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## PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NORTHWESTERN UNIVERSITY AND GEORGIA INSTITUTE OF TECHNOLOGY]

### The Binding of Metal Complexes by Polystyrene Sulfonate Ion<sup>1</sup>

BY ARNE JENSEN, FRED BASOLO AND H. M. NEUMANN

RECEIVED JUNE 25, 1958

The binding of tris-(1,10-phenanthroline) cationic complexes of iron(II), ruthenium(II) and cobalt(III) by polystyrene sulfonate ion has been studied by a dialysis method. The comparative binding tendencies of a series of nitroamminecobalt(III) ions is also reported. The effect of changes in charge, size and structure of the metal complexes on the degree of binding is discussed.

Polyanions have been observed to bind various metal ions in aqueous solution. This association has been studied for several different cations and polyanions, and a variety of experimental methods have been used to measure the extent of binding. Wall and co-workers have used electrolytic transference and diffusion methods to measure the binding of cations to polyacrylate<sup>2</sup> and polyphosphate.<sup>3</sup> Titration methods have been used with both polyacrylate<sup>4</sup> and polyphosphate.<sup>5</sup> Dialysis methods are also described for the polyacrylate ion.<sup>6</sup>

It was reported recently that the rates of dissociation and racemization of the tris-(1,10-phenanthroline)-iron(II) ion are greatly altered by the presence of polymethacrylate and polystyrene sulfonate ions.<sup>7</sup> These differences in rates of reaction were found to be due to the association of the iron(II) complex with the polyanions. Complexes of this type are known to display biological activity, and this activity may result from an at-

tachment of the complex to active sites in the biological system.<sup>8</sup>

This paper reports a study, using a dialysis method, of the binding of several different metal complexes to polystyrene sulfonate (PSS<sup>-</sup>). The effect of changes in charge, size and structure of the complex on the degree of binding was investigated.

#### Experimental

**Compounds.**—Most of the metal complexes were taken from a collection of compounds prepared in this Laboratory over a period of a few years. The identity and purity of the compounds were confirmed by comparing their absorption spectra with those of the known compounds.<sup>9</sup> Solutions of Fe(phen)<sub>3</sub><sup>3+</sup> were prepared *in situ* by the addition of three equivalents of 1,10-phenanthroline to one of iron(II) sulfate. The complex [Ru(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was prepared by the method of Dwyer,<sup>10</sup> and [Co(phen)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O was provided by B. R. Baker. Salts of the complexes Co(en)<sub>2</sub>NH<sub>3</sub>NO<sub>2</sub><sup>2+</sup>, Co(en)<sub>2</sub>(py)NO<sub>2</sub><sup>2+</sup> and Co(trien)NH<sub>3</sub>NO<sub>2</sub><sup>2+</sup> were prepared by the reaction between the corresponding chloro complexes and silver nitrite.<sup>11</sup> The sodium polystyrene sulfonate was kindly supplied by the Monsanto Chemical Company. This material known as Lustrex X-770 was prepared from polystyrene with an average mol. wt. of 70,000 and the degree of sulfonation varies between 1.0 and 1.1. The polyelectrolyte was used without further purification.

**Dialysis.**—Dialysis measurements were made by the method described earlier.<sup>7</sup> In each experiment a cellophane bag containing 10 cc. of solution of polyelectrolyte was suspended in 10 cc. of a solution of complex contained in a large

(1) This investigation was supported by a Grant-in-Aid from the National Institutes of Health, Grant No. RG-4335.

(2) J. R. Huizenga, P. F. Grieger and F. T. Wall, *THIS JOURNAL*, **72**, 2636, 4228 (1950); F. T. Wall, P. F. Grieger, J. R. Huizenga and R. H. Doremus, *J. Chem. Phys.*, **20**, 1206 (1952); F. T. Wall and R. H. Doremus, *THIS JOURNAL*, **76**, 1557 (1954); F. T. Wall and M. J. Eitel, *ibid.*, **79**, 1550, 1556 (1957).

(3) F. T. Wall and R. H. Doremus, *ibid.*, **76**, 868 (1954).

(4) H. P. Gregor, L. B. Luttinger and E. M. Loebel, *J. Phys. Chem.*, **59**, 34, 990 (1955); E. M. Loebel, L. B. Luttinger and H. P. Gregor, *ibid.*, **59**, 559 (1955).

