BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 614—619 (1968)

A New Anion Exchanger Containing Cobalticinium Cation

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(Received September 27, 1967)

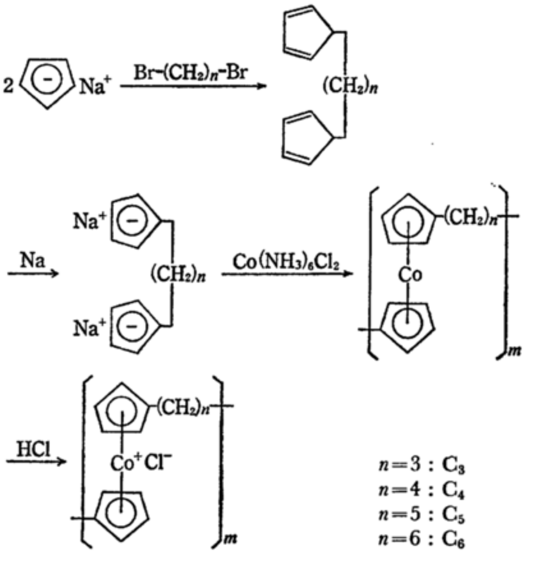
A New type of anion-exchanger, polymeric olygomethylene cobalticinium cation, was synthesized and its ion-exchange properties and stability toward heat and reagents were investigated in comparison with those of the ion-exchange resins. The preparative method of the exchanger was the same as that for polymeric olygomethylene ferrocene; hexamminecobalt(II) chloride was added to the product of α, ω-dicyclopentadienyl alkane with sodium. Although the pure products could not be obtained, the substance extracted with water showed several peaks common to a cobalticinium cation in IR spectra. The content of cobalt in tetraphenyl borate was 0.175 mmol/g, which corresponded to 91% trimethylene cobalticinium tetraphenyl borate. The saturated ion-exchange capacity of the eschanger was 1.75 meq/g, which was half the theoretical value. This discrepancy could be attributed to the shortage of cobalt according to the results of chemical analysis and magnetic susceptibility measurements. Although ion-exchange resins lose their exchange capacity by heating at 150°C in air, this exchanger was thermostable decreasing to only 70% in ion-exchange capacity. The ion-exchange capacity of the exchanger in hydrothermal water at 220°C decreased to 55—35%, while that of resins drops to as low as 20%. The selectivity coefficient for various anions became smaller in the order; $ClO_4^- > I^- > ClO_3^- > BrO_3^- > Br^- > Cl^- > IO_3^- > F^-$. This tendency was the same as that for ion-exchange resins.

The ion-exchange group as well as the structure of net-works influences the properties of ion-exchangers, such as stability toward high temperature and reagents, and selectivity for ions.

Quaternary ammonium salt type resin has been used most generally during the past decade. However, this type of resin is not stable at high temperature. This weak point can be attributed to the property of quaternary ammonium salt.

Inorganic ion-exchangers such as zirconium oxide, thorium oxide¹⁾ and bismuth hydroxide were synthesized and their properties have been investigated from the point that these inorganic materials are stable at high temperature. In spite of many studies, some weak points, *e. g.*, lower ion-exchange capacity, lower exchange rate, lower reversibility of ion-exchange and higher solubility in acid or akaline solution, have not been improved.

Recently, dicyclopentadienyl metal compounds were found.²,³⁾ Some of them (compounds of Co(III), Rh(III) and Ir(III)) exist as stable cations in an alkaline medium as well as in water, and do not decompose at high temperature.²,³⁾ Accordingly, it is expected that a polymer containing these salts exhibits more thermostable properties than the quaternary ammonium type resin. Since the compound of Rh(III) and Ir(III) can not readily obtained, a polymer containing cobalticinium cation (π-dicyclopentadienyl cobalt-(III) cation) was synthesized. The synthesis of the polymer was made according to that of polymeric olygomethylene ferrocene.⁴⁾ The reaction steps and the probable structure of the product are as follows;



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1) C. B. Amphlett, L. A. Mcdonald and M. J. Redman, *J. Inorg. & Nucl. Chem.*, **6**, 236 (1958).

