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PHOTO-LIGAND-SUBSTITUTION REACTION OF TRIS(ETHYLENEDIAMINE) COBALT(III) ION WITH N-BIS(2-HYDROXYETHYL)DITHIOCARBAMATE ION

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Tris(ethylenediamine)cobalt(III) ion underwent a ligand substitution with N-bis(2-hydroxyethyl)dithiocarbamate ion(=L^-) to form $[CoL_3]$ in aqueous solution, when the light(460-585nm) was irradiated. The quantum yield(0.343-0.845) of the reaction is unusually high compared to those of the photo-ligand-substitution reactions of cobalt(III) complexes so far known.

It has been so far known that the quantum yields of the photo-ligand-substitution reaction of cobalt(III) complexes are very low, except for the few cases such as the aquation of $[Co(CN)_6]^{3-}$ and $[Co(CN)_5H_2O]^{2-}$.1) Especially $[Co(en)_3]^{3+}$ has been believed to be inert for visible light, and undergoes aquation by only irradiation of the light of the charge transfer band region.2)

Recently, Matsubara and Kida found that $[Co(en)_3]^{3+}$ readily reacts with dtc^- (=diethyldithiocarbamate ion) in aqueous solution forming solid $[Co(dtc)_3]$, when the 550nm (or less in wavelength) light is irradiated. However, they were not successful in determining the quantum yield of the reaction, because the deposit of the product $[Co(dtc)_3]$ on the cell window disturbed quantitative measurements.3)

In this paper photo-ligand-substitution reaction of $[Co(en)_3]^{3+}$ with L^- (=N-bis(2-hydroxyethyl)dithiocarbamate ion) are reported, where the reaction product $[CoL_3]$ is somewhat soluble in water, thereby enabling us to determine the quantum yield of the reaction. The product $[CoL_3]$ can be crystallized from aqueous solution, and was characterized by elementary analysis. Found: C,30.32; H,5.15; N,6.84 %, calcd. for $C_{15}H_{30}N_3O_6S_6Co$: C,30.04; H,5.04; N,7.01 %. The potassium salt of the ligand L^- was synthesized as colorless crystals from diethanolamine, carbon disulfide and potassium hydroxide. Found: C,27.29; H,4.63; N,6.53 %, calcd. for

$C_5H_{10}NO_2S_2K$: C,27.38; H,4.60; N,6.39 %. One mililitre of an aqueous solution of $[Co(en)_3]Cl_3\cdot 3H_2O$(0.0607M) and 2ml of an aqueous solution of KL(0.183M) were mixed in a 1 cm quartz cell in the dark room. The irradiation was carried out at 585, 571, 535, 511, 486 and 460nm by use of JASCO MODEL CRM-FA SPECTRO-IRRADIATOR attached with a 3kW Xe-lamp as a light source, band width of each light being within 15nm. The irradiation times were set so that about 5% of $[Co(en)_3]^{3+}$ undergo the ligand substitution reaction for each wavelength.

The quantum yields were calculated using the formula derived by Kling et al. for the reaction, $A \xrightarrow{h\nu} B$.[4)] According to them,

$$-\phi\int_0^t Q_0 dt = \frac{\kappa_A-\kappa_B}{\kappa_A}\int_{a_0}^{a}\frac{da}{1-\exp[-\{(\kappa_A-\kappa_B)a+\kappa_B a_0\}h]} + \frac{\kappa_B}{\kappa_A}a_0\int_{a_0}^{a}\frac{da}{a\left(1-\exp[-\{(\kappa_A-\kappa_B)a+\kappa_B a_0\}h]\right)}$$

Here, ϕ is the quantum yield for a monochromatic light and $\int_0^t Q_0 dt$ represents the quanta of the irradiation in unit volume($mol\cdot \ell^{-1}$); a and h are concentration of A($mol\cdot \ell^{-1}$)(when t=0, $a=a_0$) and thickness of the reaction cell(cm), κ_A and κ_B being molar natural extinction coefficients($mol^{-1}\cdot \ell \cdot cm^{-1}$) of A and B, respectively, (if molar decadic extinction coefficient is expressed as ε, $\varepsilon=0.4343\kappa$). We assumed here that no side reaction occurs, i.e., $a+b=a_0$, where b is the concentration of B.

