# Dioxygen Binding to a Cobalt(II) Porphycene Complex and Its Auto-Oxidized Cobalt(III) Complex

**Hisashi Shimakoshi, Isao Aritome, Shun Hirota,[1] and Yoshio Hisaeda***

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University,
Hakozaki, Higashi-ku, Fukuoka 812-8581

[1]Department of Physical Chemistry, Kyoto Pharmaceutical University,
5 Nakauchi-cho, Misasagi, Yamashina-ku, Kyoto 607-8414

Received February 15, 2005; E-mail: yhisatcm@mbox.nc.kyushu-u.ac.jp

The reaction between a cobalt porphycene complex, [Co$^{II}$(TPrPc)] (TPrPc is a dianion of 2,7,12,17-tetrapropylporphycene), and dioxygen was investigated by means of UV–vis, ESR, and resonance Raman (RR) spectroscopies. These spectra indicate the formation of [Co$^{III}$–O$_2$$^{-\bullet}$]. In the presence of pyridine as an axial ligand, the formation of a six-coordinated superoxide species was confirmed by its characteristic ESR spectrum. The six-coordinated dioxygen adduct exhibits an RR band at 1144 cm$^{-1}$, which is characteristic of O–O stretching of superoxide. $\nu$(Co–O$_2$) stretching is also observed at 540 cm$^{-1}$. The $\nu$(O–O) and $\nu$(Co–O$_2$) wavenumbers in the complex were assigned by means of $^{18}$O$_2$ substitution. $\nu$(Co–O$_2$) of the O$_2$ adduct shows a higher frequency relative to those of cobalt porphyrin complexes. On standing for one day at room temperature, the compound was auto-oxidized to a Co$^{III}$ complex, which was structurally determined by X-ray analysis. The complex crystallized in the monoclinic space group $P2_1/n$, $a = 9.6266(4)$ Å, $b = 12.6343(5)$ Å, $c = 15.6566(6)$ Å, $\beta = 99.1200(10)^\circ$, $V = 1880.17(13)$ Å$^3$, and $Z = 2$. The Co$^{III}$ ion lies on the plane of the porphycenato core, and coordinates four porphycenato nitrogen atoms and two pyridine nitrogen atoms. The complex cation, [Co$^{III}$(TPrPc)(Py)$_2$]$^+$, exhibits a slightly distorted octahedral coordination geometry. The average Co–N (porphycenato pyrrole) distance and the Co–N (pyridine) distance are 1.929 and 1.952 Å, respectively.

Metal–dioxygen complexes are of chemical and biological interest because of their important role in living organisms as well as their function as artificial oxidation catalysts.[1–3] The binding of molecular oxygen to transition metal complexes has been the subject of much current research. Therefore, numerous efforts have been made to synthesize new cobalt(II)–dioxygen complexes and to characterize their dioxygen affinities.[4] In the course of these studies, cobalt complexes that bind dioxygen are available in a large variety of ligand systems, such as the Schiff base,[5–9] tetraazamacrocycle,[10,11] dimethylglyoxime,[12] and porphyrin.[13,14] Porphyrins are macrocyclic tetrapyrrole pigments that play an important role in life processes. Thus, cobalt porphyrins are among the most common models for the active sites of heme-proteins, which have a biological task of carrying dioxygen. Porphycenes, the structural isomer of porphyrins synthesized by Vogel et al.,[15] are attracting considerable attention in view of their unusual properties by comparison to those of porphyrins.[16–26] In spite of their potential application in biological processes, reactivity of the complexes toward small ligands (CO, NO, and O$_2$) as well as their catalytic activities have scarcely been studied, except for our previous studies.[27–31] Therefore, in this study we investigated the reactivity of a tetra-*n*-propylporphycene cobalt(II) complex toward dioxygen by means of UV–vis, ESR, and resonance Raman spectroscopies.

## Experimental

**Materials.** The free base 2,7,12,17-tetra-*n*-propylporphycene (H$_2$TPrPC) was synthesized according to a method previously reported by Vogel et al.[15] The corresponding cobalt complex was prepared by a previously reported method.[20] The chemicals and solvents used in the syntheses were of the highest grade available, and were used without further purification. All solvents for spectroscopies were purified by distillation before use. $^{18}$O$_2$ (Kishida Chemicals, 97% pure) was used for a resonance Raman study.