2) G. Wilkinson and F. A. Cotton, "Progress in Inorganic Chemistry," Vol. 1, ed. by F. A. Cotton, International Publishers, New York, N. Y. (1959), p. 13.

3) J. A. Page and G. Wilkinson, *J. Am. Chem. Soc.*, **74**, 6149 (1952).

4) A. Littringhaus and W. Kullick, *Makromol. Chem.*, **44/46**, 669 (1961).

Experimental

Synthesis of Polymeric Olygomethylene Cobaltocene. Four kinds of α, ω-dibromoalkanes were used; 1, 3-dibromopropane, 1, 4-dibromobutane, 1, 5-dibromopentane and 1, 6-dibromohexane. After the reaction of α, ω-dicyclopentadienyl alkane with sodium metal was completed, the reaction mixture was cooled to 0°C and hexamminecobalt(II) chloride (75 g) added. The temperature was raised gradually in a water bath. Ammonia gas began to evolve at about 25°C. The temperature was maintained until the evolution ceased. Finally the reaction was completed by refluxing for 2 hr. Unreacted sodium and sodium compounds were decomposed with methanol. Solvent was removed by evaporation under reduced pressure after the mixture was centrifuged. The precipitates were extracted with 300 m*l* benzene, and the resulting solutions separated with a centrifuge. Benzene was removed by evaporation under reduced pressure.[*1]

An aqueous layer was separated and washed with benzene several times. Tetraphenyl borate solution was added to the aqueous solution. Resulting precipitates were dried at 110°C. The cobalt content was 0.175 mmol/g. The theoretical cobalt content calculated from the formula, $Co(C_5H_4)_2(CH_2)_3(C_6H_5)_4B$, is 0.192 mmol/g.

Samples for measurement of IR and UV spectra were prepared from the preceeding aqueous solution after converting to a triiodide, or hydroxide form.

The precipitate obtained from benzene solution was treated with 1 N hydrochloric acid, washed with water and dried at 60°C. Then it was ground and sieved to two kinds of mesh size; 50/100 mesh and 100/200 mesh. The exchangers were conditioned by alternate treatment with 2 N HCl and 2 N NaOH. After washing with distilled water, it was converted to the desired salt forms.

Preparation of Cobaltocene and Cobalticinium Salts. Cobaltocene was prepared in accordance with the method of Cordes,⁵⁾ from sodium cyclopentadienide and hexamminecobalt(II) chloride. Cobalticinium salts were obtained by treating cobaltocene with dilute hydrochloric acid and purified by recrystallization of the picrate. The desired salt forms were obtained by anion exchange resin columns.

Measurements of Ion-exchange Capacity, pH-titration Curves, Selectivity Coefficient and Ion-exchange Rate. Ion-exchange capacities at different pH, and pH-titration curves were measured in a 0.1 M (KCl+HCl) solution of constant ionic strength. The volume of the solution was 25 m*l*, and the amount of sample, 0.250 g. After equilibration, pH measurements were made with a pH-meter with a glass electrode. Adsorption capacities were measured from the decrease in the concentration of chloride ion, which was determined potentiometrically by titration with silver nitrate solution. pH-titration curves for cobalticinium hydroxide and polymeric tetramethylene cobalticinium hydroxide were measured by titrating 50 m*l* of 0.146 N solution of cobalticinium hydroxide, and 50 m*l* of 0.124 N solution of polymeric tetramethylene cobalticinium hydroxide with 0.1 N HCl, respectively.

Selectivity coefficients for ions of SCN^-, I^-, Br^- and Cl^- were measured on exchangers of the NO_3 form, and others on exchangers of the Cl form. Measurements were carried out at 25.00±0.01°C. Neutral salt solutions (0.1 M) were added to a certain amount of the exchangers. After 24 hr, halogenide ion, and thiocyanate ion concentrations were determined by the method previously mentioned. The selectivity coefficient (K_B^A) was computed according to the definition:

$$K_B^A = \left(\frac{m_B}{m_A}\right)_r \Big/ \left(\frac{m_A}{m_B}\right)_w ,$$

where m_B is meq. of B^- and m_A is that of A^-, the subscript r refers to the phase of the exchanger, and w the phase of the external solution. The amount of m_A and m_B in the exchanger can be obtained from the amount of ions adsorbed, and the saturated capacity.

