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Mössbauer Emission Spectroscopic Study of Some Spin Crossover Cobalt(II) Complexes

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The Mössbauer emission spectra of $[^{57}Co(terpy)_2]X_2$ (X=Cl and ClO_4), $[^{57}Co(snn)_2](ClO_4)_2$, and $[^{57}Co(snnme)_2](ClO_4)_2$ (terpy=2,2′: 6′2″-terpyridine, snn=*N*-(2-pyridylmethylene)-2-(methylthio)aniline, and snnme=*N*-(6-methyl-2-pyridylmethylene)-2-(methylthio)aniline) were examined. These cobalt complexes show thermally induced spin crossover behavior and the temperature dependence of their magnetic moment varies with the counter anion, although the corresponding iron complexes are in a low-spin state. The high-spin iron(II) species ascribed to a metastable form are observed in the emission spectra of $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ and $[^{57}Co(snnme)_2](ClO_4)_2$, and their spectral areas increase with decreasing source temperature. The effective vibrating mass for the iron complex observed in the emission spectra of $[^{57}Co(snnme)_2](ClO_4)_2$ was calculated from the temperature dependence of the isomer shift value, and was used to distinguish whether the iron complex formed by EC-decay of a cobalt-57 atom is stable or metastable.

The Mössbauer emission spectroscopic method provides for studying the after-effects attended by EC-decay of a cobalt-57 atom in a solid state. The chemical after-effects in solids, reflected in the Mössbauer spectra, are categorized as follows: (i) The oxidation state of the iron atom formed in the EC-decay of a cobalt-57 atom in the lattice of the labeled cobalt complexes is different from that of the parent cobalt atom (formation of foreign-charge state). (ii) An iron atom after EC-decay does not have the same spin state as the corresponding iron complexes but the same oxidation state (formation of anomalous spin state). (iii) An iron atom after EC-decay is stabilized in a coordination atmosphere different from that of a cobalt atom because of the radiolysis of the ligands, although it does have the same spin and oxidation state as the corresponding iron complex. These phenomena have been explained by various mechanisms as described below:

Friedt and Danon reported on the behavior of $^{57}CoX_2$ in terms of the lattice energy.[1] Friedt *et al.* reported that iron(III) appearing in the emission spectra of $^{57}CoSO_4 \cdot nH_2O$ was due to the radiolysis of hydrated water.[2–4] The role of the radicals resulting from autoradiolysis of ligands due to photoelectrons and X-rays have been extensively examined, and Sano *et al.* concluded that the redox properties of radicals affect the final oxidation state of the daughter atom, and that these effects are due to the radiolytic self-decomposition of the molecular environment of the decaying atoms.[5–8] These mechanisms have been supported by performing an external irradiation experiment using electrons and X-rays.

On the other hand, Nath *et al.* suggested that the multiple charged iron atom after Auger cascade was rapidly neutralized by electron transfer from ligands, and the coulomb repulsion between the iron and ligands resulted in the fragmentation of molecules; the fragmentation was highly dependent on the degree of bonding conjugation in the molecule.[9,10]

The Mössbauer emission spectra of some cobalt complexes with imines or their derivatives were measured by Gütlich *et al.*[11–15] They proposed that the anomalous spin states appearing in these emission spectra had lifetimes of the order of 100—400 ns and were the immediate precursors of the stable states. Several studies were performed from the view point of the spin state of the daughter iron atom.[16–19]

In this study we measured the Mössbauer emission spectra of spin crossover cobalt complexes in order to investigate how the difference in the spin state of a parent cobalt atom affects the lifetime of a metastable state of a daughter iron atom. The effective vibrating mass calculated using the method proposed by Herber[20] was used to distinguish between the metastable and the stable state.

Experimental

The cobalt complexes used in this study were prepared described in the literature. $[Co(terpy)_2]X_2$ (X=Cl and ClO_4),[21] $[Co(snn)_2](ClO_4)_2$,[22] and $[Co(snnme)_2](ClO_4)_2$:[23] terpy; 2,2′: 6′,2″-terpyridine, snn;*N*-(2-pyridylmethylene)-2-(methylthio)aniline, and snnme;*N*-(6-methyl-2-pyridylmethylene-2-(methylthio)aniline. Iron complexes were prepared by methods similar to those of the cobalt complexes. The elemental analysis was performed with unlabeled samples and the values found for carbon, nitrogen, and hydrogen deviated by less than 0.3% from the calculated values. The compounds for the Mössbauer emission spectroscopic measurement were all labeled with 1 mCi of cobalt-57. The magnetic susceptibilities at 297 K and 80 K were measured on polycrystalline samples by the Faraday method. $HgCo(NCS)_4$ was used as the calibration substance. The effective magnetic moment was calculated using the formula $\mu_{eff} = 2.84\sqrt{\chi_M T}$, where χ_M is the molar susceptibility after dia-

