increased energy may exist for one of the oxidation states so that the structural difference between it and the other oxidation state is relatively small. The mechanism of the electron-transfer reaction would then be successive conformational change and electron transfer. A mechanism quite similar to this has recently been proposed for the electron-transfer reactions of a series of copper–polythia ether complexes.[29]

A more general lack of correlation between structural changes and self-exchange rate constants in Cu(I)/Cu(II) systems is evident when the behavior of the [Cu(TAAB)]$^{+/2+}$ couple is considered. This couple has a very large self-exchange rate constant of 5×10^5 M^{-1} s^{-1} despite its change in coordination number between the two oxidation states.[30] Perhaps a sequential mechanism is at work here also. This concept could have important consequences in cuproprotein chemistry, in that it would not be necessary for the protein to impose a rigid coordination environment in order to attain facile electron transfer.

Several reports of electron-transfer reactions involving synthetic Cu(I)/Cu(II) couples have appeared since our last publication. These include studies of the polythia ether systems in aqueous solution mentioned above.[29] There are two reports on redox reactions of copper complexes with ruthenium ammine and bipyridyl complexes in aqueous solution and in 50% methanol.[31,32] There is also a report of the reactions of several tetracoordinate copper(II) complexes with ferrocene and 1,1′-dimethylferrocene in acetonitrile.[33] The ferrocene reactions displayed saturation kinetics at high [Fe(cp)$_2$], which was interpreted in terms of a mechanism involving extensive association of the two reactants. In the studies with the ruthenium complexes, it was deduced that the coordination number about copper changed from 4 to 5 with increasing oxidation state. The polythia ether ligand systems showed quite different self-exchange rate constants, depending on whether the complexes were being reduced or oxidized; a "square" scheme was devised to account for this behavior. Thus, none of these recent studies are directly comparable with the reactions described in the present work.

Much more pertinent is the recent study by Groeneveld et al. of Cu(bidhp)$^{n+}$.[18b] In the Cu(I) state this is a pseudotetrahedral complex bearing a linear tetradentate N_2S_2 ligand. The Cu(II) analogue apparently also bears a bound aquo ligand in the solid state, but it is claimed that in DMSO solution both the Cu(I) and Cu(II) states are bound solely by the N_2S_2 ligand. Dynamic NMR techniques were used to extract a self-exchange rate constant of 4×10^3 M^{-1} s^{-1} in DMSO at 28 °C. Unfortunately it is difficult to assess the degree of structural reorganization in this system because the crystal structure of the tetracoordinate Cu(II) derivative is not yet available.

Conclusions. The present studies confirm the previous estimate of the electron self-exchange rate constant for the [Cu((imidH)$_2$DAP)]$^{2+/+}$ redox couple and demonstrate excellent agreement with Marcus theory. Unfortunately, there is still some uncertainty as to whether the mechanism is outer-sphere. Perhaps this issue can be resolved by measuring the substitution kinetics of the Cu(II) complexes. Other methods may actually be more direct, such as using (1) rigorously outer-sphere reaction partners with known self-exchange rates to verify the self-exchange rates for the copper complexes by the Marcus treatment or (2) derivatives of the [Cu(L$_2$DAP)]$^{n+}$ molecules with macrocyclic ligands designed to prevent the ligand dissociation step entirely. These efforts are in progress, with the objective of obtaining a firmer understanding of the interrelationships between structure, conformational mobility, and reaction rates of these and related model compounds.

Acknowledgment. This research was supported by the NSF (D.M.S., Grant CHE-8520515), the NIH (L.J.W., Grant GM-28451), and the Robert A. Welch Foundation (D.M.S., Grant C-846, and L.J.W., Grant C-627). We are grateful to Dr. A. Kook for help with the NMR spectra, to DeAnna Coggin for assistance during manuscript preparation, and to Prof. Geoffrey Davies for helpful conversations. The XAS work reported herein was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy, Office of Basic Energy Sciences, and the National Institute of Health, Biotechnology Resource Program, Division of Research Resources. R.A.S. is a NSF Presidential Young Investigator and an Alfred P. Sloan Research Fellow.

