

Electrochemistry and Electrokinetics of Prussian Blue Modified Electrodes Obtained Using Fe(III) Complex

Seong Bae Moon* and Jung Dae Moon

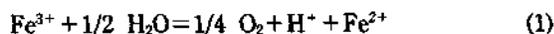
Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

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Thin films of two kinds of Prussian Blue (PB)-modified, using iron(III) complex instead of conventional FeCl_3 , were prepared on a gold substrate and these films were able to be electrochemically reduced in potassium nitrate solution. In case of PB-modified films prepared from Fe(III)-ethylenediamine-*N,N'*-diacetic acid (FeEN^{3+})/ $\text{K}_3\text{Fe}(\text{CN})_6$ solution, the mid-peak potential was 0.156 V in 0.1 M KNO_3 and it was found that potassium ion migrates into or out of the film during the electrolysis. These films were shown to be electrochromic. These films exhibited smaller peak separation than those formed from Fe(III)-tartaric acid (FeTA^{3+})/ $\text{K}_3\text{Fe}(\text{CN})_6$ system. The diffusion coefficient of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple, evaluated using the fabricated Au rotating disc electrode (rde) previously reported, was in good agreement with the existing data. Two experimental procedures, including the voltammetry at relatively low scan rates and the rde study, have been used in order to characterize the electrode kinetics. The electrode kinetics of some redox couples (FeEN^{2+} - FeEN^{3+} and FeTA^{2+} - FeTA^{3+}) on both PB-modified thin films and bare Au electrode were studied using a Au rde. In all cases the rate constants of electron transfer obtained with the PB-modified film electrodes were only slightly less than those obtained for the same reaction on bare Au disc electrodes. The conductivities, as determined from the slopes of the *i*-V curves for a ca. 1 mm sample for dried PB-modified potassium-rich and deficient bulk samples pressed between graphite electrodes, were 6.21×10^{-7} and $2.03 \times 10^{-7} (\Omega \cdot \text{cm})^{-1}$, respectively.

Introduction

Since the first study of thin films of a Prussian Blue (PB) on various metal and semiconductor substrates was carried out,¹ PB and several of its analogues have been of considerable interest in the electrochemistry. These materials have the great potentiality of practical applications such as electrochromic devices,²⁻⁴ electro-optical devices,^{5,6} secondary solid-state cells,⁷ highly reversible batteries in which two PB thin films are used for both cathode and anode,^{8,9} potassium ion-selective electrodes,^{10,11} and as electrocatalysts.^{1,12,13} The reasons for the increased interest in PB and its analogues are that these materials can be easily synthesized from cheap inorganic chemicals and electrodeposited on a great variety of substrates. Moreover, these materials, when prepared electrochemically, are very stable in both neutral and acid solutions. A mechanism of the film growth¹⁴ was proposed as follows: the first step of the reduction of free ferric ion or associated ferric ion and second reaction including the reduction of potassium ferricyanide.



From the consideration of reaction (1), one can possibly draw out to form other kinds of PB-modified thin films using some iron(III) complex instead of ferric ion. The devices consisting of PB-modified thin films can be also applied for practical applications. The reasons are that these materials may be presumed to be the very similar structure because of their physical and chemical properties similar to that of PB.

In this paper, we shall consider the details of the voltammetric curves of the oxidation and reduction of two kinds of PB-modified thin films. The rate constants of electron

transfer of a simple redox couple on thin films of two kinds of PB-modified electrodes will be described. The electronic conductivities have been made on bulk samples consisting of powdered PB-modified pressed between inert conducting electrodes.

Experimental

All chemicals used were reagent grade and were not purified except for the potassium nitrate, which was purified by recrystallization. All solutions were freshly prepared with triply distilled water and deoxygenated with nitrogen gas before the electrochemical experiments. Electrochemical experiments were performed using a conventional three electrode system. The rde was constructed in our laboratory.¹⁵ The rde was first polished with an alumina powder (0.3 micron) on a polishing cloth attached to a glass plate and rinsed thoroughly in an ultrasonic bath. The rde was inserted in a 0.5 M H_2SO_4 for electrochemical pretreatment. The auxiliary electrode was a Pt wire. All the electrode potentials are reported relative to the saturated calomel electrode (SCE) used as a reference electrode.

