from the highly-charged states of the species initially produced in EC-decay, and that some disturbance occurs in after-effect in the [^{57}Co(NCS)$_4$]$^{2-}$ species including either flipping of thiocyanato ligands or displacement of decaying atoms during the processes initiated by the EC-decay.

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