# **15.** The Conductivities of Some Complex Cobalt Chlorides and Sulphates.

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From the conductivities of dilute solutions at  $25^{\circ}$  of the chlorides and sulphates of hexamminocobalt, trisethylenediaminocobalt, and trispropylenediaminocobalt, the limiting mobilities of the cobaltic cations, and the dissociation constants of the ion pairs formed between these and chloride and sulphate ions have been determined. The increasing radii of the complex cations are found to alter systematically the limiting mobilities of these ions and the dissociation constants of their sulphates. A comparison is drawn between the sizes of these ion pairs as calculated by Stokes's law and by Bjerrum's method.

AMONG the various factors which influence the extent to which ions associate in solution is their effective size. This may be seen, for instance, by a comparison of similar salts containing organic ions in non-aqueous solvents, where the dissociation constants are found to increase with increasing size of the organic ions (Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 3614; Davies, "Conductivity of Solutions," 1933, Chap. 18). In aqueous solutions, hydration effects distort this generalisation. So far as quantitative relations are concerned, Bjerrum (Kgl. Danske Vidensk. Selskab., 1926, **7**, No. 9) has proposed, for those cases where the forces are essentially polar, the relation

where  $b = (|z_1 z_2|)^2 / aDkT$ ; a represents the distance of closest approach of the ions forming

the ion pair. Generally, this has been used to calculate values of a from experimentally found dissociation constants, when from the calculated values of Q(b), b can be obtained from tables (Bjerrum, *loc. cit.*) and hence a found. Alternatively, by assuming a, as found from data with aqueous solutions, to be constant, one can compare the variation of K with variations in the dielectric constant D when this is altered by the addition of various organic solvents to water. This implies that the extent of ion-hydration remains constant, but the agreement with experimentally found results appears to be fairly good with large ions such as lanthanum ferricyanide (James, J., 1950, 1094).

The sizes of ions, when they are of similar character, also cause variations in their mobilities. This may be seen for instance with the polydecylamine salts (Ralston and Hoerr, J. Amer. Chem. Soc., 1942, 64, 773) and some simple aliphatic anions (Bredig, Z. physikal. Chem., 1894, 13, 191). A development of this aspect of mobilities is the well-known instance of the alkalimetal cations where the mobilities are in inverse order to the radii of the bare ions owing to the effective radii of the hydrated ions being in the order Li > Na, etc., which is the order of increasing mobilities.

A quantitative relation between ion mobilities and their radii is expressed by Stokes's law

### $v = X z \varepsilon / 6 \pi \eta a$

which, in terms of conductivity in aqueous solution at 25°, becomes

$$a = 9.16 \times 10^{-7} z / \Lambda_i^{\circ}$$
 . . . . . . . . . . . (2)

*a* being the ion radius of valency *z* and limiting ionic mobility  $\Lambda_i^{\circ}$ . With small ions whose radii are of the same order of magnitude as the solvent molecules, it is doubtful if the solvent viscosity truly describes the retarding effect. Furthermore, hydration effects introduce additional complications. With large spherical ions we would expect solvation effects to be much smaller, owing to the low density of charge on their surfaces, and we would have conditions more favourably suited to the requirements of Stokes's law. With this in mind, we have followed the conductivities of the chlorides and sulphates of some rather large symmetrical complex cobalt ions, which gradually increase in size. The chlorides enable the limiting ion mobilities,  $\Lambda_i^{\circ}$ , to be found and their radii to be calculated from (2). With the sulphates, the dissociation constants of the ion pairs have fairly low values, and from these, Bjerrum's expression gives values of *a* which may be compared with those derived from Stokes's law.