**Physical Measurements.** Elemental analyses were obtained from the Service Center of Elementary Analysis of Organic Compounds at Kyushu University. $^1$H, $^{13}$C, and 2-D NMR (COSY) spectra (in CDCl$_3$) were recorded on a Bruker Avance 500 spectrometer, and the chemical shifts (in ppm) were referenced relative to SiMe$_4$ as the internal standard. IR spectra were recorded on a JASCO IR-810 spectrophotometer using KBr discs. Electrospray ionization (ESI) mass spectra were acquired using a PerSeptive Biosystem Mariner™. ESR spectra were obtained on a JEOL JES-FE1G X-band spectrometer equipped with an Advantest TR-5213 microwave counter and an Echo Electronics EFM-200 NMR field meter. Resonance Raman (RR) scattering was excited at 406.7 nm with a Kr$^+$ ion laser (Spectra Physics, 2060) and detected with a CCD (PRICETON INSTRUMENTS) attached to a single polychrometer. The slit width and slit height were set to be 200 µm and 10 mm, respectively. The excitation laser beam power (at the sample point) was adjusted to 10 mW. Measurements were carried out with a spinning cell (diameter = 2 cm). The cell was spun at 3000 rpm in a cryostat that was cooled to 233 K by cold N$_2$ gas. The data-accumulation time was 150 s. Raman shifts were calibrated with acetone, and the accuracy of the peak positions of the Raman bands was ±1 cm$^{-1}$.

**Reversible Oxygen Binding Followed by Electronic Spectroscopy.** The electronic absorption spectra at low temper-

Published on the web August 30, 2005; DOI 10.1246/bcsj.78.1619

ature were measured in dichloromethane on a Hitachi U-3300 spectrophotometer equipped with an Oxford DN nitrogen-bath cryostat controlled by an Oxford ITC601 temperature controller. A $1.0 \times 10^{-5}$ mol dm$^{-3}$ solution of [Co$^{\mathrm{II}}$(TPrPc)] was prepared and lowered to 203 K under dioxygen, and an electronic absorption spectrum of the resulting purple solution was obtained. The temperature of the solution was then raised to 263 K. This thermal cycling was repeated as necessary with electronic absorption spectra being obtained at the lower and higher temperatures of each cycle. A similar experiment was also carried out in the presence of 100 equivalents mole of pyridine ($1.0 \times 10^{-2}$ mol dm$^{-3}$).

**Oxidation of [Co$^{\mathrm{II}}$(TPrPc)] to Co$^{\mathrm{III}}$ Complex.** The complex [Co$^{\mathrm{II}}$(TPrPc)] was dissolved in $CH_2Cl_2$ under aerobic conditions at 203 K in the presence of 100 mol equivalents of pyridine, resulting in a bluish-purple colored solution. The solution was allowed to stand at room temperature in the presence of $NaClO_4$. Bluish-purple crystals were obtained by slow evaporation of the $CH_2Cl_2$–pyridine–benzene solution at room temperature. The following spectroscopic data indicate the structure as [Co$^{\mathrm{III}}$(TPrPc)-(Py)$_2$]ClO$_4$: $^1$H NMR (CDCl$_3$; ppm); $\delta$ −0.42 (d, 4H, Py), 1.39 (t, 12H, $-\mathrm{C}\underline{\mathrm{H}}_3$), 2.50 (m, 8H, $-\mathrm{CH_2C}\underline{\mathrm{H}}_2\mathrm{CH_3}$), 4.29 (t, 8H, $-\mathrm{C}\underline{\mathrm{H}}_2\mathrm{CH_2CH_3}$), 4.81 (t, 4H, Py), 5.99 (t, 2H, Py), 9.35 (s, 4H, pyrrole H), 10.23 (s, 4H, methine). $^{13}$C NMR (CDCl$_3$; ppm); $\delta$ 14.5 ($-\underline{\mathrm{C}}\mathrm{H}_3$), 24.8 ($-\mathrm{CH_2}\underline{\mathrm{C}}\mathrm{H_2CH_3}$), 31.6 ($-\underline{\mathrm{C}}\mathrm{H_2CH_2CH_3}$), 107.1, 121.8, 122.9, 136.6, 145.6, 146.4, 146.5, 154.8. IR ($\nu$/cm$^{-1}$); 1089s (Cl–O) (KBr). ESI-MS: $(\mathrm{M} - \mathrm{ClO_4})^+$, 693.3 (calcd for $\mathrm{M} - \mathrm{ClO_4}$, 693.3); $(\mathrm{M} - \mathrm{ClO_4} - 2\mathrm{Py})^+$, 535.2 (calcd for $\mathrm{M} - \mathrm{ClO_4} - 2\mathrm{Py}$, 535.2). Found: C, 63.67; H, 5.80; N, 10.70%. Calcd for $C_{42}H_{46}N_6Cl_1Co_1O_4$: C, 63.59; H, 5.85; N, 10.59%.