The PB-modified films were deposited under the constant current density of $2 \mu\text{A}/\text{cm}^2$ on Au disc and conducting indium tin oxide (ITO) glass substrates. The immersion solutions were of 0.01 M iron(III) complex compounds instead of FeCl_3 on the conventional system.¹ The above complex solutions were prepared with the ferric nitrate and two ligands, such as ethylenediamine-*N,N'*-diacetic acid (EN) and tartaric acid (TA). Electrochemical preparations of some PB-modified electrodes were investigated on conducting substrates. Two kinds of PB-modified films were obtained using Fe(III)-TA and Fe(III)-EN solutions instead of FeCl_3 . The

film thickness, estimated from the total charge for the reduction, was roughly 1000 Å. Infrared spectra of two kinds of PB-modified thin films, deposited on ITO glass, were obtained by Nicolet 740 FT-IR spectrometer. The ITO glasses were obtained from LXD Inc., Bedford, OH, USA. The single sharp CN absorption bands of PB-modified thin films prepared using FeEN^{3+} and FeTA^{3+} are given at 2175 and 2072 cm^{-1} , respectively. The frequencies of ferricyanide for both films are very similar to that already reported of PB.¹⁴

The kinetics of electron transfer for some redox systems (FeEN^{2+} - FeEN^{3+} and FeTA^{2+} - FeTA^{3+}) on PB modified thin films were studied using a fabricated Au rde. In order to evaluate the performance of the rde, we determined the diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-/4-}$ couple on a Au rde in 0.1 M H_2SO_4 . This value of $5.2 \times 10^{-6} \text{ cm}^2/\text{s}$ was very similar to the literature value of $6.1 \times 10^{-6} \text{ cm}^2/\text{s}$.¹⁶ The disc electrodes were placed in an unstirred solution at a certain potential for 1 minute and then the electrode potential was rapidly altered to the required potential value and the rotation speed was simultaneously changed over a variety of ranges. The rde was placed vertically in a solution and stirred by a variable speed motor. The rotation speeds were continuously changed until the currents achieved stationary currents. The currents were measured on the potentiostat after steady state conditions were achieved in the considered systems. The studies of the electrode kinetics were carried out by analyzing the observing currents vs. the angular velocities. The rate constants of heterogeneous electron transfer were evaluated by the Levich method from the steady-state measurements of the currents and angular velocities.¹⁷ The potassium-rich PB-modified bulk samples were prepared by mixing the equal volume of 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KNO_3 mixture solution with 50 mL of 0.01 M iron(III) complex solution and centrifuging several times with 50% mixtures of distilled water and ethanol. Potassium-deficient compounds were obtained from the solutions of 0.01 M $\text{K}_3\text{Fe}(\text{CN})_6$ transferred into the 0.01 M iron(III) complex solution. Both compounds were dried under a vacuum desiccator.

All electrochemical measurements were made with a PAR model 273 potentiostat. Voltammetric curves were recorded by using a Linseis LY 1600 XY recorder.

Results and Discussion

The electrode kinetics of simple redox couples have been studied of interest using a rotating disc electrode quite suitable for the evaluation of the heterogeneous rate constants for moderately rapid electron transfer process.²¹⁸ In order to evaluate the performance of the fabricated Au rde, the diffusion coefficient for $\text{Fe}(\text{CN})_6^{3-/4-}$ couple in 0.1 M H_2SO_4 was compared with the existing value. The anodic currents were measured at different applied potentials (0 to 0.9 V vs. SCE) and at the moderate rotation velocity (2500 rpm). The obtained value of $5.8 \times 10^{-6} \text{ cm}^2/\text{s}$ was in good agreement with the published data.¹⁶ So this rde can be quite fit for determining the rate constants for the moderately rapid charge transfer processes. There were some differences in the rate constants obtained from different metals.^{19,20} These differences could be explained by the potentials of zero charge, 0.23 V for gold and 0.48 V for platinum.²¹ Au electrodes are very sensitive to impurities in solution.¹⁹