#### EXPERIMENTAL.

The conductivity equipment and the determination of the cell constants have been described in earlier papers (Davies, J., 1937, 432; Davies and Monk, J., 1949, 413). All the measurements were at  $25^{\circ}\pm0.01^{\circ}$ . Hexamminocobalt(III) chloride,  $Co(NH_3)_6Cl_3$ , was prepared by the method of Bjerrum and Reynolds ("Inorganic Syntheses," McGraw-Hill, 1946, Vol. II, Chap. 8). The crystals were thoroughly washed with conductivity water and absolute alcohol, then dried to constant weight over phosphoric oxide and paraffin wax in a vacuum. The stock solutions were made up by weight, buoyancy corrections being applied. The resistance readings, when the cell was not disturbed, were found to drift slowly, but on shaking the cell fairly vigorously the original readings could always be reproduced. This effect, which is undoubtedly one of adsorption on the electrodes, was also noticed by Hartley and Donaldson (*Trans. Faraday Soc.*, 1937, 33, 457) in their conductivity measurements with this salt; they attempted a time extrapolation to obtain the correct readings.

Trisethylenediaminocobalt(III) chloride was formed by Work's method ("Inorganic Syntheses," Vol. II, Chap. 8). The crystals were dissolved in water and reprecipitated by addition of pure ethyl alcohol. This was repeated several tlmes, and the product dried in a vacuum oven at 50—60°. The salt was slightly hygroscopic, so the stock solutions were made up approximately by weight, and the exact concentrations found gravimetrically as silver chloride; the duplicates of these agreed to within  $\pm 0.03\%$ . These solutions had a pH of >6. Resistance readings were constant, adsorption effects being very slight.

Trispropylenediaminocobalt(III) chloride was prepared as follows. 11.6 Ml. of specially pure B.D.H. propylenediamine were diluted to 40 ml. with water and partly neutralised with 5.3 ml. of concentrated hydrochloric acid in 17 ml. of water. This mixture was poured into a solution of 5.3 g. of hydrated cobalt chloride in 17 ml. of water. Oxygen was bubbled through rapidly for 3 hours. The solution was evaporated to about 15 ml., then 4 ml. of concentrated hydrochloric acid and 30 ml. of ethyl alcohol were added to precipitate the salt. This was washed with alcohol until the washings had a pH of >6, then dried in a vacuum desiccator over phosphoric oxide and paraffin wax. The concentrations of the stock solutions were determined gravimetrically as above. A slight drift in the resistance readings when the cell was left stationary was readily overcome by shaking the cell before taking readings.

Hexamminocobalt(III) sulphate. This was prepared by dissolving 27 g. of hydrated cobalt sulphate and 15 g. of ammonium sulphate in 20 ml. of water, adding 0.5 g. of activated decolorising animal

charcoal as catalyst, and 50 ml. of concentrated ammonia solution, then drawing air through the solution for 5 hours. The product was filtered off, dissolved, and the animal charcoal filtered off, the sulphate being precipitated by addition of 100 ml. of concentrated sulphuric acid and cooling to 0°. It was washed with water, dissolved in water, and precipitated with alcohol, this process being repeated six times. Although the salt was dried in a vacuum oven at 50°, it could not be brought to constant weight, being slightly hygroscopic. Consequently, the concentrations of the stock solutions were found by quantitative sulphate analysis. Vogel's method ("Quantitative Analysis," Longmans, Green and Co., p. 478) was used, the barium sulphate being weighed in sintered porcelain crucibles; duplicates agreed to within  $\pm 0.03\%$ . The stock solutions had a pH of *ca*. 6. Adsorption effects were very small, and it was easy to get consistent resistance readings.