The ion-exchange rate was measured at 25.00±0.01°C. After ion-exchangers of the OH form (100/200 mesh) were added to 100 m*l* of 0.1 N HCl with stirring, the decrease in concentration of Cl^- ion was determined by the method previously mentioned. The fractional attainment of equilibrium was computed as the fraction of ion adsorbed at a given time to the amount of ion adsorbed after equilibration.

Measurements of Stability toward Temperature and Reagents. Stability toward heat was measured by heating exchangers of the OH form in an oven, or in hydrothermal water in an autoclave. After treatment, the ion-exchange capacity was measured. Stability toward reagents was measured by treating exchangers of the OH form with hydrochloric, sulfuric and nitric acids of varying concentrations at room temperature for 24 hr. After the adsorbed ions were eluted with 5 N NaOH, the exchangers were washed with water, dried at 60°C, and the ion-exchange capacities measured.

Analysis of Cobalt and Measurement of IR and UV Spectra. Cobalt was determined by the gravimetric method as Co_3O_4, or by chelatometric titration with 0.01 N EDTA using XO as indicator, after cobaltocene was destroyed with fuming perchloric acid. UV spectra were recorded on an EPS-2 Hitachi recording spectrophotometer, and IR spectra on an EPI-S2 Hitachi spectrophotometer with a KBr disk.

The magnetic susceptibility of the pentamethylene cobalticinium compound was measured by the Guoy method using water ($\kappa = -0.72 \times 10^{-6}$ c.g.s. unit/g) as a standard.

Results and Discussion

The IR spectrum of polymeric tetramethylene cobalticinium triiodide exhibits 5 peaks common to those of cobalticinium triiodide, as shown in Fig. 1. The UV spectrum in Fig. 2 shows that the peaks of the polymer shift to longer wavelength relative to cobalticinium ion.

The ion-exchange of Cl^- ion from 0.1 N HCl on the exchanger of the OH form is rapidly attained, almost at the same rate as with the ion-exchange

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[*1] Ferrocene compounds were separated from organic impurities (hydrocarbons) by oxidation with $FeCl_3$ solution. The compounds of cobaltocene, however, were very difficult to separate in this manner owing to the formation of an emulsion of benzene and water.

5) J. F. Cordes, *Chem. Ber.*, **95**, 3084 (1962).

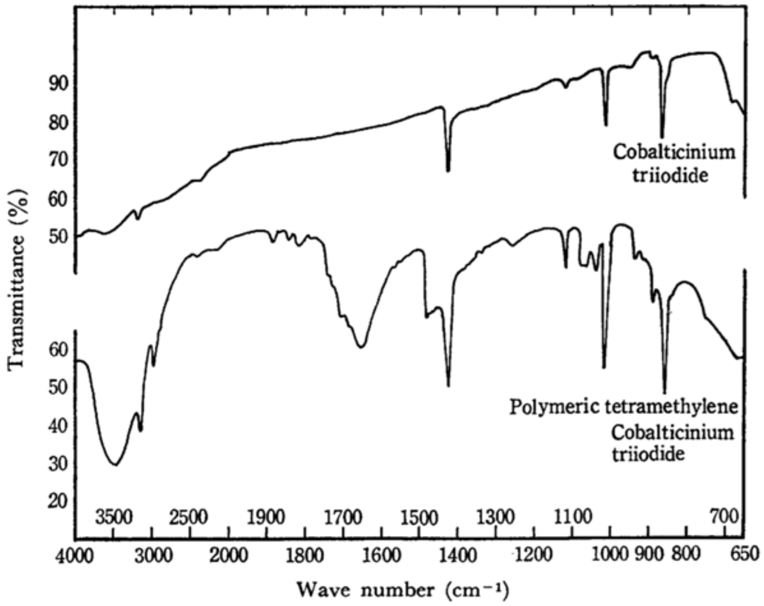

Fig. 1. IR spectra of polymeric tetramethylene cobalticinium triiodide and cobalticinium triiodide.