(5) J. R. Van Wazer and D. A. Campanella, *THIS JOURNAL*, **72**, 655 (1950).

(6) A. M. Kotliar and H. Morawetz, *ibid.*, **77**, 3692 (1955); K. Hutschneker and H. Deuel, *Helv. Chim. Acta*, **39**, 1038 (1956).

(7) A. Jensen, F. Basolo and H. M. Neumann, *THIS JOURNAL*, **80**, 2354 (1958).

(8) F. P. Dwyer, E. C. Gyarfas, R. D. Wright and A. Shulman, *Nature*, **179**, 425 (1957).

(9) F. Basolo, *THIS JOURNAL*, **72**, 4393 (1950).

(10) F. P. Dwyer, J. E. Humpoletz and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 212 (1947).

(11) "Gmelins Handbuch der anorganischen Chemie," Vol. 58B, Verlag Chemie, G. m. b. H., Berlin, 1930, pp. 139-141.

test-tube. The test-tube and its contents were mechanically shaken in a water-bath at  $25.0 \pm 0.1^\circ$  for a period of 12 hr. At the end of this time the optical density of the solution outside the dialysis bag was measured and from this the concentration of complex calculated. The amount of complex remaining inside the dialysis bag was then obtained as the difference between the amount of complex originally added and that which appeared outside the bag. Blank experiments were run with the complex alone and the polyelectrolyte alone. In this way corrections in optical density due to some complex bound to the cellophane and due to the color of the polyelectrolyte and extracted bag were made. A typical set of experimental data is given in Table I.

TABLE I

TYPICAL<sup>a</sup> DIALYSIS DATA FOR THE ESTIMATE OF CATIONIC COMPLEX BOUND BY POLYANION

Binding of  $\text{Fe}(\text{phen})_3^{2+}$  by 0.005% NaPSS in 0.05 M NaCl at  $25^\circ$

	Fe- (phen) <sub>3</sub> <sup>2+</sup> initial, moles × 10 <sup>7</sup>	Optical density, 510 mμ	Cor. optical density	Fe- (phen) <sub>3</sub> <sup>2+</sup> free, molarity × 10 <sup>6</sup>	Fe- (phen) <sub>3</sub> <sup>2+</sup> free, moles × 10 <sup>7</sup>	
1 <sup>b</sup>	7.66	0.152	0.146	1.34	2.68	
I	7.66	.395	.387	3.56	7.12	
2	7.66	.153	.147	1.35	2.70	
II	7.66	.399	.391	3.59	7.18	
3	7.66	.151	.145	1.33	2.66	
III	7.66	.400	.392	3.60	7.20	
4	0.00	.006				
IV	0.00	.008				
	Fe- (phen) <sub>3</sub> <sup>2+</sup> bound by bag, moles × 10 <sup>7</sup>	Fe(phen) <sub>3</sub> <sup>2+</sup> not bound by bag, moles × 10 <sup>7</sup>	Fe(phen) <sub>3</sub> <sup>2+</sup> bound by PSS <sup>-</sup> , moles × 10 <sup>7</sup>			r
1	0.18	7.48	4.80			} 136
I	.54					
2	.18	7.48	4.78			
II	.48					
3	.18	7.48	4.82			
III	.46					

<sup>a</sup> The results on binding of  $\text{Co}(\text{phen})_3^{3+}$  are less accurate since the optical densities of the blanks, 4 and IV are 4-5 times large at 349 mμ than at this wave length. <sup>b</sup> 1, 2, 3 and 4 are solutions of NaPSS; I, II, III and IV are blank solutions without NaPSS.

Optical density measurements for the different complexes were made at a number of wave lengths:  $\text{Fe}(\text{phen})_3^{2+}$ , 510 mμ;  $\text{Ru}(\text{phen})_3^{2+}$ , 447 mμ;  $\text{Co}(\text{phen})_3^{2+}$ , 349 mμ;  $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$ , 349 mμ; *cis*- $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^{2+}$ , 362 mμ; *trans*- $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^{2+}$ , 380 mμ; *cis*- $\text{Co}(\text{en})_2(\text{NO}_2)_2^{2+}$ , 359 mμ; *trans*- $\text{Co}(\text{en})_2(\text{NO}_2)_2^{2+}$ , 369 mμ;  $\text{Co}(\text{en})_2\text{NH}_3\text{NO}_2^{2+}$ , 367 mμ;  $\text{Co}(\text{trien})\text{NH}_3\text{NO}_2^{2+}$ , 360 mμ;  $\text{Co}(\text{en})_2\text{pyNO}_2^{2+}$ , 363 mμ;  $\text{Co}(\text{bipy})_2(\text{NO}_2)_2^{2+}$ , 387 mμ.

