113. *Ion-pair Constants of Some Chloropentamminecobalt*(III) *Salts from* pH (*Glass Electrode*) *and Solubility Measurements.*

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The thermodynamic dissociation constants of ion-pairs formed between the chloropentamminecobalt(III) ion and a variety of ligands have been estimated from pH and solubility studies at 25 and 35°. Several sodium dicarboxylates have also been examined by the pH method.

IN ORDER to interpret the effects of salts upon the rates of reactions involving ions it is necessary to assess the concentrations of ion-pairs which may be present. If independent measurements are used, they must be made in a small fraction of the half-lives of the reactions. This study is concerned with a complex ion with an aquation half-life of ~100 hours and both methods of measuring ion-pair dissociation constants required less than 1 hour.

pH *Measurements.*—These were made with the conventional system

$$\text{Glass electrode} \mid H_2L\ (m_1),\ \text{NaOH}\ (m_2),\ \text{Cp}(NO_3)_2\ (m_3) \mid \text{Sat. KCl, Calomel}$$

($\text{Cp} = Co(NH_3)_5Cl^{2+}$, L = ligands of dicarboxylic acids), as described previously,[1] first by equilibrating a solution of $m_1 + m_2$ in order to calculate E_0 of

$$E = E_0 - k'\text{pH} \qquad (1)$$

($k' = 2{\cdot}303\ \boldsymbol{RT}/\boldsymbol{F}$) where E is the measured potential and the pH is calculated from the known dissociation constants [2,3] K_1 and K_2 of H_2L. With E_0 known, pHs of mixtures of $m_1 + m_2 + m_3$ are obtainable. The expressions involved in these steps and for obtaining the dissociation constants K of the CpL ion-pairs are

$$\log K_1 = \log\,[HL^-] - \log\,[H_2L] - \text{pH} - \boldsymbol{F}(I) \qquad (2)$$

$$\log K_2 = \log\,[L^{2-}] - \log\,[HL^-] - \text{pH} - 3\boldsymbol{F}(I) \qquad (3)$$

$$\log\,[H^+] = \boldsymbol{F}(I) - \text{pH} \qquad (4)$$

$$[HL^-] = 2m_1 - m_2 - 2[H_2L] - [H^+] \qquad (5)$$

$$\boldsymbol{F}(I) = A\{I^{\frac{1}{2}}(1 + I^{\frac{1}{2}}) - 0{\cdot}3I\} \qquad (6)$$

$$I = 2m_2 + 3m_3 - m_1 - 4[\text{CpL}] + 2[H^+] + 2[H_2L] \qquad (7)$$

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[1] Archer and Monk, *J.*, 1964, 3117.

[2] Robinson and Stokes, " Electrolytic Dissociation," Butterworths Publishing Co., London, 1959.

[3] Kortum, Vogel, and Andrussow, " Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths Publishing Co., London, 1961.

$$[\mathrm{CpL}] = m_1 - [\mathrm{L}^{2-}] - [\mathrm{HL}^-] - [\mathrm{H_2L}] \qquad (8)$$

$$\log K = \log (m_3 - [\mathrm{CpL}])[\mathrm{L}^{2-}] - \log [\mathrm{CpL}] - 8\boldsymbol{F}(I) \qquad (9)$$

Expression (6) is that of Davies[4] and $A = 0{\cdot}50$ at 25° and 0·51 at 35°. The calculations were made by means of an IBM 1620 computer. The programme was arranged so that [CpL], [H^+], and [H_2L] were first taken as zero and then found to the nearest 0·000001 by an iterative procedure. Where the values of K for a particular run showed a slight trend with increasing m_3 it was assumed that E_0(calc.) was slightly wrong, and was automatically adjusted in 0·1 mv steps until the trend was removed. The appropriate E_0 (used) and E_0 (calc.) values are shown in the Tables. This device assumes that CpL_2^{2-} formation is negligible. It is supported by studies of the cobaltous and zinc systems[5] where this ion-pair only forms to a slight extent in a few cases.

TABLE 1.

Dissociation constants of chloropentamminecobalt(III) salts from pHs at 25°.