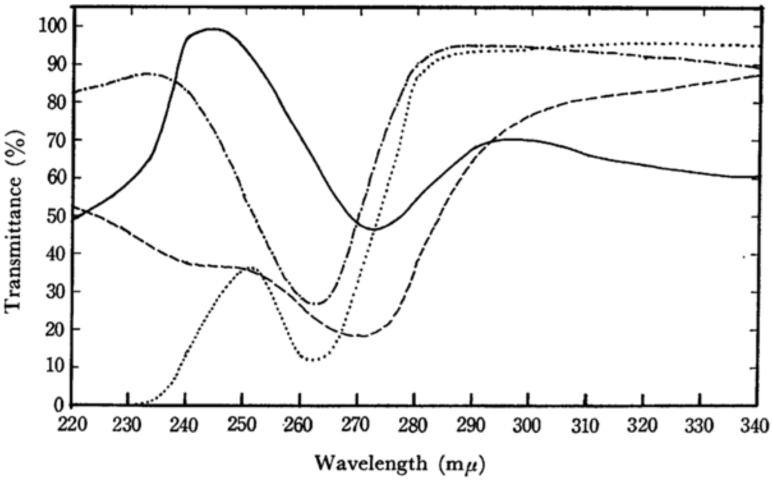

Fig. 2. UV spectra of polymeric pentamethylene cobalticinium salts and cobalticinium salts.

— — Soluble polymer ——— Solid polymer dispersed
—·— Cobalticinium picrate ······ Cobalticinium iodide

resin (Fig. 3). One day therefore is enough to attain ion-exchange equilibrium.

TABLE 1. SATURATED ION-EXCHANGE CAPACITIES OF POLYMERIC OLYGOMETHYLENE COBALTICINIUM SALTS AND COBALT CONTENT

	C_3	C_4	C_5	C_6
Ion-exchange capacity (meq/g)	1.036	1.209	1.241[*2]	1.020
Cobalt content (meq/g)	1.350	1.460	1.504	1.385

The saturated ion-exchange capacity of these compounds was 1.75 meq/g from Fig. 4. This is half the value calculated from the formula weight of the polymer, $(C_5H_4)_2Co(CH_2)_5OH$. The comparison of cobalt content with saturated ion-exchange capacities after alternate treatment with

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[*2] The saturated ion-exchange capacity was different in different batches. The values shown in Fig. 4 are for the highest one. A small decrease in the capacity was observed when the ion-exchanger was treated with hydrochloric acid as shown in following section.

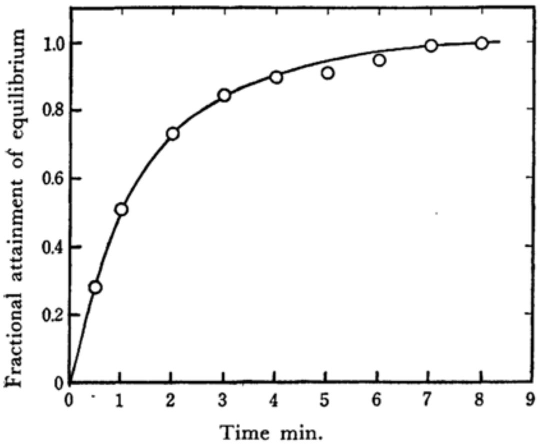

Fig. 3. Rate of attainment of ion-exchange equilibrium of the polymeric pentamethylene cobalticinium (OH form).

hydrochloric acid and sodium hydroxide is shown in Table 1.

The magnetic susceptibility of the pentamethylene cobalticinium compound was 1.3×10^{-6} c.g.s.unit/g, whereas that of cobaltocene was 6.8×10^{-6} c.g.s. unit/g,[2] and cobalticinium ion was found to be diamagnetic.[2] Therefore, this weak paramagnetism of the compound suggests that the discrepancy between the saturated ion-exchange capacity and the cobalt content may be attributed to cobaltocene which is not oxydized to cobalticinium ion.

