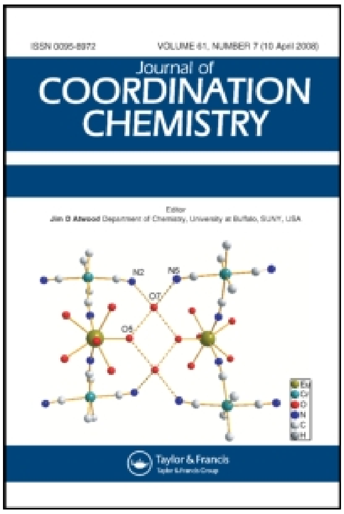

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PRELIMINARY COMMUNICATION

SUBSTITUTION OF *tris*(2,2'-BIPYRIDINE)-COBALT(III) BY CARBONATE ION

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This communication reports the instability of *tris*(2,2'-bipyridine)cobalt(III) toward ligand substitution. 2,2'-Bipyridine("bpy") has been recognized as one of the most potent ligands and used to prepare many kinds of metal complexes. Nevertheless, one of the authors[1] reported the preparation of $[Co(CN)_2(bpy)_2]Cl$, which was obtained by the reaction of $[Co(bpy)_3]^{3+}$ with cyanide ion in water. The reaction was reported to occur within five minutes at room temperature. The strong nucleophilicity of the cyanide ion might be responsible for this kind of substitution.

The instability of $[Co(bpy)_3]^{3+}$ toward substitution was not restricted to attack by potent ligands. Recently, we have found that $[Co(bpy)_3]^{3+}$ is easily substituted by several anions in aqueous solutions to produce $[Co(XX)(bpy)_2]^{n+}$. The anions which attack the complex ion are carbonate, oxalate, phosphate, sulfite and azide. Even chloride attacks $[Co(bpy)_3]^{3+}$ to produce $[Co(Cl)_2(bpy)_2]^+$ in a mixture of hydrochloric acid and ethyl alcohol. It is both striking and curious that carbonate is more reactive than oxalate and phosphate, and less reactive than azide. Thus, the azide ion attacks $[Co(bpy)_3]^{3+}$ even at room temperature.

The substitution of $[Co(bpy)_3]^{3+}$ with carbonate was investigated at 70 °C under various conditions. An induction period was observed when the reaction was carried out in the absence of free 2,2'-bipyridine, but it was not observed in the presence of appreciable amounts of ligand. Figure 1 shows the effect of 2,2'-bipyridine on the change in absorbance at 503 nm. Both runs gave *pseudo*-first-order rate constants, although the rate in the presence of 2,2'-bipyridine was somewhat slower than that in the absence of bipyridine. Since the rate seemed to be independent of 2,2'-bipyridine when its concentration exceeded 8.0 mM, the following reactions were carried out in the presence of 10.0 mM or more of bipyridine.

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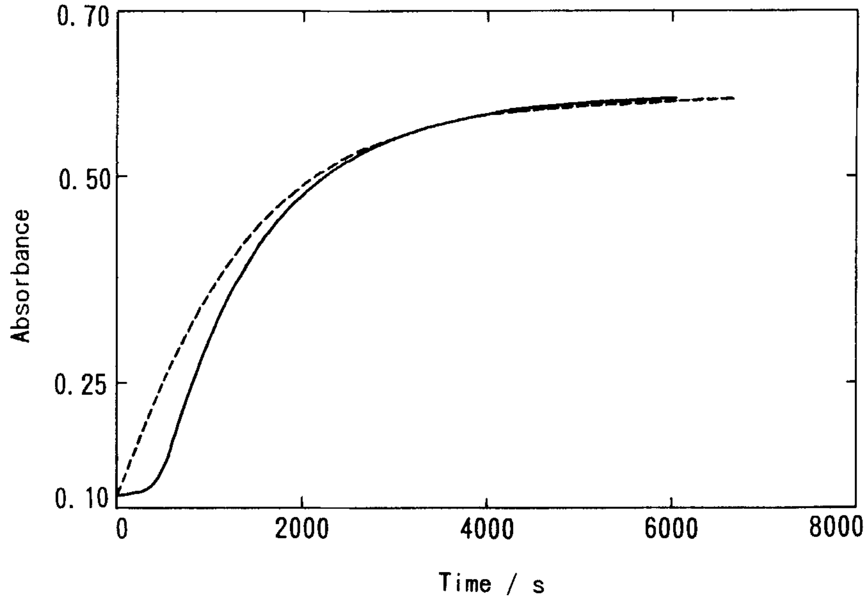

Figure 1 Change in absorbance at 503 nm in the absence and in the presence of 2,2'-bipyridine observed for the reaction of $[Co(bpy)_3]^{3+}$ with CO_3^{2-} at 70 °C under conditions of [bpy] = 0 (——) and 4.12 mM (----); $\{[Co(bpy)_3]Cl_3\}$ = 5.00 mM, $[K_2CO_3]$ = 188 mM, $[KHCO_3]$ = 188 mM, and μ = 1.0 (KCl).

The *pseudo*-first-order rate constants were found to be almost independent of pH in the range from 9.3 to 10.1, under conditions of $\{[Co(bpy)_3]Cl_3\}$ = 5.00 mM, [bpy] = 13.7 mM, $[K_2CO_3]$ = 150 mM, $[KHCO_3]$ = 37.5 ~ 300 mM, and μ = 1.0 (KCl). The slight increase of rate at lower pH may be due to increasing concentration of HCO_3^-, although the effect of HCO_3^- on the rate was small.[2]

The rate constants were found to depend on the ionic strength, *i.e.*, the *pseudo*-first-order rate constant steadily decreased from 6.6×10^{-4} s^{-1} (μ = 1.0) to 2.7×10^{-4} s^{-1} (μ = 2.0) at 70 °C, in the presence of equimolar amounts of K_2CO_3 and $KHCO_3$ with appropriate amounts of KCl for control of ionic strength.