Ligand	Symbol	$10^5m_1'$	$10^5m_2'$	$10^5m_3'$	Z	10^4E_0 (calc.)	10^4E_0 (used)
Malonate	A	1138	1880	2449	65	3719	3721
Phthalate	B	2222	3472	1879	65	3722	3722
Tartrate.........	C	2300	3900	2378	60	3802	3797
Maleate	D	2064	2667	2499	75	3692	3691
Succinate	E	2292	3890	2511	65	3706	3707
Malate	F	2006	3196	2453	75	3792	3794

$c =$	0	5	10	15	20	25	30	35	40
10^4E(A)	305	328	345	360	373	383	392	400	406
10^5K(A)	—	535	530	535	530	535	535	535	535
10^4E(B)	599	612	625	635	645	655	665	673	680
10^5K(B)	—	310	280	290	295	295	280	285	300
10^4E(C)	1140	—	—	1154	1158	1162	—	1168	1171
10^4K(C)	—	—	—	95	100	100	—	105	100
10^4E(D)	361	388	410	430	445	460	473	483	493
10^5K(D)	—	290	285	345	295	290	290	330	295
10^4E(E)	299	305	312	316	321	325	328	332	335
10^4K(E)	—	100	90	100	105	100	105	105	105
10^4E(F)	799	807	815	821	827	832	837	841	845
10^4K(F)	—	110	90	100	95	95	95	95	95

TABLE 2.

Dissociation constants of chloropentamminecobalt(III) salts from pHs at 35°.

Ligands (see Table 1)	$10^5m_1'$	$10^5m_2'$	$10^5m_3'$	Z	10^4E_0 (calc.)	10^4E_0 (used)
A	2725	4896	2389	75	3859	3862
B	2066	3200	1180	70	3988	3992
C	2328	3944	2408	75	3932	3928
D	2092	2720	2362	75	3922	3924
E	2084	2720	2401	75	3843	3843

$c =$	0	5	10	15	20	25	30	35	40
10^4E(A)	170	178	184	190	196	201	206	211	217
10^5K(A)	—	445	490	515	480	505	490	500	470
10^4E(B)	764	773	782	790	797	804	811	817	823
10^5K(B)	—	330	235	215	220	225	215	225	220
10^4E(C)	1180	1187	1192	1197	1200	1203	1206	1210	1213
10^4K(C)	—	110	90	90	105	115	120	105	105
10^4E(D)	425	449	469	487	503	516	528	539	550
10^5K(D)	—	295	305	295	300	305	300	295	295
10^4E(E)	665	—	681	688	694	699	704	709	713
10^4K(E)	—	—	93	93	85	91	88	86	84

The results are summarised in Tables 1 and 2 where Z is the initial volume of buffer of concentrations, $m_1' = \mathrm{H_2L}$, $m_2' = \mathrm{NaOH}$, and $c =$ ml. of stock solutions $m_3' = \mathrm{Cp(NO_3)_2}$.

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[4] Davies, " Ion Association," Butterworths Publishing Co., London, 1962.

[5] Seys, Rowlands, and Monk, unpublished results.

It has also been assumed in the above calculations that $CpNO_3^+$ and NaL^+ ion-pairs are not formed. The solubility results reported below indicate that the former species may be ignored and since the E_0 values are also based upon an absence of NaL^+ any consequent errors almost cancel out providing $K(NaL^+)$ is large. On the other hand this ion-pair must be considered in the analysis of the solubility data, so measurements were made with additions of m_3 = NaCl to the cell instead of $Cp(NO_3)_2$. The potentials and the resultant $K(NaL^+)$ figures (obtained in a similar way to that used above for CpL) are given in Table 3. As previously,[1] allowance was made for the effects of sodium ions by means of

$$E_0'' = E_0 + \Delta E \qquad (10)$$

where E_0'' was obtained by extrapolating a plot of E_0 (calc.) against $m_2 + m_3$ = total $[Na^+]$ and ΔE is the increase in E_0 due to $[Na^+]$ when the cell contained 0·0001M-HCl + 0—0·09M-NaCl (see Table 3). An interesting feature is that with sodium tartrate E_0(calc) is independent of $[Na^+]$. This suggests that not only does sodium tartrate dissociate completely but that the sodium ion " error " is absent. Consequently the application of (10) is suspect when applied to the other ligands but it so happens that by adopting the policy of adjusting E_0 until $K(NaL^+)$ is constant as $[Na^+]$ varies and ignoring the ΔE corrections, $K(NaL^+)$ is only slightly lower than when ΔE is included. This is shown in Table 3 for phthalate and succinate.