TABLE 1. EFFECTIVE MAGNETIC MOMENT OF COBALT AND IRON COMPLEXES

Complex	μ_{eff}/BM	
	297 K	80 K
$[Co(terpy)_2]Cl_2 \cdot 5H_2O$	2.53	2.10
$[Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$	3.70	3.10
$[Co(snn)_2](ClO_4)_2$	2.59	2.02
$[Co(snnme)_2](ClO_4)_2$	5.10	3.85
$[Fe(snn)_2](ClO_4)_2$	dia.	dia.
$[Fe(snnme)_2](ClO_4)_2 \cdot 2H_2O$	2.60	1.19

magnetic corrections. These data are listed in Table 1.

The external irradiation experiments with γ-ray for [Fe(snn)$_2$](ClO$_4$)$_2$ and [Fe(snnme)$_2$](ClO$_4$)$_2$·2H$_2$O were performed as described elsewhere.[24)]

Mössbauer spectra were measured with a constant acceleration spectrometer(Austin Science Associate). The data are stored in a 1024 channel analyzer, type 5200 (Inotech, Inc). Temperature was monitored with a calibrated copper *vs.* constantan thermocouple in a variable temperature cryostat, type ASD-4V(Austin Science Associate) and maintained with a temperature controller, type S-8(Austin Science Associate). In the emission spectroscopy, potassium hexacyanoferrate(III) enriched with iron-57 was used as a standard absorber and was maintained at room temperature. A cobalt-57 source of 10 mCi diffused into palladium foil was used for the absorption experiment. All the spectra were fitted by Lorentzian line shapes using the least-square method at the Computer Center, Kyushu University; the velocity scale was normalized with respect to the center of the spectrum of an iron foil at 297 K. The geometry effect on the spectra(dimensions of source and absorber in relation to the distance between them) were taken into consideration in the fitting procedure. The experimental errors for Mössbauer parameters(isomer shift, quadrupole splitting, and full width at half-maximum) are estimated to be about ±0.01 mm s^{-1} or less.

Results and Discussion

Figures 1—4 show the Mössbauer emission spectra recorded for [^{57}Co(terpy)$_2$]Cl$_2$·5H$_2$O, [^{57}Co(terpy)$_2$](ClO$_4$)$_2$·2H$_2$O, [^{57}Co(snn)$_2$](ClO$_4$)$_2$, and [^{57}Co(snnme)$_2$](ClO$_4$)$_2$, respectively. The values for the Mössbauer parameters are listed in Tables 2—4 together with those for the absorption spectra of the analogous iron complexes and those for the corresponding iron-57 doped cobalt complexes. It was found that the iron atoms in the iron complexes and in the matrices of the cobalt complexes were in a low-spin state, while the corresponding cobalt complexes exhibited thermally induced spin crossover behavior.

The emission spectrum of [^{57}Co(terpy)$_2$]Cl$_2$·5H$_2$O recorded at 80 K is very similar to that at 297 K; both spectra are characterized by two quadrupole doublets(A and B) assigned to low-spin iron(II). An additional resonance line C ascribed to low-spin iron (III) is observed at 80 K. The disappearance of the species C at 297 K is due to the decrease of the recoil free fraction of this species. The values of the isomer shift and the quadrupole splitting of A are similar to those for the absorption spectra of the corresponding iron complex. The similarity between their parameters indicates that A is attributable to an iron atom stabilized without undergoing any after-effect, and that the electronic ground state of A, which is formed in the lattice of the paramagnetic cobalt compound by nuclear disintegration, is not influenced by the high-spin character of the surrounding cobalt ions at room temperature. The doublet B is attributable to a species stabilized in a coordination atmosphere different from that of A. This stabilization occurs

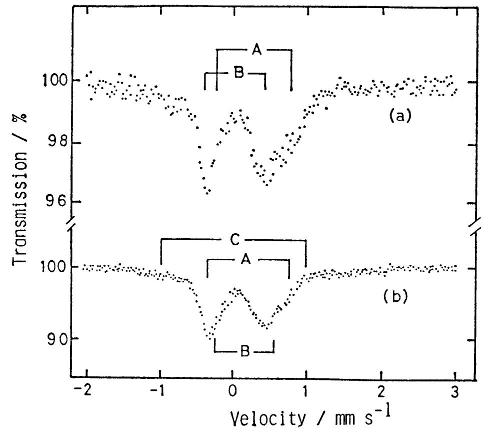

Fig. 1. Mössbauer emission spectra of [^{57}Co(terpy)$_2$]Cl$_2$·5H$_2$O at (a) 297 K and (b) 80 K.