#### TABLE I.

10 <sup>4</sup> C.	$10^{2}C^{\frac{1}{2}}$ .	Λ.	$\Lambda + bC^{\dagger}$	. a.	10 <sup>3</sup> к.	10 <b>⁴</b> C.	$10^2 C^{\frac{1}{2}}$ .	Λ.	$\Lambda + bC$	<sup>1</sup> / <sub>3</sub> . a.	10 <sup>з</sup> к.
		(i)	Conduci	tivity of h	iexammi	nocobalt(III)	chlorid	e solutio	ns.		
1.5374	1.240	171.44	175.33	0.9970	45	6.6539	2.578	166.99	174.38	0.0840	39
9.9491	1.408	170.46	175.16	0.0047	20	7.0800	2.661	165.95	174.10	0.0917	02 90
2.2421	1.670	160.75	174.00	0.0098	22	7.0000	2.001	165.95	174.19	0.0010	29
4.4657	9.112	168.10	174.73	0.0801	22	8.4888	2.015	164.02	174.07	0.0700	00 91
4.5705	2.110	100.10	174.73	0.9691	00 94	0.4490	2.910	104.90	179.00	0.9799	31
5.7910	2.130	166.04	174.74	0.9892	04 91	9.4439	3.010	104.20	179.93	0.9707	29
5.1917	2.400	100.94	174.40	0.9657	31						
		(11) Co	nductivit	y of triset	hylenedi	aminocobalt(	(111) chlo	oride sol	utions.		
2.1450	1.465	146.33	150.71	0.9917	22	5.8170	2.412	142.80	150.01	0.9779	18
2.3865	1.545	145.83	150.45	0.9876	16	6.1207	2.474	142.44	149.84	0.9749	17
2.5895	1.609	145.52	150.33	0.9854	15	7.2284	2.689	141.72	149.76	0.9729	<b>20</b>
3.4420	1.855	<b>144</b> .89	150.44	0.9864	<b>21</b>	7.8923	2.809	141.23	149.63	0.9704	18
3.8508	1.962	144.38	150.25	0.9838	18	10.090	3.177	139.79	149.29	0.9634	19
4.4106	$2 \cdot 100$	144.00	150.28	0.9834	<b>21</b>	10.143	3.185	$139 \cdot 86$	149.38	0.9647	<b>20</b>
5.4216	2.328	142.95	<b>149</b> .91	0.9767	18	12.158	3.487	138.63	149.06	0.9584	20
		(iii) Con	nductivity	of trispr	opylene	diaminocobal	t(III) ch	loride se	olutions.		
1.9246	1.387	137-18	141.01	0.9929	23	6.5440	2.558	133-31	140.36	0.9813	27
2.2269	1.492	136.93	141.04	0.9936	30	7.4520	2.730	132.50	140.03	0.9751	22
3.5599	1.887	135.48	140.68	0.9873	23	8.3983	2.898	132.05	140.04	0.9750	24
4.3626	2.087	134.93	140.69	0.9872	$27^{-1}$	9.0360	3.006	131.57	139.82	0.9710	22
5.9195	2.433	133.77	140.48	0.9835	28	10.115	<b>3</b> ·180	131.05	139.82	0.9709	$\overline{24}$
10 <b>4</b> C.	10 <b>2</b> C	<b>i</b> .	Λ.	10 <sup>5</sup> x.	10 <sup>4</sup> ĸ.	10 <b>4</b> C.	10ºC	ł.	Λ.	10 <sup>5</sup> x.	10ªĸ.
		(iv)	Conduc	tivity of I	hexammi	nocobalt(III)	) sulphai	e solutio	ons.		
0.755	0.86	้า ผู้	1.04	0.930	2.80	5.284	9.390	1 19	9.19	5.06	9.71
1.492	1.910	8 10 9 15	0.00	0.760	2.80	8.406	9.800	$11^{-12}$	2.65	10.04	2.01
0.557	1.500	5 10 D 14	0.33	1.94	2.00	0.029	2.000	2 11	0.55	10.94	2.04
2.007	1.093	5 14 2 19	4.57	1.04	2.18	19.70	9.564	10	9.10	12.30	0.70
3,390 4,380	9.000	0 10 N 19	4·07 9.16	4.96	2.10	14.94	9.959		0.00	19.90	2.10
4.671	2.090	1 19	8.95	4.30	2.13	14.04	9.007	5 9	9.77	23.00	2.10
4.071	2.10	1 12	0.00	4.19	2.15						
		(v	) Conduc	tivity of	trisethyli	enediaminoco	bbalt(111)	sulpha	te.		
1.278	1.130	) 13	6.32	0.457	3.88	8.604	2.932	2 10	1.16	10.5	3.25
3.048	1.746	3 12	4·11	1.95	3.92	9.082	3.013	3 10	3.74	10.3	3.65
3.584	1.893	311	7.74	2.92	3.18	10.68	3.208	39	7.11	14.1	3.29
4.667	2.160	) 11	6·13	<b>3</b> ⋅88	3∙96	$13 \cdot 12$	3.623	39	1.89	19·1	2.94
6·141	2.480	0 11	1.18	5.82	3.86						
		(vi)	Conduct	ivity of th	rispropy	lenediaminod	cobalt(II	I) sulph	ate.		
1.858	1.363	3 13	3.77	0.240	16.6	7.847	2.801	12	0.98	2.49	19.1
2.407	1.55	1 13	2.78	0.306	21.0	7.993	2.82	11	9.74	2.86	16.9
3 662	1.914	4 12	9.02	0.698	19.2	9.541	3.089	$\hat{\mathbf{j}}$	7.48	3.76	17.0
4.924	2.219	9 12	6.32	1.14	19.5	11.27	3.357	7 11	6.23	4.46	18.9
5.733	2.394	4 12	4.02	1.62	17.5	14.61	3.826	3 11	2.56	6.61	19.0