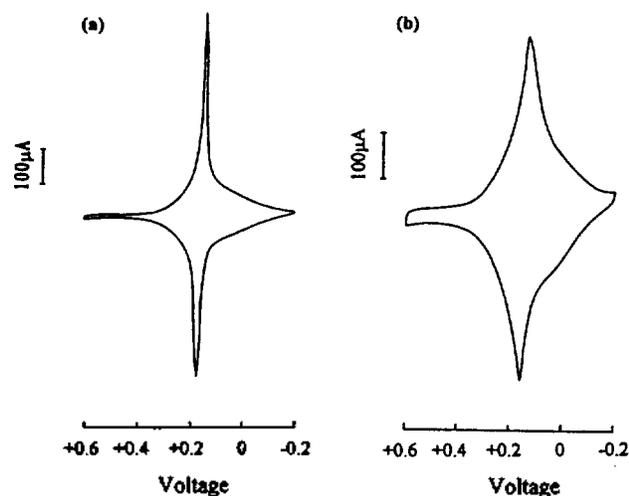


Figure 1. Voltammograms of two kinds of PB-modified films obtained in 0.1 M KNO_3 solution at the scan rate of 50 mV/s; (a) PB-modified film formed in $\text{FeEN}^{3+}/\text{K}_3\text{Fe}(\text{CN})_6$ system. (b) PB-modified film formed in $\text{FeTA}^{3+}/\text{K}_3\text{Fe}(\text{CN})_6$ system.

Therefore, Au rde was selected as electrode material for these kinetic studies in some redox couples.

In the film growth of a PB film,¹⁴ first step involving the reduction of ferric ion might be based on the rate of the film formation because the rate of the film growth increases as increasing concentration of ferric ion. PB compound was formed in the second step associated with the reduction of potassium ferricyanide. Two kinds of PB-modified films were obtained from iron(III) complex solution instead of the use of FeCl_3 in the conventional $\text{FeCl}_3/\text{K}_3\text{Fe}(\text{CN})_6$ system. This preparation could be removed the possible chloride contamination related to the process of the film growth. The presence of chloride ion, observed by the EDX (Energy Dispersion X-ray Analysis), was coordinated with ferric ion in the films and not accommodated in the interstitial sites of the unit cells.^{22,23} Electrochemical preparations of PB modified electrodes were investigated on conducting substrates. As a results, the films electrodeposited from two systems using FeEN^{3+} and FeTA^{3+} solutions were light blue in the potential range of +0.6 V to -0.2 V. The reduced films were slowly changed to a white color when hold below -0.2 V. The electrochromic effect was appeared to be reversible during at least 200 switching steps between +0.6 V and -0.2 V.

The voltammograms of PB modified thin films taken in some redox couples are shown in Figure 1. The shapes of the i -V curves and the half-widths did not change significantly in 1.0 M KNO_3 solution at the slow scan rates in the range of 1 to 100 mV/s. But, if the potassium ion concentration in the electrolyte is reduced below 0.1 M, the shapes of the i -V curves begin to alter and the half-widths for the cathodic scans become larger than for the anodic scans. Large peak widths have been associated with repulsive molecular interactions. The narrow peak widths have been indicated either the absence of such interactions or exact cancellation of repulsive and attractive interactions.²⁴ Neff *et al.*¹⁴ defined a good film as one which gives a sharp voltammogram with a half-width of ~ 15 -20 mV at the slow scan rate.