Solutions containing the polyelectrolyte were 0.005% in NaPSS and 0.05 M in NaCl; solutions containing the complex were also 0.05 M in NaCl. For the phenanthroline complexes variable concentrations of the complex were used, and for each of the nitro-amminecobalt(III) complexes only one concentration, about 0.00025 M.

Studies could not be made on either  $\text{Co}(\text{NH}_3)_5^{3+}$  or  $\text{Co}(\text{en})_3^{3+}$  because these ions formed precipitates with the polyanions. Attempts to investigate  $\text{Co}(\text{NH}_3)_5(\text{NO}_2)_3$  and  $\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4^-$  also failed. In these two cases the difficulty was that the complexes reacted during the 12 hr. equilibration period. This was established by noting that the absorption spectra of these solutions changed during the time of the dialysis experiment.

## Results and Discussion

In dialysis experiments of this type the concentration of complex inside the bag will be either greater than or equal to the concentration outside. The concentration differences result whenever there is binding of the complex to the polyelectrolyte

or when the concentrations of all ions are such as to lead to a measurable Donnan membrane effect. The sodium polystyrene sulfonate had a molecular weight of 142,000 and the degree of sulfonation was between 1.0 and 1.1. The 0.005% solution is then  $2 \times 10^{-4}$  "N" in sulfonate. The solutions were made 0.05 M in NaCl in order to make the Donnan effect negligible, and the observed concentration differences across the membrane must be attributed to actual binding of the complex.

**1,10-Phenanthroline Complexes.**—Data collected on the binding of  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Ru}(\text{phen})_3^{2+}$  and  $\text{Co}(\text{phen})_3^{3+}$  are given in Table II, and the results are illustrated in Fig. 1 and Fig. 2. The results of the binding experiments are expressed in terms of  $r$ , the number of moles of complex bound per mole of polyelectrolyte, and  $A$ , the concentration of free complex ion in the solution with the polyelectrolyte.<sup>12</sup>

TABLE II

BINDING OF  $\text{M}(\text{phen})_3^{2+}$  OR  $^{3+}$  BY 0.005% NaPSS IN 0.05 M NaCl<sup>a</sup>

Complex	Temp., °C.	A × 10 <sup>6</sup>	r	r/A × 10 <sup>-4</sup>
$\text{Co}(\text{phen})_3^{3+}$	25.0	0.14	106	76
		.52	120	23
		.85	128	15
		1.39	129	9.3
		1.47	139	9.5
$\text{Fe}(\text{phen})_3^{2+}$	25.0	0.10	79	79
		.35	107	31
		.78	120	15
		1.34	136	10
		1.33	101	31
$\text{Ru}(\text{phen})_3^{2+}$	25.0	16.9	0.33	101
		39.7	1.22	129
		0.46	94	20
		1.39	117	8.4
		0.12	82	68
		0.25	96	38

<sup>a</sup> This method gives a precision of  $\pm 2\%$ .

Within experimental error, the iron and ruthenium complexes are bound to the same extent, with the binding by the cobalt complex being slightly different. A complete description of binding in these systems must be made in terms of multiple equilibria, such as those discussed in relation to the binding of proteins.<sup>13</sup> The data cannot be fit satisfactorily by any of the simpler assumptions that sometimes apply to these systems. As a result it is concluded that binding at the various sites of the polyanion cannot be considered to be independent of one another, nor can the interaction between sites be considered to be purely electrostatic.

The general feature of the binding of these complexes is an apparent saturation of the polyanion. This does not appear to be an electrical saturation; since there are approximately 670 sulfonate groups

(12) The results are expressed in terms customarily used to describe the binding in protein systems (see ref. 13). Since the molecular weight used to calculate the number of moles is but an average value, a referee has suggested that the results would better be stated in terms of the number of moles of complex bound per sulfonate group, rather than in terms of  $r$ . Values of  $r$  can be converted to these terms merely by dividing by 670.

