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Reversible Stretching of a Polymer-Supported Cobalt-Chelate Film in Response to Oxygen

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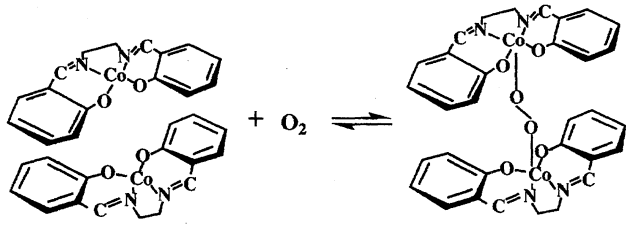
The polymer-supported *N,N'*-di(salicylidene)ethylenediaminatocobalt(II) [Co(salen)] took up oxygen through 2/1 Co/dioxygen adduct formation. The composite film of the polymer-supported [Co(salen)] and polymer layers reversibly bent under an oxygen and nitrogen atmosphere. The stretching was caused by a structural change in the [Co(salen)] crystal before and after the oxygen-binding, which was analyzed based on the near-IR spectral and density change as well as EXAFS.

N,N'-Di(salicylidene)ethylenediaminatocobalt(II) [Co(salen)] is the oldest known and simplest example of oxygen-binding chelates. Pfeiffer and Tsumaki found in 1933 that [Co(salen)] in the solid state forms a 2/1 Co/dioxygen adduct (Scheme 1).[1)] Calvin and his co-workers exhaustively studied this oxygen-binding to [Co(salen)] during the last world war to develop [Co(salen)] as an oxygen-absorbent or -releasing agent,[2)] and have already described a crystal structure change of [Co(salen)] in response to the binding and releasing of oxygen.

Macromolecule–metal complexes have been studied over the past two decades,[3)] which are a combination of metal complexes with organic polymers, in an attempt to provide materials with inorganic functions. This paper describes our recent success in preparing a polymer film composed of [Co(salen)], which reversibly stretches in response to oxygen. A series of chemical sensors selectivity responding to oxygen are known:[4)] electrochemical methods, such as Clark-type electrodes; colorimetry, such as hemoglobin-based visible absorption change, fluorescence quenching of organic dyes, and conductivity measurements with zinc and nickel oxide semiconductors; and with solid electrolytes, such as stabilized zirconia. The former and the latter two systems are sensors used for detecting oxygen dissolved in aqueous media and in gas samples, respectively. There has been, however, no report on a reversibly stretching material which responds chemically to oxygen. On the other hand, there has been continuous interest in mechanochemical polymers which reversibly stretch and mechanically work in response to the pH, ionic strength, electrode potential, temperature, etc.[5)] However, they are polymer gels, or network polymers dipped in liquid media, and little attention has being paid to a reversibly streching and dry (solvent-free) polymeric material which chemically responds to a simple gaseous molecule. This paper describes the oxygen-responding performance of the polymer-supported [Co(salen)] film and its reversible stretching mechanism.



Scheme 1.

Experimental

[Co(salen)] was prepared according to a method described in the literature,[1,2a)] and was recrystallized from chloroform in the absence of oxygen. Poly(octyl methacrylate), poly(vinyl acetate), and polystyrene were prepared via free-radical polymerization of the corresponding vinyl monomers initiated by azobisisobutyronitrile. The molecular weights of the poly(octyl methacrylate), poly(vinyl acetate), and polystyrene were 8.2×10^4, 7.0×10^4, and 1.2×10^5, respectively.

A chloroform solution (5 ml) of poly(octyl methacrylate) (0.15 g) was poured on a Teflon® plate (7×7 cm) under an oxygen-free atmosphere, and kept under reduced pressure for 1 d. A concentrated chloroform solution (4 ml) of poly(octyl methacrylate) (0.12 g) and [Co(salen)] (0.03 g) was then carefully cast on the poly(octyl methacrylate) film previously cast on the Teflon® plate, to yield a flexible composite film (thickness ca. 60 μm) containing plate-like but relatively fine crystals of [Co(salen)] in the upper layer of the film. To examine the formation and size of the [Co(salen)] crystal, poly(octyl methacrylate) was extracted from the composite film with ether. The remaining [Co(salen)] crystal was observed under a microscope: (42±6)×(18±2)×(115±26) μm, on the average of 50 crystals. The content of [Co(salen)] in the film was exactly 10 wt% in each 1 cm-square piece of the film. The following measurements were carried out at 25 °C.