**X-ray Crystallography.** [Co$^{\mathrm{III}}$(TPrPc)(Py)$_2$]ClO$_4$ crystals suitable for X-ray analysis were obtained by slow evaporation from a saturated $CH_2Cl_2$–pyridine–benzene solution at room temperature. A crystal with approximate dimensions of $0.27 \times 0.32 \times 0.41$ mm$^3$ was mounted on a glass fiber, and was used for an X-ray diffraction study. Measurements were made on a Bruker SMART APEX CCD detector with graphite-monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å) and a 2 kW rotating anode generator. The data were collected at 100 K to a maximum $2\theta$ value of 56.56° in 0.30° oscillations with 12.0 s exposure times. The crystal-to-detector distance was 50.00 mm, and the detector swing angle was 28.00°. A total of 13951 reflections were collected, of which 4659 were unique ($R_{\mathrm{int}} = 0.0202$). The data frames were integrated using SAINT (Version 6.45) and merged to give a unique data set for the structure determination. Empirical absorption corrections by SADABS[32] were carried out.

The structure was solved by a direct method, and refined by the full-matrix least-squares method on all $F^2$ data using the SHELX suite of programs.[33] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation, but not refined. Crystal data and details of the structure determinations are summarized in Table 1. Crystallographic data for the structure were deposited with the Cambridge Crystallographic Data Center as a supplementary publication (number CCDC 257055). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Data for [Co$^{\mathrm{III}}$(TPrPc)(Py)$_2$]ClO$_4$

| | |
|---|---|
| Empirical formula | $C_{42}H_{46}N_6Cl_1Co_1O_4$ |
| Formula weight | 793.23 |
| Crystal color, Habit | bluish purple, plate |
| Crystal dimensions | $0.27 \times 0.32 \times 0.41$ mm$^3$ |
| Crystal system | monoclinic |
| Unit cell dimensions | $a = 9.6266(4)$ Å |
| | $b = 12.6343(5)$ Å |
| | $c = 15.6566(6)$ Å |
| | $\beta = 99.1200(10)$ Å |
| | $V = 1880.17(13)$ Å$^3$ |
| Space group | $P2_1/n$ |
| $Z$ value | 2 |
| Density (calculated) | 1.401 Mg/m$^3$ |
| Radiation | Mo K$\alpha$ ($\lambda = 0.71073$ Å) |
| $\mu$(Mo K$\alpha$) | 0.579 mm$^{-1}$ |
| Temperature | 100(2) K |
| Theta range for data collection | 2.08 to 28.28° |
| Reflections collected | 13951 |
| Independent reflections | 4659 |
| Completeness to theta = 28.28° | 100.0% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Goodness-of-fit on $F^2$ | 1.056 |
| $R1$[a)] | 0.0421 |
| $wR2$[b)] | 0.1172 |
| Largest diff. peak and hole | 1.249 and −0.403 e Å$^{-3}$ |

a) $I > 2\sigma(I)$. $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. b) $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

