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POLYMERIC COBALT-SCHIFF-BASE AND -PORPHYRIN COMPLEXES AS A DIOXYGEN DEVICE

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Abstract: New functions of polymeric cobalt complexes were examined using their oxygen-binding reactions in the solid state. An oxygen-releasing device was prepared by compositing the oxygen-binding but electrically insulating cobalt-Schiff-base or -porphyrin complex with a conductive carbon powder. The device quickly released the absorbed oxygen in response to an applied voltage. A polymer film containing the cobalt-Schiff-base complex reversibly stretched in response to the atmospheric oxygen concentration. The driving force of the stretching of the film was attributed to the crystal structure change of the complex before and after the oxygen-binding.

INTRODUCTION

One of the characteristic chemical functions of cobalt complexes is specific and reversible binding of molecular oxygen or dioxygen from air (Refs. 1-6). Cobalt Schiff-base complexes, such as *N,N'*-disalicylidene-ethylenediaminocobalt [Co(salen)], form a μ-dioxo Co complex or a Co/dioxygen 2/1 adduct (Eq. 1). The dioxygen adduct formation or the oxygen-binding is a reversible reaction and proceeds in air at room temperature, and even in the solid state. Cobaltporphyrins with a cavity structure on the porphyrin plane bind dioxygen to form a Co/dioxygen 1/1 adduct. A cobalt picket-fence-porphyrin ligated with imidazole (Ref. 7) [CoP] is a typical example (Eq. 2). The oxygen-binding by CoP is characterized by its moderate binding affinity and kinetic activity.

Reactivity of the polymer-bound or -embedded metal complexes is often affected by the polymers, which coordinate to and/or surround the metal complex (Refs. 8-11). For example, in connection with the oxygen-binding by Co complexes, the apparent oxygen-binding equilibrium is influenced and shifted by the surrounding polymer simply because the physical oxygen solubility into the polymer depends on the polymer species. Another important effect of the polymers is increasing the working lifetime of the Co complexes as an oxygen carrier, because side reactions or irreversible oxidations of the cobalt ion are retarded by the polymers that fix and surround the complex moieties. This effect allows reversible oxygen-binding with a

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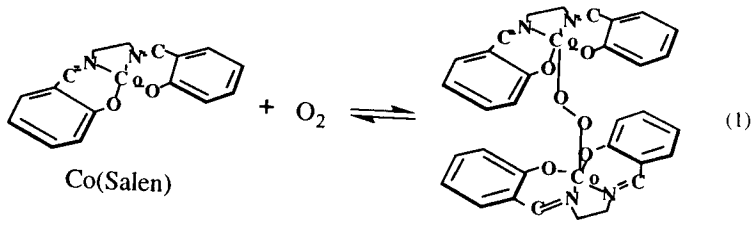
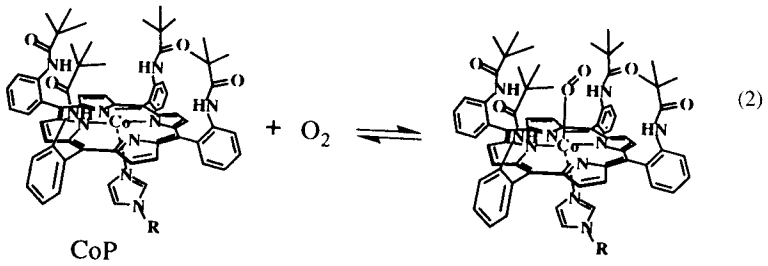
sufficient lifetime in ambient air and provides new functions for the polymeric Co complexes by using their oxygen-binding reaction in the solid state.