(13) I. M. Klotz, in "The Proteins," Vol. I, Part B, edited by H. Neurath and K. Bailey, Academic Press, Inc., New York, N. Y., 1953, pp. 727-806.

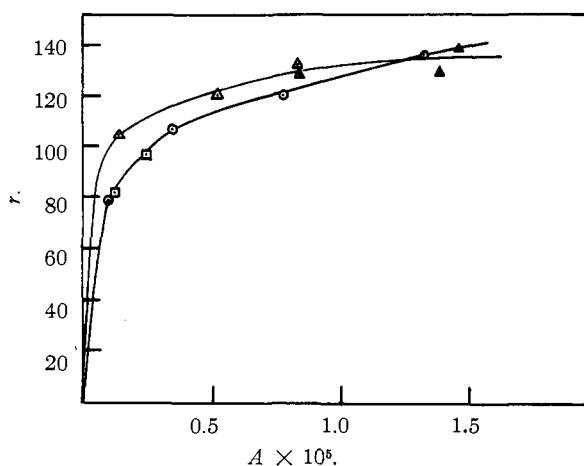


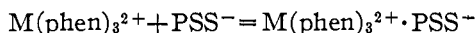
Fig. 1.—The binding of metal complexes by PSS<sup>-</sup> in 0.05 M NaCl at 25°: O, Fe(phen)<sub>3</sub><sup>2+</sup>; □, Ru(phen)<sub>3</sub><sup>2+</sup>; Δ, Co(phen)<sub>3</sub><sup>3+</sup>.

per ion of the polyelectrolyte,  $r$  would have to exceed 200 for electrical saturation by a +3 ion and would have to exceed 300 for a +2 ion.

It may be that the Co(III) complex exists to a great extent as an ion-pair with chloride ion, so that the binding for all three complexes is effectively that of +2 ions. Ion pair formation by the analogous Fe(III) complex has been reported.<sup>14</sup>

The saturation may be related to steric factors. The geometrical features of the phenanthroline complexes and the possibility of binding three sulfonate groups have been discussed previously.<sup>7</sup> Molecular models show that two of the three possible positions for sulfonates can be occupied by adjacent sulfonates, but that the third position, if occupied at all, must be filled by a sulfonate considerably down the polyelectrolyte skeleton. Using alternate, rather than adjacent, sulfonates does not improve the situation. Occupancy of the third position will require either unusual coiling of the skeleton of a single anion, or, less likely, the binding of two different polyanions to the same complex. The steric factors might then account for the similarity between the +2 and +3 complexes but do not obviously account for the particular saturation value observed.

In order to be able to make a quantitative comparison with other systems it would be expedient to determine the binding constant for the addition of only one complex cation to one polyanion.



The equilibrium constant is expressed by

$$K_1 = \frac{[M(\text{phen})_3^{2+} \cdot \text{PSS}^-]}{[M(\text{phen})_3^{2+}][\text{PSS}^-]}$$

The value of  $K_1$  can be obtained by extrapolating a plot of  $r/A$  vs.  $A$  to  $A = 0$ . At this limiting value of  $A$

$$\lim_{A \rightarrow 0} \left( \frac{r}{A} \right) = mK_A = K_1$$

where  $m$  is the number of equivalent sites on the polyanion, and  $K_A$  is the intrinsic constant for the

(14) J. E. Dickens, F. Basolo and H. M. Neumann, *THIS JOURNAL*, **79**, 1286 (1957).

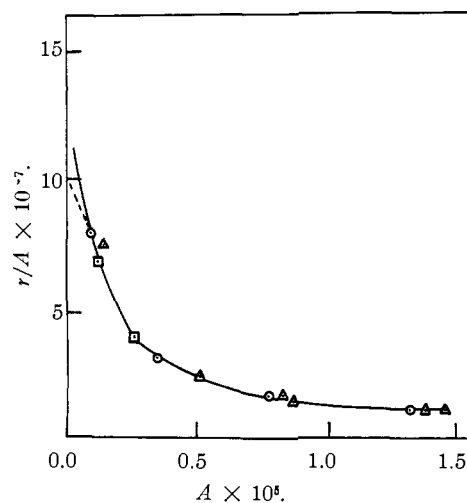


Fig. 2.—The binding of complex ions by PSS<sup>-</sup> in 0.05 M NaCl at 25°: O, Fe(phen)<sub>3</sub><sup>2+</sup>; □, Ru(phen)<sub>3</sub><sup>2+</sup>; Δ, Co(phen)<sub>3</sub><sup>3+</sup>.

