

ノート

赤外スペクトルによる $[\text{Co}(\text{en-d}_4)_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ の
 β 放射線分解の研究 (en : エチレンジアミン)

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$[\beta\text{-Radiolysis of } [\text{Co}(\text{en-d}_4)_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}]$

Infrared Study on β -Radiolysis of
 $[\text{Co}(\text{en-d}_4)_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ (en: ethylenediamine)

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Abstract

β -Radiolysis of $[\text{Co}(\text{en-d}_4)_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ was studied under a mild condition by means of infrared spectroscopy over a period of 8 months. The spectra became complex due to the appearance of many new bands in the initial process. This is explained in terms of the exchange reaction in hydrogen isotopes between water and ethylenediamine. It was found that ethylenediamine decomposed by $\sim 50\%$ in 100 days, forming ammonia coordinated to a Co^{2+} ion and an ammonium ion. On the other hand, a Co(III) ammine complex, acetylene and so on were not found. A scheme for the β -radiolysis is proposed.

We have studied β -radiolysis of $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ by means of infrared spectroscopy,^{1,2)} where it has been proposed that a decomposition reaction of $\text{en} \rightarrow 2\text{NH}_3 + \text{HCCH}$ takes place owing to β -emission, forming an ammine complex. On the other hand, infrared spectra have changed too rapid to identify and determine the

decomposition products, especially for the initial process. Very strong bands have appeared in the range of $3600\sim 3100\text{ cm}^{-1}$, whose assignments are obscure. Thus, it is desirable to observe infrared spectra under a mild condition in a radiation field as compared with the previous one (H system). This was carried out using T_2O diluted by H_2O and a N-deuterated complex. This will be reported in details in the present study.

The N-deuterated compound was obtained by recrystallization of the compound 5 times from D_2O . The anhydrate was obtained with dehydration at 120°C *in vacuo*. T_2O was prepared by means of oxidation of T_2 with CuO at 300°C . The amount of tritium used was estimated to be 0.8 Ci from the pressure of tritium gas in the reaction vessel. The isotopic purity of tritium was lowered extremely by an exchange reaction with H adsorped on the surface in a reaction vessel, though the absolute value was unknown; the lowering was suitable for a mild condition for β -radiolysis, as shown later. The absorption of T_2O into the anhydrate was carried out by exposing the anhydrate to the vapour. Infrared spectra were observed in the range of $4000\sim 330\text{ cm}^{-1}$ over a period of 8 months by use of a JASCO-IRA-302 spectrometer with a beam condenser, as reported previously.¹⁾ The observed spectra are given in Fig. 1, where t means the reaction time by day. Changes in absorbance of some bands with t are given in Fig. 2.

The infrared spectra became complex with appearance of many new bands in the initial process ($t < 20$), as shown in Fig. 1. Subsequently, further new bands appeared at $1635, 1420\text{ cm}^{-1}$ and so on with decreasing the intensity for many bands owing to ethylenediamine, as shown in Fig. 1. The second process indicates clearly the decomposition of ethylenediamine, which is quite slow in comparison with the H system, where two third of ethylenediamine decomposes at $t\sim 11$.

In the initial process ($t < 20$) the doublet of the O-X stretchings ($X = \text{H, D or T}$) was observed with the center at $3450, 2550$ or 2160 cm^{-1} , respectively. The N-X stretching was also observed in the lower frequency region by $\sim 150\text{ cm}^{-1}$ than the O-X one. Although we added T_2O diluted with H_2O to the compound, the intensity of bands for ND_2 groups decreased rapidly, as seen in the N-D stretching at 2330 cm^{-1} and the ND_2 bending at 1160 cm^{-1} .^{3,4)} This indicates clearly that the exchange reaction of hydrogen isotopes takes place easily between water and ethylenediamine at $t < 20$, forming probably isotopes of water, XOY ($X, Y = \text{H, D or T}$), and those of ethylenediamine. Further gradual decrease in intensities for O-D and N-D groups was found even at $t\sim 70$, as seen in Fig. 1. This is explained in terms of the exchange

