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MÖSSBAUER EMISSION SPECTROSCOPIC STUDIES ON SPIN EQUILIBRIUM COMPLEXES $[^{57}Co(terpy)_2]X_2$ (X=Cl and ClO_4)

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The ^{57}Fe Mössbauer emission spectroscopic technique has been applied to the study of after-effects of electron capture in $[^{57}Co(terpy)_2]Cl_2 \cdot 5H_2O$ and $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ (where terpy= 2,2',2''-tripyridyl) which exhibit an anomalous magnetic behavior. These results were interpreted on the basis of the difference in the spin multiplicity of the central cobalt ion.

The stabilization of the aliovalent state of iron-57 formed by EC-decay of cobalt-57 has been interpreted in terms of the autoradiolysis owing to the photoelectrons and X-rays,[1] and the molecular fragmentation due to the coulomb repulsion between multi-charged iron atom and positively charged ligands.[2] Recently Gütlich et al. have suggested that the anomalous spin state of iron(II) observed in the Mössbauer emission spectra of some cobalt(II) chelate compounds might correspond to the immediate precursors of the stable state of iron.[3]

In this work, we measured the Mössbauer emission spectra of $[Co(terpy)_2]Cl_2 \cdot 5H_2O$ and $[Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ labeled with 1 mCi ^{57}Co, which are known as the complexes demonstrating thermally induced spin equilibrium,[4] in order to investigate how the difference in the spin state of metal ion in the host matrix influences the stabilization of the anomalous iron-57 species formed after EC-decay.

The samples used in this work were prepared according to the methods in the literature[4] and elemental analysis was performed with the unlabeled samples. Potassium hexacyanoferrate(II) enriched with iron-57 was used as an absorber. All the spectra were fitted with Lorentzian line shape using the least-square method,

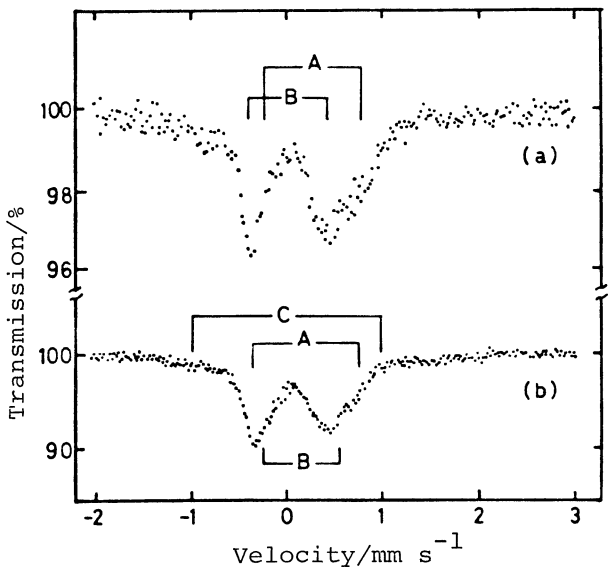

Fig. 1. Mössbauer emission spectra of $[^{57}Co(terpy)_2]Cl_2 \cdot 5H_2O$ at (a) 300 K and (b) 80 K.

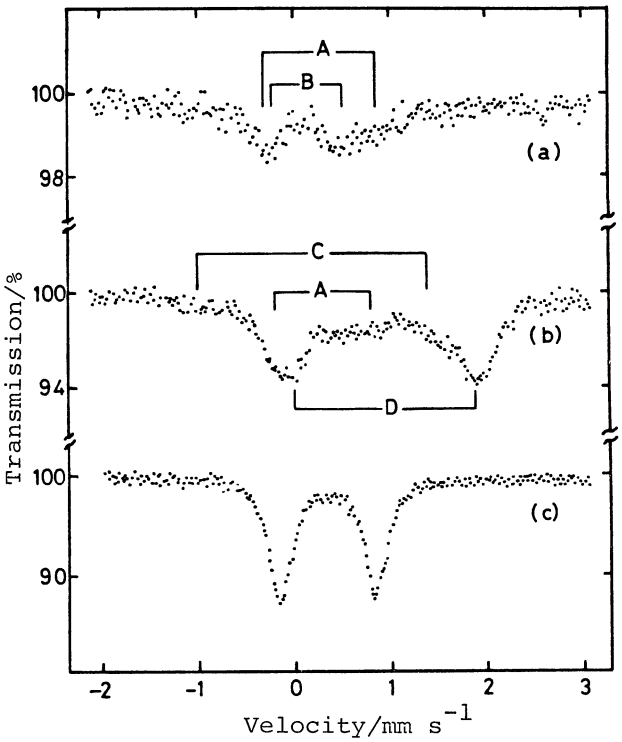

Fig. 2. Mössbauer emission spectra of $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ at (a) 300 K and (b) 80 K, and Mössbauer absorption spectrum (c) of $[^{57}Fe_{0.1}Co_{0.9}(terpy)_2](ClO_4)_2 \cdot 2H_2O$ at 80 K.

and the velocity scale was normalized with respect to metallic iron. The experimental errors for the parameters (isomer shift, quadrupole splitting, and full width at half-maximum) are estimated to be about 0.01 mm s^{-1}. Figures 1 and 2 show the Mössbauer emission spectra of $[^{57}Co(terpy)_2]Cl_2 \cdot 5H_2O$ and $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ together with the absorption spectrum of the cobalt complex doped with ^{57}Fe. The Mössbauer parameters measured for these complexes are listed in Table.