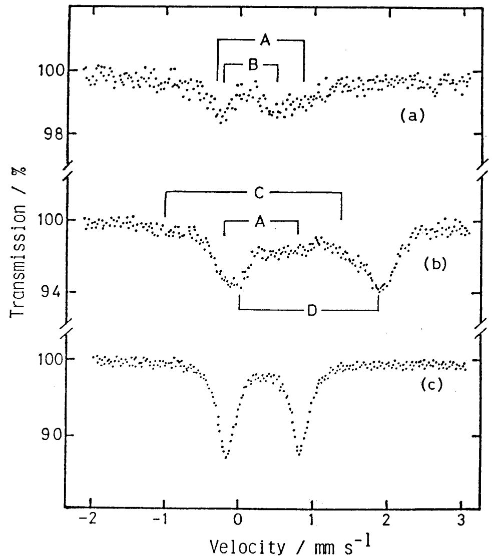

Fig. 2. Mössbauer emission spectra of [^{57}Co(terpy)$_2$](ClO$_4$)$_2$·2H$_2$O at (a) 297 K and (b) 80 K, and Mössbauer absorption spectrum (c) of [^{57}Fe$_{0.1}$Co$_{0.9}$(terpy)$_2$](ClO$_4$)$_2$·2H$_2$O at 80 K.

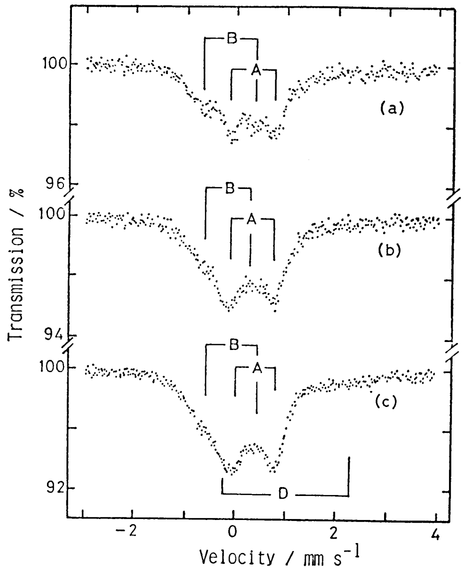

Fig. 3. Mössbauer emission spectra of [^{57}Co(snn)$_2$](ClO$_4$)$_2$ at (a) 297 K, (b) 200 K, and (c) 80 K.

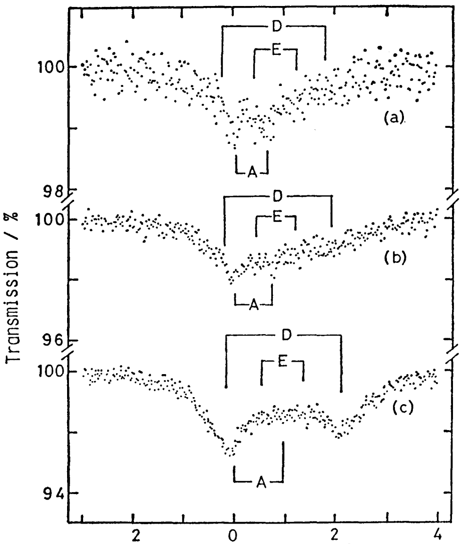

Fig. 4. Mössbauer emission spectra of [^{57}Co(snnme)$_2$](ClO_4)$_2$ at (a) 297 K, (b) 200 K, and (c) 80 K.

within the lifetimes of iron-57 m (10^{-7} s) through a secondary process after EC-decay. The coordination structure around B is distorted from the original coordination atmosphere by after-effects of nuclear disintegration.

