1428 © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 1428—1430 (1988) [Vol. 61, No. 4

# Catalytic Activity of *catena*-$\mu$-Cyano-(phthalocyaninato)cobalt(III) for the Cathodic Reduction of Oxygen

Osamu IKEDA,[†],* Shuji ITOH, and Hiroshi YONEYAMA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565

(Received August 28, 1987)

**Synopsis.** *catena*-$\mu$-Cyano-(phthalocyaninato)cobalt(III) showed a 4-electron reducibility for the cathodic reduction of oxygen at low overpotentials, which was not observed for (phthalocyaninato)cobalt(II) and chloro(phthalocyaninato)-cobalt(III).

Many of metal complexes of phthalocyanine, porphyrin and tetraazaannulene possess electrocatalytic activities for the cathodic reduction of oxygen. However, most of them catalyze the 2-electron pathway ($O_2+H_2O+2e^- \rightarrow HO_2^-+OH^-$). Therefore, the conversion of the 2-electron pathway to the 4-electron pathway ($O_2+2H_2O+4e^- \rightarrow 4OH^-$) has been tried by means of molecular designs; The preparations of face-to-face or cofacial porphyrins[1,2] and a planar binuclear complex[3] are typical examples. In the present study, catalytic activities of *catena*-$\mu$-cyano-(phthalocyaninato)-cobalt(III) ($[Co^{III}(pc)CN]_n$), which has a stacked structure bridged by cyanide ions[4] as shown in Fig. 1, have been investigated to examine the effect of molecular designs.

## Experimental

$[Co^{III}(pc)CN]_n$ was prepared from $Co^{II}(pc)$ via dichloro-(phthalocyaninato)cobal(III) $[Co^{III}(pc)(Cl)_2]$ and then via dicyano (phthalocyaninato)cobalt(III) $[Co^{III}(pc)(CN)_2]$.[4] $Co^{III}(pc)Cl$ was obtained by the thermal decomposition of $[Co^{III}(pc)(Cl)_2]$ in Ar atmosphere at 320 °C.[5] The formation of catenary $[Co^{III}(pc)CN]_n$ was confirmed by an IR spectrum ($\nu_{C\equiv N}=2158\ \mathrm{cm}^{-1}$) and a high conductivity ($\sigma=2\times10^{-3}\ \mathrm{S\ cm}^{-1}$)[5] of the resulting powders.

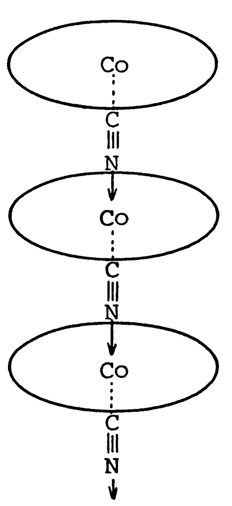

Fig. 1. Stacked structure of $[Co^{III}(pc)CN]_n$. Ellipses represent the phthalocyanine ring (pc(−2)).

(Phthalocyaninato)cobalt-coated disc electrodes were prepared by coating with use of a microsyringe *N,N*-dimethylacetamide (DMA) solutions containing either one of the above-mentioned (phthalocyaninato)cobalts onto a top surface of a glassy carbon rod (Tokai Carbon GC20; 6 mm diameter and 10 mm length) preheated to 80 °C on a hot plate. The amount of coating was $2\times10^{-7}\ \mathrm{mol\ cm}^{-2}$ for all cases. The GC rod was then installed into the disc cavity of a ring-disc electrode. The potential of the Pt ring was fixed to 0.3 V vs. SCE, where diffusion limiting currents due to oxidation of peroxide ions ($HO_2^-$) as a reduction intermediate of oxygen were observed. Aqueous 1 M ($=\mathrm{mol\ dm}^{-3}$) KOH was used as the electrolytic solution.

## Results and Discussion

Axial ligands of metallomacrocycles are apt to exchange with other competing ligands. In fact, $[Co^{III}(pc)CN]_n$ is known to be decomposed by organic bases (L) such as pyridine and piperadine to give monemeric $Co^{III}(pc)(CN)L$.[4] Since the catalytic activities for oxygen reduction were studied in an alkaline solution, it was then examined whether or not the phthalocyanines used were decomposed in contact with hydroxide ions. For this purpose, visible light absorption spectra were measured before and after addition of 1 M KOH to the DMA solutions of $Co^{III}(pc)Cl$ and $[Co^{III}(pc)CN]_n$, and before and after immersion of $[Co^{III}(pc)CN]_n$ and $Co^{III}(pc)Cl$-coated quartz plates into 1 M KOH. $Co^{III}(pc)Cl$ showed a spectrum change both in the DMA solution and in the coated films, suggesting that $Co^{III}(pc)Cl$ changed into $Co^{III}(pc)OH$ in the presence of $OH^-$. On the other hand, the spectra of $[Co^{III}(pc)CN]_n$ were little changed by contact with $OH^-$, suggesting that the Co-CN-Co bond is stable against $OH^-$. The stability of the axial ligand or the strength of the ligand-metal bond seems to roughly correspond to spectrochemical series for $Co^{III}$-complexes ($Cl^- < OH^- \ll CN^-$).