The oxygen absorption into the film was measured by the pres-

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sure decrease under the condition of constant volume using an absolute pressure gauge (MKS Instr., USA). The apparatus consisted of a vacuum line mounted in a thermocontrolled air bath. Oxygen-adduct formation of the [Co(salen)] film was measured using a visible and near-IR spectrophotometer (Shimadzu UV-3101PC) equipped with a reflectance apparatus. The diffraction angle and intensity were measured using a Rigaku RAD-IC X-ray diffractometer. The density of the [Co(salen)] crystal was measured by floating the crystals in aqueous solutions of cadmium nitrate under nitrogen and oxygen atmospheres in a glove box.

X-Ray absorption (XAS) measurements were performed in the transmission mode on samples of the deoxy- and oxy-[Co(salen)] that were mixed with BN and pressed into thin wafers. The deoxy sample was prepared in a glove box under a nitrogen atmosphere. Both samples were sealed in aluminum holders with an *O*-ring seal and aluminum-coated Mylar windows. XAS measurements were made at both 77 and 298 K at Beam Line X11A at NSLS, Brookhaven National Laboratory. A Co foil was used in conjunction with a third detector as an internal calibration for the edge spectra. The methods for analyzing of the edge data of the X-ray absorption near-edge structure (XANES) have been described.[6] The extended X-ray absorption fine structure (EXAFS) was analyzed using the XDAP program of XAFS Services International,[7] by first performing a k^3-weighted Fourier transform between $k = 3.6$ to 13.3 $Å^{-1}$, and an inverse transform between 0 and 2.1 Å. Phase and amplitude parameters were generated by the FEFF5 program.[8] The EXAFS analysis was performed by first making a k^3-weighted Fourier transform between $k = 3.6$ to 13.3 $Å^{-1}$ and an inverse transform between 0 and 2.1 Å. In the case of the deoxy-[Co(salen)], a two-shell fit was made while fixing both the N and O coordination numbers at 2. For the oxy-[Co(salen)], a three-shell fit was made with one N and two O coordination shells. The coordination numbers were fixed at 2 for N and 2 and 1 for the O coordination shells. All other parameters were allowed to float. Other details concerning the analysis methods are given elsewhere.[6]

Results and Discussion

Three chloroform-soluble polymers were tested as the supporting polymer of the [Co(salen)] crystal: poly(octyl methacrylate) (glass transition temperature: T_g = 13°C), poly(vinyl acetate) (T_g = 43°C), and polystyrene (T_g = 93°C). Poly(octyl methacrylate) as a rubbery polymer was selected as the supporting polymer, because of its good film-forming property and high compatibility with the [Co(salen)] crystal to homogeneously disperse the crystal in the polymer.

The film (10 wt% [Co(salen)]) absorbed 3.8 $cm^3\ g^{-1}$ oxygen: The mole ratio of the saturated oxygen absorption amount to the [Co(salen)] in the film was ca. 0.5, which corresponded to the stoichiometric oxygen-binding represented in Scheme 1. The IR spectrum of the [Co(salen)] film under oxygen gave absorption at 565 cm^{-1}, which has been ascribed to the stretching vibration of the cobalt-oxygen bond for the [Co(salen)]/dioxygen adduct.[9] The [Co(salen)] in the film returned to the deoxy form upon exposing the film to nitrogen or by vacuum-pump evacuation (ca. 1 cmHg, 1 cmHg = 1333.22 Pa). The oxygen absorption or the oxy–deoxy cycle could be repeated more than 100 times for the polymer-supported [Co(salen)], which was much longer compared to the cycle for the [Co(salen)] crystal, itself (< 10 times). The latter degraded to a Co(III) derivative in ambient air, while the polymer support suppressed the same degradation of [Co(salen)]. The hydrophobic property of the polymer presumably retards a water molecule (proton)-driven irreversible oxidation of the [Co(salen)]-oxygen adduct. The polymer-supported [Co(salen)] acted as an efficient oxygen absorbent.

