TABLE I
COMPLEXATION OF CATIONS TO POLY(VINYLBENZO-15-CROWN-5) AND POLY(VINYLBENZO-18-CROWN-6) AS COMPARED TO THEIR MONOMERIC ANALOGS[a]

	% alkali ion extracted[b]			
Cation	15C5	P-15C5[c]	18C6	P-18C6[c]
Li^+	<1	10.0	1.01	6.3
Na^+	10.6	24.7	13.1	20.7
K^+	22.3	85.2	85.6	90.2
Rb^+	13.0	83.7	74.0	84.2
Cs^+	3.5	68.8	71.0	87.9

[a] Concentration of picric acid, 7.0 × 10^{-5} *M;* macrocyclic polyether, 35 × 10^{-5} *M;* metal hydroxide, 0.1 *M.* [b] Based on total amount of picric acid. [c] Concentrations of the polymers are expressed as concentrations of crown units.

larger alkali ions, but also for the Na^+ and Li^+. It is interesting to notice that we have recently found spectroscopic evidence for the stable 2:1 complexes of 15C5 with fluorenylpotassium in solutions of these compounds in tetrahydrofuran.[11] Also, the crystalline complex of 15C5 and KCNS was found to be a 2:1 complex.[2] Apparently, a considerable amount of energy is gained on complexing two 15C5 molecules with alkali ions that have diameters larger than the 15C5 polyether ring. This is most likely the reason for the strong increase in the complexing efficiency of P-15C5, as two neighboring 15C5 moieties can cooperate in the complexation. CPK models of this polymer make it likely that alternating rather than adjacent crown units are cooperating. Another possible structure is that of a threefold helix with the cation sandwiched in between two crown units situated on adjacent helix turns.

The 18C6 crown ether appears to be considerably more effective in binding cations than 15C5, especially where it concerns the larger cations. This is due to the increased diameter of the polyether ring.[2] In comparing P-18C6 and 18C6, one again finds an improvement in the cation complexation of the polymer, but by no means as pronounced as with P-15C5. It is interesting that the 18C6 forms a crystalline 1:1 complex with KCNS[2] and in a THF solution with fluorenylpotassium 1:1 complexes are also observed, even with excess 18C6, contrary to the results obtained with 15C5.[11] If only one 18C6 is complexed to a cation, one does not expect a great improvement by changing to P-18C6, as cooperative effects in the cation complexation are not as important as with P-15C5. It should be pointed out, however, that 18C6 complexes of K^+ ions higher than 1:1 may exist in other media or under different conditions. It is interesting that McLaughlin, *et al.*,[12] have inferred the existence of 3:1 complexes of di-*tert*-butyldicyclohexyl-18-crown-6 for all of the alkali metal cations in the interior of phospholipid bilayer membranes.

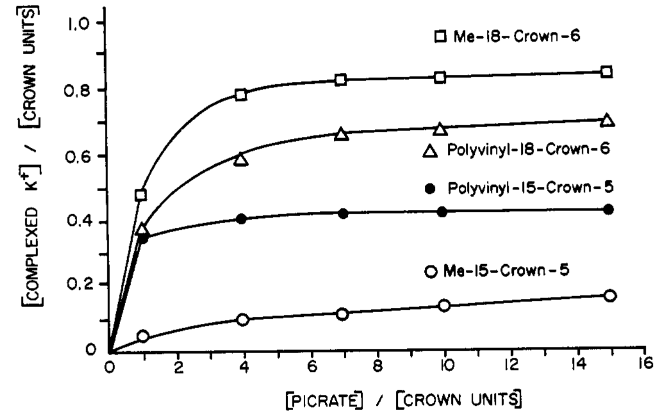

Figure 1. Complexation of potassium ions to P-15C5, P-18C6, and their monomeric analogs. Determination of number of cations complexed per crown unit; [crown] = 7 × 10^{-5} *M*, [base] = 0.1 *N*.