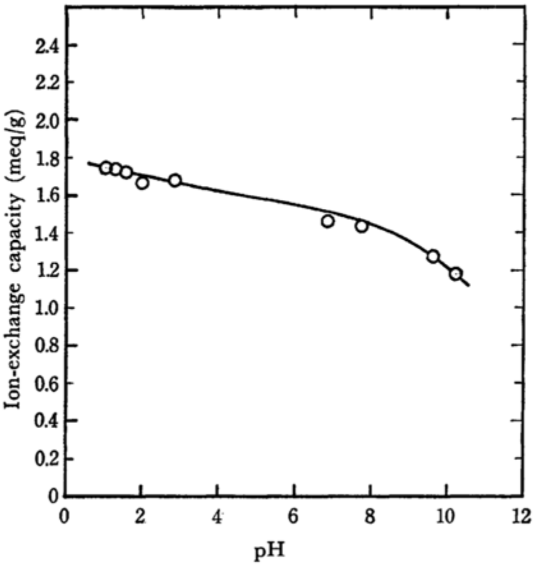

Fig. 4. pH dependence of the ion-exchange capacity of the polymeric pentamethylene cobalticinium (OH form).

A discrepancy between the saturated ion-exchange capacity, and the value calculated from the formula weight indicates the presence of organic impurities. Although it is unknown what the impurities are, the main impurity could be supposed to be α,ω-dicyclopentadienyl alkane which did not react with sodium. Although these impurities decreased

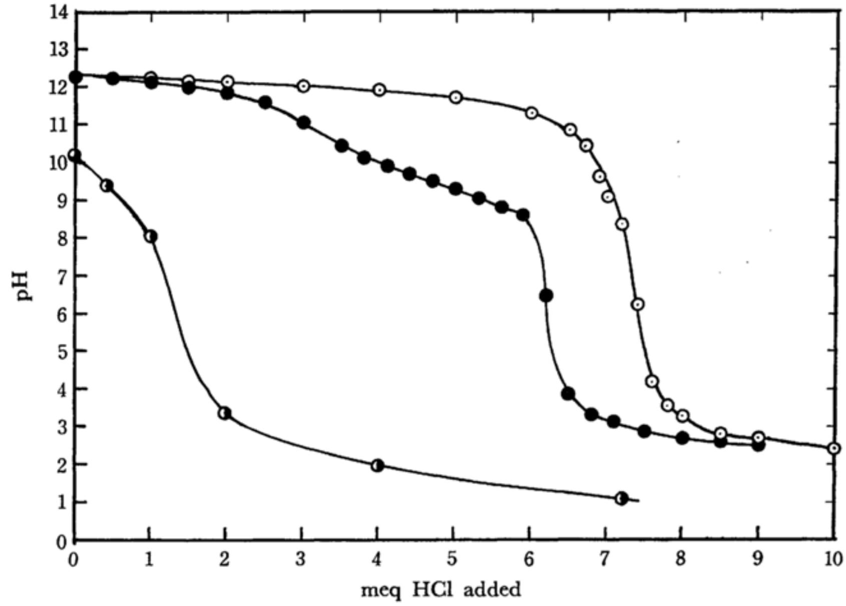

Fig. 5. Titration curves of polymeric olygomethylene cobalticinium hydroxide and cobalticinium hydroxide.

○ Cobalticinium hydroxide
● Soluble tetramethylene cobalticinium hydroxide
◑ Solid pentamethylene cobalticinium hydroxide

the saturated ion-exchange capacity, they also decreased the solubility of the exchanger.

Ion-exchange capacity does not change greatly with pH, as may be seen in Fig. 4. This fact suggests that the exchanger is of a strong base type. Although cobalticinium hydroxide is a very strong base, it seems to become weaker with polymerization, as can be seen from the comparison of the pH-titration curve of cobalticinium hydroxide with that of polymeric tetramethylene hydroxide (Fig. 5).

