CHEMISTRY LETTERS, pp. 1403−1406, 1991.

Substituent Effects on the Formal Potential of the Co^{II}/Co^{III} Redox Couple for Co(salen) Derivatives

Akira NISHINAGA, Kunihiko TAJIMA,+ Bernd SPEISER,++ Emerich EICHHORN,++ Anton RIEKER,++ Hiroaki OHYA-NISHIGUCHI,+++ and Kazuhiko ISHIZU+

Department of Applied Chemistry, Osaka Institute of Technology, Ohmiya 5, Asahi-ku, Osaka 535

+ Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

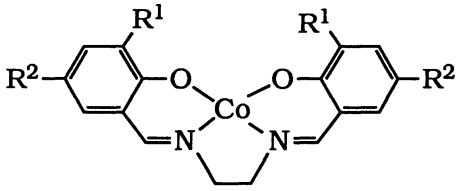
++ Institut fur Organische Chemie, Auf der Morgenstelle 18, D-7400 Tubingen 1, Germany

+++ Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

The formal potential of the Co^{II}/Co^{III} redox couple in Co(salen) derivatives determined in DMF varies with the electronic as well as the steric properties of substituents at the aromatic rings in the salen ligand, where *t*-butyl groups shift the potential to more positive values, indicating strong steric interactions with solvent molecules.

Cobalt(II) Schiff-base complexes [Co^{II}(SB)] have been of particular interest for a long time because they form oxygen adducts reversibly and catalyse the oxygenation of organic molecules resembling oxidoreductases including dioxygenases, monooxygenases, and peroxidases.[1] It has been shown that derivatives of Co(salen) [H_2salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] with an electron-withdrawing substituent at the aromatic ring accelerate the oxygenation of phenolic substrates,[2] and that a twisted structure of Co^{II}(SB) favors monooxygenation reactions of olefins with molecular oxygen[1c] and with NaOCl.[3] The correlation between structure, redox potential, and catalytic activity of the Co^{II}(SB) complexes is essential to discuss the mechanism of these reactions. Little is, however, known about the effect of substituents in the aromatic rings on E^0 of Co(salen) type complexes.[4] On the other hand, a relation between the redox potential and the equilibrium constant for oxygen binding has been discussed for some Co^{II}(SB) complexes.[5]

Thus, Co(salen) derivatives **1** - **4** were synthesized by the reaction of $Co(OAc)_2\ 4H_2O$ with the appropriate Schiff bases,[6] and their formal potentials were determined from cyclic voltammograms in DMF/0.1 M NBu_4PF_6 as the mean value of the oxidation and



	1a	1b	1c	1d	1e	1f
R^1	H	H	H	H	H	H
R^2	MeO	Me	*t*-Bu	H	Cl	NO_2

	2a	2b	2c	2d	2e	2f
R^1	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu
R^2	MeO	Me	*t*-Bu	H	Cl	NO_2

	3	4
R^1	Me	Me
R^2	*t*-Bu	H

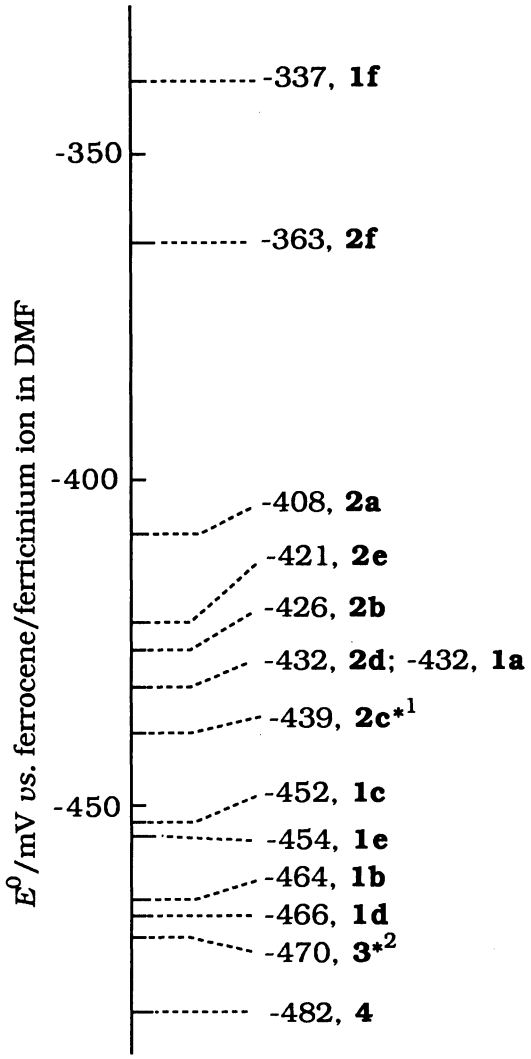


Fig. 1. Formal potentials (E^0) of Co^{II}(SB) (**1**)-(**4**). *1 ΔE_p values vary from 160 to 82 depending on the scan rate due to a slow electron transfer process. E^0 calculated by multi-parameter estimation.[8] *2 Large values for ΔE_p may be due to a slow electron transfer process.

reduction peak potentials, E_p^I and E_p^{II} at a Pt disk working electrode. All potentials are given relative to an external Fc/Fc^+ (Fc = ferrocene) reference. The iR drop was compensated by positive feed back in the Bruker E310 potentiostat to an extent that oscillations were just avoided. In some cases, a numerical correction of the remaining iR error was employed.[7] The values of E_p^I and E_p^{II} were obtained at room temperature at scan rates v = 10 - 200 mV/s . The resulting E^0 are shown in Fig. 1 (mean values over all *v*).