If in P-15C5 two crown units cooperate in the complexation of a cation, one may expect a maximum cation/crown ratio of 0.5. To observe the saturation point of cation complexation of P-15C5 and P-18C6, a number of experiments were carried out with increasing ratio of picrate to crown units. The results for K^+ ions are shown in Figure 1. One notices again the much greater complexation ability of P-15C5 as compared to 15C5. More important, the cation/crown ratio for P-15C5 never exceeds 0.5, while that for P-18C6 reaches about 0.7. Cooperation of two adjacent 15C5 moieties is apparently important for the complexation of at least the larger cations (*e.g.*, K^+), while this appears not to be essential for K^+ with P-18C6. However, a ratio of one K^+ per crown unit in P-18C6 may never be reached because of electrostatic repulsion between the bound cations. Experiments are in progress to determine more exactly the importance of this repulsion effect, as well as the cation binding in other types of solvents. Also, the mechanism of anionic polymerization of the vinyl monomers itself should be interesting, as the propagating carbanion pairs are probably of the separated kind due to intramolecular complexation of the cation by the crown unit. This reaction is therefore being investigated in more detail.

The preparation of the vinyl macrocyclic ethers and the polymerization procedures will be described in a future publication.

Acknowledgment. The support of this research by the National Institutes of Health through Grant No. GM 15965 is gratefully acknowledged.

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(11) U. Takaki, T. E. Hogen Esch, and J. Smid, to be published.

(12) S. G. A. McLaughlin, G. Szabo, G. Eisenman, and S. Ciani, *Biophys. Soc. Abstr.*, **10,** 96a (1970).

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Organometallic Polymers. IX. Polyesters of 1,1′-Bis(chlorocarbonyl)cobalticinium Hexafluorophosphate

Cobalticinium salts, in contrast to their isoelectronic ferrocene derivatives, are resistant to strong oxidizing agents such as fuming nitric acid and ozone.[1,2] However, unlike their ferrocene analogs, cobalticinium salts have not been incorporated into condensation polymers. The only metallocinium polymers previously reported have been a series of polymethylenecobalticinium salts prepared by Ito and Kenjo[3] and a series of polyferricinium salts prepared in our laboratories by oxidation of vinylferrocene and ferrocene acrylate

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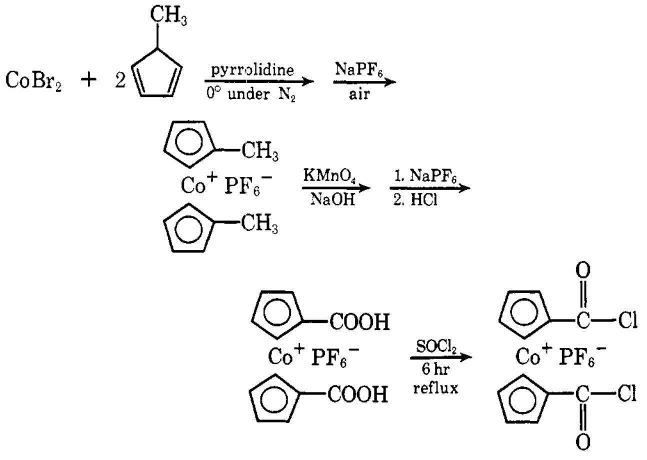
(1) E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94,** 1517 (1961).
(2) J. E. Sheats and M. D. Rausch, *J. Org. Chem.*, **35,** 3245 (1970).
(3) T. Ito and T. Kenjo, *Bull. Soc. Chem. Jap.*, **41,** 614 and 1600 (1968).

