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Chemical Effects Due to the (γ, n) Reaction and Isomeric Transition Studied by a Vacuum Sublimation Technique

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Chemical effects of the ^{59}Co(γ,n)^{58m,g}Co reaction and of the isomeric transition of ^{58m}Co in Co(acac)$_3$, Co(acac)$_2$, and Co(acac)$_2$·2H$_2$O were studied by using a vacuum sublimation technique. In the isomeric transition, highly enriched ^{58g}Co(acac)$_2$ was separated from ^{58m}Co(acac)$_3$. By the (γ,n) reaction, about a half of the radioactive nuclides produced were found in the form of Co(acac)$_2$ after irradiation of Co(acac)$_3$. The present results were compared with those obtained by other authors.

A vacuum sublimation method has been successfully applied to hot atom chemical study and enrichment of radioactive isotopes in our laboratory.[1-3] It was found that this method was an effective radiochemical separation method for the following reasons. It can separate chemical species of tracer scale in dry environment immediately after irradiation. If the volatile metal organic complex of suitable stability is chosen for the study, sublimation can be made at a moderate temperature under which ordinary inorganic compounds can not sublime. It is well known that β-diketones, such as 2,4-pentanedione (acetylacetone, Hacac), 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, Hdpm or Hthd), form volatile complexes with many metallic elements, and these complexes are available as irradiation targets for hot atom chemical studies.

For neutron-irradiated Co(acac)$_3$, it was found previously that highly enriched ^{60}Co(acac)$_2$ was separated from the target by sublimation in an evacuated tube with a temperature gradient.[2] However, detailed studies of chemical effects due to the (γ, n) reaction have not yet been carried out, except for the few papers mentioned below. In order to obtain high specific activity of ^{58}Co, Hoffman tried a hot atom chemical enrichment by using ion exchange separation.[4] Nath studied the change of the retention value of Co(acac)$_3$ in the (n, 2n) reaction.[5] Shoji *et al.* investigated the hot atom chemistry of the tetraphenylporphyrin complex of cobalt due to ^{58m}Co decay, and they found a retention value higher than 75%.[6] Lazzarini and Lazzarini reported the survival probabilities for several cobalt complexes in isomeric transition of ^{58m}Co.[7]

In order to study the hot atom chemistry of the (γ, n) reaction of cobalt, the accumulative effects of the (γ, n) reaction and the isomeric transition of ^{58m}Co must be evaluated. In the present study, these effects were separately analysed. Chemical effects of the (γ, n) reaction and of the isomeric transition of ^{58m}Co were investigated by applying a sublimation method which is specifically useful to separate Co(acac)$_2$ from Co(acac)$_3$.

Experimental

Sample Preparation. Two kind of cobalt complexes, tris(2,4-pentanedionato)cobalt(III) (Co(acac)$_3$) and diaquabis(2,4-pentanedionato)cobalt(II) (Co(acac)$_2$·2H$_2$O), were synthesized from CoCl$_2$·6H$_2$O and acetylacetone (both were commercially obtained from the Wako Pure Chemical Co. Ltd., Guaranteed) by the previously reported methods.[8,9] The tracer of ^{60}Co was spiked in the synthesis to enable us to estimate the processes of radiation and thermal decomposition. Each complex was purified twice by sublimation.

The sample of Co(acac)$_2$·2H$_2$O transfers to Co(acac)$_2$ in the vacuum sublimation, while the former is obtained by allowing Co(acac)$_2$ to stand in the atmosphere for one day after the sublimation. As for Co(acac)$_2$, which is strongly hydroscopic, the sample was sealed in a plastic package as soon as possible after breaking the vacuum of the sublimation tube so that hydration could be avoided. The chemical form of Co(acac)$_2$ was examined by X-ray diffraction in order to evaluate the effectiveness of sealing. By this examination, it was found that most of the Co(acac)$_2$ remained unchanged for a few days. Therefore, Co(acac)$_2$ used for the target was prepared just before the irradiation with γ-rays.

Irradiation. Irradiation with bremsstrahlung (maximum energy: 60 MeV) was carried out by an electron linear accelerator of the Laboratory of Nuclear Science, Tohoku University. A platinum converter was used to obtain bremsstrahlung from electrons; unconverted electrons were removed by a sweep magnet, and the targets were cooled by Dry Ice during an irradiation period of about seven hours.

