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Substitution Reaction of In-plane Ligand in Bis(dimethylglyoximato)-cobalt(II) Complex with *N,N'*-Disalicylideneethylenediamine

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Synopsis. A spectrophotometric study of the reaction $Co(dmgH)_2 + salenH_2 \hookrightarrow Co(salen) + 2\,dmgH_2$, in which $dmgH_2$ is dimethylglyoxime and $salenH_2$ is *N,N'*-disalicylideneethylenediamine, was carried out in methanol at 22 °C. The reaction rate decreased with increased amounts of added pyridine, and reached a stationary value at the molar ratio $[pyridine]/[Co(dmgH)_2] = 1$. The form of the rate expression was $d[Co(salen)]/dt = k[Co(dmgH)_2]$ where the rate constant $k = 0.023\ min^{-1}$.

In vitamin B_{12}, it has been reported that the 5,6-dimethylbenzimidazole axial base dissociates from the central cobalt atom very easily and that probably the base-off form contributes as a reactive intermediate during enzymatic reactions.[1] Therefore it is significant to study the properties of the base-off form in vitamin B_{12} or in a suitable model system. The high reactivity of the base-off form has been known in the electrochemical reduction of central cobalt atom[2] or in the cleavage of carbon-cobalt bond for vitamin B_{12} or for the model compounds.[3] However there have been few reports concerning the difference between the base-off form and base-on form in the reactivity of the in-plane ligand.

In the present work the substitution reaction of in-plane ligand in $Co(dmgH)_2$ complex (dmgH is the monoanion of dimethylglyoxime), which has been known as a good model compound of vitamin B_{12r}, was carried out in the presence and in the absence of axial base pyridine. $SalenH_2$ (*N,N'*-disalicylideneethylenediamine) was chosen as the substrate for the substitution reaction, because the reaction with $salenH_2$ was found to be a clean reaction, as expressed by

$$Co(dmgH)_2 + salenH_2 \longrightarrow Co(salen) + 2dmgH_2 \qquad (1)$$

and it proceeds at an appropriate reaction rate in methanol solution at room temperature.

Experimental

A 30 cm^3 deoxygenated methanol solution of $Co(dmgH)_2$ complex was prepared at 2.0 mM† with 14.94 mg (0.06 mmol) of cobalt acetate tetrahydrate, 13.92 mg (0.12 mmol) of dimethylglyoxime, 4.8 mg (0.12 mmol) of sodium hydroxide and an appropriate amount of pyridine by the method of Schrauzer.[4] *N,N'*-Disalicylideneethylenediamine and Co(salen) was prepared by the method of Pfeiffer.[5]

The substitution reaction of $Co(dmgH)_2$ with $salenH_2$ was initiated by the injection of the deoxygenated methanol solution of $salenH_2$, which was prepared just before use, into the solution of $Co(dmgH)_2$ complex. After a small quantity of the reaction mixture was transferred to a 1 mm quartz cell, which was joined to the reaction vessel, the reaction progress was monitored by the measurement of the change in the visible absorption spectra in the thermostated cell compartment. The concentration of $Co(dmgH)_2$, $salenH_2$ and Co(salen) could then be determined by solving the equation described elsewhere.[6]

Results and Discussion

Methanol solutions of $Co(dmgH)_2$ were prepared from cobalt acetate tetrahydrate and dimethylglyoxime without pyridine in concentrations ranging from 1 to 3 mM, and the visible absorption spectra were measured. When pyridine was added to the solutions no detectable change in the spectra was observed. When the absorbances of the spectra of those solutions at 472 nm were plotted against the amount of cobalt acetate tetrahydrate used for the complexation reaction, the plot showed a straight line with zero intercept. The results exhibit that, both in the presence and in the absence of pyridine, the complexation reaction between cobalt acetate tetrahydrate and dimethylglyoxime is complete in the present experimental conditions and that in both cases the spectra are almost the same. Similarly, at the concentrations ranging from 1 to 3 mM, cobalt acetate tetrahydrate and $salenH_2$ formed the 1 : 1 complex completely and the spectra of the solution showed no detectable change with the addition of pyridine.

The time-dependent change of spectra in the reaction between $Co(dmgH)_2$ and $salenH_2$ at equimolar ratio was measured in the molar ratios of pyridine to $Co(dmgH)_2$, $[py]/[Co(dmgH)_2]_0$, =0.5, 0.8, 1.0, and 2.0 respectively. All of them showed distinct isosbestic points at 449 and 488 nm. A typical example is shown in Fig. 1. After the reaction was completed, the spectrum, for example of in Fig. 1, was found to be

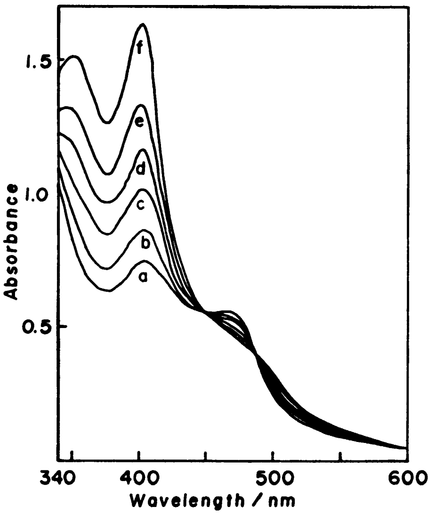

Fig. 1. Visible absorption spectra in the reaction between $Co(dmgH)_2 \cdot py$ and $salenH_2$ in methanol at 22 °C after mixing 10(a), 15(b), 25(c), 35(d), 55(e), and 120 min(f) respectively.
Initial concentration: $Co(dmgH)_2$; 1.80, $salenH_2$; 1.80, and pyridine; 1.80 mM.