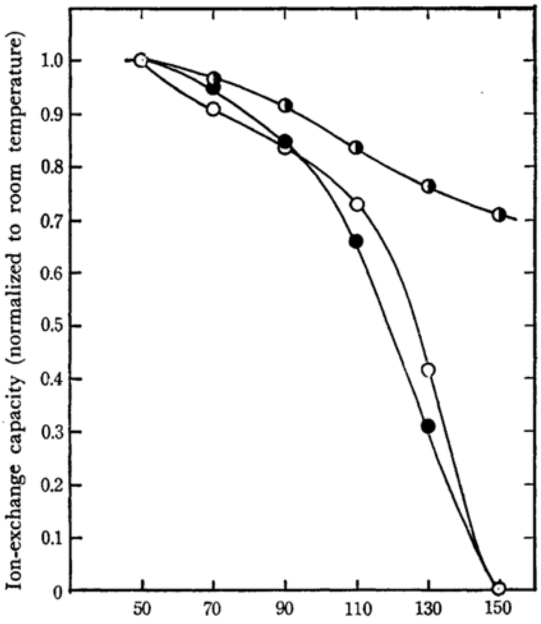

Fig. 6. Decreases of the ion-exchange capacities with temperature in air.

- ◐ Polymeric pentamethylene cobalticinium (OH form)
- ● Dowex 1 X-2 (OH form)
- ○ Amberlite IRA-410 (OH form)

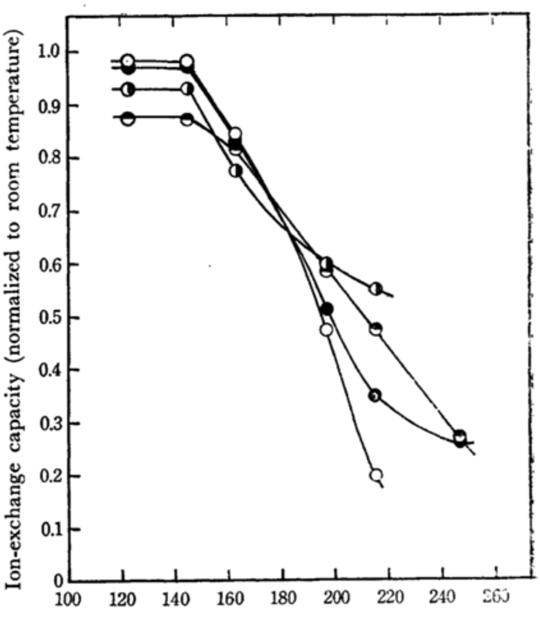

Fig 7. Decrease of the ion-exchange capacities with temperature in hydrothermal water.

- ○ Dowex 1 X-2 (OH form)
- ◓ Polymeric tetramethylene cobalticinium (OH form)
- ● Polymeric pentamethylene cobalticinium (OH form)
- ◑ Polymeric hexamethylene cobalticinium (OH form)

Table 2. Decrease of ion exchange capacity of the polymeric olygomethylene cobalticinium salts by alternate treatments of mineral acids and sodium hydroxide solution

Concentration of acid (N)	C_3	C_4	C_5	C_6
		HCl		
0	1.181	1.405	1.511	1.200
0.1	1.084	1.284	1.383	1.122
1	1.006	1.291	1.416	1.072
5	1.101	1.300	1.339	1.138
ca. 12	1.122	1.251	1.244	1.080
		H_2SO_4		
1	1.079	1.342	1.431	0.993
9	1.071	1.324	1.463	0.971
18	1.067	1.331	1.418	0.967
		HNO_3		
1	0.931	1.265	1.337	0.895
6	0.704	0.979	1.232	0.882
13	0.438	0.687	0.753	0.433

Decreases in ion-exchange capacities with temperature in air are given in Fig. 6. Resins were decomposed completely at 150°C, while this exchanger decreased to 70% in ion-exchange capacity. Decreases in ion-exchange capacity in water are shown in Fig. 7. The exchanger did not decrease so greatly as ion-exchange resin in capacity. The resins were more stable toward heat in water than in air. This fact may be explained as being due to the sensitivity of the quaternary ammonium ion to air. From the fact that cobalt hydroxide was detected in water after heating in the autoclave, it is apparent that the cobalticinium ion decomposes to the hydroxide and hydrocarbons. As for the stability of other forms of exchangers to heat, salt forms were more stable than the OH form. After heating at 205°C for 1 hr in hydrothermal water, the capacity of the OH form decreased to 0.327 meq/g, while that of the Cl form, and the NO_3 form decreased to