$[Co(terpy)_2]Cl_2 \cdot 5H_2O$ is confirmed to be in low-spin state at 297 and 80 K based on the effective magnetic moment (μ_{297}=2.53 B.M. and μ_{80}=2.10 B.M.), while the high-spin character in $[Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ is enhanced at both temperatures (μ_{297}=3.70 B.M. and μ_{80}=3.10 B.M.), and the corresponding iron complexes are always in low-spin state. The magnetic properties of the complexes prepared in this study are consistent with the Staufer's study.[4] We measured the Mössbauer absorption spectrum of $[^{57}Fe_{0.1}Co_{0.9}(terpy)_2](ClO_4)_2 \cdot 2H_2O$ in order to

clarify the ground state of the iron in the atomosphere of the host cobalt complexes. It was confirmed from the absorption spectra at 80 K and 300 K that iron-57 is in low-spin state. The X-ray diffraction measurements indicate the doped sample, $[^{57}Fe_{0.1}Co_{0.9}(terpy)_2](ClO_4)_2\cdot 2H_2O$, retains the same crystal structure as that of the host material, $[Co(terpy)_2](ClO_4)_2\cdot 2H_2O$.

The emission spectra of $[^{57}Co(terpy)_2]Cl_2\cdot 5H_2O$ and $[^{57}Co(terpy)_2](ClO_4)_2\cdot 2H_2O$ consist mainly of two sets of quadrupole doublets (A) and (B) at 300 K. The Mössbauer parameters of species (A) observed in all the emission spectra, are similar to those in the absorption experiments ($[Fe(terpy)_2](ClO_4)_2$[5] and $[^{57}Fe_{0.1}Co_{0.9}(terpy)_2](ClO_4)_2\cdot 2H_2O$), and such similarity evidences that a certain amounts of iron-57 formed by EC-decay is stabilized in the analogous environment to the iron in iron or cobalt complexes. The doublet (B) is ascribed to low-spin iron(II) species stabilized in the different situation from species (A) within the lifetime of iron-57m through the hot process described later. The emission spectra of two samples at 300 K consist almost the same components in spite of their different cobalt spin states. It is concluded from this result that the spin state of iron stabilized in the time scale of 10^{-7} s after EC-decay does not depend on the spin multiplicity of cobalt in these systems at this temperature.

Table. The Mössbauer parameters of the emission and absorption spectra of the complexes

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

a) Isomer shift. b) Quadrupole splitting.
c) Full width at half-maximum. d) Relative peak area.
e) Data from reference 5).

The Mössbauer spectra of the both complexes at 80 K, however, exhibit additional resonance lines (C) which are assigned to low-spin iron(III) based on its Mössbauer parameters. The absence of this species in the spectra at 300 K is presumably due to the decreased recoilless fraction at increased temperatures. The spectrum of $[^{57}Co(terpy)_2]Cl_2 \cdot 5H_2O$ at 80 K is mainly composed of low-spin iron(II). On the other hand, the spectrum of $[^{57}Co(terpy)_2](ClO_4)_2 \cdot 2H_2O$ has another intense doublet (D) at 80 K, which is assigned to high-spin iron(II) on the basis of its isomer shift, 0.93 mm s^{-1}, although the doublet (D) is not observed at 300 K. This indicates that the doublet (D) is ascribed to a metastable-state species. Namely the ligand field's strength about ^{57}Fe is weaker than that of corresponding iron compounds in the Mössbauer time scale of ca. 10^{-7}-10^{-8} s after EC-decay. The sequence of the events following EC-decay at 80 K appears to be as follow:

^{57}Co(high-spin state) $\longrightarrow$ ^{57}Fe(high-spin metastable-state like (D)) $\longrightarrow$ ^{57}Fe(low-spin state like (A) or (B)).

It is considered that the species (D) is in the metastable-state prior to the stable state such as (A) or (B). The absence of this state (D) in other three emission spectra indicates that the lifetime of this metastable-state depends on the spin multiplicity of cobalt and changes according to the temperature. In these cases, hot processes such as autoradiolysis of the ligands by photoelectrons and X-rays and coulomb repulsion by highly charged iron must be further taken into account.

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