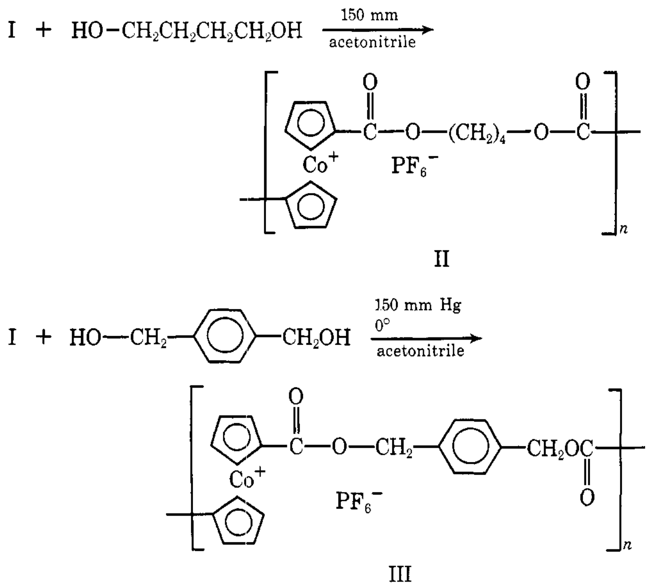
polymers with dichlorodicyanoquinone and *o*-chloranil.[4a] As an extension of our study of polymers of 1,1′-bis(chlorocarbonyl)ferrocene[5] and as part of an extensive study of polymers containing transition metals,[4] 1,1′-bis(chlorocarbonyl)cobalticinium hexafluorophosphate (I) was synthesized (Scheme I) and allowed to react with both 1,4-bis(hydroxymethyl)benzene and 1,4-butanediol to give polyesters (Scheme II).

SCHEME I



I

SCHEME II



Preparation of 1,1′-Bis(chlorocarbonyl)cobalticinium Hexafluorophosphate.[6] 1,1′-Dimethylcobalticinium hexafluorophosphate was prepared by treatment of cobalt(II) bromide with methylcyclopentadiene followed by oxidation to 1,1′-dicarboxycobalticinium hexafluorophosphate using the published procedure of Sheats and Rausch.[2] This method was previously applied to the preparation of monosubstituted cobalticinium salts.[2] A 10-g sample of the dicarboxylic acid was refluxed for 6 hr in 100 ml of thionyl chloride. As the reaction progressed, the carbonyl peak in the ir at 1705 cm^{-1} disappeared, and new peaks appeared for the chlorocarbonyl groups at 1770 and 1740 cm^{-1}. The thionyl chloride solution was chilled and 8.5 g of yellow crystals of the bischlorocarbonyl derivative were obtained, probably as a mixture of chloride and hexafluorophosphate salts: ir (KBr) 3130, 1770, 1740, 1445, 1389, 1230, 1045, 933, 890, 870, 832, 701, 560, 503, 460, and 278 cm^{-1}; nmr (CF_3–CO_2H) δ 6.25 (m, 4) and 6.50 (m, 4). Compound I darkened at 235° and decomposed gradually over the range 270–335°.[7] Before use in polymerization reactions, I was recrystallized from dry acetonitrile, in which the dicarboxylic acid is insoluble.

Preparation and Characterization of Polymer II. A solution of 1,4-butanediol (0.44 g, 4.88×10^{-3} mol) in 15 ml of acetonitrile (both dried over anhydrous $MgSO_4$, distilled, and stored over molecular sieves) was added to a solution of monomer I (2.26 g, 4.88×10^{-3} mol) over a 15-min period at room temperature under a partial vacuum of 150 mm. The pressure was maintained at 150 mm for an additional 2 min after the completion of addition to ensure effective removal of the HCl formed during the reaction. Additional acetonitrile was added to replace that which was lost during this evacuation procedure. The reaction mixture was then heated to a gentle reflux for 30 min under a nitrogen atmosphere. The resulting solution was filtered and the polymer was precipitated by dropwise addition of the filtrate to 1200 ml of 75–25 petroleum ether (30–60°)-acetone. A green waxy product was collected and purified by repeated precipitations from acetone into the petroleum ether–acetone solution. The polymeric product was obtained in 60% yield after drying overnight at 25 mm: ir strong band at 1725 cm^{-1} (ester carbonyl), no trace of the 1770-cm^{-1} carbonyl band of monomer I, powerful C–O stretching bands at 1287 and 1168 cm^{-1} with other bands at 3120, 1037, 930, 872, 836, 778, and 755 cm^{-1}. The polymer had carboxyl-group end-group absorption maximizing at 3420 cm^{-1}.