Registry No. [Cu^{I}((imidH)$_2$DAP)]$^+$, 69021-97-2; [Cu^{I}((py)$_2$DAP)]$^+$, 75688-55-0; [Zn^{II}(CH$_3$CN)$_6$]$^{2+}$, 21519-23-3.

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Effects of Transition-Metal Ions on the Reduction of Di-2-pyridyl Ketone with Sodium Borohydride

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Received February 3, 1988

The Co(II) complexes of di-2-pyridyl ketone (dpk), di-2-pyridylcarbinol (dpc), and di-2-pyridylmethanediol (dpk-H$_2$O) were prepared and characterized. In methanol, the Co(II) complex of dpk [Co(dpk)$_3$](ClO$_4$)$_2$·3H$_2$O was reduced with NaBH$_4$, yielding [Co(dpc)$_3$](ClO$_4$)$_2$, and was hydrated to give [Co(dpk-H$_2$O)$_3$](ClO$_4$)$_2$·$^3/_2$CH$_3$OH. Kinetics of the reduction of dpk with NaBH$_4$, yielding dpc, were studied in ethanol containing 14% (v/v) diglyme in the presence of Co(II) or Zn(II) ion and in the absence of the divalent metal ions. The catalytic effects of the Zn(II) ion are attributed to the inductive effects of the metal ion acting as a Lewis acid, leading to enhancement in the electrophilicity of the carbonyl group of the coordinated dpk. On the other hand, the Co(II)-promoted reduction of dpk with NaBH$_4$ involves two successive intermediates containing Co(I) ion. From the rate data observed for the conversion of the first intermediate into the second one, the structures of the two intermediates were assigned. Thus, the Co(II)-promoted reduction of dpk with NaBH$_4$ appears to involve the initial reduction of the central metal ion with NaBH$_4$ and subsequent electron transfer from the metal ion to the carbonyl group of the coordinated dpk.

Introduction

Previously, we reported that the reduction of the Co(II) complex of di-2-pyridylamine (dpa) [Co(dpa)$_2$Cl$_2$] with NaBH$_4$ under an inert atmosphere followed by oxidative addition with CH$_3$I led to the organometallic Co(III) complex [Co(dpa)$_2$(CH$_3$)$_2$]I.[2] In this reaction it was proposed that the reduction of the Co(II) complex with NaBH$_4$ initially produced the Co(I) species as an intermediate.

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[1] (a) Department of Chemistry Education. (b) Department of Chemistry.

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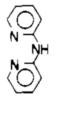
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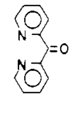
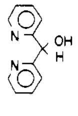

dpk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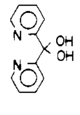
dpk·H_2O

In a subsequent study, we substituted di-2-pyridyl ketone (dpk) for dpa. When the same reactions were attempted, however, the Co(III)–methyl complex was not obtained. This was rather unexpected since dpk would stabilize the Co(I) ion better than dpa because of its better π-accepting properties. In order to explain the failure to obtain the Co(III)–methyl complex containing dpk, we presumed that the Co(I) complex of dpk produced by the reduction of the corresponding Co(II) complex with $NaBH_4$ underwent electron transfer from the Co(I) metal center to the carbonyl group of the dpk ligand, losing nucleophilicity toward CH_3I. In order to test this possibility, we isolated the product formed from the reaction of $[Co(dpk)_3]^{2+}$ with $NaBH_4$ and found it to be the Co(II) complex of di-2-pyridylcarbinol (dpc) $[Co(dpc)_3]^{2+}$. We also performed a mechanistic study on the reduction of dpk with $NaBH_4$ in the presence of various metal ions. Kinetic data for the reduction reactions and electronic spectra of accumulating intermediates are presented in this paper together with the mechanistic information derived therefrom.