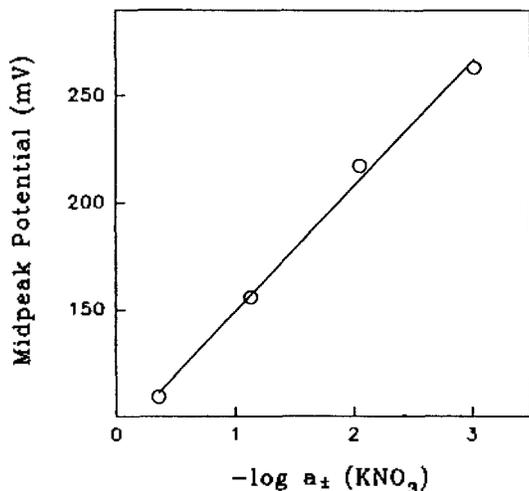


Figure 2. Nernst plot of midpeak potential vs. mean activity of potassium nitrate for a PB-modified film obtained using $\text{FeEN}^{3+}/\text{K}_3\text{Fe}(\text{CN})_6$ system.

In these experiments, the former film displayed only 13 mV half-width and the latter 113 mV at the scan rate of 50 mV/s. The mid-peak potentials for these films were nearly same, but the shapes of the i - v curves and the values of half-width were somewhat different. Peak separations for both thin films were 13.3 and 53.3 mV, respectively. This factor are closely related to the IR drop across the film. The above definition figures that we can select the former film as a good film and carry out the details of the reduction reaction of these films. The mid-peak potential between cathodic and anodic curves in 0.1 M KNO_3 solution was found to be 0.156 V. The peak currents for both reactions increased linearly with the slow scan rates. This dependence suggests that the electrode redox processes are kinetically controlled by electrolyte cation migration in and out of the PB lattice.^{14,23} Here are at least two interfaces, namely, that between metal and semiconductor and that between semiconductor and solution. The film must admit ions from solution in order to preserve the balance of charge. The fact that potassium ion actually diffuses into or out of the film can be demonstrated by considering the i - V curves for solutions containing cations other than potassium ion. The voltammograms of the former films were obtained in the nitrate solutions of group I cations and ammonium ion. In the cases of Li^+ and Na^+ , the reactions were blocked and no i - V curves were observed after one or two cycles. In other cations, the processes were completely reversible as changing in the supporting electrolyte from one to another. This imply that, in the electrocatalytic effects of group I cations and ammonium ion, all cations (except Li^+ and Na^+) were allowed to enter and leave the films. These selectivities of the ion transport are closely related to the hydrated ionic radius and the channel radius in the PB-modified lattice.²⁵ In order to consider further evidence for the role of the potassium ion, the voltammograms were obtained at different potassium ion concentrations. The mid-peak potentials, for both the oxidation and reduction reactions, were determined as a function of the mean ionic activity of potassium nitrate. This behavior is remarkably Nernstian with 59 mV/decade for both reactions. These results

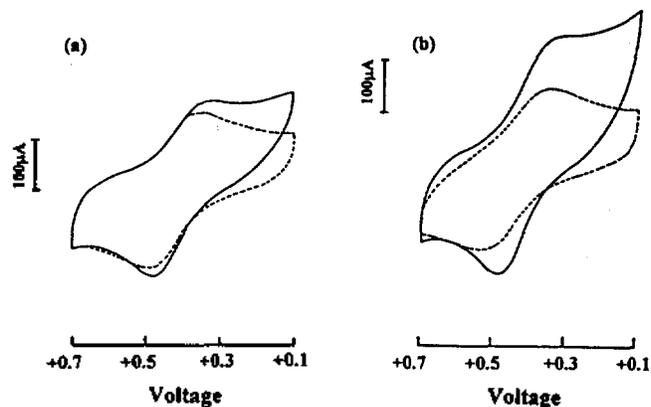


Figure 3. The voltammograms for the PB-modified thin films and bare Au disc electrode obtained in both (a) 10^{-3} M $\text{FeEN}^{3+}/\text{FeEN}^{2+}$ solution and (b) 10^{-3} M $\text{FeTA}^{3+}/\text{FeTA}^{2+}$ solution at the scan rate of 50 mV/s; (solid line): PB-modified electrode, (dashed line): bare Au disc electrode.

are shown in Figure 2.