Radioactivity Measurement. Radioactivity was measured with a 4K γ-ray spectrometer equipped with a Ge(Li) detector of 80 cm^3. Determenation of ^{58g}Co can be made by measuring its γ-ray of 810 keV. Owing to the very low energy of this γ-ray and to its large internal conversion coefficient ($\approx$2000), ^{58m}Co was determined indirectly from the growth curve of ^{58g}Co, which allowed analysis of ^{58m}Co decay.

Sublimation System. The sublimation system used in this experiment is shown in Fig. 1. Though the electric furnace (Type 1) in the figure was designed to have little temperature gradient inside, a steep temperature gradient outside the furnace was effective to separate Co(acac)$_3$ from Co(acac)$_2$, which was more volatile than the former complex. This type of furnace was found useful in purification of the cobalt complexes. Another electric furnace (Type 2) used in this study has a temperature gradient inside; it can effectively

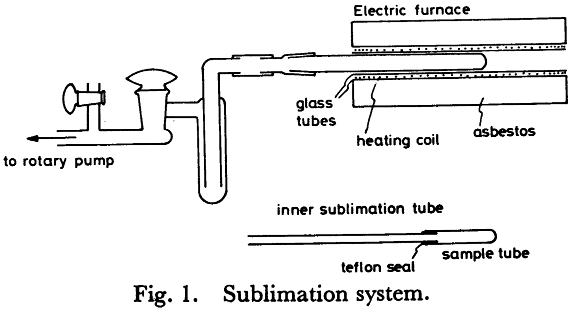

Fig. 1. Sublimation system.

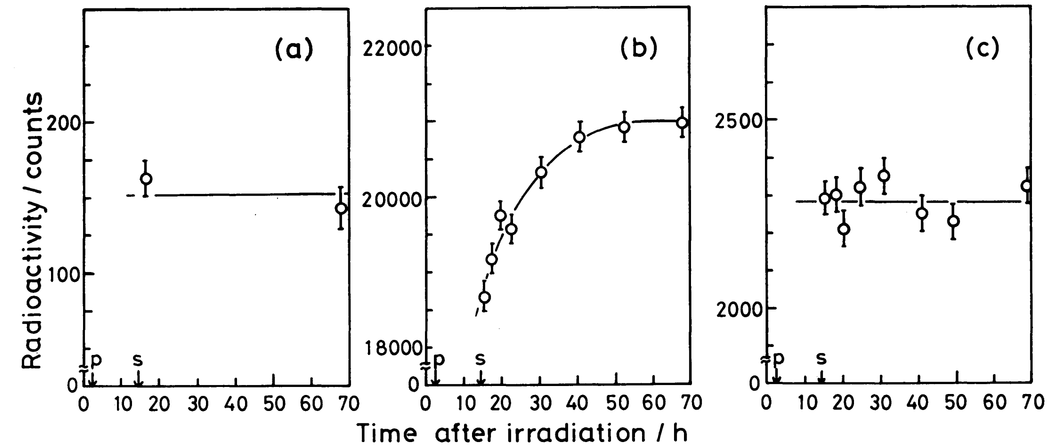

Fig. 2. Radioactivity change with time for each fraction separated by sublimation.
a): Residue, b) $Co(acac)_3$ fraction, c) $Co(acac)_2$ fraction; P and S denote the time when purification is over, and that when resublimation is over, respectively.

separate various volatile chelate compounds.[3] The temperature for sublimation was set at 170 °C. Beyond this temperature $Co(acac)_3$ would be decomposed to $Co(acac)_2$ in a considerably higher rate and, on the other hand, below this temperature a much longer time would be needed to sublime the sample completely. At 170 °C, sublimation started at about five minutes after inserting the sample tube under the vacuum of about 0.13 Pa. Almost complete sublimation finished after about fifteen minutes.