(1)



(2)

REVERSIBLE DIOXYGEN-RELEASE FROM A CoP AND Co(salen) COMPOSITE IN RESPONSE TO AN APPLIED VOLTAGE

N, *N'*-3-Ethoxydisalicylidene-ethylenediamino-cobalt [Co(Esalen)] was prepared as the derivative of Co(salen) according to *lit* (Ref. 12). CoP was obtained by recrystallizing the complex of *meso*-tetrakis(α , α , α , α -*o*-pivalamidophenyl)porphyrinatocobalt (picket-fence cobaltporphyrin, Ref. 7) and *N*-benzylimidazole from THF/hexane. The CoP and Co(Esalen) complexes were ground, then sieved into a particle size range of 40-50 μm. The CoP or Co(Esalen) powder and electrically conductive carbon powder (Fujikura Chemical Co., particle size 40-50 μm, specific gravity 0.9-1.0) were mixed, sandwiched between copper mesh, and pressed to produce a disk having a diameter of 2 cm and thickness of 2 mm. Homogeneous mixing of the Co complex and carbon was recognized by the homogeneous deep red-brown color of the broken pieces of the disk. The disk was not mechanically tough but remained intact during the following repeated temperature elevation and depression and oxygen releasing and absorbing tests.

The oxygen-binding reactions in Eqs. 1 and 2 are exothermic with an enthalpy gain of *ca.* 30 and *ca.* 14 kcal/mol for the Co(salen)/dioxygen 2/1 adduct formation in Eq. 1 and for the CoP/dioxygen 1/1 adduct formation in Eq. 2, respectively. That is, the dioxygen adduct formations are reduced at higher temperature. Fig. 1 shows the oxygen absorption amount per gram of the CoP/ and Co(Esalen)/carbon composites placed set in a thermocontrolled bath. The CoP and Co(Esalen) composites absorbed 11 and 21 cm^3 oxygen/g at room temperature, respectively, which almost corresponds to the stoichiometric oxygen adduct formation represented in Eqs. 1 and 2. The oxygen-binding affinity was reduced or the absorbed oxygen

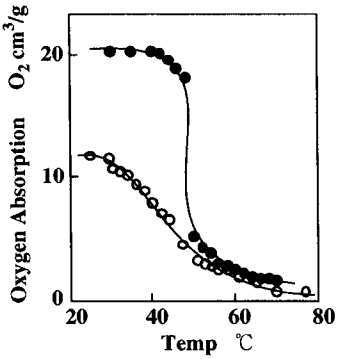


Fig. 1. Oxygen absorption with the 60% CoP/carbon disk (○) and the 70% Co(Esalen)/carbon disk (●)

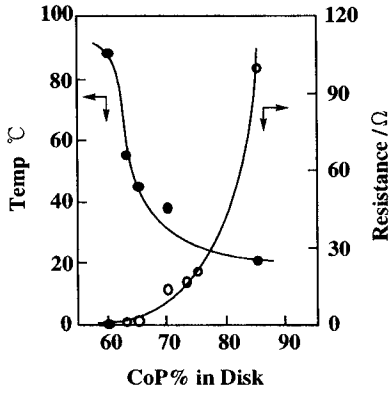
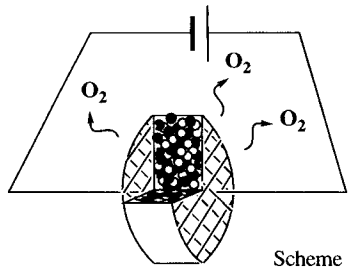


Fig. 2. Electrical resistance and heat elevation upon the application of 1.5 V to the CoP/carbon disk



Scheme 1

was released when the thermobath temperature was increased, and the oxygen release was completed at *ca.* 75℃ for both composites.

Copper wires were connected to the mesh of the composite disk and a voltage was applied to the disk (Scheme 1). We have previously reported the result for the composite disk of Co(salen) (Ref. 13), and describe in this paper the composite disks of CoP and Co(Esalen). Electrical resistance and temperature of the disk under the applied voltage were measured. Fig.