TABLE 3.

Dissociation constants of sodium salts from pHs at 25°.

Z = 75 ml.; E, E_0, and ΔE in v. Symbols as in Table 1.

$10^2[Na^+]$	1	2	3	4	5	6	7	8	9
$10^4\Delta E$	3	5	7	8	10	11	12	13	14

Ligand	$10^5m_1'$	$10^5m_2'$	$10^4m_3'$	$10^4E_0'$	10^4E_0 (used)		c = 0	1	2	3	4	5
A	2770	4874	9056	—	—	10^4E(A)	336	351	362	372	383	392
				3698	—	10^2K(A)	18	18	19	20	17	18
B	2222	3472	9056	—	—	10^4E(B)	600	618	633	645	657	668
				3802	—	10^2K(B)	24	24	23	23	23	24
				—	3810	10^2K(B)	19	20	19	19	18	17
C	2300	3900	8340	—	—	10^4E(C)	1038	1047	1054	1062	1068	1073
				—	3700	10^4E_0(C)	3700	3701	3698	3699	3700	3700
D	2064	2667	9056	—	—	10^4E(D)	364	389	407	421	433	445
				3670	—	10^2K(D)	20	18	18	20	20	19
E	2292	3890	9056	—	—	10^4E(E)	300	313	325	335	344	350
				—	3695	10^2K(E)	73	66	53	56	53	56
				—	3697	10^2K(E)	41	38	34	34	34	34

Solubility Measurements.—The solubility of chloropentamminecobalt(III) iodate is sufficiently low to apply Davies's method of obtaining dissociation constants.[4] This consists of obtaining the activity solubility product K_s from the solubility in water [$s(H_2O)$] and equation (6), to measure the solubility [s(Soln.)] in salt solutions, and to calculate $[Cp^{2+}]$ from K_s and (6). Then $[CpL] = s(\text{Soln.}) - [Cp^{2+}]$ and K is obtained from (9). Allowance is made for subsidiary ion-pairs,[4] namely $NaIO_3$, $NaNO_3$, $NaSO_4^-$, and NaL^+. In spite of numerous washings, $s(H_2O)$ of freshly prepared iodate crystals decreased very slowly to a constant value (0·00465M at 25°, 0·00625 at 35°), so $s(H_2O)$ was determined before each s(Soln.) determination. When using the sodium salts of weak acids a slight excess of acid was left in the solution and allowance made for HL^- by means of (5) (H_2L and H^+ are negligible). The results are summarised in Table 4.

DISCUSSION

The average results are in Table 5. There are few previous figures for comparison. Davies and Williams[6] have calculated K = 0·0028 for the sulphate from solubility data[7]

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[6] Davies and Williams, *Trans. Faraday Soc.*, 1958, **54**, 1547.

[7] Bronsted and Petersen, *J. Amer. Chem. Soc.*, 1921, **43**, 2265.

TABLE 4.

Dissociation constants of chloropentamminecobalt(III) salts from solubilities.

Ligand symbols as in Table 1, also G = sulphate, H = nitrate, J = chloride, K = acetate, L = azide, M = glycollate, N = perchlorate.

25°

Ligand	A	A	A	B	B	C	C	D	D
10^5 [Sodium salt]	1457	2277	3505	731	939	1193	1237	448	1792
10^5 [Acid]	596	277	548	33	10	47	41	60	242
$10^5 s$ (H_2O)	471	471	468	466	466	469	469	467	467
$10^5 s$ (Soln.)	617	674	730	581	610	596	600	542	689
$10^4 K$	47	49	47	32	30	76	75	36	32

Ligand	E	E	F	F	G	G	G	H	H
10^5 [Sodium salt]	1080	2161	1380	2759	740	1520	2885	7136	8120
10^5 [Acid]	130	262	145	289	—	—	—	—	—
$10^5 s$ (H_2O)	466	466	467	467	465	465	497	469	469
$10^5 s$ (Soln.)	573	638	597	672	581	608	803	602	670
$10^4 K$	120	110	103	100	33	36	32	900	850