Trisethylenediaminocobalt(III) sulphate. 61 Ml. of 70% ethylenediamine in water were partly neutralised with 1.5 ml. of concentrated sulphuric acid in 10 ml. of water. To this, a solution of 24 g. of cobalt sulphate in 75 ml. of water was added, and a vigorous stream of air passed through for 5 hours. The mixture was evaporated on a water-bath until a crust formed on the surface. On addition of 15 ml. of concentrated sulphuric acid and 30 ml. of ethyl alcohol, the salt was precipitated. It was filtered off and washed with alcohol until the washings were colourless. The sulphate was recrystallised by dissolving it in water and adding alcohol, this process being repeated five times. The stock solutions were analysed gravimetrically as in the previous case, duplicates agreeing within  $\pm 0.03\%$ . The stock solutions had a pH of ca. 4, which in spite of the numerous recrystallisations was probably due to traces of free acid. In place of the usual solvent correction, a pH-concentration curve was obtained and the pH's of the solutions whose resistances were measured were obtained by interpolation. Since hydrogen

ions contribute to the major part of the solvent conductivity, and the specific conductivity due to these is given by  $\kappa = 350[H'] \times 10^{-3}$ , where 350 is the mobility of the ion (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, p. 172), this amount was subtracted from the measured specific conductivities before calculation of the equivalent conductivities.

Trispropylenediaminocobalt(III) sulphate. 11.6 Ml. of specially pure B.D.H. propylenediamine were diluted to 41 ml. with water, and poured into 17 ml. of water containing 5.3 g. of cobalt sulphate. Air was bubbled through vigorously for 5 hours. The solution was evaporated to 15 ml., and the salt precipitated by addition of 4 ml. of concentrated sulphuric acid and 40 ml. of ethyl alcohol. After cooling, the salt was filtered off. Initially, it formed an oil, but crystallised out after vigorous stirring. Methyl alcohol was used during the recrystallisations, and it caused the salt to settle out as a fine yellow powder. After several recrystallisations from water and alcohol, the salt was dried in a vacuum oven at  $30-50^{\circ}$  for 2 days. The concentrations of the stock solutions were found gravimetrically as sulphate, duplicates agreeing to within  $\pm 0.03\%$ . The pH of the strongest solution was 4.9, and solvent corrections were applied as in the previous case.

The results are given in Table I.