The Mössbauer emission spectrum recorded at 80 K for [^{57}Co(terpy)$_2$](ClO_4)$_2\cdot 2H_2O$ is quite different from that at 297 K. The spectrum at 297 K is fitted to doublet A and B. However, when the source temperature was lowered, two additional resonance lines, D ascribed to high-spin iron(II) and C to low-spin iron(III) appeared in the emission spectra. These C and D lines are obviously attributable to a new chemical species because their chemical states are different from that of iron-57 doped in the host matrix [Co(terpy)$_2$](ClO_4)$_2\cdot 2H_2O$ as shown in Fig. 2. The decrease in the recoil free fraction with increasing temperature have resulted in the disappearance of C in the Mössbauer spectra at 297 K; C is a minor absorption peak even at 80 K. There is a possibility that the high-spin species D is in the stable state produced by the radiolytic reaction between the ligands and ClO_4^-. However we ascribe D to a metastable species leading to stable low-spin iron(II) for the following reasons:[15,25] It is assumed that the average ligand field strength experienced by the iron-57 daughter atom on the Mössbauer time scale of *ca.* 10^{-7}—10^{-8} s tends to decrease effectively because of coulomb repulsion between central iron-57 atom and ligands after Auger cascade. The absence of D in other emission spectra is caused by rapid relaxation of energy produced by EC-decay. Berlin and Schmand[26] have concluded that the existence of a metastable state is proved in the emission spectra of $^{57}CoSO_4\cdot 7H_2O$ because the metastable state has a long relaxation time of energy deposited on an iron atom after EC-decay; and they determined the lifetime of high-spin iron (II) species as a function of temperature.

The chemical structure of ligands snn and snnme are the same except for the methyl group located at the 6-position of pyridine. Therefore, the effects of autoradiolysis on both ligands by photoelectron and X-rays emitted following EC-decay are assumed to be similar. However, the methyl group of [Co(snnme)$_2$](ClO_4)$_2$ causes magnetic behavior different from that of [Co(snn)$_2$](ClO_4)$_2$.

The Mössbauer emission spectra of [^{57}Co(snn)$_2$](ClO_4)$_2$ at various temperatures are mainly composed of two kinds of quadrupole doublets A and B, and the ratios of the absorption areas of A and B to the total absorption area are almost the same in the range of the source temperature(80 K—297 K). This indicates that these species are in a stable state. The Mössbauer parameter of A appearing in the emission spectra is in good agreement with that obtained for the Mössbauer absorption spectra of [^{57}Fe$_{0.1}$Co$_{0.9}$-

TABLE 2. THE MÖSSBAUER PARAMETERS OF THE EMISSION AND ABSORPTION SPECTRA OF [^{57}Co(terpy)$_2$]X_2 AND RELATED IRON COMPOUNDS

Complex	T / K	δ[a] / mm s^{-1}	ΔE_Q[b] / mm s^{-1}	Γ[c] / mm s^{-1}	A[d] / %	Assignment[e]
[^{57}Co(terpy)$_2$]$Cl_2\cdot 5H_2O$	297	0.21	0.99	0.44	44	A
		0	0.82	0.28	56	B
	80	0.07	1.97	0.40	11	C
		0.24	1.11	0.24	21	A
		0.14	0.73	0.43	68	B
[^{57}Co(terpy)$_2$](ClO_4)$_2\cdot 2H_2O$	297	0.22	1.18	0.30	34	A
		0.06	0.74	0.33	66	B
	80	0.16	2.50	0.41	9	C
		0.24	0.99	0.32	13	A
		0.93	1.92	0.60	78	D
[^{57}Fe$_{0.1}$Co$_{0.9}$(terpy)$_2$](ClO_4)$_2\cdot 2H_2O$	297	0.23	1.05			
	80	0.34	1.00			
[Fe(terpy)$_2$](ClO_4)$_2$[f]	300	0.21	1.06			
	4.2	0.29	1.06			

a) Isomer shift. b) Quadrupole splitting. c) Full width at half-maximum. d) Relative peak area. e) A: Low-spin Fe(II), B: low-spin Fe(II), C: low-spin Fe(III), and D: high-spin Fe(II)(metastable). f) Data from Ref. 27.

