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Ion Pair Formation between Some Complexes of Chromium(III), Cobalt(III) and the Anions of the Benzenecarboxylic Acids

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Ion pair formation constants for the outer sphere interaction between the complex ions $Co(NH_3)_6^{+3}$, $Co(NH_3)_5Cl^{+2}$, $Cr(NH_3)_5Br^{+2}$, $Cr(NH_3)_5Cl^{+2}$, *and* $Cr(MeNH_2)_5Cl^{+2}$ *and the ions of the benzenecarboxylic acids have been determined potentiometrically at 25 °C. Comparison of the ion pair formation constants for the series of complex cations with a single anion revealed an expected dependence upon the cation charge and size. However, for an individual cation the stability of the ion pair formed with the anions varied linearly with the basicity of the anions. The correlation between* $\log K_f$ *and* pK_a *for the individual anions took the form*

$$\log K_f = mpK_a + b$$

This dependence was interpreted to mean that H-bonding interaction makes a significant contribution to the stability of the ion pairs.

Introduction

Aqueous solutions of polyvalent ions frequently show deviations from ideal behavior which may be interpreted in terms of the specific interaction between ions of opposite charge which, as a first approximation, would be expected to be dependent upon the charge and radius of the associating ions [1]. Although this seems to be generally true there is a fine structure associated with the variation of the interacting ions that suggests the involvement of a variety of second order effects. For instance, Archer and Monk [2] found that the interaction between acetate and a series of similarly sized cations depended only upon the charge on the cation and Peacock and James [3] interpreted the difference in ion-pair association constant of hexammine cobalt(III) with various dicarboxylates on the basis of the size and structure of the anion. However, Colman-Porter and Monk [4] observed that for ion pairs formed between the alkaline earth cations and a series of carboxylate anions the formation constants increased in the order Mg < Ca < Sr < Ba, for a given anion. Similar behavior was observed for the interaction of alkali metal ions with some oxyanions [5]. This observation was explained in terms of ion induced dipole and dispersion forces. It may be that the disruption of solvent structure in the vicinity of the cation or equilibrium between inner and outer sphere ion pair complexes also play a role in determining the relative stability of an ion pair. Presumably these effects could be distinguished if the enthalpy and entropy changes accompanying association were known. Unfortunately, most systems that have been examined are not susceptible to a unique interpretation of the role of the solvent in modulating the interaction between the ions. Actually much of the work that has appeared in recent years has been directed toward the evaluation of the Debye–Hückel formulation, and its extensions, as valid representations of electrolyte solution behavior. This activity has been reasonably summarized by Petrucci [6]. However, there has been increasing interest in ions pairs as intermediates in both organic [7] and inorganic reactions [8, 9]. This in turn has sparked renewed interest in the characteristics of specific ion–ion interaction with EPR techniques being particularly effective [10, 11]. However, there are still very few instances where the distinction between inner and outer sphere complexes has been cleanly drawn [1, 12].

The present work, which arises out of a study of the effect of ion pair formation upon the rate of hydrolysis of chromium(III) complexes [13], involves the study of the association of a series of substitutionally inert positively charged complex ions with a series of interrelated anions. In these ion pairs the anions do not penetrate the inner coordination sphere of the cations, and it ought then to be possible to disentangle the first order charge and size effects from such second order effects as might influence the association of the ions.

Experimental

Preparation of Materials

Both bromopentamminechromium(III) bromide and chloropentamminechromium(III) chloride were prepared according to the method of Mori [14] and analyzed as described previously [15]. The preparation of chloro(pentakismethylamino)chromium(III) has also been described previously [16]. The cobalt(III) complexes obtained from Alpha Inorganics were found to contain traces of ammonium chloride and were recrystallized from hydrochloric or perchloric acid before use. Perchlorate salts of the complexes were used unless otherwise indicated. All other materials were of Reagent Grade and were used without further purification.

Water used in the preparation of solutions was obtained by distilling deionized water from alkaline permanganate in an all glass system. The water was protected from absorption of atmospheric carbon dioxide by storage under nitrogen.

Buffer solutions used for standardization of the pH meter were potassium acid phthalate (pH = 4.005) and dihydrogen phosphate–hydrogen phosphate (pH = 6.865). The solutions used in the determination of ion pair association constants were prepared by dissolving known amounts of the salts Na_xA and $Na_{(x-1)}$ HA in purified, carbon dioxide free water. The concentration of dissolved salt was known and was usually 1.000 X 10^{-3} *M* with respect to the acid radical A. The pH of the solution was then adjusted to the required value by the addition of measured amounts of sodium hydroxide or hydrochloric acid.

pH Measurements

The pH measurements (to ±0.002 pH) were made at 25.00 ± 0.05 °C using a Beckman Research pH meter or a Radiometer 4 pH meter in conjunction with a glass-saturated calomel electrode system. Carbon dioxide was excluded from all the solutions by flushing with nitrogen.

The variations in ionic strength inherent in the change from 10^{-3} *M* NaA to 10^{-3} *M* Na_6A when the acid component was changed from benzoic to 1,2,3,4,5,6-benzenehexacarboxylic acid did not produce experimentally measureable changes in the pH. In consequence it was satisfactory for our purposes to equate a_{H^+} with $[H^+]$ (see Eqs. 5 and 6).

Dissociation Constants of the Acids

The dissociation constants of the acids were determined from the pH titration curve [17] obtained by the incremental addition of standard hydrochloric acid solution from a micrometer syringe to an approximately 10^{-3} *M* solution of the sodium salt of the acid.