Results and Discussion

Isomeric Transition Effect of ^{58m}*Co Decay.* One of the difficulties in investigating the isomeric transition effects due to ^{58m}Co decay is to prepare the complexes labeled with ^{58m}Co and to purify them in a very short time. However, we have solved this problem by sublimatographic separation of the irradiated cobalt complexes using an electric furnace of Type 1. This procedure can be performed easily. Examination of chemical properties by alumina column chromatography using chloroform as a solvent, or by thin layer chromatography using benzene-ether (50/50) guaranteed the chemical identity and purity of each complex.[10]

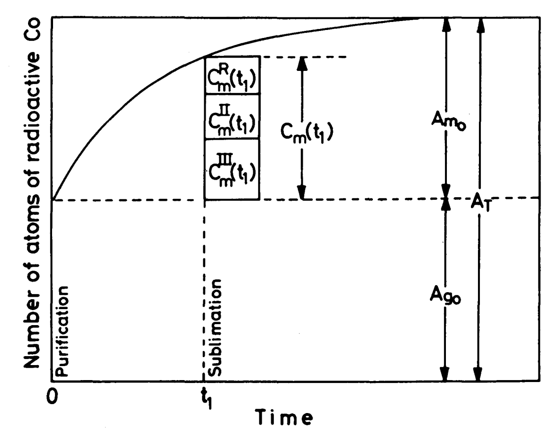

Fig. 3. Relationship between the number of atoms and time in the study of ^{58m}Co decay effect.

The complex $Co(acac)_3$ labeled with ^{58m}Co was stored in a small glass tube under Dry Ice cooling. Its portions were taken as samples for sublimation from time to time. Concentrated hydrochloric acid was added to three different fractions separated by sublimation, and their radioactivity was measured at appropriate time intervals. As an example, the results of radioactivity measurements are shown in Fig. 2. Only the radioactivity of the $Co(acac)_3$ fraction increased. Whereas the radioactivities for the residue and the $Co(acac)_2$ fractions showed no change with time. Almost all the radioactivity of ^{60}Co which was spiked before irradiation was detected in the $Co(acac)_3$ fraction. From these results, ^{58g}Co radioactivities detected in the residue and also in the $Co(acac)_2$ fraction could be ascribed to the decay product of ^{58m}Co during the storage. Calculation of the retention value can be done as schematically shown in Fig. 3. When the m/g ratio of ^{58m}Co to ^{58g}Co at $t=0$ is expressed as A_{m0}/A_{g0}, the total radioactivity of ^{58}Co after a cooling time which is long enough to allow ^{58m}Co to decay out is $A_T(=A_{m0}+A_{g0})$. And the disintegrating amount of ^{58m}Co from $t=0$ to $t=t_1(C_m(t_1))$ can be calculated from the same growth curve.

$$C_m(t_1) = A_{m0}(1-e^{-\lambda_m t_1}) = A_T(1-f)(1-e^{-\lambda_m t_1}), \quad (1)$$

where $f=A_{g0}/A_T$. Then the retention value (R) is obtained by the following equation:

$$R(\%) = \frac{C_m^{III}(t_1)}{C_m(t_1)} \times 100 = \left\{1 - \frac{C_m^R(t_1)+C_m^{II}(t_1)}{A_T(1-f)(1-e^{-\lambda_m t_1})}\right\} \times 100, \quad (2)$$

where $C_m^{III}(t_1)$, $C_m^{II}(t_1)$, and $C_m^R(t_1)$ are radioactivities of the decayed components in $Co(acac)_3$ and $Co(acac)_2$ and of the residue at $t=t_1$, respectively. The retention values obtained from these analyses are plotted against storage times in Fig. 4. This result shows that some annealing effect during storage can not be avoided even under Dry Ice cooling; a constant value of about 60% was obtained after ten days. The increase in the retention value with storage time was balanced by the decrease in the yield of $^{58g}Co(acac)_2$. In a study of ^{58m}Co decay effects by using a wet separation method, Lazzarini

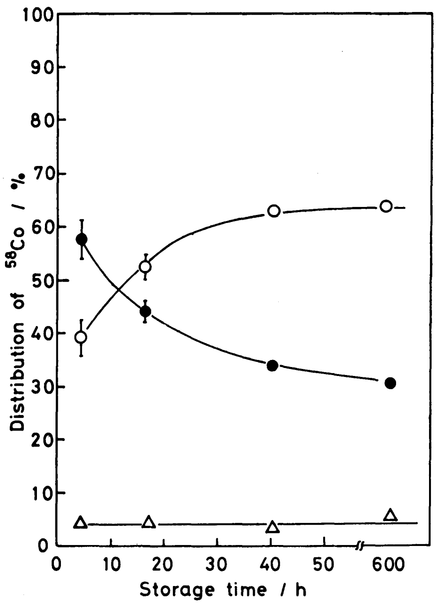

Fig. 4. Change of distribution of ^{58}Co with storage time. ○: Fraction of Co(acac)$_3$, ●: fraction of Co(acac)$_2$, △: residue.

