

In-plane Ligand Effects on Oxygenation of Cobalt(II) Schiff Base Complexes

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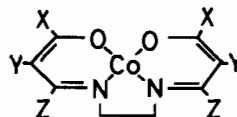
A series of cobalt(II) complexes of Schiff base with some peripheral substituents was employed for the measurements of redox potentials of the cobalt(II) complexes and stability constants for those pyridine and oxygen adducts. The electron-withdrawing substituents favor the reduction of a cobalt(II) ion, but make its oxidation difficult. While a Hammett reaction constant for $\log K_{py}$ is positive, that for $\log KO_2$ is negative, indicating that pyridine nucleophilically attacks the cobalt(II) ion, but molecular oxygen attacks the ion electrophilically.

Introduction

The study of reversible oxygenation of cobalt(II) complexes has received considerable attention in order to determine the chemical behavior of heme in hemoglobin and myoglobin [1]. Since the first report of a synthetic reversible oxygen carrier, (N,N'-disalicylideneethylenediaminato)cobalt(II) in 1938 [2], many studies on the reversibility of cobalt(II) Schiff base complexes have been reported. An ESR study showed that a nearly complete electron transfer from cobalt(II) to molecular oxygen occurs in some oxygenated-cobalt(II) complexes [3]. IR and Resonance Raman spectra of the oxygenated-cobalt(II) complexes have also been utilized to elucidate the nature of the oxygen-cobalt(II) bonding [4, 5]. Recently, Schaefer *et al.* have reported the crystal structures of a series of oxygen adducts of the cobalt(II) Schiff base complexes to study the influence of a change in substituents of the in-plane ligand on the cobalt(II)-molecular oxygen geometry [6].

Basolo *et al.* suggested that the system which enhances the electron density on the cobalt(II) ion increases the oxygen affinity; a linear correlation was found between the stability constants for oxygen adducts and the ease of oxidation of cobalt(II) to cobalt(III) [7]. However, in the course of investigations of the effects of the equatorial chelate groups, they reported that the stability constant for the

oxygen adduct of the complex with X = Y = Z = methyl in Fig. 1. was smaller than that with X = Z = methyl and Y = hydrogen [7]. This seems to be confused because the methyl group should contribute the electron density to the cobalt(II) ion, and thus enhances its oxygen affinity. In this paper, the relation of the redox potentials and the stability constants for pyridine- and oxygen adducts of the cobalt(II) complexes shown in Fig. 1 with Hammett σ constants of the peripheral substituents is comprehensively discussed to reveal the *cis*-effect of the substituents on the oxygen affinity of the complexes.



| | X = | Y = | Z = |
|--------------|--------|-------------|----------|
| 1 Co(A-H) | methyl | hydrogen | methyl |
| 2 Co(A-Cl) | methyl | chloro | methyl |
| 3 Co(A-succ) | methyl | succinimido | methyl |
| 4 Co(A-OPh) | methyl | phenoxy | methyl |
| 5 Co(B-H) | phenyl | hydrogen | methyl |
| 6 Co(B-Cl) | phenyl | chloro | methyl |
| 7 Co(B-succ) | phenyl | succinimido | methyl |
| 8 Co(J-en) | methyl | acetyl | hydrogen |

Fig. 1. Symbols for the cobalt(II) Schiff base complexes.

Results and Discussion

Redox Potentials

The redox potentials were determined by current-sampled dc polarography in N,N-dimethylformamide (DMF). The data obtained are listed in Table I. The gradients of the plots of E against $\log i/(i_d - i)$ are close to the theoretical value (0.0592 V) for diffusion-controlled currents. The typical cyclic voltammogram is displayed in Fig. 2. The peak currents on the cathodic and anodic branches are nearly equal to each other, also implying reversible redox processes. The reaction at the electrode surface is as follows:

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TABLE I. Data for the Current-sampled DC Polarograms, and the Stability Constants for Pyridine- and Oxygen Adducts of Cobalt(II) Schiff Base.