#### DISCUSSION.

From the conductivities of the chlorides, the limiting mobilities of the cations may be obtained with a high degree of accuracy. For this purpose Onsager's method of extrapolation



was used (*Physikal. Z.*, 1927, 28, 277). An approximate value of  $\Lambda^{\circ}$ , the equivalent conductivity at zero concentration, is obtained in the usual manner, *i.e.*, by plotting  $\Lambda$  against  $C^{\frac{1}{2}}$ . From this the theoretical slope *b* is calculated by means of Onsager's conductivity equation, and then  $\Lambda + bC^{\frac{1}{2}}$  is plotted against *C*. These sensitive plots are shown in Fig. 1, and  $\Lambda_i^{\circ}$ , the limiting mobilities of the cations thereby obtained, are listed in Table II. The experimental conductivity curves,  $\Lambda$  being plotted against  $C^{\frac{1}{2}}$ , lie slightly below the theoretical line; this is illustrated in the case of hexamminocobalt(III) chloride in Fig. 2. This slight difference may be attributed to ion-pair formation between the cation and chloride ions. The dissociation constant corresponding to the equilibrium  $Co(NH_3)_6^{\cdots} + Cl' \Longrightarrow Co(NH_3)_6Cl^{\cdots}$  has been calculated as follows. Let  $(1 - \alpha)m$  represent the concentration of  $Co(NH_3)_6^{\cdots}$  is then  $\alpha m$ , and the solution is treated as a mixture of (i) the 1: 3-valent salt  $[Co(NH_3)_6^{\cdots}, 3Cl']$  of molar concentration  $\alpha m$ , for which the Onsager equation is  $\Lambda_{31} = 175 \cdot 55 - 221 \cdot 5I^{\frac{1}{2}}$ , where *I* is the actual ionic strength  $= \frac{1}{2}[[Cl'] + 4[Co(NH_3)_6Cl^{\cdots}] + 9[Co(NH_3)_6^{\cdots}]^{\frac{1}{2}} = (1 + \alpha)C$ , where *C* is the

equivalent concentration, and (ii) the 1:2-valent salt  $[Co(NH_3)_6Cl^*,2Cl']$  of molar concentration  $(1 - \alpha)m$ , for which the Onsager equation is  $\Lambda_{21} = 142 \cdot 5 - 146 \cdot 5I^{\frac{1}{2}}$ . In this case, the mobility of the bivalent ion-pair is taken as two-thirds of that of the tervalent cation. The solvent-corrected specific conductivity of the solution is given by

$$\begin{split} 10^{3}\kappa &= 3\alpha m \Lambda_{\rm Co(NH_{2})_{6}} + 2(1-\alpha) m \Lambda_{\rm Co(NH_{2})_{6}Cl'} + (2+\alpha) m \Lambda_{\rm Cl'} \\ &= 3\alpha m \Lambda_{31} + 2(1-\alpha) m \Lambda_{21} \end{split}$$

Whence

$$\begin{split} \Lambda &= 10^{3} \kappa / 3m = \alpha \Lambda_{31} + \frac{2}{3} (1 - \alpha) \Lambda_{21} \\ &= 94.94 - 97.7I^{\frac{1}{2}} + \alpha (80.6 - 123.8I^{\frac{1}{2}}) \end{split}$$

At first,  $\alpha$  is assumed to be unity and the corresponding value of *I* is used in this equation, thereby giving a truer value to  $\alpha$  with which to calculate a truer value of *I*, and so on, until constant figures are obtained. The dissociation constant results

$$K = \frac{\{\text{Cl}'\}\{\text{Co(NH_3)}_6^{\bullet\bullet\bullet}\}}{\{\text{Co(NH_3)}_6\text{Cl}^{\bullet\bullet}\}} = \frac{(2+\alpha)\alpha m f_1 f_2}{(1-\alpha) f_3}$$