On reduction (*i.e.* the metal is the cathode) there are three potential rate determining processes. These are: 1) electron transfer at the metal/film interface. 2) electron transport through the film. 3) electron transfer at the film/solution interface. For most conducting polymer films, the rate of the reaction was controlled by electron transfer at the film/solution interface.²⁶ Two experimental procedures have been used in order to characterize the kinetics. There were voltammetry at relatively low scan rates and the rde study described previously. The voltammograms were obtained in a given redox couple on the film and on a pure gold electrode for comparison. These data were shown in Figure 3. The results were rather surprising, particularly in comparison to those of the bare metal electrodes. In both cases it was found that the voltammograms for a given couple on the PB-modified films were very similar to those obtained for the same couple on the bare metal electrode. The shapes of the i - V curves and the half-widths did not change significantly in 10^{-3} M redox couples at the slow scan rates (normally 1 to 100 mV/s). From this, we should draw out the conclusion that the film is not catalytic but is having as a simple electron transport medium (*i.e.* like a metal). The above observations are coincident with the extensive kinetic data obtained using the rde. The kinetics of electron transfer rates for some redox systems (10^{-3} M $\text{FeEN}^{2+}/\text{FeEN}^{3+}$ and $\text{FeTA}^{2+}/\text{FeTA}^{3+}$) on PB-modified thin films were carried out using a Au rde. The electron-transfer rate constants were evaluated by the Levich method from the steady-state measurements of the currents and angular velocities in the considered system.¹⁷ In both cases, plots, shown in Figure 4 and 5, are linear. The standard heterogeneous electron-transfer rate constants for both the former film and bare electrode in 10^{-3} M $\text{FeEN}^{2+}/\text{FeEN}^{3+}$ solution were 1.13×10^{-3} cm/s and 1.42×10^{-3} cm/s, respectively. The rate constants for both the latter film and bare electrode in 10^{-3} M $\text{FeTA}^{2+}/\text{FeTA}^{3+}$ solution were 3.41×10^{-4} cm/s and 7.34×10^{-4} cm/s, respectively. The rate constants of electron transfer obtained with PB-modified thin films are slightly less than that obtained for the same reaction on bare Au electrode. Substi-

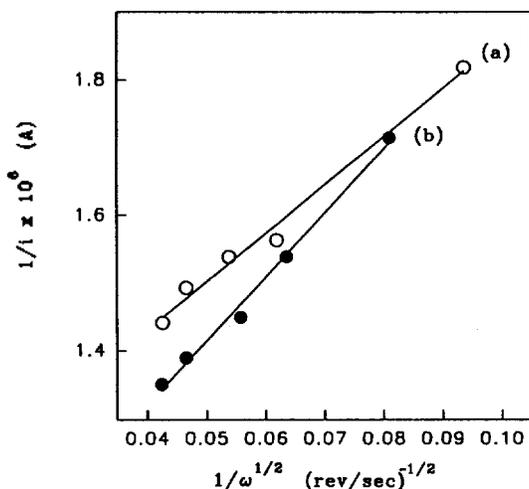


Figure 4. The plots of $1/i$ vs. $1/\omega^{1/2}$ obtained both (a) PB-modified thin films prepared using FeEN^{3+} solution (b) bare Au disc electrode, applied at +0.65 V vs. SEC, in 10^{-3} M $\text{FeEN}^{3+}/\text{FeEN}^{2+}$ solution.