| Complex | Redox potentials/V vs. SCE ^a | | | | log K _{py} ^b (λ/nm) ^c | log KO ₂ ^d (λ/nm) ^c |
|--------------|---|-------|--------------------|-------|--|--|
| | Co ^{III/II} | slope | Co ^{II/I} | slope | mol ⁻¹ dm ³ | Torr ⁻¹ |
| 1 Co(A-H) | 0.045 | 0.055 | -1.775 | 0.052 | 1.25 ± 0.10 (378) | -2.03 ± 0.05 ^e (510) |
| 2 Co(A-Cl) | 0.099 | 0.059 | -1.512 | 0.050 | 1.55 ± 0.29 (392) | |
| 3 Co(A-succ) | 0.053 | 0.052 | -1.549 | 0.054 | 1.53 ± 0.11 (382) | -2.48 ± 0.01 ^f (320) |
| 4 Co(A-OPh) | 0.063 | 0.058 | -1.609 | 0.054 | 1.03 ± 0.04 (396) | |
| 5 Co(B-H) | 0.080 | 0.055 | -1.610 | 0.054 | 1.57 ± 0.09 (413) | -2.58 ± 0.01 ^g (550) |
| 6 Co(B-Cl) | 0.097 | 0.054 | -1.383 | 0.049 | 1.73 ± 0.31 (411) | |
| 7 Co(B-succ) | 0.048 | 0.060 | -1.431 | 0.051 | 1.76 ± 0.02 (394) | -2.85 ± 0.01 ^f (530) |
| 8 Co(J-en) | 0.182 | 0.058 | -1.281 | 0.054 | 2.13 ± 0.05 (380) | |

^aMeasured in the DMF solution of TEAP (0.1 mol dm⁻³), E_{1/2} ± 0.001/V. ^bMeasured in the benzene solution. ^cWave-lengths used for the measurements. ^dMeasured in the 1% pyridine solution of 1,2-dichloroethane. ^eThe value of -2.08/Torr⁻¹ was reported in toluene at 0 °C [3]. ^fData from ref. 10. ^gThe value of -2.03/Torr⁻¹ was reported in toluene at -21 °C [3].

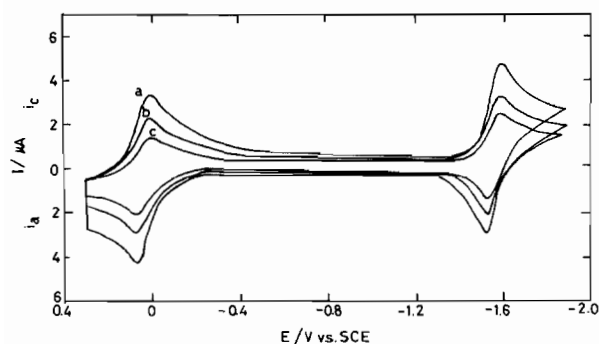
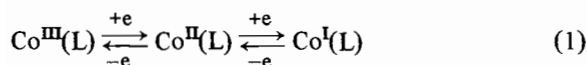


Fig. 2. A typical cyclic voltammogram of Co(A-succ) in DMF, 0.1 mol dm⁻³ TEAP. Scan rate: a, 0.050; b, 0.100; c, 0.200 V/s.



where L denotes the Schiff base ligands. Even though six-coordinate species were proposed for the Co^{III/II} couples of some cobalt(II) Schiff base complexes in a pyridine solution by Basolo *et al.* [7], the exact species at the electrode surface are not clear in this case. However, all that is required for the present purpose is that the species have the same coordination number for all of the E_{1/2} values. A plot of the Co^{III/II} couples vs. the Co^{II/I} couples shows the inverse trend in the case of oxidation of the cobalt(II) ion vs. reduction (Fig. 3).

The trend can be explained as a variation in the electron density on the cobalt(II) ion by the effect of different substituents. The inductive effect of the substituents on the central cobalt(II) ion may well be explained by Hammett linear free energy relationship:

$$\log K = \log(K^{\text{X}}/K^{\text{H}}) = \sigma\rho' \quad (2)$$

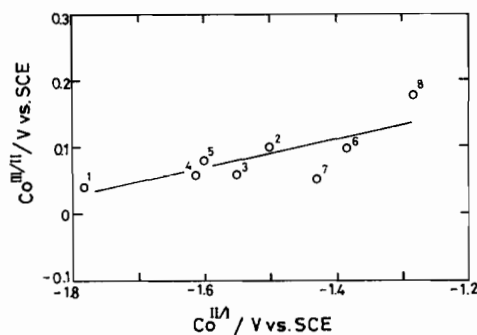


Fig. 3. Comparison of polarographic half-wave potentials (E_{1/2}) for Co^{III/II} to those for Co^{II/I}.

