Electrical Properties of PPV Derivatives

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Electrical Properties of Poly(1,4-phenylene vinylene-co-2,5-dimethoxy-1,4-phenylene vinylene)s and Poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene)s

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The temperature dependence of electrical conductivities and thermoelectric power of I_2-doped poly(1,4-phenylene vinylene-co-2,5-dimethoxy-1,4-phenylene vinylene)s [poly(PV-co-DMPV)] and poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene)s [poly(PV-co-TV)] were studied. The former copolymers were also doped with $FeCl_3$. All the samples used were in thin film forms. The temperature dependence of electrical conductivity implies that the variable range hopping conduction mechanism applies to these systems. The activation energy for the electrical conduction in dimethoxy-phenylene vinylene (DMPV) copolymers ranged from about 7 to 30 meV depending on the polymer composition and the nature of the dopant. It was significantly higher for I_2-doped thienylene vinylene (TV) copolymers, namely 90-200 meV. The values of the room temperature thermoelectric power were 30-70 $\mu V/K$ for DMPV copolymer and 100-800 $\mu V/K$ for TV copolymers. Anisotropy in the electrical conductivities was also studied for oriented films obtained by uniaxial stretching of the precursor polymer films.

Introduction

Polyconjugated copolymers consisting of p-phenylene vinylene (PV) units and other conjugated units such as 2,5-dimethoxy-1,4-phenylene vinylene (DMPV) or 2,5-thienylene vinylene (TV) structure can be prepared in high molecular weight by a two-step synthetic method originally described by Wessling and Zimmerman.[1-3] These copolymers can be obtained in film form and are readily doped with I_2 or other dopants to produce materials having a wide range of electrical conductivity depending upon their composition and the degree of doping. Moreover, they can be obtained in uniaxially oriented films by stretching the precursor polyelectrolyte films prior to thermal elimination to form the final polyconjugated polymers. In contrast to these copolymers, poly(1,4-phenylenevinylene)(PPV) can not be doped with I_2 or $FeCl_3$ but requires stronger oxidizing dopants such as AsF_5.[2,3]

In this study, we again prepared a series of copolymers of poly(1,4-phenylene vinylene-co-2,5-dimethoxy-1,4-phenylene vinylene)s [poly(PV-co-DMPV)][4] and poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene)s [poly(PV-co-TV)][5] and their electrical properties were further studied. Especially, temperature dependence of their electrical conductivity and the thermoelectric power were studied in detail. Anisotropy in the electrical conductivity of unstretched and stretched films was also measured. Iodine and $FeCl_3$ were utilized as dopants for poly(PV-co-DMPV) series and only I_2 for poly(PV-co-TV)'s.

Experimental

Synthesis of Copolymers. Synthetic methods of the copolymers were the same as that reported in the literatures.[4,5] The precursor polyelectrolyte polymers were dialyzed in a dialysis tube with molecular cut-off of 12,000 and then were cast into films from the aqueous solution. Thermolysis of the precursor films into polyconjugated copolymer films was conducted at 215 °C for 21 hr. When an oriented film was to be made, the precursor film was stretched uniaxially at 110-160 °C using a zone heating apparatus.

Doping. I_2-doping was performed in a vacuum line whose pressure was maintained at 1.0×10^{-6} torr. For $FeCl_3$-doping, the films were soaked in a nitromethane solution (0.05 M) of $FeCl_3$. The degree of doping was calculated from the weight uptake. $FeCl_3$-doped films were washed with fresh nitromethane before drying in a vacuum oven at room temperature.

Measurement of DC Conductivity and Thermoelectric Power. DC conductivity of the samples was measured by Montgomery method.[6] The film samples were pumped at 10^{-6} torr for about 1 hr to avoid the conduction due to moisture. Displex system was used to lower the temperature from 300 to 10 K and 3700 ADPE digital temperature indicator/controller was used to maintain a desired temperature. Keithley 181 nanovoltmeter or 642 electrometer was used for the measurement of voltage drop.