are given in Table I (i). The activity coefficients  $f_1$ ,  $f_2$ , and  $f_3$  have been calculated from the Debye-Huckel equation,  $-\log f_i = 0.509 z_i^2 I^{\frac{1}{2}}$  where  $z_i$  is the ion valency. Exactly the same treatment has been applied to the other two chlorides, and the average results are 0.032 for  $Co(NH_3)_6CI^*$ , 0.019 for Co en<sub>3</sub> CI<sup>\*</sup>, and 0.025 for Co pn<sub>3</sub> CI<sup>\*</sup>. Since these are dependent on very slight differences between theory and practice, and are sensitive to very small changes in  $\Lambda^\circ$ , we cannot expect these figures to do more than indicate the orders of the dissociation constants, but it is noteworthy that they are comparable with the values obtained with 1: 3-valent salts where the anion is tervalent, namely, 0.068 for NaP<sub>3</sub>O<sub>9</sub>" (Davies and Monk, J., 1949, 413), and 0.06 for KFe(CN)<sub>6</sub>" and KCo(CN)<sub>6</sub>" (James and Mork, Trans. Faraday Soc., in the press).

The limiting cation mobilities obtained from the chlorides, together with 80.00 for the sulphate ion (Jenkins and Monk, J. Amer. Chem. Soc., 1950, 72, 2695), have been used in discussing the conductivities of the sulphates. This method of obtaining  $\Lambda^{\circ}$  is preferable to obtaining it by extrapolation of the sulphate conductivities, since this is a rather uncertain method with higher-valent electrolytes. In Fig. 2, where the conductivity curve for hexamminocobalt(III) sulphate is compared with the theoretical Onsager line for the fully ionised electrolyte, there is a large discrepancy, through strong association between the complex cation and the sulphate ions. This is also the case with the other two sulphates, and the dissociation constants of these, e.g., for the equilibrium  $Co(NH_3)_6(SO_4)^* \Longrightarrow Co(NH_3)_6^{**} + SO_4^{*'}$ , have been obtained as follows. The three Onsager equations for the three types of ion are

For Co(NH<sub>3</sub>)<sub>6</sub><sup>•••</sup> 
$$\Lambda_1^i = 99.2 - 224.4I^{\frac{1}{2}}$$
  
,, SO<sub>4</sub><sup>••</sup>  $\Lambda_2^i = 80.00 - 168.4I^{\frac{1}{2}}$   
,, Co(NH<sub>3</sub>)(SO<sub>4</sub>)<sup>•</sup>  $\Lambda_3^i = 33.07 - 74.8I^{\frac{1}{2}}$ 

The limiting mobility of the ion-pair is taken as one-third of that of the tervalent cation. The total ionic strength is given by

$$I = \frac{1}{2} \{9[Co(NH_3)_6^{**}] + 4[SO_4^{''}] + [Co(NH_3)_6(SO_4)^{*}] \}$$

and if we let x be the concentration of the ion-pair at a total molar concentration m, then  $I = 15m - 6x = 2 \cdot 5C - 6x$ . The observed conductivity,  $\Lambda$ , is related to the calculated conductivity by

$$6\Lambda m = 3(2m - x)\Lambda_1^{i} + 2(3m - x)\Lambda_2^{i} + x\Lambda_3^{i}$$
  
*i.e.*, 
$$\Lambda_1^{i} + \Lambda_2^{i} - \Lambda = (x/C)(3\Lambda_1^{i} + 2\Lambda_2^{i} + \Lambda_3^{i})$$