Elemental analyses were very difficult to perform with P, F, and Co in the same sample. However, these analyses were clearly low in P, indicating significant anion exchange. *Anal.* Calcd: Co, 13.4; H, 3.66; C, 43.80; P, 7.15. Found: Co, 15.84; H, 3.53; C, 42.84; P, 1.35. The exchange of PF_6^- with chloride ion appears to account almost entirely for the low phosphorus content. Reanalysis showed 4.96% Cl present, which is close to the theoretical amount predicted for exchange of 81% PF_6^-. It should be emphasized the amount of anion exchange varied from run to run.

Intrinsic viscosity measurements[8] in dimethylformamide varied from 0.034 to 0.078 dl/g for a series of polymers made using this technique. Those samples below 0.04 could be dimers and trimers, while the higher viscosities indicate low-molecular-weight polymers.

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[4] (a) C. U. Pittman, Jr., J. C. Lai, D. P. Vanderpool, M. Good, and R. Prados, Preprints of the Division of Organic Coatings and Plastics, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, p 72; *Macromolecules*, **3**, 746 (1970); (b) C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **5**, 2927 (1967); (c) *J. Ala. Acad. Sci.*, **38** (1967); (d) *Polym. Lett.*, **6**, 19 (1968); (e) *Tetrahedron Lett.*, 3619 (1967); (f) *J. Paint Technol.*, **39**, 587 (1967); (g) C. U. Pittman, Jr., J. C. Lai, and D. P. Vanderpool, *Macromolecules*, **3**, 105 (1970).

[5] C. U. Pittman, Jr., *J. Polym. Sci., Part A-1*, **6**, 1687 (1968).

[6] The synthesis of a series of 1,1′-disubstituted cobalticinium salts, including I, was reported by J. D. Sheats, C. E. Whitten, and W. M. Minihane, Proceedings of the Fourth International Conference on Organometallic Chemistry, Bristol, U. K., July 27–Aug 1, 1969, p J-1. The complete characterization of these compounds including infrared and nmr spectra, melting behavior, and elemental analyses will be published subsequently.

[7] Diacid chloride I was further identified by conversion to its diester. I (500 mg) was refluxed for 30 min in 50 ml of methanol and the dimethyl ester precipitated by dropwise addition of a solution of sodium tetraphenylborate in methanol. The product recrystallized from acetone–chloroform: mp 182°; ir (KBr) 3120, 3080, 2980, 2960, 1740 (s), 1580, 1470, 1422, 1398, 1380, 1285 (s), 1193, 1150 (s), 1068, 1032, 965, 858, 790 (s), 740 (s), 705 (s), 610, 510, 485, 415, and 320 cm^{-1}; nmr (acetone) 6.39 (t, 4, J = 2 Hz), 6.18 (t, 4, J = 2 Hz), and 3.99 (s, 6). *Anal.* Calcd for $C_{38}H_{34}BCoO_4$: Ca, 73.09; H, 5.49; O, 10.25; Co, 9.44. Found: C, 72.89; H, 5.42; O, 10.30; Co, 9.40.

[8] Viscosity measurements were made with Cannon-Ubbelohde viscometers at 30°.