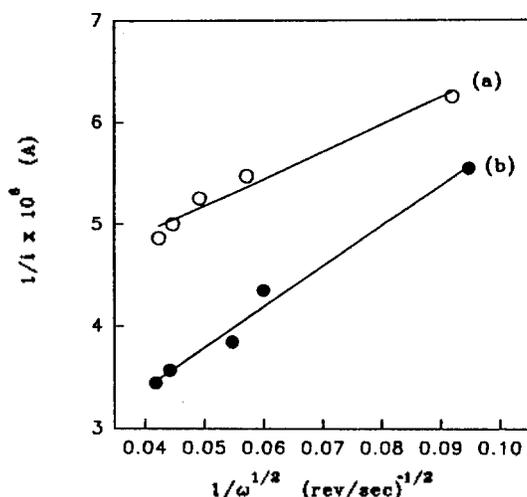


Figure 5. The plots of $1/i$ vs. $1/\omega^{1/2}$ obtained both (a) PB-modified thin films prepared using FeTA^{3+} solution (b) bare Au disc electrode, applied at +0.65 V vs. SEC, in 10^{-3} M $\text{FeTA}^{3+}/\text{FeTA}^{2+}$ solution.

tution of the slopes of the $1/i$ vs $1/\omega^{1/2}$ plots into the Levich equation gave the diffusion coefficients for 10^{-3} M $\text{FeEN}^{2+}/\text{FeEN}^{3+}$ ions at both the former PB and a bare electrode as 1.74×10^{-5} and 1.03×10^{-5} cm^2/s , respectively. In other case, the diffusion coefficients in 10^{-3} M $\text{FeTA}^{2+}/\text{FeTA}^{3+}$ at both the latter PB and a bare electrode are 2.17×10^{-6} and 1.23×10^{-6} cm^2/s , respectively. As seen in Figure 3, the voltammograms obtained in $\text{FeEN}^{2+}/\text{FeEN}^{3+}$ and $\text{FeTA}^{2+}/\text{FeTA}^{3+}$ couples exhibited similar shapes on the i - V curves for both PB-modified thin films and a bare substrate. As a result, we believe that the rate constants between the PB-modified films and a bare substrate are exhibited almost similar values. The conductivities, as determined from the slopes of the i - V curves for a ca. 1 mm sample of well dried PB-modified powdered pressed between graphite electrodes,

are 6.21×10^{-7} ($\Omega \cdot \text{cm}$) $^{-1}$ for potassium-rich compound and 2.03×10^{-7} ($\Omega \cdot \text{cm}$) $^{-1}$ for potassium-deficient compound, respectively. We have known that the conductivity for bulk samples depend on the potassium ion contents.

Conclusion

Two kinds of PB-modified thin films were electrochemically prepared using Fe(III) complex. This method could be fairly reduced the chloride ion entering into the crystal lattice during the film growth. As compared to the voltammetric shapes, the former film exhibited smaller peak separation, indicated by the ohmic resistance of the film, rather than conventional PB thin film. The rate constants between the films and a bare substrate were almost similar magnitude. The electronic conductivity of PB-modified bulk sample, obtained in $\text{FeEN}^{3+}/\text{K}_3\text{Fe}(\text{CN})_6$ system, was a little higher value than that of PB of 2.45×10^{-7} ($\Omega \cdot \text{cm}$) $^{-1}$. The devices consisting of PB-modified thin films could have been a good candidate for the practical applications.

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The Crystal Structure of a Sulfur Sorption Complex of the Dehydrated Partially Co^{2+} -Exchanged Zeolite A

Young Hoon Yeom, Seong Hwan Song[†], and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

[†]*Department of Chemical Engineering, Dongseo University, Pusan 616-010, Korea*