Ligand	J	J	K	K	L	M	M	N	N
10^5 [Sodium salt]	6008	8348	5537	8274	5758	3329	4994	5880	9408
10^5 [Acid]	—	—	Trace	Trace	—	Trace	Trace	—	—
$10^5 s$ (H_2O)	473	473	491	477	481	470	470	483	479
$10^5 s$ (Soln.)	633	674	613	646	645	618	664	646	713
$10^4 K$	1000	1050	2100	2200	850	330	350	680	710

35°

Ligand	A	A	A	B	B	C	C	D	D
10^5 [Sodium salt]	812	1624	2538	714	1300	1546	2656	1294	1635
10^5 [Acid]	113	227	191	1	20	37	18	377	253
$10^5 s$ (H_2O)	638	638	627	630	629	632	632	637	644
$10^5 s$ (Soln.)	765	855	911	760	848	809	892	855	904
$10^4 K$	53	48	48	31	28	85	78	32	30

Ligand	E	E	F	F	G	G	G	J	J
10^5 [Sodium salt]	1928	2620	1447	2516	982	1289	1860	4615	7386
10^5 [Acid]	64	109	118	290	—	—	—	—	—
$10^5 s$ (H_2O)	628	629	648	640	627	635	639	626	626
$10^5 s$ (Soln.)	815	860	813	895	796	848	919	790	860
$10^4 K$	120	115	104	103	31	30	29	1000	950

Ligand	K	K	L	L	N	N
10^5 [Sodium salt]	4677	7490	3575	5360	3530	5861
10^5 [Acid]	Trace	Trace	—	Trace	—	—
$10^5 s$ (H_2O)	625	628	628	628	628	628
$10^5 s$ (Soln.)	761	808	758	802	761	828
$10^4 K$	2800	4000	1100	1200	950	850

TABLE 5.

Average dissociation constants.

Ligands (see Tables 1 and 4)	A	B	C	D	E	F	G	H
pH 25°	0·0053$_5$	0·0029	0·0100	0·0030	0·0101	0·0097	—	—
pH 35°	0·0048$_5$	0·0023$_5$	0·0105	0·0030	0·0089	—	—	—
Soly. 25°	0·0048	0·0031	0·0075	0·0034	0·0115	0·0102	0·0035	0·09
Soly. 35°	0·0050	0·0030	0·0082	0·0031	0·012	0·0104	0·0030	—
Na Salts	0·18	0·2	—	0·2	0·5	—	—	—

Ligands	J	K	L	M	N
Soly. 25°	0·1	0·2	0·08$_5$	0·03$_5$	0·07
Soly. 35°	0·1	0·35	0·11	—	0·09

for the bromide salt of the chloro-ion at 0°; this agrees well with our estimate. In addition, as the following Paper shows, dissociation constants close to ours are deduced from kinetic data for the sulphate, malonate, and phthalate.

In general, when both methods have been used the answers agree well. The largest discrepancy is for tartrate (C) where the uncertainty is ±15%. Further solubility measurements agreed with those given here but fresh pH measurements at 35° revealed slow potential drifts. These would lead to a lower dissociation constant but these drifts may be due to a slower response of the glass electrode or to aquation of the complex.

EXPERIMENTAL

Chloropentamminecobalt(III) iodate crystals were made by slow addition of potassium iodate solution to a warm almost saturated solution of chloropentamminecobalt(III) chloride followed by refrigeration overnight. The crystals were washed with water by decantation, " fines " being removed at the same time. Solubility measurements were made with a Davies type of saturator [8] in a bath kept to ±0·03°. The same standard thiosulphate was used to find the solubility in each water and salt solution. The ligand salt solutions were made up by weight from the acids of the dicarboxylates and standard sodium hydroxide. For the other ligands, solutions were made up by weight from the sodium salts, except glycollate which was made from the acid and sufficient standard sodium hydroxide for a pH of 6.

pH Measurements were obtained with a Radiometer type PHM 4C pH-meter and the cell system developed for acetates.[1] The more soluble nitrate of the chloro-ion was used. Crystals of it were made by pouring a warm solution of the chloride into concentrated nitric acid, filtering, washing with ethanol till acid-free, then drying at 50°.

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[8] Money and Davies, *J.*, 1934, 400.