Experimental Section

$[Co(dpk)_3](ClO_4)_2·3H_2O$. **$[Co(dpk)_3](ClO_4)_2·3H_2O$.** To a methanol solution (20 mL) of $Co(ClO_4)_2·6H_2O$ (1.98 g) was added with stirring a methanol solution (30 mL) of dpk (2.99 g). The solution was allowed to stand at room temperature for 24 h. The pink crystals formed were filtered, washed with methanol, and dried in vacuo; yield 85%. Anal. Calcd for $CoC_{33}H_{30}N_6O_{14}Cl_2$: C, 45.85; H, 3.50; N, 9.72. Found: C, 46.16; H, 3.26; N, 9.72. IR (cm^{-1}): ν_{O-H}, 3500; $\nu_{C=O}$, 1695; $\nu_{C=C}$, $\nu_{C=N}$, 1580, 1595; ν_{Cl-O}, 1100. Λ_M (Ω^{-1} cm^2 M^{-1}): 194 in MeOH at 20 °C.

$[Co(dpc)_3](ClO_4)_2$. To a methanol solution (50 mL) of $[Co(dpk)_3](ClO_4)_2·3H_2O$ (3.98 g) was slowly added $NaBH_4$ (2.41 g) over a period of 30 min with stirring. The solution was stirred for 4 h and then kept in a refrigerator for 24 h. The pink crystals formed were filtered, washed with methanol, and dried in vacuo. These synthetic steps were carried out in the presence of air; yield 37%. Anal. Calcd for $CoC_{33}H_{30}N_6O_{11}Cl_2$: C, 48.54; H, 3.70; N, 10.30. Found: C, 48.25; H, 3.51; N, 10.10. IR (cm^{-1}): ν_{O-H}, 3350; $\nu_{C=C}$, $\nu_{C=N}$, 1570, 1600; ν_{Cl-O}, 1100. Λ_M (Ω^{-1} cm^2 M^{-1}): 172 in MeOH at 20 °C.

$[Co(dpk\text{-}H_2O)_3](ClO_4)_2·{}^3/_2CH_3OH$. When 95% methanol or another mixture of methanol and water was used as a solvent for the synthesis of $[Co(dpk)_3](ClO_4)_2$, the Co(II) complex of dpk-H_2O precipitated prior to that of dpk. Anal. Calcd for $CoC_{34.5}H_{36}N_6O_{15.5}Cl_2$: C, 45.41; H, 3.98; N, 9.21. Found: C, 45.55; H, 3.89; N, 9.15. IR (cm^{-1}): ν_{O-H}, 3340, 3580; $\nu_{C=C}$, $\nu_{C=N}$, 1568, 1603; ν_{Cl-O}, 1100. Λ_M (Ω^{-1} cm^2 M^{-1}): 139 in DMF at 20 °C.

dpc. To an aqueous solution (50 mL) of $[Co(dpc)_3](ClO_4)_2$ (4.9 g) was added 36% HCl solution (50 mL). A saturated aqueous solution of Na_2CO_3 (86 g) was added to the resultant green solution, and then the mixture was extracted with $CHCl_3$. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo to afford an oily substance; yield 65%. The NMR spectrum of the product is consistent with that of dpc reported previously.[3]

Physical Measurements. Conductance measurements were performed by using an Industrial Instruments Model RC 216 B 2 conductivity bridge. Infrared spectra were recorded on a Jasco IR 810 spectrophotometer with Nujol mulls. Electronic absorption spectra were recorded with a Beckman 5260 UV/vis spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Reaction rates were measured with a Beckman 5260 UV/vis spectrophotometer. The temperature was maintained at 25 ± 0.1 °C with a Lauda Brinkmann Model RC3 circulator. Stock solutions of $NaBH_4$ were made in diglyme under a nitrogen atmosphere, and those of dpk, $[Co(dpk)_3](ClO_4)_2·3H_2O$, and $ZnCl_2$ were made in ethanol. Kinetic and spectral measurements were carried out in ethanol containing 14% (v/v) diglyme. For the kinetic measurements made in the absence of oxygen, oxygen was removed from organic solvents by bubbling nitrogen through the solvents and the cuvettes containing reaction mixtures were tightly covered with serum caps under a nitrogen atmosphere.