In most cases, nearly reversible voltammograms were obtained, but for compounds **2c** and **3** an increased peak potential difference due to a slightly quasireversible process was observed.

The values of E^0 depend on the substituents. In series **1** a shift of 129 mV is found between the complexes oxidized at the lowest (**1d**) and highest (**1f**) potentials. The E^0 values of all compounds except **1f**, however, are not very different. The nitro complex **1f** is much more difficult to be oxidized: the electron-withdrawing nature of the NO_2 substituent decreases the electron density at the metal center.

In series **2** the small substituent effect generally observed has further decreased to 76 mV (cf. **2c** and **2f**). All formal potentials, with the exception of E^0 (**2f**), are *more positive* than those for the respective compounds in series **1**. From the electronic effects of the *t*-Bu substituent, we would expect a shift in the negative direction. Obviously, the electronic effects of this bulky alkyl substituent are overcompensated by steric effects.

Two steric consequences of a *t*-Bu substituent may be envisaged: the largely planar structure of the complexes **1** (cf., for example, Ref. 9) could become distored and/or the coordination of an additional axial donor ligand could be hindered. The former effect is demonstrated by an X-ray analysis of compound **2a**, which shows a slightly twisted conformation of the complex.[10]

Furthermore, it is known that Co^{II}(SB) complexes coordinate an additional donor molecule (here: the solvent DMF). The donor supplies electron density and the formal potential attains more negative values. If the bulky *t*-Bu groups hinder solvent coordination in series **2**, the influence of the donor is reduced. This will result in an overall positive variation of E^0. The data for **2d** and **4** as well as **2c** and **3**, where the Me and the *t*-Bu substituents with similar electronic but different steric effects are located *ortho* to the O atom, confirm our explanation. Further investigations to prove the predominance of steric effects on the electrochemistry of Co^{II}(SB) complexes are under way.

The small substituent effect finally may be explained by the fact that the electron is taken from the d_{z^2} orbital which is influenced by the SB ligand only slightly.[11] In pyridine adducts of Co^{II}(SB) complexes the Co atom is known to move out of the ligand plane in the direction of the donor.[12] Streric hindrance of the donor access causes a more planar arrangement and may result in an even smaller effect of the ring substituents. The exception of the NO_2 complexes may be due to some additional change in solvation or the geometry of the molecules.

The present work has been supported by the Grant-in-Aid for Scientific Research, Ministry of Education, Japan and partly by the Volkswagen-Stiftung, Hannover, FRG.

References

1) a) E. C. Niederhoffer, J. H. Timmons, and A. E. Martell, *Chem. Rev.*, **84**, 137 (1984); b) A. Nishinaga, *Tampakushitsu Kakusan Koso*, **26**, 214 (1983); c) A. Nishinaga, T. Yamada, H. Fujisawa, K. Ishizaki, H. Ihara, and T. Matsuura, *J. Mol. Catal.*, **48**, 249

(1988); d) A. Nishinaga, I. Sugimoto, and T. Matsuura, *Nippon Kagaku Kaishi*, **1988**, 489.
2) A. Nishinaga, H. Tomita, K. Nishizawa, T. Matsuura, S. Ooi, and K. Hirotsu, *J. Chem. Soc., Dalton Trans.*, **1981**, 1504.
3) A. Nishinaga, M. Kakutani, T. Umeda, and T. Mashino, *Proceeding of 4th International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidation*, **1990**, in press.
4) D. F. Averill and R. F. Broman, *Inorg. Chem.*, **17**, 3389 (1978); D. F. Rohbach, W. R. Heineman, and E. DeuTsch, *ibid.*, **18**, 2536 (1979).
5) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
6) A. Nishinaga, H. Moriyama, K. Maruyama, and T. Mashino, to be published.
7) E. Eichhorn, A. Rieker, and B. Speiser, to be published.
8) B. Speiser, *Anal Chem.*, **57**, 1390 (1985).
9) N. Bresciani, M. Calligaris, G. Nardin, and L. Randacchio, *J. Chem. Soc., Dalton Trans.*, **1974**, 1606.
10) W. Hiller, A. Nishinaga, and A. Rieker, *J. Chem. Soc., Chem. Commun.*, to be published.
11) A. M. Tate, F. V. Lovecchio, and D. H. Bush, *Inorg. Chem.*, **16**, 2206 (1974).
12) N. Bresciani, M. Calligaris, G. Nardin, and L. Randacchio, *J. Chem. Soc. Dalton Trans.*, **1974**, 498.

(Received May 21, 1991)