TABLE 3. THE MÖSSBAUER PARAMETERS OF THE EMISSION AND ABSORPTION SPECTRA OF $[^{57}Co(snn)_2](ClO_4)_2$ AND RELATED IRON COMPOUNDS

Complex	T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	Γ/mm s^{-1}	A/%	Assignment
$[^{57}Co(snn)_2](ClO_4)_2$	297	0.33	0.90	0.55	68	A
		−0.17	1.08	0.49	32	B
	200	0.32	0.93	0.60	71	A
		−0.19	0.99	0.66	29	B
	80	0.37	0.89	0.55	56	A
		−0.12	1.04	0.71	31	B
		1.01	2.61	1.19	13	D
$[^{57}Fe_{0.1}Co_{0.9}(snn)_2](ClO_4)_2$	297	0.31	0.73	0.23		
	80	0.39	0.72	0.27		
$[Fe(snn)_2](ClO_4)_2$	297	0.29	0.75	0.31		
	80	0.37	0.72	0.36		
$[Fe(snn)_2](ClO_4)_2$ irrad.[a]	80	0.39	0.74	0.31		

a) Total exposure dose is 5.2×10^8 R.

TABLE 4. THE MÖSSBAUER PARAMETERS OF THE EMISSION AND ABSORPTION SPECTRA OF $[^{57}Co(snnme)_2](ClO_4)_2$ AND RELATED IRON COMPOUNDS

Complex	T/K	δ/mm s^{-1}	ΔE_Q/mm s^{-1}	Γ/mm s^{-1}	A/%	Assignment
$[^{57}Co(snnme)_2](ClO_4)_2$	297	0.33	0.68	0.32	31	A
		0.78	0.78	0.29	13	E[a]
		0.72	2.07	1.38	56	D
	200	0.35	0.77	0.35	18	A
		0.76	0.82	0.43	15	E
		0.84	2.11	1.29	67	D
	80	0.44	0.99	0.47	13	A
		0.93	0.91	0.38	7	E
		0.95	2.33	1.22	80	D
$[^{57}Fe_{0.1}Co_{0.9}(snnme)_2](ClO_4)_2$	297	0.38	0.88	0.28		
	80	0.47	0.87	0.29		
$[Fe(snnme)_2](ClO_4)_2\cdot2H_2O$	297	0.35	0.83	0.34		
	80	0.41	0.80	0.36		
$[Fe(snnme)_2](ClO_4)_2\cdot2H_2O$ irrad.[b]	80	0.45	0.81	0.33		

a) E: high-spin Fe(II). b) Total exposure dose is 5.2×10^8 R.

$(snn)_2](ClO_4)_2$. The high-spin chemical species D appearing in the emission spectrum recorded at 80 K for $[^{57}Co(snn)_2](ClO_4)_2$ disappeared as the source temperature was increased due to the decrease of the recoil free fraction.

The high-spin character of $[Co(snnme)_2](ClO_4)_2$ is enhanced in comparison with $[Co(snn)_2](ClO_4)_2$ as indicated by the effective magnetic moments. The emission spectra of $[^{57}Co(snnme)_2](ClO_4)_2$ at various temperatures are composed of three species (A, D, and E). It is worthy of note that high-spin iron(II) D appearing in the emission spectra of $[^{57}Co(snnme)_2](ClO_4)_2$ can be ascribed to a metastable state, because the ratio of the peak area of D to the total absorption area increases as the source temperature decreases, and this phenomenon is in good accord with that of $[^{57}Co(terpy)_2](ClO_4)_2\cdot2H_2O$. The three emission spectra of $[^{57}Co(snnme)_2](ClO_4)_2$ consist of two kinds of high-spin iron(II) (D and E) and low-spin iron(II) A. The species E ascribed to high-spin iron(II) is in a stable state with the ligands partly decomposed by autoradiolysis. The assumption that E is in a stable state is supported by the temperature independent ratio of the peak area of E to the total absorption area, and by the high value (>57) of the effective vibrating mass(EVM) as described later.

The absence of E in $[^{57}Co(snn)_2](ClO_4)_2$ or of B in $[^{57}Co(snnme)_2](ClO_4)_2$ can account for the fact that snn makes a stronger ligand field around the center atom than snnme; that is, the iron atom after EC-decay in the former complex is still in a low-spin state even if snn is exposed to secondary process following EC-decay because of its strong ligand field. On the other hand, the high-spin species is believed to be produced easily in the latter complex because the slight increase of the bond length between the iron atom and the coordination atom brings about a predominance of high-spin character.

External irradiation experiments with γ-rays were performed for $[Fe(snn)_2](ClO_4)_2$ and $[Fe(snnme)_2]$-

$(ClO_4)_2 \cdot 2H_2O$ and no chemical effect was observed in the irradiated samples.