Figure 2 shows disc currents and ring currents of the rotating ring-disc electrodes as a function of the disc potential in oxygen-saturated 1 M KOH. There are differences in the electrochemical behaviors of the three kinds of (phtalocyaninato)cobalts at rising portion of the disc currents. In the case of $Co^{II}(pc)$ and $Co^{III}(pc)Cl$, though the actual form of the latter will be $Co^{III}(pc)OH$, disc and ring currents have the same onset potential. In the case of $[Co^{III}(pc)CN]_n$, however, there are negligible ring currents in an onset potential region of the disc currents. The results seem to suggest that oxygen is reduced to $OH^-$ through the 4-electron pathway at the $[Co^{III}(pc)CN]_n$ but not at the $Co^{II}(pc)$ and $Co^{III}(pc)Cl$ electrodes.

In order to evaluate the 4-electron reducibility of the three kinds of (phtalocyaninato)cobalts, the apparent

---

[†] Present address: Department of Chemistry, College of Liberal Arts, Kanazawa University, 1-1 Marunouchi, Kanazawa 920.

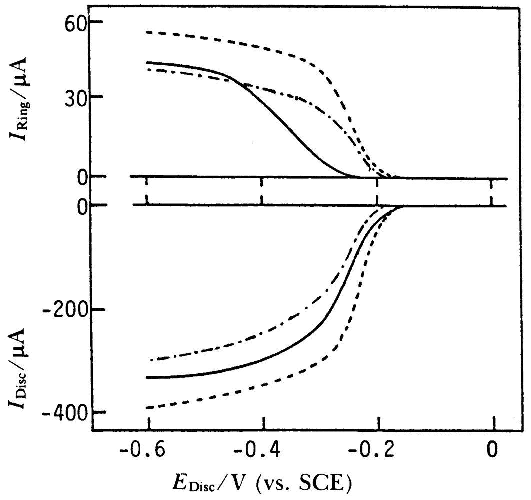

Fig. 2. Disc currents and ring currents at the ring(Pt)-disc(GC) coated with (----) Co$^{II}$(pc), (-·-·-) Co$^{III}$(pc)Cl, and (——) [Co$^{III}$(pc)CN]$_n$ electrodes as a function of disc potential in $O_2$-saturated 1 M KOH. Rotation rate, 1000 rpm; ring potential, 0.3 V vs. SCE; sweep rate at the disc, 20 mV s$^{-1}$; the disc area, 0.28 cm$^2$.

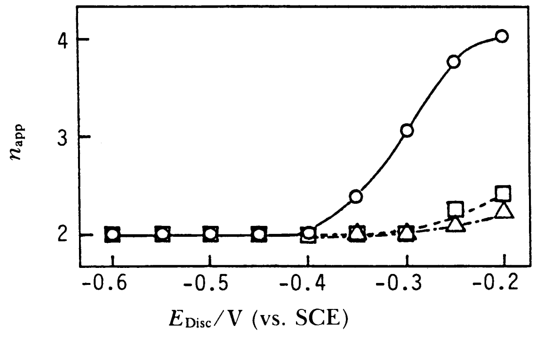

Fig. 3. Variation of $n_{app}$ (apparent number of electrons involved in $O_2$ reduction) with disc potential for (○) [Co$^{III}$(pc)CN]$_n$, (△) Co$^{III}$(pc)Cl, and (□) Co$^{II}$(pc), respectively.

number of electrons involved in the oxygen reduction ($n_{app}$) was determined as a function of the disc electrode potentials. In the determination $n_{app}$, it was assumed that the $O_2$ reduction at the disc consisted of a mixed reaction of the 2-and 4-electron pathways. Thus, $n_{app}$ was evaluated by the next relation: $n_{app}=4I_{Disc}/(I_{Disc}+I_{Ring}/N_{corr})$, where $I_{Disc}$ and $I_{Ring}$ are the disc and ring currents at a potential, respectively, and $N_{corr}$ is the collection efficiency for $HO_2^-$, corrected for a deviation from coplanality between the Pt ring and the (phtalocyaninato)cobalt-coated disc.[4] The results are shown in Fig. 3. It is obvious from this figure that catenary [Co$^{III}$(pc)CN]$_n$ has a high 4-electron reducibility compared with monomeric Co$^{II}$(pc) and Co$^{III}$-(pc)Cl for oxygen reduction at low overpotentials.

In order to clarify the participation of redox of metal sites in the above oxygen reduction, the electrochemistry of Co$^{II}$(pc), Co$^{III}$(pc)Cl and [Co$^{III}$(pc)CN]$_n$ was studied by means of cyclic voltammetry of these (phtalocyaninato)cobalt-coated glassy carbon electrodes in deaerated 1 M KOH. However, clear redox peaks were not observed in the cyclic voltammograms between 0 V and −0.6 V vs. SCE for all catalysts. Furthermore, no detectable change was observed in visible absorption spectra of Co$^{II}$(pc), Co$^{III}$(pc)Cl, and [Co$^{III}$(pc)CN]$_n$ on an optically transparent electrode ($In_2O_3$/quartz) between 0 V and −0.6 V vs. SCE. Each spectrum was almost the same as that at open circuit in 1 M KOH. These results suggest that the oxygen reduction mechanism in the present catalysts is not controlled by the redox of metal sites.