## Results and Discussion

**Reversible Binding of Dioxygen.** The electronic spectrum of [Co$^{\mathrm{II}}$(TPrPc)] was changed to a new spectrum in dichloromethane under a dioxygen atmosphere when the temperature was decreased from 263 to 203 K, as shown in Fig. 1. This spectral change was not observed under a nitrogen atmosphere. This behavior corresponded to the change in the oxidation state of cobalt, Co$^{\mathrm{II}}$ to Co$^{\mathrm{III}}$, while the absorption maxima changed from 385 and 594 nm to 390 and 613 nm, respectively.[19] In the presence of 100 equivalents mole of pyridine, the absorption maxima of the $O_2$ adduct were further shifted to 394 and 615 nm, respectively. The ESR spectrum of [Co$^{\mathrm{II}}$(TPrPc)] exhibited a symmetrical signal at $g = 2.03$ under a dioxygen atmosphere in dichloromethane at 77 K, which was ascribed to the formation of a superoxide (Fig. 2a). In the presence of pyridine as axial ligands, the formation of a six-coordinated superoxide species was also confirmed by the ESR spectrum, which was resolved into $g_{\parallel}$, $g_{\perp}$, and the respective coupling constants ($g_{\parallel} = 2.08$, $g_{\perp} = 2.00$, $A_{\parallel} = 20$ G, $A_{\perp} = 11$ G) (Fig. 2b). The ESR spectrum, having eight hyperfine splitting ($I = 7/2$ for $^{59}$Co) with $A_{\parallel} = 20$ G, was interpreted in terms of the formation of the [Co$^{\mathrm{III}}$–O$_2{}^{-\bullet}$] superoxide. Thus, the presence of four isosbestic points in Fig. 1, coupled with the ESR data, clearly demonstrates a simple equilibrium between [Co$^{\mathrm{II}}$(TPrPc)] and the 1:1 oxygen adduct, as shown in Chart 1. Indeed, the electronic spectral change was reversible at temperatures of 263 to 203 K, as shown in Fig. 3.

**RR Spectra.** The $O_2$ stretching vibrations of dioxygen adducts of metal complexes provide valuable information about the nature of the metal–$O_2$ bond and the geometry of the metal–$O_2$ moiety. Figure 4 shows the RR spectra of [Co(TPrPc)(O$_2$)(Py)] in chloroform containing 100 mol equivalents of pyridine at 233 K obtained with a spinning cell. As

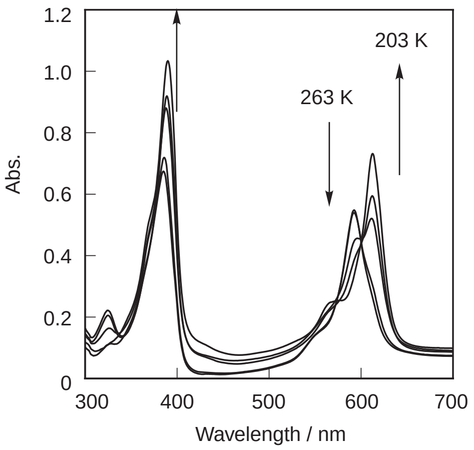

Fig. 1. Electronic spectral change for [Co$^{II}$(TPrPc)] ($1.0 \times 10^{-5}$ mol dm$^{-3}$) in $CH_2Cl_2$ at 263 to 203 K.

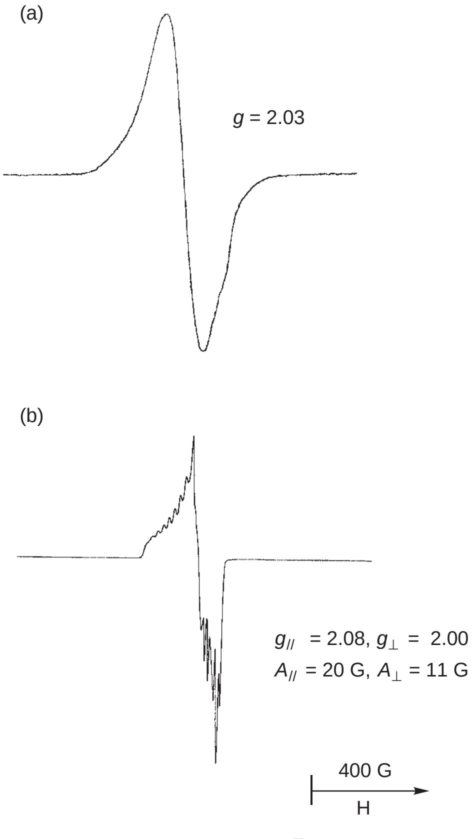

Fig. 2. ESR spectra of (a) [Co$^{II}$(TPrPc)] ($2.0 \times 10^{-3}$ mol dm$^{-3}$) in $CH_2Cl_2$ at 77 K under $O_2$ and (b) in the presence of pyridine ($2.0 \times 10^{-1}$ M).

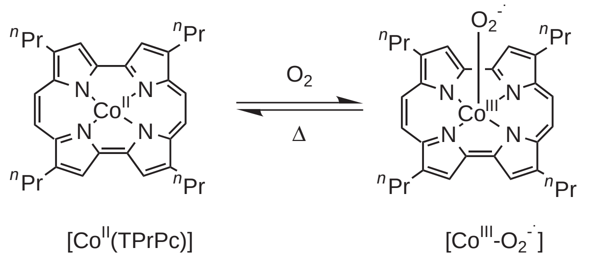

Chart 1.