Measurement method of thermoelectric power was the same as described elsewhere.[7] A rectangular sample (about 2 × 10 mm in size) was mounted between platinum plates adhered onto the hot and the cold plates. Electrodag 502 was utilized for the contact between the sample and the platinum plates. The temperature of the sample holder was fixed at a desired temperature using displex system and a temperature controller. Then a temperature gradient, typically 2 K, was applied using a Keithley 220 current source. While measuring the actual temperature difference using a Keithley 195 A digital multimeter, voltage difference was measured with Keithley 181 nanovoltmeter.

Results and Discussion

The chemical structures of the two series of copolymers studied in this investigation are as follow;

Table 1. Electrical Properties of Poly(1,4-phenylene vinylene-co-2,5-dimethoxy-1,4-phenylene vinylene)s

Polymers[a]	Draw Ratio L/L_o	Degree of Doping[b]	Electrical Conductivity		Activation Energy, meV	Thermoelectric Power, $\mu V/K$
			$\sigma_{\parallel}$ Scm^{-1}	$\sigma_{\parallel}/\sigma_{\perp}$		
PDMVP	1	0.6 I_3/RU	31	1.3	22	71
	1	0.22 FeCl$_4$/RU	170	1.2	17	37
80-poly	1	0.7 I_3/RU	183	1.2	15	71
(PV–co–DMPV)	1	0.53 FeCl$_4$/RU	40	0.9	22	41
53-poly	1	1.8 I_3/RU	26	1.0	23	53
(PV–co–DMPV)	2.5	2.8 I_3/RU	900	78	6.6	59
19-poly (PV–co–DMPV)	1	1.5 I_3/RU	3.1	0.9	29	70

[a]The numbers 80 53 and 19 describe the contents of DMPV units in the copolymer.[4] [b]Degree of doping per average repeating unit, RU. It is well known "...t, when dopant is I_2 or FeCl$_3$, counter ion present after doping is mainly I_3^- or FeCl$_4^-$, respectively.

poly (PV-co-DMPV)

poly (PV-co-TV)
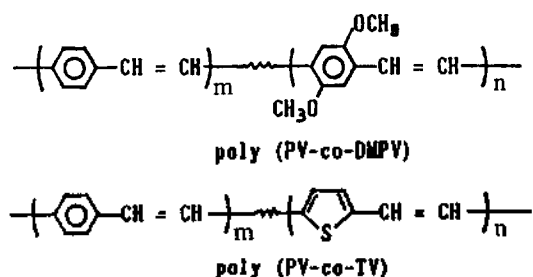
Synthesis of these copolymers and their electrical conductivities at room temperature after being doped with I_2 were described by Han et al.[4] and by us.[5] Although PPV itself is not dopable either with I_2 or with FeCl$_3$, these copolymers are readily doped with the weakly oxidizing dopants to produce highly conducting materials. In order to further understand the electrical transport behavior of these copolymers, we studied the temperature dependence of their electrical properties and of thermoelectric power. The poly(PV–co–DMPV) series were doped with I_2 and FeCl$_3$ whereas the poly(PV–co–TV) series were doped only with I_2.

Table 1 summarizes the electrical properties of DMPV copolymers after being doped with either I_2 or FeCl$_3$. For the purpose of comparison, similar data for poly(2,5-dimethoxy-1,4-phenylene vinylene), PDMPV, were also included in the table. The thickness of the films was in the range of 5-25 um. The values of the room temperature conductivities of the I_2- or FeCl$_3$-doped copolymers are in the same range as reported by Han et al.[4] and by Jen et al.[6] The conductivity of 53-poly(PV–co–DMPV) film containing 53 mole % of DMPV units with the draw ratio of 2.5 was particularly high reaching to 900 S cm^{-1}. This can be ascribed to the high degree of doping as well as to its oriented polymer chains as indicated by the high value, 78 of anisotropy in conductivity. Conductivity along the stretching direction, $\sigma_{\parallel}$ is about 2 orders of magnitude greater than that across the stretching direction, $\sigma_{\perp}$.