Therefore, the results for oxygen reduction in Figs. 2 and 3 are discussed on the basis of d-electron configuration of cobalt ions and molecular conformation of the phtalocyanines as follows. The effective magnetic moment $\mu_{eff}$ of Co$^{II}$(pc) has been reported to be 2.7 $\mu_B$ (Bohr Magneton),[7] and the d-electron configuration of Co(II) is estimated to be $(d_{xy})^2(d\pi)^4(d_z{}^2)^1$.[8] Exerimental values of $\mu_{eff}$ for Co$^{III}$(pc)Cl and [Co$^{III}$(pc)CN]$_n$ were 3.1 and 1.0 $\mu_B$, respectively. The spin only equation for magnetically diluted substances roughly predicts that the number of unpaired electrons is 2 for Co$^{III}$(pc)Cl and 0 for [Co$^{III}$(pc)CN]$_n$. Consequently, the d-electron configuration of Co$^{III}$(pc)OH which will be the actual form of Co$^{III}$(pc)Cl in 1 M KOH, will be the same as that of Co$^{III}$(pc)Cl, because the ligand field strength would not be so different between Cl$^-$ and OH$^-$.

Both Co$^{II}$(pc) and Co$^{III}$(pc)Cl have an unpaired electron on $d_z{}^2$ orbital of the central cobalt ions, which facilitates an interaction with the oxygen $1\pi_g^*$ orbital. This interaction leads to the 2-electron pathway for oxygen reduction through its end-on coordination.[9] The cobalt ion in [Co$^{III}$(pc)CN]$_n$ has an empty $d_z{}^2$ orbital, which offers a favorable condition for the 4-electron pathway, because the $\sigma$-coordination of the oxygen $1\pi_u$ electron to the empty cobalt $d_z{}^2$ orbital and the $\pi$-back donation of $d_\pi$ electrons to the oxygen $1\pi_g^*$ orbital facilitate the side-on coordination of oxygen.[10] However, such a side-on coordination is expected only at the terminal cobalt ions in the stacked structure of [Co$^{III}$(pc)CN]$_n$. In order to obtain the observed peculiar effect of the Co-CN-Co bridge for the 4-electron reduction of oxygen, we have to assume that an oxygen makes a bridge type coordination between two cobalt ions.[11] The intermetallic distance separated by the cyanide ions of [Co(pc)CN]$_n$ was estimated to be 4—5 Å, which is fitted well in making the bridge type coordination of oxygen.[1] However, the interaction between a filled $d\pi$ orbital or paired electrons and the oxygen $1\pi_g^*$ orbital electron seems to be weak, because the latter has a radical character. The $\mu_{eff}$ of [Co(pc)CN]$_n$ was not real zero but 1.0 $\mu_B$, suggesting that there is a small unparing character in the $d\pi$ orbital. Probably, this unpairing character allows the bridge type coordination of oxygen leading to the 4-electron pathway, but it may disappear with increasing the overpotential. Thus, the 2-electron pathway becomes predominant.

The potential dependence of $n_{app}$ for [Co$^{III}$(pc)CN]$_n$ was reproduced even after 100 potential sweep cycles between 0 V and −0.6 V vs. SCE. The result suggests that the molecular conformation of [Co$^{III}$(pc)CN]$_n$ is also stable against the potential sweep cycles.

## References

1) J. P. Collman, M. Marrocco, C. Koval, and F. C. Anson, *J. Am. Chem. Soc.*, **103**, 6027 (1980).

2) H. Y. Liu, M. Weaver, C. Wang and C. Chang, *J. Electroanal. Chem. Interfacial Electrochem.*, **145**, 439 (1983).

3) E. Yeager, *Electrochim. Acta*, **29**, 1527 (1984).

4) J. Metz, and M. Hanack, *J. Am. Chem. Soc.*, **105**, 828 (1983).

5) M. Hanack, *Mol. Cryst. Liq. Cryst.*, **105**, 133 (1984).

6) O. Ikeda, H. Fukuda, and H. Tamura, *J. Chem. Soc., Farady Trans. 1*, **82**, 1561 (1986).

7) R. L. Carlin, "Transition Metal Chemistry," Marcel Dekker, New York (1965), Vol. 1, p. 30.

8) G. A. Williams and B. N. Figgis, *J. Chem. Soc., Dalton Trans.*, **1981**, 734.

9) L. Pauling, *Nature (London)*, **203**, 182 (1964).

10) J. S. Griffith, *Proc. R. Soc. London, Ser. A*, **235**, 23 (1956).

11) E. Yeager, *J. Electrochem. Soc.*, **128**, 160C (1981).