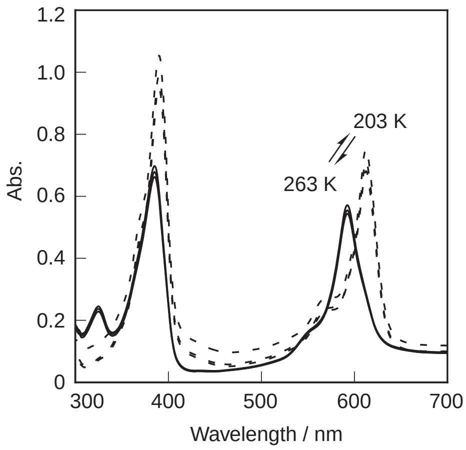

Fig. 3. Reversible electronic spectral changes (3 cycles) for [Co$^{II}$(TPrPc)] ($1.0 \times 10^{-5}$ mol dm$^{-3}$) in $CH_2Cl_2$ at 263 K (solid line) and 203 K (broken line).

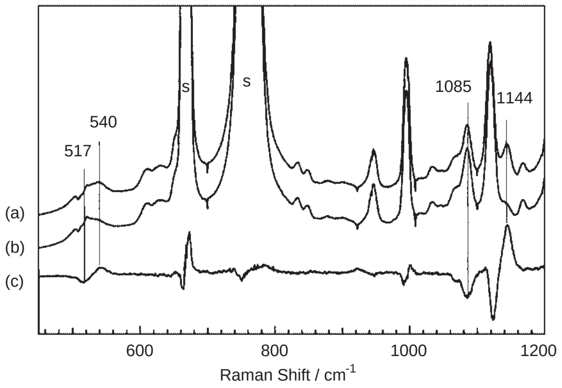

Fig. 4. Resonance Raman spectra of [Co$^{II}$(TPrPc)] ($2.0 \times 10^{-4}$ mol dm$^{-3}$) in $CHCl_3$ containing 100 mol equivalents of pyridine at 233 K: (a) [Co(TPrPc)(Py)] + $^{16}O_2$, (b) [Co(TPrPc)(Py)] + $^{18}O_2$, (c) the difference spectrum between (a) and (b).

shown in Fig. 4a, the $^{16}O_2$ derivative of [Co(TPrPc)($O_2$)(Py)] gives an RR band at 540 cm$^{-1}$ in the Co–$O_2$ stretching region and a band at 1144 cm$^{-1}$ in the O–O stretching region with superoxo adducts.[34,35] With the use of $^{18}O_2$, the 540 and 1144 cm$^{-1}$ bands shift to 517 and 1085 cm$^{-1}$, respectively (Fig. 4b). The observed $\nu$(O–O) shift from 1144 to 1085 cm$^{-1}$ (59 cm$^{-1}$) is close to that of a perturbed diatomic molecule (65 cm$^{-1}$). Similarly, the observed $\nu$(Co–$O_2$) shift from 540 to 517 cm$^{-1}$ (23 cm$^{-1}$) is close to that of a perturbed diatomic molecule (20 cm$^{-1}$). Therefore, these bands are associated with vibrations involving oxygen. The observed $\nu$(O–O) value is similar to that of [Co(TPP)($O_2$)(Py)] with 1143 cm$^{-1}$; TPP is a dianion of 5,10,15,20-tetraphenylporphyrin and [Co(OEP)($O_2$)(Py)] with 1145 cm$^{-1}$, and OEP is a dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin. In contrast, it is interesting to note that the $\nu$(Co–$O_2$) of the cobalt porphycene complex shows a higher frequency of 540 cm$^{-1}$ relative to those of cobalt porphyrin complexes, which were observed

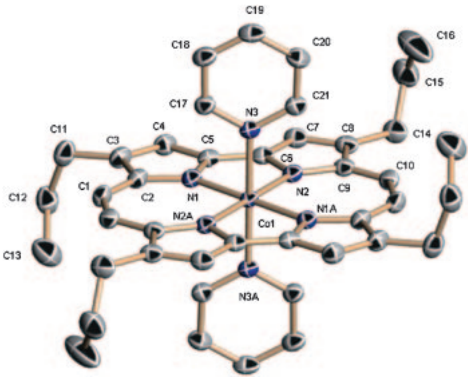

Fig. 5. ORTEP drawing of the $[Co^{III}(TPrPc)(Py)_2]^+$ cation with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Co^{III}(TPrPc)(Py)_2]ClO_4$