From this, and from the ionic-strength relation, by approximating until constant x and I values are derived, the dissociation constant

$$K = \frac{\{\operatorname{Co}(\operatorname{NH}_3)_6^{(**)} \{ \operatorname{SO}_4^{(*)} \}}{\{\operatorname{Co}(\operatorname{NH}_3)_6 (\operatorname{SO}_4)^* \}} = \frac{(2m-x)(3m-x)f_1f_2}{xf_3}$$

has been obtained; the activity coefficients were calculated as in the previous case. The results are given in the tables, and the average values are:  $Co(NH_3)_6(SO_4)^* = 2.77 \times 10^{-4}$ ,  $Co en_3 (SO_4)^* = 3.55 \times 10^{-4}$ , and  $Co pn_3 (SO_4)^* = 1.75 \times 10^{-3}$ . The trend in these as the

size of the cobalt cation increases is in the expected direction.  $LaSO_4^{\bullet}$ , where we have a similar type of association, has a dissociation constant of the same order as these, namely  $2.4 \times 10^{-4}$  (Jenkins and Monk, *loc. cit.*).

In Table II, the variation in the limiting mobilities of the complex cobaltic cations also follows the expected trend; *i.e.*, as the size increases, the mobility becomes less. Inserting these results in equation (2), we obtain the ionic radii *a* given in Table II. By applying the same treatment to the data for the chloride ion (Harned and Owen, *loc. cit.*) and sulphate, the radii of the anions are obtained also. Addition of these cation and sulphate ionic radii gives the size of the ion pair, which may be compared with those derived from Bjerrum's equation (1).

#### TABLE II.

			Radii of ion-pairs (A.).		
Λ <b>;°</b> .	a (A.).	Ion-pair.	Eqn. (1).	Eqn. (2).	
<b>99</b> ·2	2.77	$Co(NH_3)_6(SO_4)^*$	2.56	5.06	
74.7	3.68	$Co(en)_3(SO_4)$	4.28	5.97	
65.06	4.23	$Co(pn)_{3}(SO_{4})^{\bullet}$	5.76	6.52	
76.34	1.20				
<b>80.00</b>	2.29				
	Λ;°. 99·2 74·7 65·06 76·34 80·00	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\Lambda_4^{\circ}$ . $a$ (A.).       Ion-pair. $99 \cdot 2$ $2 \cdot 77$ $Co(NH_3)_6(SO_4)^{\circ}$ $74 \cdot 7$ $3 \cdot 68$ $Co(en)_3(SO_4)^{\circ}$ $65 \cdot 06$ $4 \cdot 23$ $Co(pn)_3(SO_4)^{\circ}$ $76 \cdot 34$ $1 \cdot 20$ — $80 \cdot 00$ $2 \cdot 29$ —	Radii of io $\Lambda_4^{\circ}$ .       a (A.).       Ion-pair.       Eqn. (1). $99 \cdot 2$ $2 \cdot 77$ $Co(NH_3)_6(SO_4)^*$ $2 \cdot 56$ $74 \cdot 7$ $3 \cdot 68$ $Co(en)_3(SO_4)^*$ $4 \cdot 28$ $65 \cdot 06$ $4 \cdot 23$ $Co(pn)_4(SO_4)^*$ $5 \cdot 76$ $76 \cdot 34$ $1 \cdot 20$ —       — $80 \cdot 00$ $2 \cdot 29$ —       —	

Although the sizes of the ion pairs are of the right order, it is only in the last case that the two methods give comparable results. Even with the use of Stokes's law, however, which gives the larger radii, it is probable that the calculations are on the small side, since the radius of the unhydrated chloride ion is 1.81 A. (Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1939, Chap. 10) whereas our calculations for the hydrated ion give 1.20 A. It is possible that with cases where both ions forming the ion-pair are large and symmetrical, truer results might be obtained. A pointer in this direction is provided by the case of lanthanum ferricyanide (Davies and James, *Proc. Roy. Soc.*, 1948, A, 195, 116), which has a dissociation constant of  $1.83 \times 10^{-4}$  at  $25^{\circ}$ , corresponding to a "Bjerrum distance" of 7.20 A. From the mobilities of the lanthanum and ferricyanide ions (Harned and Owen, *loc. cit.*), Stokes's law gives 6.67 A.

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