In the Co(II)-catalyzed reduction of dpk with $NaBH_4$, a solution of $[Co(dpk)_3](ClO_4)_2·3H_2O$ was mixed with $NaBH_4$ for the kinetic measurements. In the Zn(II)-promoted reduction, however, $ZnCl_2$ was added to the solutions of dpk prior to the kinetic measurements. The initially added concentration of $[Co(dpk)_3]^{2+}$ was ca. 3×10^{-5} M when the rates were measured at 240–250 nm. When the reactions were followed at 400 nm, however, much greater (ca. 3×10^{-3} M) initial concentrations of $[Co(dpk)_3]^{2+}$ were employed due to the smaller molar extinction coefficient at this wavelength. For the Zn(II)-promoted reaction, the reaction was followed at 280 nm and the initially added concentrations of Zn(II) and dpk were 2×10^{-4} M. The initially added concentrations of $NaBH_4$ ($[NaBH_4]_0$) was adjusted to be at least 20 times greater than that of dpk for all of the kinetic runs.

Table I. Electronic Absorption Spectra for Cobalt Complexes of dpk, dpc, dpk-H_2O, and dpa[a]

compd	λ_{max}, nm (ϵ, cm^{-1} M^{-1})
$[Co(dpk)_3](ClO_4)_2·3H_2O$	564 sh, 460 (47.3)
$[Co(dpc)_3](ClO_4)_2$	570 sh, 465 (55.9)
$[Co(dpk\text{-}H_2O)_3](ClO_4)_2·{}^3/_2CH_3OH$	480 (65.7)
$[Co(dpa)_3](ClO_4)_2$	524 sh, 470 (27), 384 sh
1_{Co}	540 sh, 405 (1360)
2_{Co}	505 (1150), 360 (1350)
$[Co(dpa)_3]^+$	660 sh, 420 (1000), 400 (1050)

[a] Spectra of Co(II) complexes were measured in ethanol, and those of Co(I) complexes were measured in ethanol containing 14% (v/v) diglyme under a nitrogen atmosphere.[9]

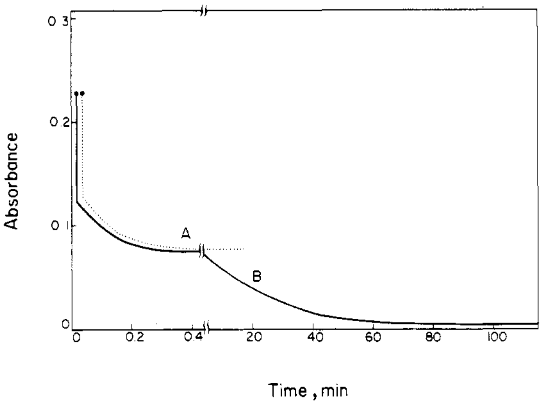

Figure 1. Absorbance changes observed at 240 nm for the reaction of $[Co(dpk)_3]^{2+}$ (2.9×10^{-5} M) with $NaBH_4$ (4.2×10^{-3} M). Curve A represents the absorbance change observed under the nitrogen atmosphere and curve B that in the presence of air.

Results

Elemental analysis, IR spectral data, and the values of molar conductance of the Co(II) complexes $[Co(dpk)_3](ClO_4)_2·3H_2O$, $[Co(dpc)_3](ClO_4)_2$, and $[Co(dpk\text{-}H_2O)_3](ClO_4)_2·{}^3/_2CH_3OH$ are summarized in the Experimental Section, and the UV/vis spectral data are given in Table I.

The pseudo-first-order rate constant for the reduction of dpk with $NaBH_4$ measured in the absence of the transition-metal ions was proportional to $[NaBH_4]_0$, with the second-order rate constant of $(6.9 \pm 0.6) \times 10^{-2}$ M^{-1} s^{-1}.

The kinetics of the reduction of dpk with $NaBH_4$ were also measured in the presence of an equimolar amount of $ZnCl_2$.[4] The pseudo-first-order rate constant was proportional to $[NaBH_4]_0$, with the second-order rate constant being 2.3 ± 0.4 M^{-1} s^{-1}. The UV spectrum of the product obtained by the reduction of dpk with $NaBH_4$ in the presence of Zn(II) ion was identical with that of dpc measured in the presence of Zn(II) under the same conditions.