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Co–N(1) | 1.9283(13) | Co–N(2) | 1.9304(13) |
| Co–N(3) | 1.9520(13) | N(1)–N(2) | 2.5839(19) |
| N(1)–N(2*) | 2.8659(18) | | |
| | Bond Angles | | |
| N(1)–Co–N(2) | 84.07(6) | N(1)–Co–N(2*) | 95.93(6) |
| N(1)–Co–N(3) | 90.33(6) | N(3)–Co–N(3*) | 180.00(8) |
| N(2)–Co–N(3) | 90.04(5) | Co–N(3)–C(17) | 121.05(11) |

at 519 and 521 cm$^{-1}$ for $[Co(TPP)(O_2)(Py)]$ and $[Co(OEP)(O_2)(Py)]$, respectively.[36] When the $O_2$ molecule binds to $Co^{II}$, the $Co–O_2$ bond is formed mainly by $\sigma$-donation from $d_{z^2}$ (Co) to the antibonding $\pi_g^*$ ($O_2$) orbital.[37] The present RR data indicate that the porphycene ligand increases the electron donation to the metal d orbital compared to porphyrin ligands, thus enhancing the $Co–O_2$ bond strength.

**Auto-Oxidation to $Co^{III}$ Complex.** On standing for one day in dichloromethane containing pyridine at room temperature, the $[Co^{II}(TPrPc)]$ was auto-oxidized to a $Co^{III}$ complex, which was structurally determined by NMR and ESI-mass spectroscopies as well as X-ray analysis. The proton NMR analysis of the complex showed sharp peaks at the diamagnetic region, which indicates the formation of a low-spin $d^6$ $Co^{III}$ complex. ESI-MS analysis affords a positive-ion mass spectrum with the most prominent peak clusters at $m/z$ 693 and 535, which have mass values and isotope patterns consistent with the ions $[Co(TPrPc)(Py)_2]^+$ and $[Co(TPrPc)]^+$, respectively. The X-ray structural determination is depicted in Fig. 5, and crystallographic data are given in Table 1, while selected bond distances and angles are given in Table 2. In this complex, the $Co^{III}$ ion coordinated within the porphycene core and two pyridine molecules are coordinated at axial positions. The equatorial and axial Co–N lengths of the octahedral $CoN_6$ coordination group average 1.929 and 1.952 Å, respectively. The four nitrogen atoms of the porphycene skeleton are coplanar, and the cobalt atom is not displaced from the mean skeletal plane. To the best of our knowledge, this is the first example showing the crystal structure of the six-coordinated cobalt(III) porphycene complex. Although it is interesting to compare the structural data with those of corresponding porphyrin complexes, there is no report about the crystal data for the bispyridine cobalt(III) porphyrin complex.

In conclusion, a dioxygen adduct of cobalt porphycene was formed and characterized by various spectroscopic methods. The $\nu(Co–O_2)$ of the $O_2$ adduct shows a higher frequency relative to those of the cobalt porphyrin complex. The structure of the auto-oxidized complex was determined by X-ray analysis. The application of the cobalt porphycene complex as an oxygenation catalyst is now in progress in our laboratory.

We thank Prof. T. Kitagawa, Institute for Molecular Science, for the use of the resonance Raman equipment. We also thank Prof. Y. Naruta, Kyushu University, for the use of the equipment of the low-temperature electronic spectrometer. The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (434) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, Grant-in-Aid for Scientific Research (Nos. 16750121 and 16350076) from the Japan Society for Promotion of Science (JSPS).

## References

1 R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).

2 "Metal Ions in Biology," ed by T. G. Spiro, Wiley-Interscience, New York (1980), Vol. 2.

3 H. A. O. Hill, "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Vol. 2, p. 315.

4 D. H. Busch and N. W. Alcock, *Chem. Rev.*, **94**, 585 (1994).

5 T. Tsumaki, *Bull. Chem. Soc. Jpn.*, **13**, 252 (1938).

6 C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, **1969**, 946.

7 A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1970).

8 R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *J. Am. Chem. Soc.*, **98**, 5135 (1976).

9 H. Furutachi, S. Fujinami, M. Suzuki, and H. Okawa, *Chem. Lett.*, **1998**, 779.

10 J. C. Stevens and D. H. Busch, *J. Am. Chem. Soc.*, **102**, 3285 (1980).

11 A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, **112**, 2273 (1990).

12 G. N. Schrauzer and L. P. Lee, *J. Am. Chem. Soc.*, **92**, 1551 (1970).

13 F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1154 (1973).

14 J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, S. E. Hayes, and K. S. Suslick, *J. Am. Soc. Chem.*, **100**, 2761 (1978).