Uniaxial stretching of the precursor polymer film before thermolysis greatly improves the chain orientation of the polyconjugated polymers. Another interesting point that should be emphasized is the fact that even the conductivity of copolymers containing significant levels of PV unit is comparable with that of the homopolymer, PDMPV. This obser-
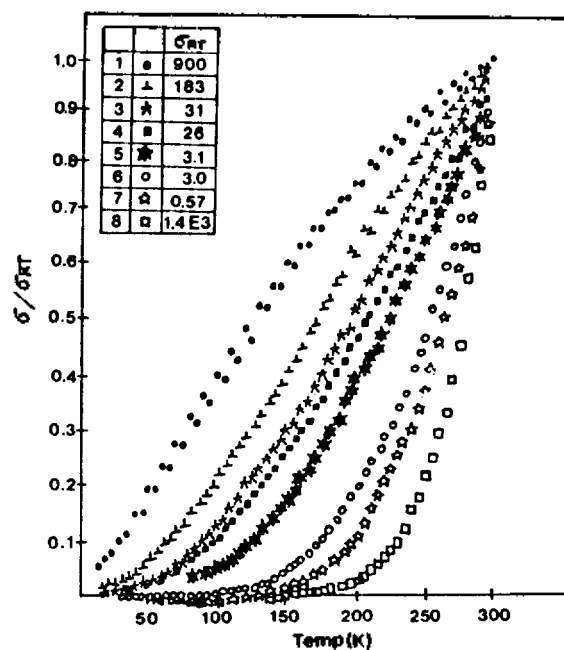
Figure 1. σ/σ_{RT} vs. T graph for PPV-derivatives doped mith iodine. 1; 53-poly(PV-co-DMPV)(2,5Lo), 2; 80-poly(PV-co-DMPV) (1Lo), 3; PDMPV(1Lo), 4; 53-poly(PV-co-DMPV)(1Lo), 5; 19-poly (PV-co-DMPV) (1Lo), 6; 32-poly(PV-co-TV)(5Lo), 7; 32-poly(PV-co-TV)(1Lo), 8; 7-poly(PV-co-TV)(1Lo).

vation implies that preferential doping of the DMPV units, due to its greater susceptibility toward oxidation than the PV units, promotes generation of charge carriers. Once the charge carriers are formed in the DMPV moieties, they are readily delocalized throughout the copolymer chains including PV units. When the concentration of DMPV units are too low, the number of charge carriers drops very low as evidenced by the relative low degree of doping for the last composition in Table 1. This, in turn, lowers the conductivity of the doped material. As described in the introduction, PPV is not doped with either I_2 or FeCl$_3$.

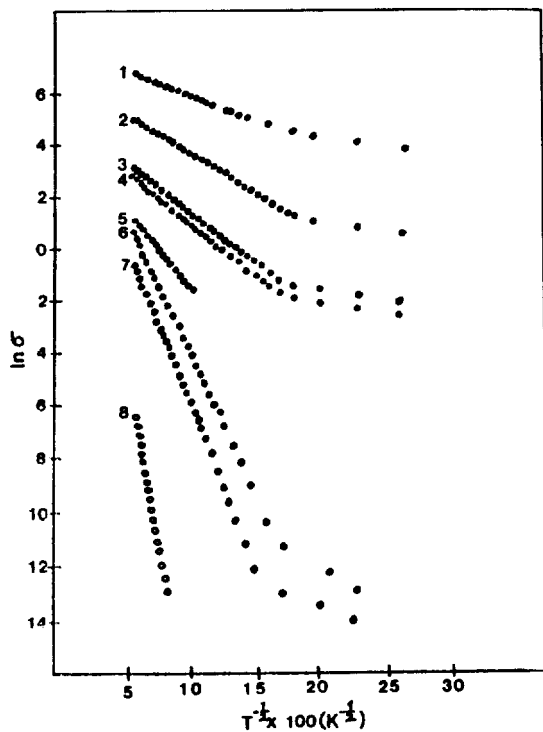Figure 1 demonstrates the temperature dependence of conductivities of I-doped samples. For all of the samples,