The absorbance changes observed at 240–250 nm for the reduction of dpk with $NaBH_4$ in the presence of Co(II) ion were biphasic in the absence of oxygen and were triphasic in the presence of oxygen as illustrated in Figure 1. The rapid initial absorbance changes were complete within the manual mixing period of the reaction mixtures. Pseudo-first-order kinetics were observed for the subsequent slow processes. The pseudo-first-order rate constant (k_2) for the second process of a biphasic reaction

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[3] Newkome, G. R.; Roper, J. M. *J. Org. Chem.* **1979**, *44*, 502.

[4] If the dissociation constant for the Zn(II) complex of dpk is sufficiently small in the reaction medium, an excess amount of Zn(II) is present.

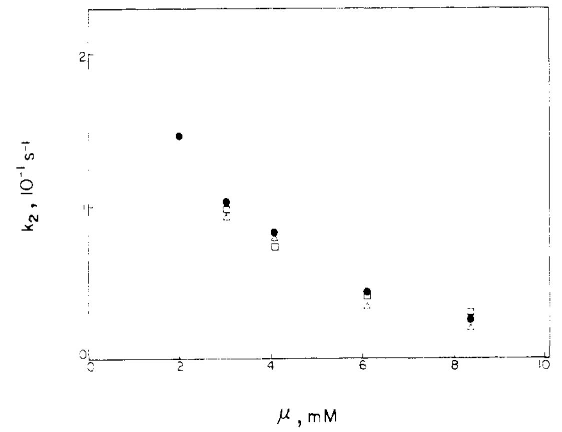
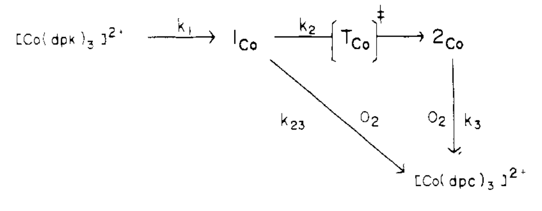


Figure 2. Value of k_2 for the reduction of $[Co(dpk)_3]^{2+}$ (2.9×10^{-5} M) with $NaBH_4$ ((2.1–$8.3) \times 10^{-3}$ M) plotted against total salt concentration (μ). For data points ●, μ represents $[NaBH_4]_0$ and the data represent the dependence of k_2 on $[NaBH_4]_0$. For data points □ and △, kinetic data were measured in the presence of both $NaBH_4$ and various amounts of $NaClO_4$ (□) or $NaBF_4$ (△). In the presence of $NaClO_4$ or $NaBF_4$, $[NaBH_4]_0$ was fixed at 2.1×10^{-3} M and μ was adjusted with the added electrolytes.

Scheme I



was identical with that of the second process of the corresponding triphasic reaction measured in the presence of oxygen. The value of k_2 decreased when $[NaBH_4]_0$ was raised as illustrated in Figure 2. Essentially identical kinetic behavior was observed when $NaClO_4$, $NaBF_4$, or NH_4PF_6 was substituted for a part of added $NaBH_4$ as illustrated in Figure 2. The pseudo-first-order rate constant (k_3) of the third process of the triphasic absorbance changes observed in the presence of oxygen was not affected by the concentration of $NaBH_4$ or added electrolytes. The value of k_3 measured in the UV region was 5.9×10^{-4} s^{-1}.

When the kinetic measurements were performed in the visible region, $[NaBH_4]_0$ was 0.14–0.18 M. The k_2 value measured in the absence of oxygen was 4.8×10^{-3} s^{-1} with 0.18 M $[NaBH_4]_0$. This is much smaller than that measured in the UV region because of high $[NaBH_4]_0$. When the reaction was followed in the visible region in the presence of oxygen by employing high $[NaBH_4]_0$, the second and third steps coalesced into a single step, apparently because their rates became comparable to each other.

The spectra of the final products obtained in the presence of oxygen were identical with that of the Co(II) complex of separately isolated dpc.

The multiphasic absorbance changes observed during the reduction of dpk in the presence of Co(II) with $NaBH_4$ indicate accumulation of two successive intermediates. Thus, the reaction paths can be summarized as Scheme I. Here, the two intermediates are denoted as $\mathbf{1}_{Co}$ and $\mathbf{2}_{Co}$, and the transition state for the conversion of $\mathbf{1}_{Co}$ into $\mathbf{2}_{Co}$ is designated as $\mathbf{T}_{Co}$. The visible spectra of $\mathbf{1}_{Co}$ and $\mathbf{2}_{Co}$ measured in the absence of oxygen are illustrated in Figure 3 and summarized in Table I together with those of Co(II) and Co(I) ions coordinating dpk, dpc, dpk-H_2O, or dpa.