and Lazzarini reported 47.9% of the daughter nuclides remained in the chemical form of the parent, and 47.2% were found in the Co^{2+} ion fraction.[7] The Co(acac)$_3$ retention in our experiments is slightly below 40% at an earlier stage and then gradually increases up to 60%. It is very interesting to see that there is an agreement between our values and Lazzarini's, although they gave the percentage of Co^{2+} instead of the Co(acac)$_2$ reported in our experiments. These facts show that annealing during sublimation in the present study *per se* does not contribute much to the overall results. The presence of Co(acac)$_2$ in a large amount is a rather striking finding, and this was made possible by the application of sublimatographic procedures in this study. However, the detailed mechanism of formation of Co(acac)$_2$ is not so simple.

Though the increase of the retention values with storage time is not yet explained very clearly, some possibilities can be considered. One is a charge transfer reaction between Co^{2+} and surrounding molecules, which Kalliat and Nath suggested.[11] Another explanation is the existence of a reaction which proceeds with very low activation energy even under Dry Ice temperature, although this would be unusual. The last explanation, which seems to be more plausible than the earlier ones, is an electrostatic interaction between recoils and their partners or surrounding matrices. This does not require much thermal agitation. This type of interaction is found in some cases involving positively charged species after nuclear decay and negatively charged oxygen impurities; detailed features of this mechanism will appear in forthcoming papers.[12]

The most significant result in this experiment is that a considerable amount of ^{58g}Co was found as the chemical form of Co(acac)$_2$. This fraction seems to correspond to the fraction analysed by Lazzarini and Lazzarini as the fraction of Co^{2+} ion which corresponds to the "complete fragmentation" in the decay event. It is known that radioactive atoms produced by nuclear reactions form a considerable amount of ligand-deficient species.[13] Tominaga and Saito pointed out the possibility of the presence of ligand-deficient complexes of the types Co(acac)$_{3-n}$$^{n+}$.[14] If $n=1$ is assumed, Co(acac)$_2$ and Co(acac)$_2$$^+$ are present in the solid: the former is observed in our experiment and the latter may be sensitive to annealing reactions. Therefore, it is considered that ^{58g}Co(acac)$_2$ separated by sublimation has its own chemical form and/or charge state in solids just before separation.

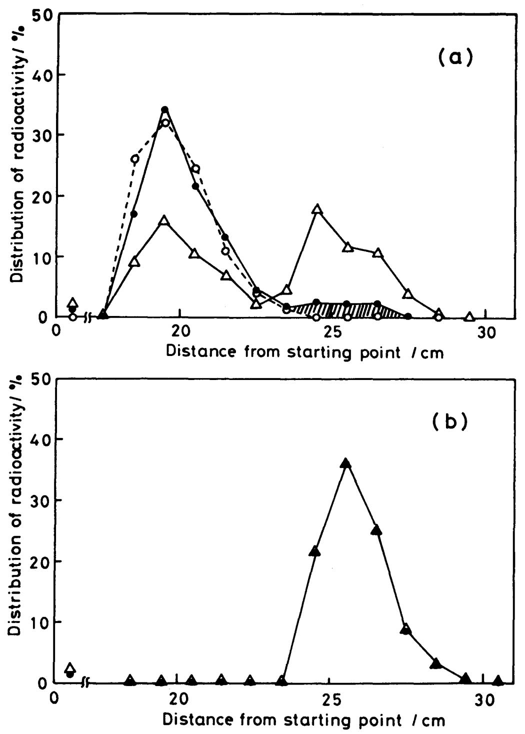

Fig. 5. Distribution of radioacrivity along sublimation tube.

(a): Irradiated Co(acac)$_3$, (b): irradiated Co(acac)$_2$–2H$_2$O. ○: ^{60}Co sublimation before irradiation, ●: ^{60}Co sublimation after irradiation, △: ^{58}Co.

The yield of the residue was almost constantly 3—4%. Although the chemical components of the residue are not clear, the residual amount of ^{58g}Co radioactivity agreed with that which Lazzarini and Lazzarini denoted as partial fragmentation.

A similar experiment was carried out for the Co(acac)$_2$ complex. Highly enriched ^{58g}Co(acac)$_3$ was not obtained; the retention value as Co(acac)$_2$ was 99% and did not vary with storage time. Almost all the ^{60}Co radioactivity was found in the parent complex, and 1% of ^{58g}Co remained in the residue; this result seems to show the extent of decomposition induced by the isomeric transition.