The *pseudo*-first-order rate constants increased with increasing concentration of CO_3^{2-}, as Figure 2 shows. Taking the ion association into account, the observed rate constant can be written as[3]

$$k_{obs} = \frac{k_1K_1[CO_3^{2-}] + k_2K_1K_2[CO_3^{2-}]^2}{1 + K_1[CO_3^{2-}] + K_1K_2[CO_3^{2-}]^2} \qquad (1)$$

where K_1 is the association constant between $[Co(bpy)_3]^{3+}$ and CO_3^{2-}, K_2 is that between $[Co(bpy)_3]^{3+}CO_3^{2-}$ and CO_3^{2-}, and k_1 and k_2 are the rate constants for the ion pair, $[Co(bpy)_3]^{3+}CO_3^{2-}$ and the ion triplet, $[Co(bpy)_3]^{3+}(CO_3^{2-})_2$, respectively. From experimental values for the $[Co(bpy)_3]^{3+}SO_4^{2-}$ system[4] and the electrostatic theory,[5] K_1 and K_2 values at μ = 0.01 and 25 °C were estimated to be $\log K_1$ = 2.09 and $\log K_2$ = 0.42. Although there were further ambiguities to extrapolate these values to the present high ionic strength regions, K_1 and K_2 were

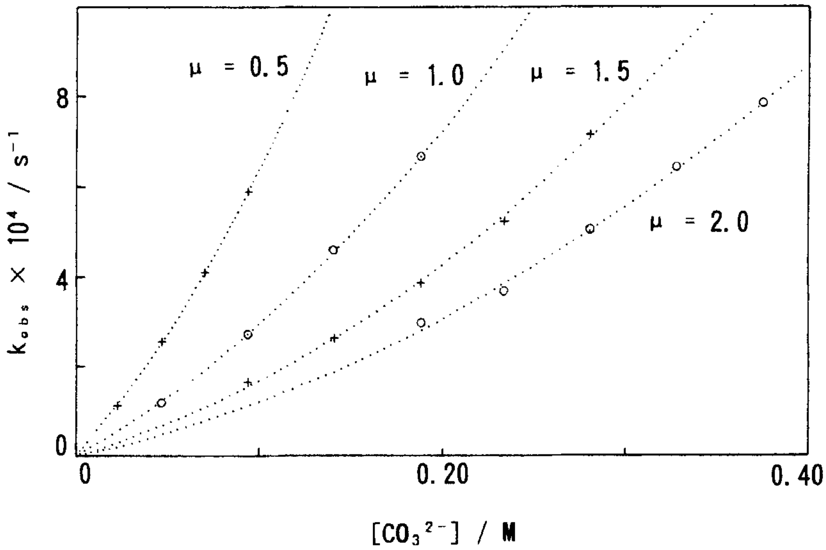

Figure 2 Dependence of the *pseudo*-first-order rate constant on the concentration of carbonate ion, observed for the substitution of $[Co(bpy)_3]^{3+}$ by CO_3^{2-} at 70 °C under conditions of $\{[Co(bpy)_3]Cl_3\}$ = 5.00 mM, [bpy] = 13.7 mM, [$KHCO_3$] = [K_2CO_3], and μ = 1.0 (KCl). The dotted lines denote least-squares curves assuming equation *(1)* using appropriate association constants (see text).

estimated at various ionic strengths studied. Then, rate constants were calculated using equation *(1)*. It is striking that the calculated k_2 values are larger than the k_1 values, taking the small ratio of K_2/K_1 into account. This means that the lesser species is more reactive than the species of higher concentration. It is difficult to understand why the ion triplet $\{[Co(bpy)_3](CO_3)_2\}^-$ is so much more effective than the ion-pair, $\{[Co(bpy)_3](CO_3)\}^+$ for this kind of substitution. Moreover, there exists another problem about these kinetics. Although the ion association constant of CO_3^{2-} with $[Co(bpy)_3]^{3+}$ may be smaller than the one with, for example, $[Co(en)_3]^{3+}$, the present kinetics do not explain why $[Co(bpy)_3]^{3+}$ is abnormally unstable to substitution.

There may be an alternative pathway for the present substitution. It has long been known that racemization of $[Co(phen)_3]^{3+}$ is catalyzed by addition of $[Co(phen)_3]^{2+}$.[6] The present substitution is also found to be accelerated by the presence of small amounts of added $[Co(bpy)_3]^{2+}$. However, we cannot detect any cobalt(II) ion in the starting material, $[Co(bpy)_3]^{3+}$, by measurement of magnetic

Table I Rate constants assuming equation *(1)* and estimated ion-association constants.

ionic strength	rate constants/$M^{-1}s^{-1}$		assoc. constants/M^{-1}	
	10^4k_1	10^4k_2	K_1	K_2
0.5	3.8	89	9.3	1.1
1.0	2.2	64	5.9	1.0
1.5	0.18	56	4.6	0.87
2.0	- 1.7	55	3.9	0.82

moments and of NMR spectra using coaxial tubes. Further investigations should be needed to rationalize fully the abnormal reactivity of $[Co(bpy)_3]^{3+}$. However, it should be stressed that any experiment which employs $[Co(bpy)_3]^{3+}$ must take into account its unusual reactivity toward substitution as well as toward racemization.

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