The electrochemical redox potential (E_{1/2}) is also related with the Hammett σ constants as follows [8];

$$\Delta E_{1/2} = E_{1/2}^{\text{X}} - E_{1/2}^{\text{H}} = \sigma\rho \quad (3)$$

where σ and ρ are a substituent constant and a reaction constant, respectively, and ρ is also related to ρ' by the factor 2.303 RT/F. The σ values used in this work originate from the article reported by Jaffe [9]. In Figure 4, the oxidation (Co^{II/III}) and reduction (Co^{II/I}) potentials of the cobalt(II) complexes are plotted against the sum of the σ values, respectively.

The straight line was obtained in the case of the Co^{III/II} couples. However, in the case of the Co^{II/I} couples, the plot of Co(A-OPh) deviated from a straight line. The yellow Co(A-OPh) complex was reported to change to dark brown in polar-solvent moistures such as methanol and acetone presumably because of the oxidative decomposition [10]. Thus, a small amount of oxygen contaminated in the DMF solution might affect the redox potential of Co(A-OPh). Further investigations of its behavior in solution should be performed. The ρ values for the oxidation and reduction of the cobalt(II) complexes

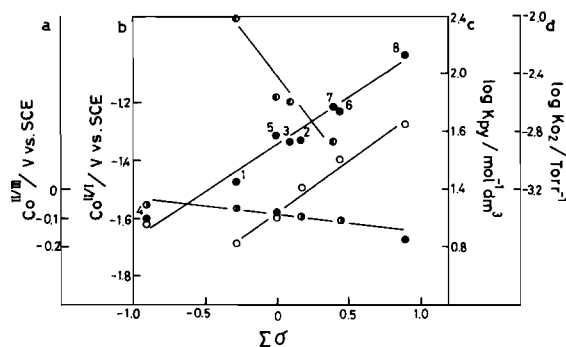
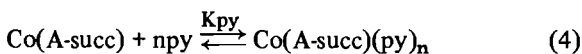


Fig. 4. A plot of the Co^{II/I} couples, the Co^{II/III} couples, log Kpy, and log KO₂ vs. the sum of the Hammett σ values: (○) Co^{II/I} couples, a; (●) Co^{II/III} couples, b; (●) log Kpy, c; (●) log KO₂, d.

are negative and positive respectively, indicating that the electron-withdrawing substituents favor the reduction of the cobalt(II) complex, but make difficult its oxidation. The ρ value for the Co^{II/I} couples ($\rho = 0.36$) is larger than the absolute one for the Co^{II/III} couples (-0.06). This indicates that the *cis*-effect is more sensitive to the Co^{II/I} couples than to the Co^{II/III} couples, as was seen in the case of *para*-substituted tetraphenylporphyrin complexes of cobalt(II) [11]. This fact is interpreted by the concept that the Co^{II/I} couples are dominated by a strong equatorial ligand interaction, while the Co^{II/III} couples are affected more strongly by an axial ligand interaction, consistent with the result of vitamin B₁₂ model compounds [12]. In the case of the succinimido derivatives, the σ constant for the succinimido group is unknown so that it is tentatively estimated at 0.19 from the straight line of the Co^{II/I} couples in Fig. 4.

Stability Constants for the Pyridine Adducts

An equilibrium between the cobalt(II) complex and pyridine in a benzene solution was studied to elucidate the factors governing the pyridine-adduct formation. Co(A-succ) showed an absorption band at 382 nm in the benzene solution. By adding pyridine to the solution, the band was gradually decreased with an isosbestic point at 403 nm. Subsequently, the intensity of the absorption became constant when the concentration of pyridine reached 0.6 mol dm⁻³.



Then, the stability constant (K_{py}) of the equation (4) is given by the relation (5).

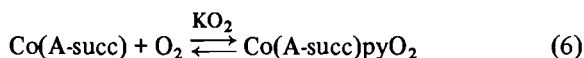
$$1/(A_0 - A) = 1/(A_0 - A_\infty)K_{\text{py}}[\text{py}]^n + 1/(A_0 - A_\infty) \quad (5)$$

where A_0 , A , and A_∞ are the absorbances at 382 nm in the absence of pyridine, in the presence of a proper amount of pyridine, and in the presence of larger

excess of pyridine, respectively. The plots of $1/(A_0 - A)$ against $1/[\text{py}]$ gave a straight line with a slope nearly equal to 1, indicating that the main species is Co(A-succ)py, and the presence of Co(A-succ)(py)₂ is negligible in the solution. The plots with the other complexes also gave straight lines. The stability constants obtained are listed in Table I, and are plotted against the σ values in Fig. 4. The straight line with the positive slope of 0.72 indicates that the stability of the pyridine adduct increases with a decrease of the electron density of the cobalt(II) ion.