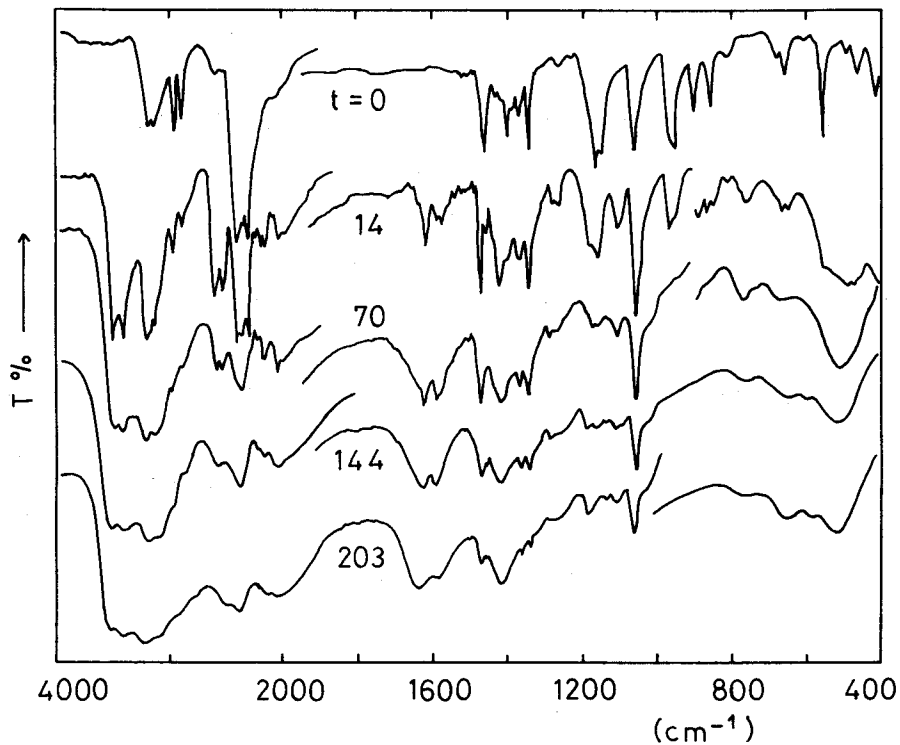


Fig. 1. The infrared spectra of [Co(en-d₄)₃] Cl₃ · 3T₂O at various times. *t* means a reaction time by day.

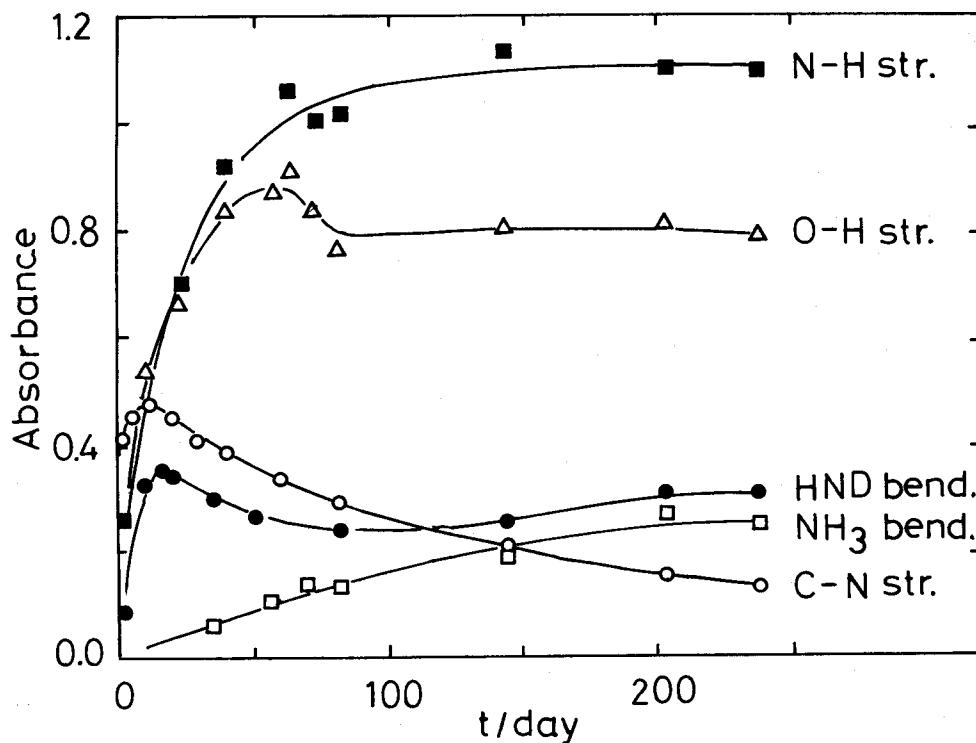


Fig. 2. Change in absorbance of some bands with time.

reaction in hydrogen isotopes between solid and vapour phases, by referring to the fast exchange reaction in the solid phase at $t < 20$.