The UV/vis spectra of the Co(II) complexes of dpc were unaffected by incubation with $NaBH_4$ for several hours. Thus, the Co(II) ions coordinating dpc are not reduced by $NaBH_4$, in marked contrast to those coordinating dpk.

Ethanolysis of $NaBH_4$ is known to occur to an insignificant degree over the period of time employed in the present experiments.[5]

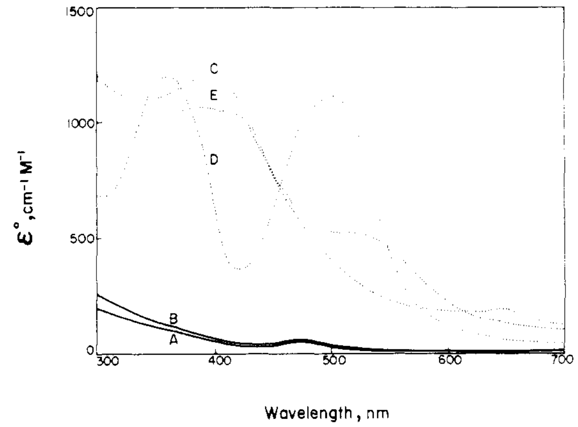


Figure 3. Visible spectra of $[Co(dpk)_3]^{2+}$ (A), $[Co(dpc)_3]^{2+}$ (B), $\mathbf{1}_{Co}$ (C), $\mathbf{2}_{Co}$ (D), and $[Co(dpa)_3]^{2+}$ treated with $NaBH_4$ (E). The solvent used for A and B is ethanol, and that for C–E is ethanol containing 14% (v/v) diglyme.

Discussion

Characterization of Complexes. In the complex $[Co(dpk)_3](ClO_4)_2 \cdot 3H_2O$, dpk is coordinated to Co(II) ion through the two nitrogen atoms of the pyridine rings. This is evidenced by the $\nu_{C=O}$ value of 1695 cm^{-1}, which is greater than that (1675 cm^{-1}) of the free dpk or that (1600–1670 cm^{-1}) of coordinated carbonyl. The complex contains water molecules in the lattice. Some lanthanide complexes of dpk were also reported to contain lattice water molecules.[6]

$[Co(dpc)_3](ClO_4)_2$, which was synthesized by the reduction of $[Co(dpk)_3](ClO_4)_2 \cdot 3H_2O$ with $NaBH_4$, was identified by the ν_{O-H} band at 3350 cm^{-1} and the disappearance of the $\nu_{C=O}$ band of the dpk complex. In the reduction of $[Co(dpk)_3]^{2+}$ with $NaBH_4$, Co(II) ion might assist the transfer of hydride from $NaBH_4$ to the carbonyl carbon of dpk by acting as a Lewis acid, increasing the electrophilicity of the carbonyl carbon. Alternatively, Co(II) ion might be reduced by $NaBH_4$ and then transfer the electron to dpk. It is also possible that the Co(II) ion and the carbonyl group of dpk might be reduced simultaneously by $NaBH_4$. The facile reduction of dpk with $LiAlH_4$ (or Na^0) in the presence of $TiCl_3$ leading to dpc has been reported,[3] and it was speculated that a low-valent titanium ion was generated by $LiAlH_4$ (or Na^0), which subsequently reduced dpk.

Although dpk is not hydrated significantly in the absence of metal ions, the coordinated dpk is hydrated readily, producing a complex of dpk-H_2O.[7] The facile hydration of $[Co(dpk)_3]^{2+}$ giving $[Co(dpk\text{-}H_2O)_3]^{2+}$ may be attributed to the inductive effect of the metal ion, which acts as a Lewis acid, and/or to the relief of the angle strain[7] of the carbonyl group of the chelate ring upon the formation of the tetrahedral diol.