binding. The best that can be said from Fig. 2 is that  $K_1$  must be greater than  $10^6$ . From the steric considerations previously discussed it is not clear whether  $m$  should be taken as 670 or  $1/2$  of that value. It appears to be safe to say that  $K_A$  is greater than  $2 \times 10^6$ .

The binding of Fe(phen)<sub>3</sub><sup>2+</sup> was measured at three temperatures in order to be able to determine the enthalpy of binding. The data reveal that the binding is practically the same at the three temperatures, indicating that the enthalpy of binding must be very small. This is consistent with the small heat of binding observed with Cu<sup>++</sup> and polyacrylate<sup>4</sup> and for certain protein systems.<sup>13</sup>

**Nitroamminecobalt(III) Complexes.**—The results of the comparative dialysis experiments carried out to determine the relative binding of several nitroamminecobalt(III) complexes by PSS<sup>-</sup> are given in Table III. Nitroamminecobalt(III)

TABLE III  
BINDING OF NITROAMMINECOBALT(III) IONS BY 0.005% NaPSS IN 0.05 M NaCl at 25°

Complex <sup>a</sup>	$A \times 10^4$	$r \times 10^{-1}$
Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> <sup>2+</sup>	2.39	11
<i>cis</i> -Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	2.44	3.4
<i>trans</i> -Co(NH <sub>3</sub> ) <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	2.62	2.3
<i>cis</i> -Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	2.44	0.0
<i>trans</i> -Co(en) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	2.44	.0
Co(en) <sub>2</sub> NH <sub>3</sub> NO <sub>2</sub> <sup>2+</sup>	2.09	.0
Co(trien)NH <sub>3</sub> NO <sub>2</sub> <sup>2+</sup>	2.40	.0
Co(en) <sub>2</sub> pyNO <sub>2</sub> <sup>2+</sup>	2.37	8.8
Co(bipy) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> <sup>+</sup>	2.12	23

<sup>a</sup> These symbols are used in the above complexes: en = ethylenediamine; trien = triethylenetetramine; py = pyridine; bipy = 2,2'-bipyridine.

complexes were chosen for this investigation because they are known not to undergo extensive hydrolysis during the 12 hr. period required for equilibration. The data in Table III permit the comparison of the effect of several factors on the binding of metal complex ions by polyanions. The first three complexes show that the greater the positive charge on the complex the greater the

extent of binding. Attempts to include  $\text{Co}(\text{NH}_3)_6^{3+}$ ,  $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$  and  $\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4^-$  in this study failed. The first complex,  $\text{Co}(\text{NH}_3)_6^{3+}$ , formed a precipitate with  $\text{PSS}^-$  and the other two underwent some decomposition during the experiment. The threefold difference in binding between the monovalent and divalent cations suggests that electrostatic forces are involved. It should be recalled that for the larger complex ions containing aromatic ligands,  $\text{Fe}(\text{phen})_3^{2+}$  vs.  $\text{Co}(\text{phen})_3^{3+}$ , there is essentially no difference in binding. This would indicate that the electrostatic contribution to binding becomes relatively less important as the size and/or aromaticity of the complex increases.

A comparison of the data given for the last four complexes in Table III shows the effect that the presence of aromatic ligands in a complex ion has on its degree of binding. The complex  $\text{Co}(\text{en})_2\text{NH}_3\text{NO}_2^{2+}$  is not bound to  $\text{PSS}^-$  under the conditions of these experiments whereas the corresponding complex  $\text{Co}(\text{en})_2\text{pyNO}_2^{2+}$  where pyridine, py, takes the place of  $\text{NH}_3$ , is definitely bound. Furthermore the monovalent complex  $\text{Co}(\text{bipy})_2(\text{NO}_2)_2^+$ , bipy = 2,2'-bipyridine, is bound approximately 2.5 times more than is the pyridine complex. Likewise  $\text{Fe}(\text{phen})_3^{2+}$ , even in a sixteen-fold more dilute solution, is bound about 1.5 times more than is  $\text{Co}(\text{en})_2\text{pyNO}_2^{2+}$ . It is therefore apparent that the greater the number of aromatic ligands in a complex, the greater the extent of binding of the complex cation by an aromatic polyanion. This would appear to result from an increase in the van der Waals interaction forces.