Side-shot photographs of the [Co(salen)] film strip (1×5 cm) (Fig. 1) represents reversible bending of the film in response to oxygen. The left film side in the photo contains [Co(salen)] and the right is the bulk polymer side, and the two layers remain in intimate contact. The [Co(salen)] layer expands and shrinks in response to oxygen, which induces a bending of the composite film.

The film strip (0.5×1.8 cm, and 60 μm thickness) was repeatedly exposed to oxygen and nitrogen, and the end-to-end length of the strip was measured for an average of 10 specimens. The [Co(salen)]-containing layer stretches and the film rapidly bends upon exposure to oxygen, and then slowly reverts to the original shape (Fig. 2). This reversible stretching was observed more than 10 times. Oxygen-binding to the [Co(salen)] was monitored at the same time using a reflectance near-IR spectrophotometer[10] (Fig. 2, inset). The time-course of oxygen-binding and -releasing on the film almost coincided with the bending sequence of the film. Similar stretching was observed for [Co(salen)] films (the

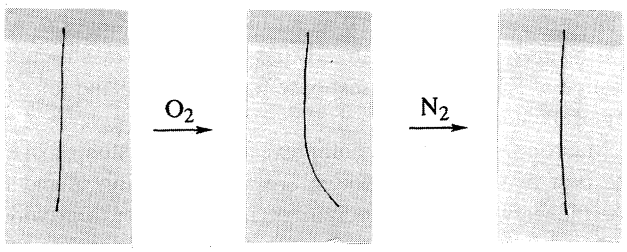


Fig. 1. Bending of the polymer-supported film in response to oxygen. Side-shot of the film strip (1×5 cm).

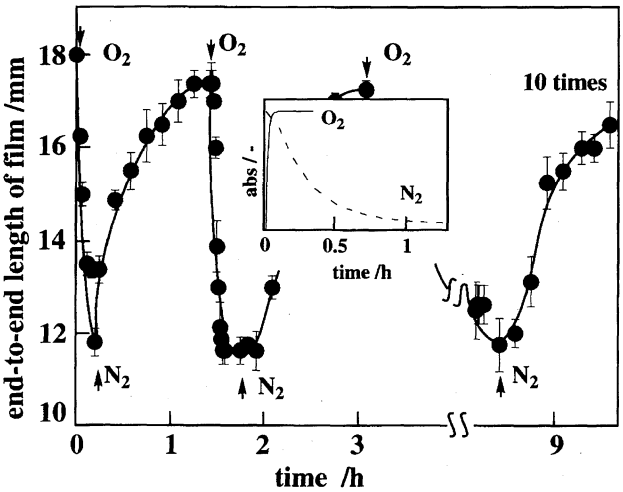


Fig. 2. End-to-end change in length during the bending of the [Co(salen)] film upon exposure to oxygen and nitrogen. Inset: time course of oxygen-binding and -releasing for the polymer-supported [Co(salen)] monitored by near-IR.

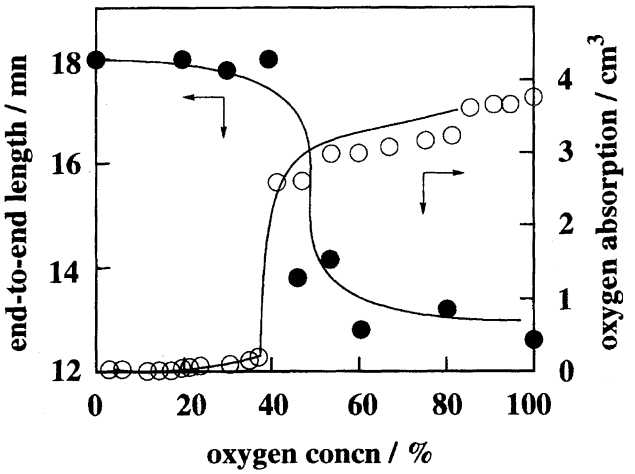


Fig. 3. End-to-end length and oxygen-absorption amount of the [Co(salen)] film under different oxygen/nitrogen gas mixtures.