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Figure 2. $\ln \sigma$ vs. $T^{-\frac{1}{2}}$ graph for PPV-derivatives doped with iodine. 1; 53-poly(PV-co-DMPV)(2.5Lo), 2: 80-poly(PV-co-DMPV) (1Lo), 3; PDMVP(1Lo), 4; 53-poly(PV-co-DMPV)(1Lo), 5; 19-poly(PV-co-DMPV)(1Lo), 6; 32-poly(PV-co-TV)(5Lo), 7; 32-poly(PV-co-TV)(1Lo), 8; 7-poly(PV-co-TV)(1Lo).
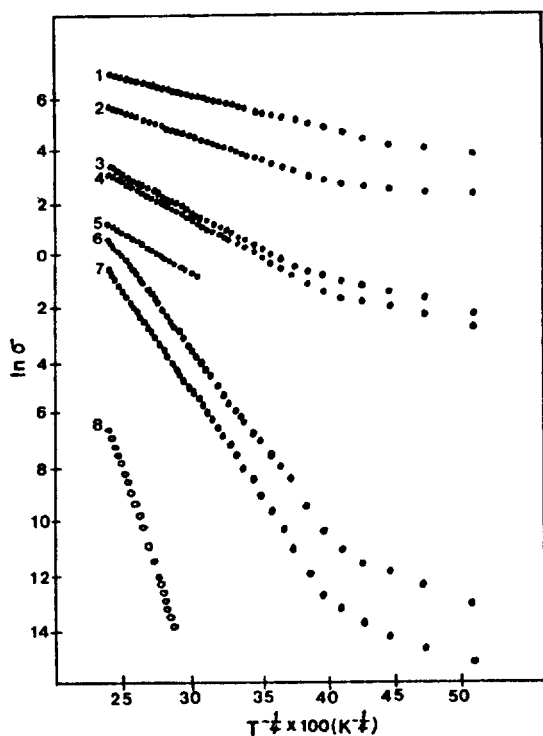

Figure 4. T.E.P. vs. T graph for PPV-derivatives doped with iodine.

Figure 3. $\ln \sigma$ vs. $T^{-\frac{1}{4}}$ graph for PPV-derivatives doped with iodine. 1; 53-poly(PV-co-DMPV)(2.5Lo), 2: 80-poly(PV-co-DMPV) (1Lo), 3; PDMPV(1Lo), 4; 53-poly(PV-co-DMPV)(1Lo), 5; 19-poly(PV-co-DMPV)(1Lo), 6; 32-poly(PV-co-TV)(5Lo), 7; 32-poly(PV-co-TV)(1Lo), 8; 7-poly(PV-co-TV)(1Lo).
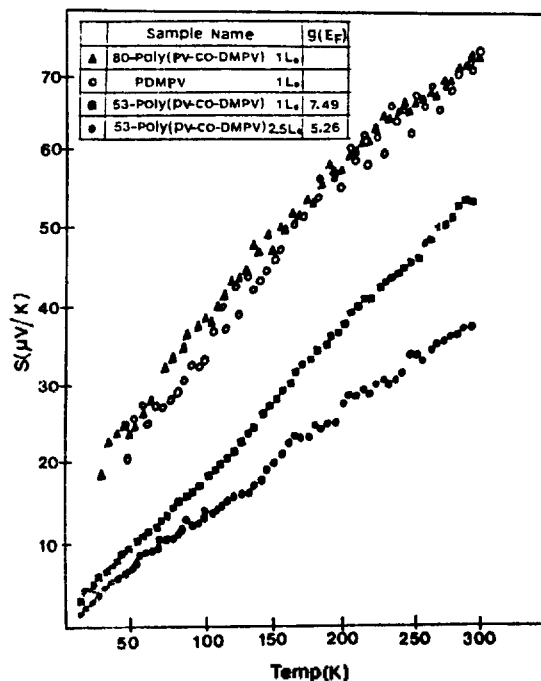
conductivity increases with temperature, which is usually observed for semi-conductors. Although the data for $FeCl_3$-doped samples are not shown, their behavior is somewhat similar to those of I_2-doped samples. It is however surprising enough to note that the upper three curves exhibit a curvature change from a positive(+) value to a negative(-) value as temperature decreases. This can be taken as an indication of semiconductor-to-metal transition at low temperatures. On the contrary the bottom two cruves maintain positive curvatures over the examined temperature range. This difference deserves a further study.