The Chemical Effect by the (γ, n) Reaction. The sublimatographic results obtained by using the electric furnace (Type 2) with temperature gradient are shown in Fig. 5. The dotted line in Fig. 5(a) for Co(acac)$_3$ shows the distribution of ^{60}Co radioactivity obtained by the sublimation before irradiation. Thermal decomposi-

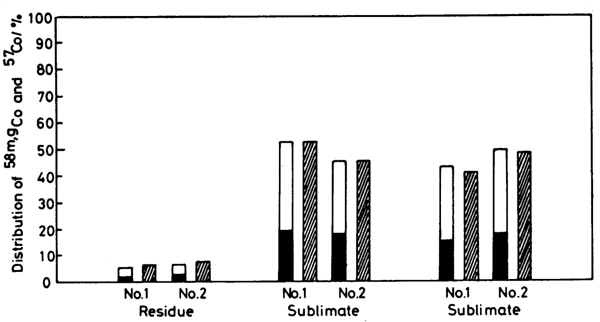

Fig. 6. Distribution of ^{58m,g}Co and ^{57}Co in each fraction. ^{58g}Co: closed area, ^{58m}Co: open area, ^{57}Co: shaded area. Nos. 1 and No. 2 denote experimental number.

tion of Co(acac)$_3$ is almost negligible under these conditions. In the case of sublimation after irradiation, about 4% of total ^{60}Co radioactivity was observed (shaded area) in the form of Co(acac)$_2$. The radioactivity of ^{58}Co was measured after long period during which almost all ^{58m}Co decayed out. A half of ^{58}Co radioactivity was found in the Co(acac)$_2$ fraction.

Figure 6 shows the distribution of ^{58}Co in each fraction separated by sublimation made immediately after the irradiation. This is compared to the distribution of ^{57}Co produced simultaneously by the (γ, 2n) reaction. This result shows that the radioactivity of ^{58}Co almost equally distributed in the Co(acac)$_3$ and Co(acac)$_2$ fractions; the same tendency appears for the distribution of ^{57}Co.

The ^{58m}Co/^{58g}Co ratio in each fraction was obtained by the growth curve of each fraction, and is shown in Fig. 7. The residue showed the smallest value, while the Co(acac)$_3$ fraction showed the largest value. This pattern was found to be sufficiently reproducible. Each fraction was considered to consist of three components at the end of irradiation; ^{58g}Co and ^{58m}Co produced directly by (γ, n) reaction (A_g, A_m), and a part of ^{58g}Co produced by the decay from ^{58m}Co during the irradiation ($A_{m\to g}$). A_g, A_m, and $A_{m\to g}$ are represented as follows:

$$A_g = N\phi\sigma_g(1-e^{-\lambda_g t}) \tag{3}$$

$$A_m = N\phi\sigma_m(1-e^{-\lambda_m t}) \tag{4}$$

$$A_{m\to g} = N\phi\sigma_m\left\{(1-e^{-\lambda_g t}) - \frac{\lambda_g}{\lambda_g-\lambda_m}(e^{-\lambda_m t} - e^{-\lambda_g t})\right\}, \tag{5}$$

where ϕ is flux of γ-rays, N is the amount of cobalt atoms in the target, t is irradiation time, λ_g and λ_m are the decay constants of ^{58g}Co and ^{58m}Co, respectively, σ_g and σ_m are the independent reaction cross sections of (γ, n) reactions to produce ^{58g}Co and ^{58m}Co, respectively. $A_{m\to g}$ can be obtained from the Eqs. 3 and 5 and A_T, which is the total amount of radioactivity of ^{58}Co after long cooling when all the ^{58m}Co atoms have decayed out.