15 E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex, and O. Ermer, *Angew. Chem., Int. Ed. Engl.*, **26**, 928 (1987).

16 J. P. Gisselbrecht, M. Gross, M. Köcher, M. Lausmann, and E. Vogel, *J. Am. Chem. Soc.*, **112**, 8618 (1990).

17 W. A. Oertling, W. W. Juan, López-Garriga, Y. Kim, and C. K. Chang, *J. Am. Chem. Soc.*, **113**, 127 (1991).

18 J. Waluk, M. Müller, P. Swiderek, M. Köcher, E. Vogel, G. Hohlneicher, and J. Michl, *J. Am. Chem. Soc.*, **113**, 5511 (1991).

19 C. Bernard, J. P. Gisselbrecht, M. Gross, E. Vogel, and M. Lausmann, *Inorg. Chem.*, **33**, 2393 (1994).

20 F. D'Souza, P. Boulas, A. M. Aukauloo, R. Guilard, M. Kisters, E. Vogel, and K. M. Kadish, *J. Phys. Chem.*, **98**, 11885 (1994).

21 K. M. Kadish, P. L. Boulas, M. Kisters, E. Vogel, A. M. Aukauloo, F. D'Souza, and R. Guilard, *Inorg. Chem.*, **37**, 2693 (1998).

22 M. Kadish, A. Tabard, E. V. Caemelbecke, A. M. Aukauloo, P. Richard, and R. Guilard, *Inorg. Chem.*, **37**, 6168 (1998).

23 T. Ikeue, Y. Ohgo, M. Takahashi, M. Takeda, S. Neya, N. Funasaki, and M. Nakamura, *Inorg. Chem.*, **40**, 3650 (2001).

24 Y. Ohgo, S. Neya, T. Ikeue, M. Takahashi, M. Takeda, N. Funasaki, and M. Nakamura, *Inorg. Chem.*, **41**, 4627 (2002).

25 Y. Ohgo, S. Neya, M. Takahashi, M. Takeda, N. Funasaki, and M. Nakamura, *Chem. Lett.*, **32**, 526 (2003).

26 S. Neya, T. Hoshino, M. Hata, and N. Funasaki, *Chem. Lett.*, **33**, 114 (2004).

27 T. Hayashi, K. Okazaki, H. Shimakoshi, F. Tani, Y. Naruta, and Y. Hisaeda, *Chem. Lett.*, **2000**, 90.

28 T. Hayashi, K. Okazaki, N. Urakawa, H. Shimakoshi, J. L. Sessler, E. Vogel, and Y. Hisaeda, *Organometallics*, **20**, 3074 (2001).

29 T. Hayashi, H. Dejima, T. Matsuo, H. Sato, D. Murata, and Y. Hisaeda, *J. Am. Chem. Soc.*, **124**, 11226 (2002).

30 T. Matsuo, H. Dejima, S. Hirota, D. Murata, H. Sato, T. Ikegami, H. Hori, Y. Hisaeda, and T. Hayashi, *J. Am. Chem. Soc.*, **126**, 16007 (2004).

31 H. Shimakoshi and Y. Hisaeda, *J. Inorg. Biochem.*, **67**, 123 (1997).

32 G. M. Sheldrick, "SADABS," University of Göttingen, Germany (1996).

33 G. M. Sheldrick, "SHELXL97 and SHELXS97," University of Göttingen, Germany (1997).

34 K. Nakamoto, *Coord. Chem. Rev.*, **100**, 363 (1990).

35 L. M. Proniewicz and J. R. Kincaid, *Coord. Chem. Rev.*, **161**, 81 (1997).

36 K. Bajdor, J. R. Kincaid, and K. Nakamoto, *J. Am. Chem. Soc.*, **106**, 7741 (1984).

37 L. M. Proniewicz, A. Kulczycki, A. Weselecha-Birczynska, H. Majcherczyk, and K. Nakamoto, *New J. Chem.*, **23**, 71 (1999).