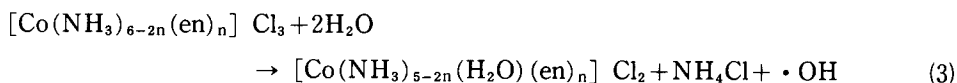
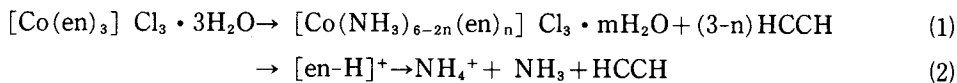
It is seen from the infrared spectra at $t = 14$ and 70 that the intensity of the C-N stretching at 1060 cm^{-1} ¹⁻⁴⁾ decreases considerably as well as those for CH_2 groups at 1470 and 1340 cm^{-1} , whereas the absorbance in such positions as the O-H stretching and 1635 cm^{-1} increases, as summarized in Fig. 2. The absorbance of the C-N stretching at 1060 cm^{-1} increases owing to the hydration at $t < 10$ in Fig. 2. Hence, the absorbance at $t = 0$ should be corrected to be 0.5, by extrapolating the absorbance to $t = 0$; we have 30 % decomposition at $t = 70$ from Fig. 2. It is clear that the decomposition results in difference between spectral features at $t = 14$ and >70 in Fig. 1. That is, the bands owing to decomposition products overlap with those owing to the parent ones in the infrared spectra, especially at $t > 70$. In Fig. 2 the absorbance for N-H and O-H stretchings is almost constant in spite of decomposition of the crystal at $t > 70$. This constancy indicates clearly appearance of new bands at 3300 cm^{-1} , which have been reasonably ascribed to N-H stretchings of ammonia.¹⁾ The band at 1635 cm^{-1} in Fig. 1 is attributed to ammonia; the band owing to H_2O is 1620 cm^{-1} .¹⁾ Thus, the formation of ammonia is obvious in agreement with the H system. In Fig. 2 the absorbance for the HND bending at 1420 cm^{-1} has the maximum at $t = 16$. The decrease at $t > 16$ corresponds to the decomposition of ethylenediamine. The successive increase at $t > 82$ is attributed to a decomposed product, NH_4^+ , as seen in the H system; the band at 1420 cm^{-1} is assigned to the asymmetric bending of an ammonium ion.

The NH_3 symmetric bending and the rocking in ammine complexes are quite sensitive in frequency to a metal ion and its valency,⁵⁾ which have been observed at 1325 and 818 cm^{-1} for $[\text{Co}(\text{NH}_3)_6] \text{Cl}_3$ and 1163 and 654 cm^{-1} for $[\text{Co}(\text{NH}_3)_6] \text{Cl}_2$, respectively. There was no band at 820 cm^{-1} in Fig. 1, though the corresponding band has been found in the H system. On the other hand the band at 650 cm^{-1} was observed in Fig. 1, which has been also found in the H system. These suggest that ammonia coordinates to a Co^{2+} ion in the present system, which is also supported through the appearance of the band at 1190 cm^{-1} for the NH_3 symmetric bending. The reduction of a Co^{3+} ion is consistent with the formation of an ammonium ion, as described above, by supposing reduction by H.

The formation of acetylene has been proposed in the H system. On the other hand, there was no band for acetylene in the present study. This may indicate that acetylene escapes from the crystal to the gas phase for a slow reaction, as suggested in the H system. The Co(III) ammine complex has been found in the H system, whereas the Co

(II) ammine complex is found under the slow condition. Thus, the Co(III) ammine complex is regarded as an intermediate. The reductant is probably water owing to a reaction $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e \rightarrow \text{H}^+ + \cdot\text{OH}$, though no product due to OH radicals was found from infrared spectra.

In the present study the spectral change owing to β-emission was, as a whole, simple rather than that in the H system. That is, the products confirmed in the present study are ammonia coordinated to a Co²⁺ ion and an ammonium ion, whereas those in the H system have the additional ones: [en-H]⁺, CO₂, HCCH and ammonia coordinated to a Co³⁺ ion.¹⁾ Since a Co(III) ammine complex as well as a [en-H]⁺ ion is regarded as the intermediate, we may, thus, summarize β-radiolysis for [Co(en)₃] Cl₃ · 3H₂O as follows:



where the formation of aquo complexes in Eq. 3 is reasonably expected from a libration at ~500 cm⁻¹, as reported previously.¹⁾

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