Stability Constants for the Oxygen Adducts

Previously the stability constants for the oxygenation of Co(A-succ) and Co(B-succ) had been measured in a 1,2-dichloroethane solution containing small amounts of pyridine at 6 °C by means of a spectral change in oxygenation [10]:



In this work, the stability constants of Co(A-H) and Co(B-H) were also measured in the 1,2-dichloroethane solution by a method similar to that used for the previous measurements, for the purpose of estimation of the trend of K_{O_2} vs. the σ values. The values of K_{O_2} obtained are listed in Table I, and are plotted against the σ values in Fig. 4. The other complexes such as Co(A-Cl), Co(A-OPh), Co(B-Cl), and Co(J-en) did not give straight lines in the plots of PO_2 vs. $\text{PO}_2/(A - A_0)$, where PO_2 , A , and A_0 are the partial pressure of oxygen, the absorbance in the absence of oxygen, and the absorbance in the proper partial pressure of oxygen, respectively. This may show the existence of a 1:2 oxygenated species. In the case of the Co(J-en) complex, it was also reported that the 1:1 and 1:2 oxygenated complexes exist in the 1,2-dichloroethane solution in oxygenation, and the latter is predominant in the higher partial pressure of oxygen [5 and 13]. The straight line with the negative slope of -0.96 in Fig. 4 suggests that the oxygen affinity of the complex increases with an increase of the electron density on the cobalt(II) ion.

While the slope of log K_{py} and the Co^{II/I} couples are positive, those of log K_{O_2} and the Co^{II/III} couples are negative. With a decrease of the electron density on the cobalt(II) ion, both the reduction of cobalt(II) and the formation of the pyridine adduct turn to advantage, but the oxidation of cobalt(II) and the oxygenation of the complex become too difficult (*vice versa*). That is, in-plane ligand effects on oxygenation of the cobalt(II) complexes may be elucidated by the electronic factors of the substituents by using the Hammett σ values. Furthermore, some cobalt(II) complexes gave the 1:2 oxygenated species in the solution. It is known that an equilibrium between the 1:1 and 1:2 oxygenated species in solution is affected by the factors such as type of base

added, polarity of solvents, and temperature [1]. Further studies will be undertaken for the effect of the substituents of the in-plane ligand on the equilibrium.

Experimental

Materials

Tetraethylammonium perchlorate (TEAP) was recrystallized twice from water. DMF was dried by refluxing over calcium chloride anhydrous, and then distilled under a nitrogen atmosphere. Benzene, 1,2-dichloroethane, and pyridine were reagent grade, and were used without further purification.

Preparation of the Complexes

The structure and symbols of the cobalt(II) complexes prepared for this study are shown in Fig. 1; Co(A-H), Co(B-H), and Co(J-en) were prepared by the methods described before [13, 14 and 15], while Co(A-Cl), Co(A-succ), Co(A-OPh), Co(B-Cl), and Co(B-succ) were prepared by the method described in [10]. The purity of the complexes was confirmed by elemental analyses and electronic spectra.

Electrochemical Measurements

All measurements were carried out in the 0.1 mol dm⁻³ TEAP solution of DMF at 25.0 ± 0.1 °C. A Fuso model 312 polarograph and a DME (or HMDE) were employed for polarographic and cyclic voltammetric measurements. The reference electrode was SCE with a salt bridge [16]. Before running electrochemical measurements, nitrogen was passed through the solution for 20 min, being subsequently passed above it throughout the measurements.

Measurements of K_{py} for the Pyridine Adducts

Co(A-succ)py: absorption spectra of Co(A-succ) in the benzene solution (2.00 × 10⁻⁴ mol dm⁻³) containing pyridine were measured at 20.0 ± 0.4 °C by successively altering the pyridine content (0–0.6 mol dm⁻³) under a nitrogen atmosphere. The stability constant was determined from the absor-

bance change at 394 nm. The values of K_{py} for the other complexes were measured in a similar way to that mentioned above.

Measurements of KO₂ for the Oxygen Adducts

The stability constants for the oxygen adducts of Co(A-H) and Co(B-H) were measured by a method similar to that used for the Co(A-succ) and Co(B-succ) complexes [10].

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