The electronic spectra (Table I) indicate that $[Co(dpk)_3]^{2+}$, $[Co(dpc)_3]^{2+}$, and $[Co(dpk\text{-}H_2O)_3]^{2+}$ contain high-spin Co(II) ions and that the ligand field strength decreases in the order dpk > dpc > dpk-H_2O. The conductance data indicate that these Co(II) complexes are 1:2 type electrolytes.

Mechanism of the Transition Metal Ion Promoted Reduction of dpk. Kinetics and mechanisms of the reduction of aldehydes or ketones with $NaBH_4$ have been intensively investigated.[8] The reduction of dpk with $NaBH_4$ in the absence of transition-metal ions would involve a similar mechanism. The reactivity of dpk toward $NaBH_4$ is enhanced by ca. 30 times upon the addition of an equimolar amount of Zn(II) ion. The pseudo-first-order rate constant measured in the presence of Zn(II) ion was proportional

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(5) Brown, H. C.; Ichikawa, K. *J. Am. Chem. Soc.* **1961**, *83*, 4372.

(6) Jagannathan, R.; Soundarajan, S. J. *J. Inorg. Nucl. Chem.* **1981**, *42*, 145.

(7) Feller, M. C.; Robson, R. *Aust. J. Chem.* **1968**, *21*, 2919; **1970**, *23*, 1997.

(8) (a) Sun, S. F.; Neidig, P. R. *J. Org. Chem.* **1969**, *34*, 1854. (b) Rickborn, B.; Wuesthoff, M. T. *J. Am. Chem. Soc.* **1970**, *92*, 6894. (c) Volpi, E.; Biggi, G.; Pietra, F. *J. Chem. Soc., Perkin Trans. 2* **1973**, 571.

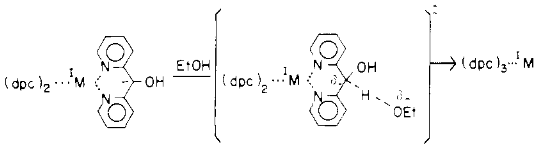
to $[NaBH_4]_0$, in contrast to those constants obtained in the presence of Co(II) ion. In addition, accumulation of intermediate species was not observed in the presence of Zn(II) ion. The catalytic effects of Zn(II) ion, therefore, may be attributed solely to the inductive effects exerted by Zn(II) ion as a Lewis acid to enhance the electrophilicity of the carbonyl group of the coordinated dpk.

In the presence of Co(II) ion, a distinctly different reaction path is involved. Although it is not possible at present to determine the mechanism in detail, the outline of the reaction path may be described on the basis of the unique spectral and kinetic data concerning the accumulating intermediates.

The visible spectra of $\mathbf{1}_{Co}$ and $\mathbf{2}_{Co}$ are noticeably different from those of the Co(II) complexes of dpk or dpa (Table I). In our previous study,[2] we proposed that treatment of the Co(II) complexes of dpa with $NaBH_4$ led to the reduction of the metal ion to Co(I). The visible spectrum of the Co(I) complexes containing dpa is illustrated in Figure 3, which can be compared with those of $\mathbf{1}_{Co}$ and $\mathbf{2}_{Co}$.[9] The strong absorption in the range of 340–430 nm may be taken as being characteristic of Co(I) compounds. Thus, $\mathbf{1}_{Co}$ and $\mathbf{2}_{Co}$ are very likely assigned as the Co(I) complexes.[10,11]

Rate constant k_2 (Scheme I) is decreased by the addition of electrolytes. Since the anions of the added electrolytes would hardly interact with the metal ions, it appears that the rate retardation is simply associated with increases in ionic strength and, consequently, in the polarity of media. An increase in $[NaBH_4]_0$ exerts the same electrolyte effects on k_2 as $NaClO_4$, $NaBF_4$, or NH_4PF_6. The intrinsic rate constant for the k_2 step appears to be independent of $[NaBH_4]_0$ under the experimental conditions. Thus, T_{Co} is in the same oxidation state as $\mathbf{1}_{Co}$. In addition, the unique rate-retarding effects of added electrolytes strongly suggest that T_{Co} is less polar than $\mathbf{1}_{Co}$.[12]

Several species containing the central metal ion and the ligand in various oxidation states would be formed during the reduction process. On the basis of the unique spectral and kinetic data observed in the present study, the structures of $\mathbf{1}_{Co}$, $\mathbf{2}_{Co}$, and transition state T_{Co} are tentatively assigned as in eq 1.