same 1.8 cm strips) composed of poly(vinyl acetate) and polystyrene: The response time-course was almost the same as in Fig. 2, while the bending degree was not large for them (1.4 and 1.6 cm under oxygen for poly(vinyl acetate) and polystyrene, respectively). High compatibility with the [Co(salen)] crystal and a rubbery property of the poly(octyl methacrylate) would induce the stronger stretching behavior.

The response time of the streching was greatly reduced for a film prepared by quickly casting the solution of the polymer and [Co(salen)] and contained extremely fine crystals (size $< 10\mu m$) of [Co(salen)]. The response time is assumed to be controlled by the crystal size, but not by the gas diffusivity in the polymer matrix. However, the bending degree was very

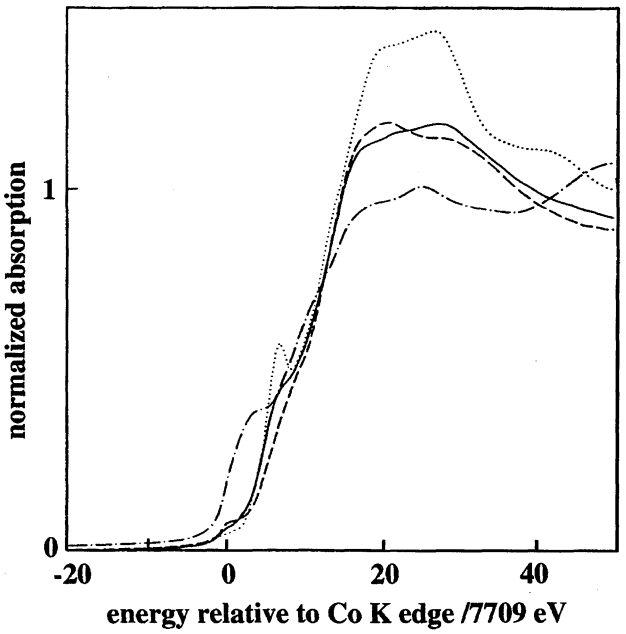
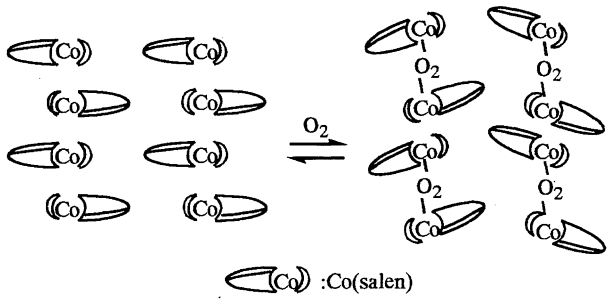


Fig. 4. Normalized XANES for deoxy (—) and oxy (- - -) [Co(salen)]. XANES for Co foil (–·–) and CoPc (····) as an internal calibration and a control sample, respectively, are also shown.



Scheme 2.

small (the decrease in the end-to-end length of film < 5%) for the film containing the fine [Co(salen)] crystal. The bending cycle shown in Fig. 2 was not influenced by the presence of carbon monoxide and carbon dioxide.

The film strip was allowed to stand for 20 min under various oxygen and nitrogen gas mixtures at 1 atm (an equilibrium was apparently established within 15 min for each condition). The film bent and the end-to-end length of the film strip decreased under a mixed gas of > ca. 50 % oxygen concentration (Fig. 3). The oxygen absorption is also plotted in Fig. 3. The oxygen-absorption curve did not obey Langmuir's isotherm or a hyperbolic one, but the oxygen-absorption increased according a S-like or on-off type profile with the oxygen concentration, which has been explained by the effect of a crystal-structure rearrangement on the oxygen-binding.[2c,11] Anyway, the bending of the film strip and the oxygen-absorption into the film coincided with each other, as shown in Fig. 3.