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† 1 M = 1 mol dm^{-3}.

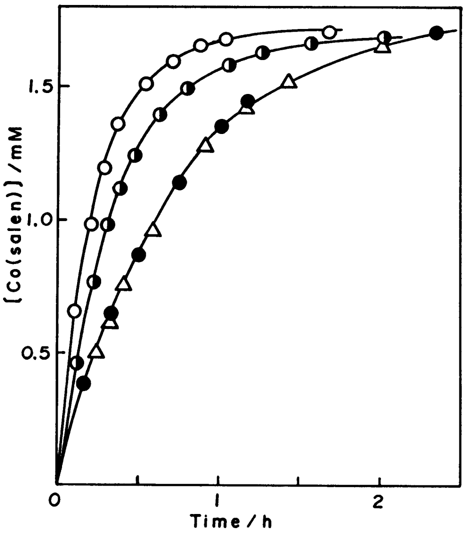

Fig. 2. Plots of the concentration of Co(salen) against reaction time for the substitution reaction at 22 °C. Initial concentration of $Co(dmgH)_2$: 1.71 (○), 1.75 (◑), and 1.80 mM (△, ●). $[py]/[Co(dmgH)_2]_0=0.5$ (○), 0.8 (◑), 1.0 (△), and 2.0 (●).

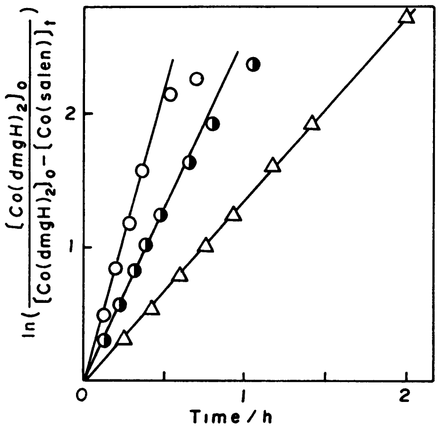

Fig. 3. First-order plots for the substitution reaction. $[py]/[Co(dmgH)_2]_0=0.5$ (○), 0.8 (◑), and 1.0 (△).

similar to that of Co(salen) which was prepared in the same concentration as that of $Co(dmgH)_2$ at the reaction time $t=0$. The results of stoichiometry and the presence of isosbestic points indicate that they are clean reactions as expressed by Eq. 1.

The change of concentration of Co(salen) during the reaction was determined by using the above mentioned time-dependent change of the spectra. The results are shown in Fig. 2. In the absence of pyridine the reaction rate is so rapid that the result is not shown in the figure. From this result and Fig. 2 it was found that the reaction rate decreased with an increase of pyridine concentration and reached a stationary value at $[py]/[Co(dmgH)_2]_0=1$.

Then $\ln(C_0/(C_0-C_t'))$, where C_0 is the concentration of $Co(dmgH)_2$ at reaction time 0 and C_t' is the concentration of Co(salen) at reaction time t, was plotted against reaction time for the reaction between $Co(dmgH)_2$ and $salenH_2$ at $[py]/[Co(dmgH)_2]_0=0.5$, 0.8, and 1.0 respectively. Each of the plots, as is shown in Fig. 3, gives a straight line with a slope of 0.075, 0.042 and 0.023. Especially in the case of $[py]/[Co(dmgH)_2]_0=1$, the plot showed linearity over at least 90% reaction. When $salenH_2$ was used in 2 times the concentration of $Co(dmgH)_2$ for the reaction, no detectable change was observed in the reaction rate. These results indicate that the reaction is first-order with respect to the concentration of $Co(dmgH)_2$ and zero-order with respect to the entering ligand concentration and that the rate equation is given by Eq. 2.

$$d[Co(salen)]/dt = k[Co(dmgH)_2] \qquad (2)$$

in which rate constant $k=0.023$ at 22 °C in $[py]/[Co(dmgH)_2]_0=1$.

Recently Corey *et al.* have proposed a mechanism for the catalytic action of vitamin B_{12}.[1] A key feature of the proposal is the cleavage of the bond between carbon 1 and 19, which directly joins the A and D ring, and tridentate ligation of the seco-corin, by prior axial base ligand dissociation. The authors[7] and Tyrlik *et al.*[8] have proposed a mechanism involving lability of an in-plane dimethylglyoxime ligand for the hydrogenation of benzil catalyzed by $Co(dmgH)_2py$. These results do not contradict the present results.

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