Activation energy for conduction at each composition was estimated from the Arrhenius plot of $\ln \sigma$ vs. T^{-1} and the results are included in Table 1. The value varies from about 7 to 30 meV depending on the composition of the copolymers and the degree of doping. In general, activation energy is lower for the films of higher conductivity, which is usual for conducting polymers.

In order to understand the conduction mechanism, the conductivity data $(\ln \sigma)$ were plotted against $T^{-\frac{1}{2}}$ and $T^{-\frac{1}{4}}$ as shown in Figure 2 and 3, respectively. Each curve shows a straight line relation from about 50 to 300 K. Such behavior is expected for the systems where variable range hopping mechanism applies.[9] The simple hopping model between localized states predicts the $T^{-\frac{1}{4}}$ dependence of $\ln \sigma$,[9] whereas $T^{-\frac{1}{2}}$ dependence was proposed for percolation mechanism applicable to finely dispersed metal particles in a insulating in a insulating matrix. A perfect electrical contacts between copolymer chains can not be achieved and thus, coexistence of highly conducting microregions (copolymer chains) and poorly conducting microregions is visualized for the morphology of these copolymer films. This may be the reason why the conductivity data satisfy both $T^{-\frac{1}{2}}$ and $T^{-\frac{1}{4}}$ dependence.

Thermoelectric power (TEP) is an index indicating the

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Table 2. Electrical Properties of Poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene)s

Polymers[a]	Draw Ratio L/L_0	Degree of Doping I_3^-/avg. RU[b]	Electrical Conductivity		Activation Energy, meV	Thermoelectric Power, μV/K
			$\sigma_\parallel$ Scm^{-1}	$\sigma_\parallel / \sigma_\perp$		
32-poly	1	1.5	0.57	1.0	91	103
(PV-co-TV)	4	1.7	1.2	6.4	93	95
	5	1.5	3.0	33	95	97
7-poly (PV-co-TV)	1	1.7	1.4×10^{-3}	1.0	200	800

[a] The numbers 32 and 7 describe the contents of TV units in the copolymers.[5] [b] RU stands for repeating unit.
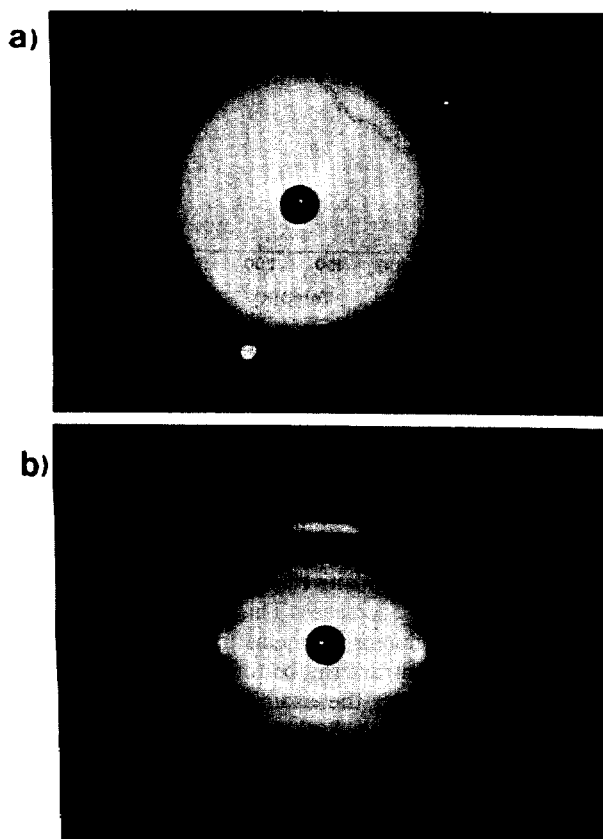
a)

b)

Figure 5. Wide angle diffraction patterns of 32-poly(PV-co-TV) films (a) unstreched, (b) streched.

magnitude of entropy per carrier.[10] Since thermoelectric power is measured at zero current, unavoidable artifacts in the measurement of electrical conductivity of the present samples resulting from the imperfect interchain contacts do not influence the results. The room temperature TEP values are included in Table 1. All of the values are of positive sign, which is consistent with the known fact that I_2 and $FeCl_3$ oxidize the polymer chain leading to p-doping. The magnitude (30-70 μV/K) of TEP values of these polymers lies in the metallic region.