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The crystal structure of a sulfur sorption complex of the dehydrated partially Co^{2+} exchanged zeolite A ($a=12.058(2)$ Å) has been determined by single-crystal X-ray techniques. The crystal structure was solved and refined in cubic space group $Pm\bar{3}m$ at 21(1) °C. Ion Exchange with aqueous 0.05 M $\text{Co}(\text{NO}_3)_2$ was done by the static method. The crystal of $\text{Na}_4\text{Co}_4\text{-A}$ was dehydrated at 380 °C and 2×10^{-6} Torr for 2 days, followed by exposure to about 100 Torr of sulfur at 330 °C for 72 h. Full matrix least-squares refinement converged to $R_1=0.084$ and $R_w=0.074$ with 102 reflections for which $I>3\sigma(I)$. Crystallographic analysis shows that 2.8 Co^{2+} ions and 4 Na^+ ions per unit cell occupy 6-ring sites on the threefold axes. 1.2 Co^{2+} ions occupy the 8-ring sites on fourfold axes. 2.8 Co^{2+} ions at Co(1) are recessed 0.66 Å into the large cavity and 4 Na^+ ion at Na(1) are recessed 0.77 Å into the sodalite cavity from the (111) plane of O(3)'s. Approximately 16 sulfur atoms were sorbed per unit cell. Two S_8 rings, each in a butterfly form, are found in the large cavity. The bond length between S and its adjacent S is 2.27(3) Å. The distance between 6-ring Co^{2+} ion and its adjacent sulfur is 2.53 (2) Å and that between 8-ring Co^{2+} ions and its adjacent sulfur is 2.72(9) Å. The angles of S-S-S and S'-S-S' in octasulfur rings are 119.0(2)° and 113.0(2)°, respectively.

Introduction

The crystal structure of a sulfur sorption complex of $\text{Na}_{12}\text{-A}^1$ has been reported. Reversible isotherms for sulfur sorption onto Ca^{2+} -exchanged zeolite A and the sodium form of zeolite X have been determined previously.² About 16 sulfur atoms per unit cell were sorbed in the crystal of dehydrated $\text{Na}_{12}\text{-A}$. The heats of sorption (-25 and -31 Kcal/mol, respectively)² also indicate that these complexes are relatively stable. Such systems afford an unique opportunity for investigating the configurations of physical sorption complexes crystallographically.

Many different forms of sulfur allotropes occur in the solid, liquid, and gas phase such as S_n ($1 < n < 12$, $n=18$, 20 and ∞).³ During last 30 years about 24 allotropes containing cyclic S_8 have been described.³ The S_8 is the most stable configuration at STP. The stability is probably due to crossing resonance.⁴ The other properties of S_8 are well reviewed.⁵ Furthermore, Spitzer,⁶ Ward,⁷ Ozin,⁸ Anderson,⁹ and Gautier¹⁰ have studied S_8 in solution and in single crystals.

Zeolites provide an attractive host for the encapsulation of semiconductor, organic and inorganic complexes. The present work was initiated to investigate what kind of sulfur allotropes can be formed inside the limited dimensions of

zeolite cavities. If a cyclic S_8 is formed, it will be interesting to study the locations and the bonding characteristics of the sorbed S_8 molecules and the interaction between sulfur and cations in the zeolite cavities.

Experimental Section

Crystals of zeolite A were prepared by a modification of Charnell's method,¹¹ including a second crystallization using seed crystals from the first synthesis. Ion exchange with aqueous solution of 0.1 M $\text{Co}(\text{NO}_3)_2$ was done by the static method.¹² This yielded material whose approximate stoichiometry was $\text{Na}_4\text{Co}_4\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot x\text{H}_2\text{O}$ per unit cell, subsequently to be referred to as $\text{Na}_4\text{Co}_4\text{-A}$, exclusive of water molecules.¹³ One of the largest single crystals from this experiment, about 0.08 mm along an edge, was selected for X-ray diffraction study. The crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by gradual increasing its temperature (ca. 25 °C/h to 360 °C at the constant pressure of 2×10^{-6} Torr). Finally, the system was maintained at this state for 48 h. The crystal became deep blue after dehydration. Similarly, about 2 g of finely divided and sublimed sulfur powder was dehydrated at 100 °C and 10^{-6} Torr for 96 h. The crystal was contacted