If the binding of metal complexes containing aromatic ligands is primarily due to van der Waals interaction forces then the similar binding of the  $\text{Co}(\text{phen})_3^{3+}$  and  $\text{Fe}(\text{phen})_3^{2+}$  can be accounted for.

The slightly greater binding of *cis*- $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^+$  than the *trans*-isomer is in agreement with observations on the ion-exchange<sup>15</sup> and chromatographic<sup>16</sup> separation of these isomers. This difference between the *cis* and *trans* isomers has been attributed to the unsymmetrical electrical dipole of the *cis* form giving rise to greater binding or adsorption than does the electrically symmetrical *trans* isomer. There is one other case where the results of these studies on the binding of complex cations by polyanions agree with the ion-exchange and chromatographic experiments. This is the observation that the replacement of two ammonia molecules in a complex by an ethylenediamine(en) molecule, *i.e.*,  $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2^+$  vs.  $\text{Co}(\text{en})_2(\text{NO}_2)_2^+$  (Table III), is accompanied by a decrease in binding of the complex. Since the complex containing ethylenediamine is larger than that containing ammonia, it may be argued that in these systems the binding is primarily due to electrostatic forces so that the smaller complex cation is bound to the greater extent. One other feature which also changes and may be of some importance is the number and accessibility of the hydrogens on nitrogen atoms in the complex. If hydrogen bonding is a contributing factor to the binding of the complex, then it follows that the ammonia system may be bound more than is the ethylenediamine system.

**Acknowledgment.**—The authors wish to thank Prof. I. M. Klotz for helpful suggestions and discussions.

(15) E. L. King and R. R. Walters, *THIS JOURNAL*, **74**, 4471 (1954).

(16) A. Jensen, J. Bjerrum and F. Woldbye, *Acta Chem. Scand.*, to be published.

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## Competitive Binding of Cations by Polymethacrylate Ion<sup>1</sup>

BY ARNE JENSEN, FRED BASOLO AND H. M. NEUMANN

RECEIVED JUNE 25, 1958

The binding of tris-(1,10-phenanthroline) cationic complexes of iron(II), ruthenium(II) and cobalt (III) by polymethacrylate ion has been studied by a dialysis method. By an extension of the method it was possible to use the distribution of the ruthenium(II) complex to measure the binding of alkali metals. It was found that the alkali metal ions are all bound to approximately the same extent but appreciably more than is the tetramethylammonium ion.

The dialysis method which proved useful in the study of association between complex ions and polystyrene sulfonate<sup>2</sup> has been applied to a study of the association between complexes of (1,10-phenanthroline) and polymethacrylate ( $\text{PMA}^-$ ) ion. Kinetic evidence for association in this latter system already has been presented.<sup>3</sup> By a slight modification of the dialysis conditions the binding of alkali metal ions to the polyelectrolyte also has been measured.

(1) This investigation was supported by a Grant-in-Aid from the National Institutes of Health, Grant No. RG-4335.

(2) A. Jensen, F. Basolo and H. M. Neumann, *THIS JOURNAL*, **81**, 509 (1959).

(3) A. Jensen, F. Basolo and H. M. Neumann, *ibid.*, **80**, 2354 (1958).

### Experimental

**Materials.**—The tris-(1,10-phenanthroline)-ruthenium(II) perchlorate was prepared by the method of Dwyer.<sup>4</sup> The polymethacrylic acid, with a reported mol. wt. of 560,000 as determined by light scattering technique, was supplied by the Monsanto Chemical Company. This polymethacrylic acid was used without further purification. The sodium salt was prepared by the addition of an equivalent amount of sodium hydroxide to a solution of the acid. All of the alkali metal chlorides and the tetramethylammonium chloride are commercially available.

**Dialysis.**—Dialysis measurements were made by the method described in the accompanying article.<sup>2</sup> All experiments, including blank runs, were performed in triplicate, and the average values are reported.

(4) F. P. Dwyer, J. E. Humpoletz and R. S. Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 212 (1947).