2 shows the resistance and the temperature of the CoP disks for various compositions of CoP and carbon. Although the disks containing more than 80% CoP have excessively high electric resistances, the disk containing *ca.* 60% CoP possessed a moderate conductivity of 5 Ω, enabling the disk to increase in the temperature after one min to *ca.* 80℃, while maintaining its oxygen absorption capability.

Temperature of the 60% CoP disk and the 70% Co(Esalen) disk increased with the voltage application of 1.5 and 6 V, respectively, and reached 80℃ after one min. In response to the temperature elevation, the disk released 11 and 21 cm^3 oxygen gas per gram of the disk, respectively (Fig. 3). Without the voltage application, the CoP and Co(Esalen) disk re-absorbed oxygen within 5 and 20 min, respectively. The oxygen-releasing and -absorbing cycle could be repeated more than 10 times, with a 10 and 30 min switching on-off interval for the CoP and Co(Esalen) disks, respectively. The oxygen-releases and -absorptions were not influenced by carbon monoxide, carbon dioxide, or 80% humidity.

An oxygen-releasing device has been successfully prepared with a composite of the oxygen-binding but electrically insulating Co complex, CoP or Co(Esalen), and electrically conductive carbon powder.

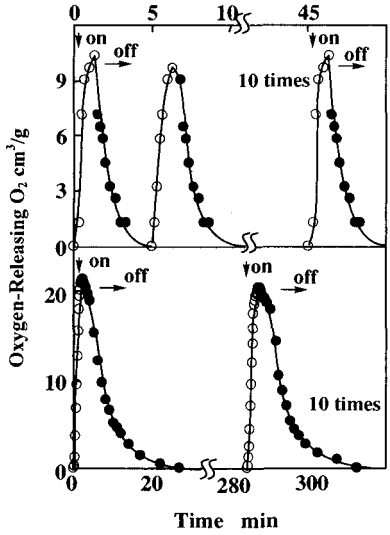
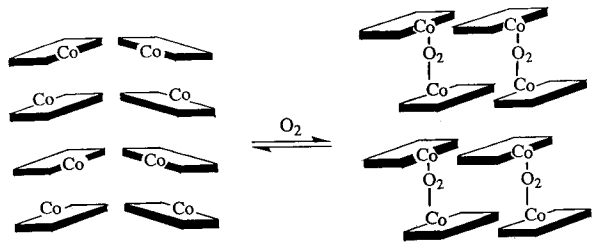


Fig. 3. Oxygen-releasing cycle for the CoP/carbon disk (upper) and the Co(Esalen)/carbon disk (lower) ; (○) 1.5 V and 6 V application to the CoP and Co(Esalen) desk, respectively, (●) voltage off, at room temperature in ambient air

REVERSIBLE STRETCHING OF A Co(salen) FILM IN RESPONSE TO DIOXYGEN

Calvin *et al.* exhaustively studied the oxygen-binding to Co-Schiff base complexes such as Co(salen) and Co(Esalen), and have suggested a crystal structure change in Co(salen) during the oxygen-binding (Ref. 1). A plate-like single crystal was obtained by recrystallizing Co(salen) from chloroform in the absence of oxygen, and the density of the crystal was first