(1)

1_{Co} T_{Co} 2_{Co}

Species $\mathbf{1}_{Co}$ and T_{Co} illustrated in eq 1 are in the same oxidation state, as required by the kinetic data. Furthermore, the negative charge is more dispersed in T_{Co} than in $\mathbf{1}_{Co}$, in agreement with the electrolyte effects.

The slow conversion of $\mathbf{2}_{Co}$ into the Co(II) complex of dpc in the presence of O_2 indicates that the central metal ions and/or the ligand of $\mathbf{2}_{Co}$ are reduced forms of the final product. On the basis of the spectral data of $\mathbf{2}_{Co}$, $\mathbf{2}_{Co}$ is likely assigned as the Co(I) complex of dpc.

The Co(II) ions coordinated to dpk or dpa are readily reduced by $NaBH_4$. On the other hand, the metal ion of the Co(II) complex of dpc resists reduction by $NaBH_4$. This may be attributed to the π orbitals of the carbonyl carbon of dpk and the nonbonding orbital of the amino nitrogen of dpa. By use of these orbitals, the electron density of the Co(I) ion can be delocalized over the cyclic system, which includes both pyridine rings as well as the carbonyl carbon or the amino nitrogen atom. In dpc, the carbinol carbon contains neither a π nor a nonbonding orbital, which is needed in the formation of a conjugated cyclic system for the stabilization of the Co(I) ion. Thus, the Co(I) ion becomes less stable when dpc is substituted for dpk.[13]

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Registry No. dpk, 19437-26-4; dpc, 35047-29-1; $[Co(dpk)_3](ClO_4)_2 \cdot 3H_2O$, 117689-10-8; $[Co(dpc)_3](ClO_4)_2$, 117709-86-1; $[Co(dpk\text{-}H_2O)_3](ClO_4)_2 \cdot {}^3/_2CH_3OH$, 117689-12-0; $NaBH_4$, 16940-66-2; $ZnCl_2$, 7646-85-7.

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(9) The Co(I) complex of dpa was generated in situ by treatment of the corresponding Co(II) complex (1.5 mM) with $NaBH_4$ (0.14 M) in ethanol containing 14% (v/v) diglyme under a nitrogen atmosphere. The absorbance reading of $\mathbf{1}_{Co}$ at a fixed wavelength was calculated by extrapolating the exponential absorbance change of the k_2 step back to the mixing time. From the absorbance readings measured at various wavelengths with 10-nm intervals, the visible spectra of $\mathbf{1}_{Co}$ were constructed. On the other hand, the spectra of $\mathbf{2}_{Co}$ were measured with the product obtained by the reduction reaction under a nitrogen atmosphere.

(10) Visible spectra of other Co(I) complexes are reported in: (a) Kaizu, Y.; Torii, Y.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3296. (b) Sacconi, L.; Midollini, S. *J. Chem. Soc., Dalton Trans.* **1972**, 1213. (c) Sacconi, L.; Ghilardi, C. A.; Mealli, C.; Zanobini, F. *Inorg. Chem.* **1975**, *14*, 1380. (d) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *J. Am. Chem. Soc.* **1976**, *98*, 86.

(11) The initial absorbance changes observed in the presence of Co(II) ion were much faster than the reaction between dpk and $NaBH_4$ in the absence of transition-metal ions or in the presence of Zn(II). This supports the initial reaction of $NaBH_4$ with Co(II) ion instead of the dpk ligand.

(12) (a) Jones, R. *Physical and Mechanistic Organic Chemistry*, 2nd ed.; Cambridge University Press: London, 1984; Chapter 12. (b) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970; Chapters 7 and 8.

(13) Since the high electron density in the Co(I) ion is better stabilized by dpk than by dpc, the transition state for the overall rate-determining step would involve a minimum number of dpk ligands. The numbers of dpc ligands in the structures of $\mathbf{1}_{Co}$ and T_{Co} indicated in eq 1 are assigned on this basis.