Next we discuss the difference in the EVM for each chemical species of $[^{57}Co(snnme)_2](ClO_4)_2$, cobalt(II) complexes reported by other authors, and the corresponding iron complexes. The EVM can frequently be estimated from the second order Doppler shift, and is given by

$$M_{\mathrm{eff}} = -\frac{3}{2} \times \frac{E_\gamma K}{c^2}\left(\frac{\mathrm{d}IS}{\mathrm{d}T}\right)^{-1}, \tag{1}$$

where E is the energy of the Mössbauer transition. The calculated data are listed in Table 5. The values of EVM obtained from the Mössbauer emission spectra is less than that from the absorption spectra for the corresponding iron compounds. The values for the metastable species D are smaller than the free-atom value 56.95 amu. On the other hand, it is interesting that the value obtained for E is larger than 56.95 amu. These results can reasonably be accounted for as follows. Equation 1 is based on a harmonic system. It is reasonable to conclude that the iron atom emerging in the emission spectra is in a excited state after EC-decay. Thus the local lattice vibrating behavior is no longer expressed in a harmonic system if anharmonicity remains on the time scale of 10^{-7}—10^{-8} s after EC-decay. It is reasonable to rewrite EVM as follows by considering the anharmonicity of the lattice vibration in order to supplement this model.

$$M_{\mathrm{eff}} = -\frac{3}{2} \times \frac{E_\gamma K}{c^2}\left(\frac{\mathrm{d}IS}{\mathrm{d}T}\right)^{-1}(1+2\alpha KT) \tag{2}$$

where α is a positive coefficient derived from Thirring expansion.[27] This equation is useful for evaluating the EVM value for the chemical species in a metastable state. Namely, the value of EVM will exceed 56.95 amu if the second term in the parentheses (Eq. 2) is taken into account. The vibrational motion of the molecular moiety containing a daughter iron atom in a metastable state is disturbed by the "hot process" defined as all those processes occuring after EC-decay. Unfortunately, we cannot estimate the coefficient α because we cannot know the absolute value of EVM for a species in the metastable state. The value for E is calculated to be larger than 56.95 amu from Eq. 1, and this implies that E, rather than D, is in a stable state. The data for the other cobalt complexes listed in Table 5 are also interpreted in a similar manner. In this way, the daughter atoms in a metastable state can be distinguished from those in a stable state by evaluating the EVM value.

TABLE 5. EFFECTIVE VIBRATING MASS OF EACH SPECIES APPEARING IN ABSORPTION AND EMISSION MÖSSBAUER SPECTRA

Complex	l.s.	h.s.	h.s.[d]
$[Fe(snn)_2](ClO_4)_2$	128		
$[Fe(snnme)_2](ClO_4)_2 \cdot 2H_2O$	129		
$[Fe(phen)_2(NCS)_2]$	300		
$[Fe(phen)_2(CN)_2]$	134		
$[^{57}Co(snnme)_2](ClO_4)_2$	80	58	39
$[^{57}Co(pmi)_3](ClO_4)_2$[a]	90	73	27
$[^{57}Co(phen)_2(CN)_2]$[a]	115		44
$[^{57}Co(2\text{-}CH_3\text{-}phen)_3](ClO_4)_2$[b]	154±15		41±2
$[^{57}Co(phen)_2(NCS)_2]$[c]		56±3	

a—c) Data for the isomer shifts are quoted from Refs. 14, 12, and 11, respectively. d) Metastable state.

The origin of a metastable state is believed to be as follows in connection with bonding between an iron and a coordination atom.

(i) The bonds between the metal and the ligands are excited by the photoelectrons and X-rays emitted after Auger cascade.

(ii) Auger cascade produces a highly charged iron atom. The coulomb repulsion occurs between the highly-positive charged iron atom and the positively charged ligands; these arise from electron transfer from ligands to an iron atom in order to neutralize the positive charge on the iron atom, and the coulomb repulsion changes the bond length.

At the same time, inter- or intramolecular vibration modes are excited through the secondary process and the energy deposited on a daughter atom is released to this vibrational system. This relaxation time would be dependent on the temperature of the lattice system. The decrease and disappearance of D as the source temperature rises in the emission spectra of $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ and $[^{57}Co(snnme)_2](ClO_4)_2$, respectively, suggest that the energy deposited by EC-decay is easily transferred to the lattice system as phonons. In these cases the spin-orbit coupling of the iron atoms is presumed to play an important role in the rapid relaxation of the energy to the lattice system.

It is concluded that the stronger the low-spin character of the cobalt complexes and the lower the source temperature, the longer the lifetime of a metastable state. At low temperatures, several parts of the decayed atoms become observable in the metastable state because of the greater lifetime of this state.

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