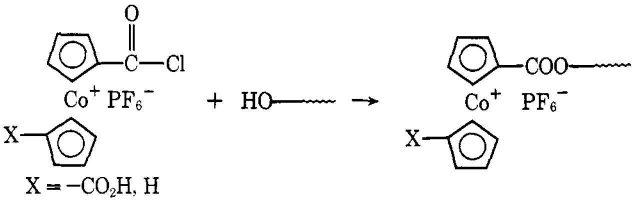
Preparation and Characterization of Polymer III. Monomer I (1.87 g, 4.06×10^{-3} mol) was dissolved in 200 ml of dry, freshly distilled acetonitrile. To this, a solution of 1,4-bis(hydroxymethyl)benzene (0.60 g, 4.35×10^{-3} mol, recrystallized from hexane) in 30 ml of acetonitrile was added over a 20-min period at 0° under a partial vacuum of 150 mm. After the addition was completed, the partial vacuum was maintained for 30 min and then the solution was refluxed in extra acetonitrile for 2 hr. A green solid was obtained upon removing most of the acetonitrile which was only partially soluble in heated acetonitrile. Extraction with acetone gave two fractions. The acetone-soluble fraction was purified by repeated precipitations from acetone into petroleum ether to give a 50% yield of a yellow powder after drying overnight at 20 mm. The acetone-insoluble fraction was soluble in DMF, and it was purified by repeated precipitations from DMF into 30–70 acetone–ether to give a 30% yield of a yellow powder. The acetone-soluble portion darkened in air at 130–160°, while the acetone insoluble fraction darkened only above 200°.

The infrared spectra of the acetone-soluble fraction showed an intense ester carbonyl stretch at 1720 cm^{-1}, no trace of residual acid chloride, and strong C–O stretching bands at 1160 and 1280 cm^{-1}. Other bands appeared at 3130, 1440, 1363, 1035, 971, 872, 833, 792, and 533 cm^{-1}.

Elemental analysis indicated some anion exchange. *Anal.* Calcd: Co, 12.1; P, 6.41; H, 3.29; C, 49.5. Found: Co, 11.4; P, 3.54; H, 3.58; C, 46.8. Exchange of PF_6^- for chloride is indicated by analysis which found 2.71% Cl.

Viscosity measurements[8] in dimethylformamide confirmed that polymeric product had been formed. Intrinsic viscosities between 0.120 and 0.095 dl/g were obtained on a series of polymers prepared as described above. Further confirmation of polymer formation was provided by gel permeation chromatography (using a Waters Associates Model 301 instrument). Applying a universal calibration approach to the calculation of molecular weight from the chromatogram indicated an $\bar{M}_n$ of about 2500. However, the intrinsic viscosity used in these calculations was measured in DMF while the chromatograms were run in THF where the polymer molecules are less solvated and more coiled. A standard calibration with an approximated Q factor indicated an $\bar{M}_n$ of about 3000–4000. High-molecular-weight tailing out to 8000 is observed. It must be concluded that the polymer is a low-molecular-weight species of from 4 to 20 repeating units. Some dimer and trimer are also resolved by gel permeation chromatography.

The synthesis of polyesters from I appears promising, and high-molecular-weight polymers should be obtained when samples of I free of carboxyl groups or traces of monosubstituted derivatives are obtained. Small percentages of carboxyl group in monomer I will cause termination of the polymerization under these mild conditions.[9] To obtain high-molecular-weight derivatives, we are attempting to obtain I of high purity. Alternatively, we are evaluating the use of the dimethyl ester of acid chloride I in transesterification polycondensations.



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(9) The monocarboxylic acid, which is present as a trace contaminant, could be formed from traces of cyclopentadiene in methylcyclopentadiene or by decarboxylation of the dianion of the 1,1′-diacid.

(10) (a) University of Alabama; (b) Huntsville Campus, University of Alabama; (c) Rider College; (d) NSF Undergraduate Research Participant, Bowdoin College, Brunswick, Me., 1967–1969.

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Murray Goodman and Shih-chung Chen: Optically Active Polyisocyanates

Page 399, column 1, third paragraph. In the section "Synthesis of the Monomer," *nitrate* should read *nitrite*.