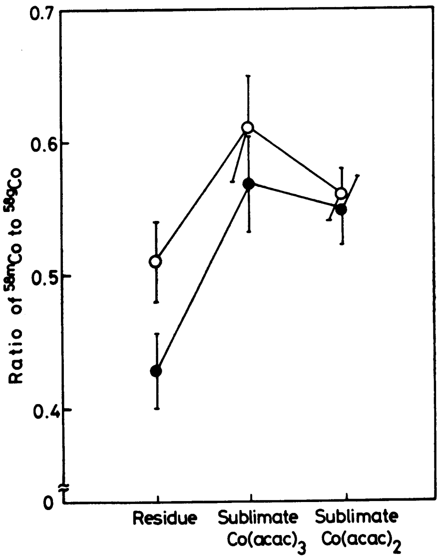

Fig. 7. Ratio of ^{58m}Co to ^{58g}Co in each fraction. ○: Experiment No. 1, ●: Experiment No. 2.

$$A_T = N\phi(\sigma_m+\sigma_g)(1-e^{-\lambda_g t}) \tag{6}$$

From Eqs. 3, 5, and 6,

$$\frac{\sigma_m}{\sigma_g} = \frac{(1-e^{-\lambda_g t})\{A_T-(A_{m\to g}+A_g)\}}{(1-e^{-\lambda_g t})(A_{m\to g}+A_g)-\left\{(1-e^{-\lambda_g t})-\frac{\lambda_g}{\lambda_g-\lambda_m}(e^{-\lambda_m t}-e^{-\lambda_g t})\right\}A_T} \tag{7}$$

Since the ratio of σ_m/σ_g is determined experimentally to be 1.16±0.06, the percent ratio of $A_{m\to g}$ to A_T is given by the equation:

$$\frac{A_{m\to g}}{A_T} \times 100 = \frac{\sigma_m/\sigma_g\left\{(1-e^{-\lambda_g t})-\frac{\lambda_g}{\lambda_g-\lambda_m}(e^{-\lambda_m t}-e^{-\lambda_g t})\right\}}{(\sigma_m/\sigma_g+1)(1-e^{-\lambda_g t})} \times 100 \tag{8}$$

In this case, a value of 11.84±0.75% was obtained for the percent ratio of $A_{m\to g}$ to the total activity A_T. By sublimation each component can be separated into the residue, the Co(acac)$_3$ fraction, and the Co(acac)$_2$ fraction. The proportion of distribution of A_g and $A_{m\to g}$ in each fraction can not be determined directly in this experiment, but the latter can be estimated by assuming that the proportions of initial distribution of A_g in each fraction are equal to that of A_m. This assumption is reasonable, judging from the relationship of the recoil energy-percentage of product found by Yoshihara and Kudo,[15] because similar recoil energies (beyond 1 keV)

TABLE 1. RETENTION VALUE AND ^{58m}Co/^{58g}Co RATIO FOR IRRADIATED Co(acac)$_2$ AND Co(acac)$_2$·2H$_2$O OBTAINED BY SUBLIMATION SEPARATION

		^{58}Co (%)	^{57}Co (%)	^{60}Co (%)	m/g ratio[a]
Co(acac)$_2$	Sublimate	98.2±0.4	98.0±1.0	98.7±0.1	0.52±0.10
	Residue	1.8±0.1	2.0±0.1	1.3±0.1	0.45±0.07
Co(acac)$_2$·2H$_2$O	Sublimate	97.2±0.4	97.3±0.7	97.4±2.0	0.58±0.07
	Residue	2.8±0.1	2.7±0.1	2.6±0.1	0.50±0.06

a) It means a ratio of ^{58m}Co to ^{58g}Co.

of both nuclides will give the same plateau value of the product percentage. This relationship is further justified by the equal product distribution of the (γ, n) and (γ, 2n) reactions described before. The distribution of $A_{m\to g}$ in each fraction was calculated to be 9.8±1.2% in the residue, 41.9±9.8% in the Co(acac)$_3$ fraction, and 48.3±6.3% in the Co(acac)$_2$ fraction. The contribution to the residue for $A_{m\to g}$ was larger by about 4.4% than that for A_m. Therefore, it is considered that the two kinds of effects by (γ, n) reaction and isomeric transition have superimposed additively.

A similar study was made for the irradiation of Co(acac)$_2$ and Co(acac)$_2$·2H$_2$O, and the results are shown in Table 1. The retention value in Co(acac)$_2$·2H$_2$O was slightly smaller than that in Co(acac)$_2$. This tendency is the same as reported by Yoshihara *et al.* in the case of the (γ, γ') reaction in In·hedta complexes with and without crystalline water.[16] This difference may be attributed to the decrease of back reaction probability by obstruction in the presence of water molecules.

The m/g ratio in the sublimate and the residue did not show the same value as those in the case of Co(acac)$_3$. It is suggested that ^{58g}Co produced by the decay of ^{58m}Co tends to form more nonvolatile species than that produced directly by nuclear reaction.

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