The temperature dependence of TEP for selected I_2-doped samples are shown in Figure 4. All of the compositions exhibit more or less linear decrease in TEP with decrease in temperature. Such a temperature dependence of TEP is typical for metallic state. This observation may appear to be contradictory to the temperature dependence of conductivity,

which did not suport the metallic behavior. These observations can be explained by the assumption that these samples have the morphology in which metallic regions are separated by poorly conducting regions. This picture is consistent also with the $T^{-\frac{1}{2}}$ and $T^{-\frac{1}{4}}$ dependence of lnσ values as described easlier. Perhaps the intrinsic conductivities of these copolymer chains are much higher than those listed in Table 1 and the conductivity values experimentally measured are limited by imperfect interchain contacts originating from the limited chain length of polymer chains and the disordered morphology of the samples. The disorderedness should be even greater for unstretched samples whose conductivities are significantly lower than that of the oriented samples.

Table 2 summarizes the electrical properties of two poly(PV-co-TV)'s stretched to varying draw ratios and doped with I_2. In general, electrical conductivities of TV copolymers are lower than those of DMPV copolymers. Here again, one can see that stretching causes anisotropy in conductivity through chain orientation. Figure 5 shows X-ray diffraction patterns for one of the copolymers before and after stretching. The unstretched sample reveals a diffraction pattern usually observed for unoriented crystalline samples (Figure 5a), whereas the stretched sample exhibits a pattern of highly oriented polymer chains.

The values of activation energy for conduction and the room temperature TEP of these copolymers are significantly higher than those of DMPV copolymers. The TEP values belong to a semiconducting region. Figure 1 includes their temperature dependence of conductivities. Curvature changes are not observed for all of the compositions throughout the examined temperature range, indicating these compositions do not experience semiconductor-to-metal transition. The reason why such a difference is observed in the temperature dependence of conductivities for DMPV and TV copolymers is not clear. As in the case of DMPV copolymers, TV copolymers also show linear dependence of lnσ on $T^{-\frac{1}{2}}$ as well as $T^{-\frac{1}{4}}$ (Figure 2 and 3) indicating the same conduction mechanism applies to these copolymers.

References

1. R. A. Wessling and R. G. Zimmerman, U. S. Pat. 3,706,677 (1972) and 3,405,152 (1968).
2. I. Murase, T. Ohnishi, T. Noguchi, and M. Hirooka,

Crystal Structure of (18−Crown−6.K)₂K[(Co(OH)₆Mo₆O₁₈]·12H₂O

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Synth. Met., 17, 639 (1987).

3. D. R. Gagnon, J. D. Capistran, F. E. Karasz, and R. W. Lenz, *Polym. Bull.*, 12, 293 (1984); *Polymer*, 28, 567 (1987).

4. C.-C. Han, R. W. Lenz, and F. E. Karasz, *Polym. Commun.*, 28, 261 (1987).

5. (a) J.-I. Jin, H.-K. Shim, and R. W. Lenz, *Synth. Met.*, 19, E53 (1989); (b) H.-K. Shim, R. W. Lenz, and J.-I. Jin, *Markromol. Chem.*, 190, 389 (1989).