Calvin and his co-workers had already indicated a crystal structure change in [Co(salen)] during the oxygen-binding,[2] as represented in Scheme 2. We first measured the density of the [Co(salen)] crystal by floating deoxy and oxy crystals in

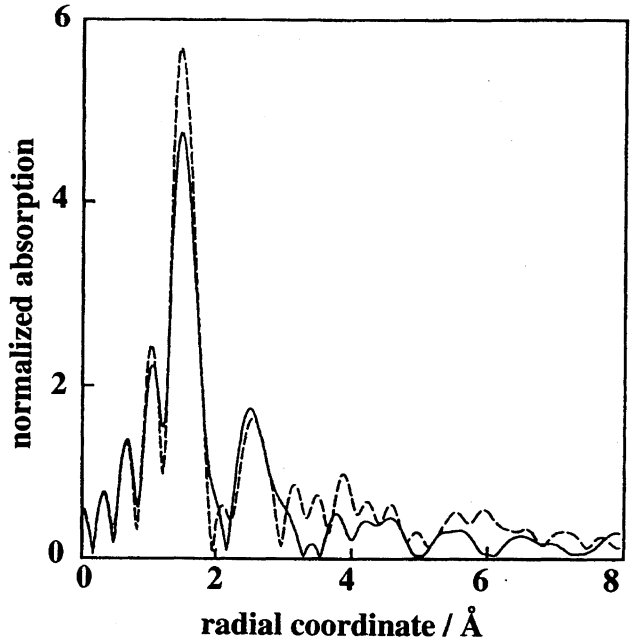


Fig. 5. Fourier transform of EXAFS for deoxy (—) and oxy (- - -) [Co(salen)], k^3 weighted, k = 3.6 to 14 Å^{-1}.

Table 1. Fitting Parameters for the First Peak of the Fourier Transforms of the EXAFS for Deoxy- and Oxy-[Co(salen)]

Material	Shell	Coord. no.	Bond distance / Å	$\Delta\sigma^2$ / Å^2	ΔE_0 / eV
Deoxy-[Co(salen)]	Co–N	2	1.90 (1.88, 1.93)[a]	0.0081	10.0
	Co–O	2	1.82 (1.86)[a]	0.0058	−1.27
Oxy-[Co(salen)]	Co–N	2	1.90	0.0200	0.88
	Co–O	2	1.85	0.0078	1.13
	Co–O[b]	1	1.90	−0.0021	0.69

a) Determined by the X-ray structure analysis on the deoxy Co(salen) crystal. b) To be ascribed to a Co-dioxygen bond.

an aqueous cadmium nitrate solution; the density ($g\,cm^{-3}$) was 1.42 for the [Co(salen)] crystal under nitrogen and 1.34 for the crystal under an oxygen atmosphere. This density change between the nitrogen and oxygen atmospheres indicates an expansion of the crystal during the oxygen-binding to the [Co(salen)] crystal.

The crystal structure change of [Co(salen)] before and after the oxygen-binding was estimated with a powder X-ray diffraction pattern of the [Co(salen)] film to give the *d*-spacing of [Co(salen)]. The *d*-spacing, presumably attributed to the face-to-face distance of the [Co(salen)] molecules, changed from 3.3_7 Å (relative intensity $I/I_0 = 0.3$) to 3.6_1 Å ($I/I_0 = 0.2$) after oxygen-binding.[12] These agreed with the previously reported X-ray data of the [Co(salen)] crystal itself,[2] and a crystal, structure rearrangement during the oxygen-binding was suggested, even after its fixation in polymer.

The *d*-spacing for deoxy-[Co(salen)] agreed with the non-binded Co–Co contact of 3.4 Å determined by the X-ray structure analysis on a plate-like single crystal of deoxy-[Co(salen)].[13] However, oxy-[Co(salen)] never gave any suitable single crystal for an X-ray structure determination. EXAFS, which probes the short-range order, was used to elucidate any changes in structure that occurred on the oxygen-binding.