Scheme 2

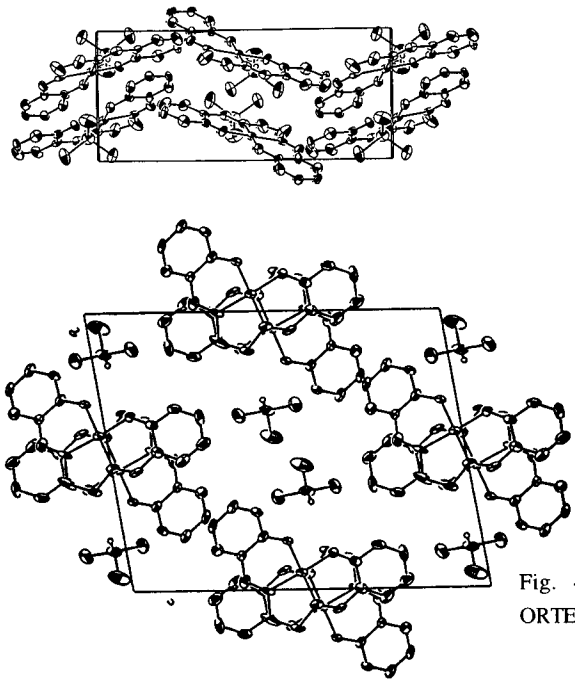


Fig. 4. X-ray crystallographic ORTEP diagram of deoxy Co(salen)

measured by floating the crystals in an aqueous cadmium solution under an oxygen and nitrogen atmosphere (Tab. 1). The density decrease after the exposure to oxygen indicates an expansion of the Co(salen) crystal as a result of the oxygen-binding.

The deoxy crystal was sealed with an epoxy cement to prevent oxygen-binding and was analyzed using a four-circle diffractometer. The crystal packing structure is shown in Fig. 4. Four deoxy Co(salen) molecules exist in a unit cell and a solvated chloroform molecule was attached to each Co(salen), as has been reported by Schaffer and Marsh (Ref. 14). Non-bonded Co-Co contact between Co(salen) molecules was estimated to be 3.4_5 Å.

Tab. 1. Density and *d*-spacing of the Co(salen) crystals

Co(salen)	deoxy	oxy
d-Spacing (Å)	3.3_7	3.6_1
Density (g cm^{-3})	1.42	1.34

However, oxy Co(salen) never gave any suitable single crystal for an X-ray structure determination, so that the crystal structure change of Co(salen) before and after the oxygen-binding was estimated using a powder X-ray diffraction pattern of the Co(salen) crystals, to give the *d*-spacings of Co(salen) (Tab. 1). The *d*-spacing attributed to the Co-Co distance changed from 3.4 to 3.6 Å after the oxygen-binding. A crystal structure change or an expansion of the Co(salen) crystal through the oxygen-binding is probably represented as in Scheme 2.

Co(salen) film was prepared by supporting or embedding the Co(salen) crystal in poly(octyl methacrylate) (Fig. 5). The concentrated chloroform solution of Co(salen) and poly(octyl methacrylate) was cast, under an oxygen-free atmosphere, upon the poly(octyl methacrylate) film with the thickness of 30 μm, to yield a flexible double-layered film (total thickness 60 μm). The film contains plate-like crystals of Co(salen) in the upper layer, and the Co(salen) and bulk polymer layers remain in intimate contact in the film.

When the film was exposed to oxygen, the Co(salen) layer expanded and the film bent. Upon exposure to nitrogen, the film slowly reverted to its original shape. This stretching of the Co(salen) film is demonstrated in Fig. 6, by making "a flower" with the Co(salen) film. The reversible stretching could be repeated more than 10 times. The Co(salen) layer expanded and shrunk due to the crystal structure change of Co(salen) in the presence and absence of oxygen, respectively, which induced a bending of the double-layered film.

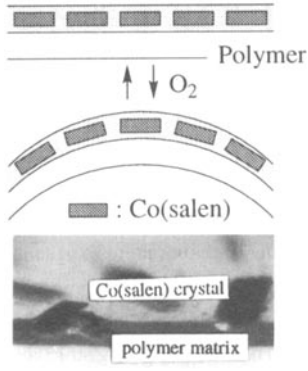


Fig. 5. Preparation of the double-layered Co(salen) film

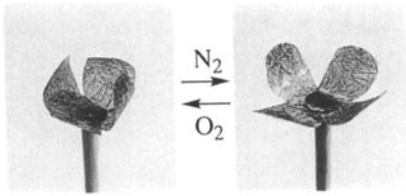


Fig. 6. Reversible stretching of the Co(salen) film in the presence and absence of oxygen

ACKNOWLEDGMENT

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