6. H. C. Montgomery, *J. Appl. Phys.*, 41, 2971 (1971).

7. Y. W. Park, W. K. Han, C. H. Choi, and H. Shirakawa, *Phys. Rev.*, B30, 5847 (1984) and references therein.

8. K. Y. Jen, M. Maxfield, L. W. Shacklette, and R. L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 309 (1987).

9. V. K. S. Shaute and C. M. Verma, *Phys. Rev.*, B8, 4885 (1973).

10. I. G. Austin and N. F. Mott, *Adv. Phys.*, 18, 41 (1969).

Structural Characterization of Crown Ether Complexed Potassium Ion (C₁₂H₂₄O₆·K)₂K[Co(OH)₆Mo₆O₁₈]·12H₂O

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The crystal structure of $(C_{12}H_{24}O_6 \cdot K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$ has been determined by X-ray diffraction. Crystal data as fallows; monoclinic, space group C_2/m, $a = 22.512(4)$ Å, $b = 18.304(4)$ Å, $c = 7.641(1)$ Å, $\beta = 90.52(2)$ Å, and $Z = 2$. A final conventional R value of 0.044 was obtained by least-squares refinement of 4173 independent observed $[|Fo| \geq 3\sigma(|Fo|)]$ reflections. The $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion shows the well-known Anderson-structure and has approximate $3m$ symmetry. A $[Co(OH)_6Mo_6O_{18}]^{-3}$ polyanion is located between two crown ether complexed cations forming a sandwich structure. One potassium ion interacts with the crown ether *via* electrostatic interactions. The other potassium ion only interacts with the water molecules and terminal oxygen atoms of the polyanion.

Introduction

Crystals of polyoxometalate salts often contain much water of crystallization. Therefore, the crystals occasionally are not stable during X-ray work because of release of the water molecules. The crown ether complexed ion as counter cation was used in order to obtain X-ray quality crystalline samples. The successful results were reported by authors.[1-3] The heteropolyanion of Anderson-structure, $[X^{+n}Mo_6O_{24}]^{-(12-n)}$ (X: heteroatom) is similar to the 18-crown-6 complexed cation in its size and shape, so that the stable packing in a crystal lattice can be anticipated in the arrangement of both polyanion and complexed cation. In this paper we report the structure of the $(18\text{-Crown-}6.K)_2K[Co^{III}(OH)_6Mo_6O_{18}] \cdot 12H_2O$ which is Anderson-structure heteropolyanion having lower oxidation state heteroatom.

Experimental

Crystals of $(18\text{-Crown-}6.K)_2K[Co(OH_6Mo_6O_{18}] \cdot 12H_2O$ were prepared as fallows. A solution of 0.05 mol of $Co(NO_3)_2 \cdot 6H_2O$ and 10 m*l* of 35% H_2O_2 in 40 m*l* of water was added dropwise with stirring the slurry, cooled by a dry ice-ethanol bath(-5 °C), of 1.0 mol of K_2CO_3 in 100 m*l* of water. The mixture was stirred for one hour at -5 °C and filtered off rapidly.

The olive-green filtrate was added to the solution cooled at 0 °C of 0.03 mole of $(NH_4)_7[Mo_7O_{24}] \cdot 4H_2O$ in 500 m*l* of water. The mixture was stirred for three hours under 10 °C, a dark-green material was precipitated gradually. The precipitate was solved in 350 m*l* of water at room temperature and filtered off, an excess of KCl was added to the filtrate, a sordid-green precipitate was deposited immediately; the precipitate changes from sordid-green to emerald-green by the repetition of this procedure. Recrystallization of the emerald-green product from an aqueous solution gave the crystal of $K_3[Co(OH)_6Mo_6O_{18}] \cdot 7H_2O$. However, it is difficult to obtain the suitable crystals for the structure determination. The solution of 0.018 mol of 18-crown-6 added to the solution of 0.006 mol of $K_3[Co(OH)_6Mo_6O_{18}] \cdot 7H_2O$. The mixed solution was allowed to stand for three weeks, the suitable crystals of $(C_{12}H_{24}O_6.K)_2K[Co(OH)_6Mo_6O_{18}] \cdot 12H_2O$ for X-ray study were obtained.

A summary of crystal data, together with the details concerning intensity measurements is given Table 1. Intensities of standard reflections no significant changes were observed the period of data collection. The data were corrected for the Lorentz and polarization effects. Neither absorption nor extinction corrections were applied. Calculations carried out with *UNICS*[4] on the 8800/8870 computer at the *Computer Center of the University of Tokyo.* The final atomic and aniso-