In this study the reaction is expressed as

$$[Co(en)_3]^{3+} \quad + \quad 3L^- \xrightarrow{h\nu} [CoL_3] \quad + \quad 3en \ .$$

Here, L^- and en(ethylenediamine) have no absorption in the region under investigation. κ_A and κ_B were obtained from the absorption spectra of the pure $[Co(en)_3]Cl_3\cdot 3H_2O$ and $[CoL_3]$ solutions(Fig. 1), respectively. The values of a were determined by use of the relation $a=a_0-b$, where b values were determined by the use of the absorption at 622.5nm($\varepsilon=549 mol^{-1}\cdot \ell\cdot cm^{-1}$) of $[CoL_3]$ in the irradiated solution. Although no dark reaction occurs practically at room temperature and within two hours, the absorbance at the same wavelength of the unirradiated solution placed in the same room of the spectro-irradiator in order to exclude the error due to the imperfect darkness while setting the cell in the spectro-irradiator. The quanta of the irradiation in unit volume, $\int_0^t Q_0 dt$, was obtained from Reinecke salt actinometry, where the standard quantum yields used for this work were 0.270, 0.278, 0.282, 0.294, 0.310 and 0.310 for 585, 571, 535, 511, 486 and 460nm, respectively, which were determined by interpolating into the Wegner and Adamsons' data.[5)]

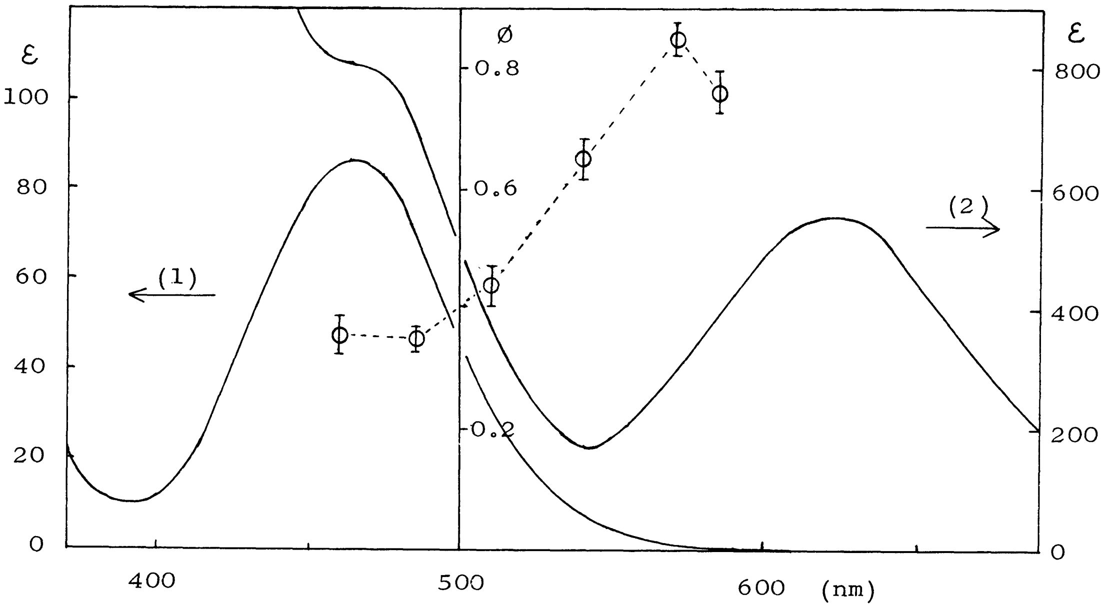

Fig. 1 Quantum yields and absorption spectra of $[Co(en)_3]Cl_3 \cdot 3H_2O$ and $[CoL_3]$ in aqueous solution

Φ: quantum yield, ——: absorption spectra of (1) $[Co(en)_3]Cl_3 \cdot 3H_2O$ and (2) $[CoL_3]$

Table 1 Quantum yields of photo-ligand-substitution reaction

Wavelength (nm)	ε_A*	ε_B*	Quantum yield (∅)	$\pm\Delta$**
585	0.831	393	0.759	0.039
571	1.08	283	0.845	0.023
535	4.92	189	0.649	0.033
511	23.1	357	0.436	0.034
486	61.2	704	0.343	0.021
460	83.0	921	0.351	0.036

* ε_A and ε_B represent molar extinction coefficients of $[Co(en)_3]^{3+}$ and $[CoL_3]$, ** $\pm\Delta$ denotes scattering of the values of the quantum yields around the mean value, ∅, when the experiments were done for three times.

The numerical calculation of the integrals was carried out at the computer center of Kyushu University.

The results are shown in Table 1 and Fig. 1. It is remarkable that the quantum yields obtained are unusually high compared with those so far known for the ligand substitution reactions of the cobalt(III) complexes by the irradiation of the visible light. It is also to be noted that the high quantum yields were obtained even at the long-wavelength-side foot of the first spin-allowed band, even higher than those at the top of the band, as seen in Table 1 and Fig. 1.

Kane-Maguir et al. reported that $[Co(en)_3]^{3+}$ gave a red product in the presence of $[Fe(CN)_6]^{3-}$ on irradiating the light of the ligand field band region. The quantum yields of the reaction were so high as 0.19, 0.23 and 0.60 at 436, 514 and 647nm, respectively.[6,7] The tendency that the quantum yields increase with going to longer-wavelength side is similar to that of the present reaction, although their reaction does not appear to be a simple photo-ligand-substitution, but is likely to be a redox one.

At present, there has been found no satisfactory explanation yet for this tendency and for the mechanism of the reaction. Further investigation is in progress.

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