TABLE 3. THE EFFECT OF REPETITION OF ALTERNATE TREATMENT OF 0.1 N HCl AND 5 N NaOH ON THE ION-EXCHANGE CAPACITIES OF POLYMERIC OLYGOMETHYLENE COBALTICINIUM SALTS

Number of acid-base treatment	C_3	C_4	C_5	C_6
0	1.251	1.416	1.511	1.372
1	1.084	1.322	1.403	1.122
2	1.020	1.270	1.366	0.943
3	1.039	1.270	1.348	0.912
4	1.062	1.228	1.247	0.903
5	1.046	1.262	1.307	0.896
6	1.029	1.209	1.272	0.909

0.764 meq/g, and 0.784 meq/g, respectively, under the same conditions.

The decrease in ion-exchange capacity with treatment by reagents is shown in Table 2. Hydrochloric, and sulfuric acids do not affect the exchangers as seriously as nitric acid. Possibly, nitric acid liberates cobalticinium cation from the polymer by destroying the olygomethylene links.

After a rather large decrease in the ion-exchange capacity due to the first treatment with acid, the anion-exchange capacity remained almost constant after several alternate treatments with acid and sodium hydroxide, as shown in Table 3. This means that almost all ions adsorbed were eluted with sodium hydroxide.

As for the influence of the number of carbon chains connecting cobalticinium cations, compounds with carbon chains of 4 or 5 are the most stable toward reagents (Table 2). As the number increases, however, grinding the sample becomes difficult owing to the increase of elasticity. From the point of practical application, compounds with carbon chains of 4 or 5 are the most suitable.

The selectivity coefficient of this exchanger is summarized in Table 4. The order of the coefficient is the same as that for resins. The properties of the cobalticinium salts are therefore nearly the same as those of the quaternary ammonium ion.

TABLE 4. SELECTIVITY COEFFICIENTS FOR VARIOUS ANIONS

	Dowex 1 X-1		Dowex 1 X-8		Amberlite IR-4B		Amberlite IR-45		C_5	
	K_{NO_3}	X_{NO_3}	K_{NO_3}	X_{NO_3}	K_{NO_3}	X_{NO_3}	K_{NO_3}	X_{NO_3}	K_{NO_3}	X_{NO_3}
SCN^-	3.95	0.120	4.69	0.079	2.16	0.196	1.53	0.155	3.08	0.200
I^-	3.59	0.122	3.43	0.100	1.23	0.270	1.01	0.205	2.14	0.283
NO_3^-	1	—	1	—	1	—	1	—	1	—
Br^-	0.764	0.315	0.763	0.275	0.625	0.372	0.470	0.317	0.303	0.708
Cl^-	0.366	0.430	0.243	0.453	0.455	0.418	0.219	0.439	0.048	0.935
	K_{Cl}	X_{Cl}	K_{Cl}	X_{Cl}	K_{Cl}	X_{Cl}	K_{Cl}	X_{Cl}	K_{Cl}	X_{Cl}
ClO_4^-	88.1	0.029	56.3	0.014	8.70	0.038	5.46	0.056	36.1	0.0475
I^-	7.79	0.135	5.04	0.070	2.99	0.108	2.38	0.126	25.3	0.035
ClO_3^-	2.45	0.164	3.35	0.097	2.05	0.143	2.43	0.122	4.46	0.164
Cl^-	1	—	1	—	1	—	1	—	1	—
BrO_3^-	0.939	0.208	0.918	0.241	1.67	0.439	1.21	0.198	1.25	0.220
IO_3^-	0.425	0.411	0.198	0.480	1.63	0.168	0.528	0.317	0.202	0.242
F^-	0.287	0.404	0.0856	0.706	0.409	0.365	0.288	0.412	0.129	0.313

X_{Cl} and X_{NO_3} = equivalent fraction in the exchanger phase.