Since the results at 77 and 298 K were very similar, only the date at 298 K are discussed here. Figure 4 shows a comparison of the XANES for the deoxy- and oxy-[Co(salen)]. XANES for a Co foil and phthalocyaninatocobalt(II) [Co(pc)] are also given. The absorption edge for the deoxy-[Co(salen)] coincides with that for [Co(pc)]. The white line or the absorption at a plateau is lower than that for [Co(pc)] because of the lower symmetry of the [Co(salen)]. The [Co(pc)] has a preedge peak at about 7 eV, which is typicial of D_{4h} symmetry. The deoxy-[Co(salen)] has a shoulder at the same position, but no peak. An interesting feature of the [Co(salen)] XANES is the very broad white line. Because of this, data below 50 eV could not be used in the EXAFS analysis. The surprising result is that there are very little changes in the Co XANES on oxygen-binding. The shoulder at 7 eV disappears and there are changes in the shape of the white line. The disappearance of the shoulder at 7 eV can be attributed to a change in symmetry on axial bonding of oxygen to the Co. There are no significant shifts in the edge spectra that can be attributed to the formation of Co(III).

Fourier transforms of EXAFS for deoxy- and oxy-[Co(salen)] are shown in Fig. 5. Table 1 gives the fitting parameters for the deoxy- and oxy-[Co(salen)]. In the case of the deoxy-[Co(salen)], there is reasonable agreement between the EXAFS and X-ray structure-determination results. There were no changes in the Co–N bond lengths through the oxygen-binding. This would indicate that there was no significant amount of Co(III) formation, which is in agreement with the XANES results. Unfortunately, no information could be found on the Co–Co distances, even in the data at 77 K. The lack of such interactions in the EXAFS is typical for layer-type structures, such as $Ni(OH)_2$ or metallophthalocyanines. However, the EXAFS Fourier transforms shown in Fig. 5 clearly indicate a structural change of [Co(salen)] before and after oxygen-binding; also, Table 1 supports the formation of a new cobalt–oxygen (dioxygen) bond with a bond distance of 1.90 Å on [Co(salen)] through oxygen-binding.

Conclusion

A composite film of the polymer-supported [Co(salen)] and polymer layers took up oxygen and reversibly bent under an oxygen and nitrogen atmosphere. The driving force of the bending or the stretching of the polymer-supported [Co(salen)] can be ascribed to a crystal-structure change of [Co(salen)] before and after the oxygen-binding.

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10) Reversible oxygen-binding to the [Co(salen)] fixed in the film was measured by near-IR reflectance spectroscopy. The spectrum in the absence of oxygen gave the absorption peak at 1190 nm which has been ascribed to Co(II)(salen). (Ref.: C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J. Chem. Soc., Dalton Trans.*, **1973**, 754.) After exposure of the film to oxygen, the [Co(salen)] turned black and the overall absorption in the visible and near-IR region increased; this deoxy-oxy- spectral change was reversible and responded to oxygen.

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12) *d*-Spacing was obtained from a 2θ–d control table. Other *d*-spacing values for deoxy-: 7.6_8 Å ($I/I_0 = 1$) and $13._0$ Å ($I/I_0 = 0.8$), for oxy-: 7.4_1 Å ($I/I_0 = 0.7$) and $13._1$ Å ($I/I_0 = 1.0$).

13) The plate-like single crystal was obtained from 0.35 wt% chloroform solution of [Co(salen)] in the absolutely absence of oxygen and was analyzed using a Rigaku AFC-5R four-circle diffractometer. The crystal packing structure showed that four deoxy-[Co(salen)] molecules existed in a unit cell and a solvated chloroform molecule was attached to each [Co(salen)], as has been reported by Schaffer and Marsh: W. P. Schaffer and R. E. Marsh, *Acta Crystallogr., Sect. B*, **B25**, 1675 (1969).