Ion Pair Formation Constants

A buffer solution containing the anion under study was placed in the reaction vessel of the pH meter, flushed with nitrogen and allowed to equilibrate at 25 °C. The initial pH of the solution was adjusted to the desired value using carbon dioxide free sodium hydroxide/perchloric acid. The complex salt, usually to make the solution 10^{-3} M in complex, was added, and dissolved as quickly as possible by vigorous stirring (approximately 0.5 minutes). The pH of the solution was again recorded at intervals for ten minutes and the zero time value was obtained by extrapolation. Generally the final pH did not vary greatly with time except when bromopentamminechromium(III) was the added complex.

The metal complexes were all acidic in aqueous solution and measureable amounts of base were required to change the pH of these solutions. Consequently some anion was consumed in a simple acid–base reaction in bringing the complex from the natural pH of its aqueous solution to the initial pH of the buffer. The correction (B in Equation 5) for this effect was derived from a pH titration curve for the appropriate complex. This excess acidity arose from acid that was carried into the solid during the recrystallization procedure. It could be removed by washing the precipitated salts with aqueous alcohol at considerable sacrifice of yield. Some neutral chloropentammine chromium(III) perchlorate was prepared and used in the ion pairing experiment with results that were indistinguishable from those obtained with the more “impure” compounds. Consequently, most of the experiments were conducted with the salts that contained the small amount of excess acid.

Results

Dissociation Constants for the Benzenecarboxylic Acids

The dissociation constants for the weak acids used in the determination of the ion pair association constants are shown in Table I. The literature values [18] are compared with those obtained in the course of this work by the method described by Albert and Serjeant [17]. The agreement is generally satisfactory but where a discrepancy occurs the pK’s obtained in this study were used. No attempt was made to extrapolate the constants to zero ionic strength, but all measurements were made in aqueous solutions that contained the acid at a total concentration of about 10^{-3} *M*. Hence, any correction for activity effects would be too small to be significant in the correlations to be attempted here.

Ion Pair Formation Constants

Outer sphere ion pair formation is represented in generalized form by

$$ML_6^{+z} + A^{m-} \longrightarrow [ML_6 \ldots\ldots A]^{(+z-m)} \qquad (1)$$

It is possible that highly charged cations (ML_6^{+z}) and anions (A^{m-}) will interact to form ion clusters. However, in the absence of cooperative effects, it is expected that clusters will have lower formation

TABLE I. pK_a for Benzenecarboxylic Acids at 25 °C.

Acid	Symbol	$^a pK_n$		$^a pK_{n-1}$	
		This work[c]	Prev.[b]	This work[c]	Prev.[b]
Benzoic	1	d	4.17		
Phthalic	12	d	5.28	d	2.98
135 Benzenetricarboxylic	135	4.75 ± 0.04	4.70	3.82 ± 0.04	3.89
124 Benzenetricarboxylic	124	5.50 ± 0.04	5.20	3.86 ± 0.01	3.84
123 Benzenetricarboxylic	123	5.90 ± 0.04	5.87	4.35 ± 0.02	4.20
1234 Benzenetetracarboxylic	1234	6.26 ± 0.02	6.21	4.71 ± 0.04	4.73
1235 Benzenetetracarboxylic	1235	5.84 ± 0.02	5.81	d	4.44
1245 Benzenetetracarboxylic	1245	5.70 ± 0.04	5.63	d	4.49
12345 Benzenepentacarboxylic	12345	6.54 ± 0.01	6.46	d	5.25
123456 Benzenehexacarboxylic	123456	6.78 ± 0.03	6.96	5.83 ± 0.04	5.89

[a] pK_n corresponds to dissociation of the last proton of a poly functional acid to give the free anion A^{-n} while pK_{n-1} refers to loss of the $(n-1)^{th}$ proton to give $HA^{-}(n-1)$. [b] Values taken from Ref. 18. [c] Uncertainties given represent variation from the average on three determinations. [d] Not determined.

constants than simple ion pairs. So unless either anion or cation is present in considerable excess over the other partner it is likely that the 1:1 ion pair will be the predominant solution species. Accordingly solutions for study were prepared in such a way that at equilibrium unassociated anion and cation and ion pair are all present at roughly equal concentrations. Under these circumstances the ion pair formation constants, are independent of the relative concentrations of anion and cation over a narrow range. This is just as expected if clusters make a negligible contribution to the species present in solution. The ion pair formation constant is given by

$$K_f = \frac{[MA]}{[M][A]} \tag{2}$$

where MA = ion pair
M = unassociated metal complex
A = unassociated anion

When A is the anion of a weak acid its concentration in solution will be governed both by ion pair formation and by protonation according to

$$H^+ + A^{m-} = HA^{(1-m)} \tag{3}$$

When a buffer solution containing A and HA in equilibrium is disturbed by the addition of a metal complex which forms ion pairs with A a pH change will be observed. This pH change can then be used as a measure of the change concentration of A. Eq. 2 can be recast in the form of [4]

$$K_f = \frac{A_i - A_f}{[M_T - (A_i - A_f)]\,A_f} \tag{4}$$

where

$$A_i = \frac{K_a[HA]_T}{K_a + [H^+]_i} - B \tag{5}$$

and

$$A_f = \left\{[HA]_T\left(1 - \frac{K_a}{K_a + [H^+]_i}\right) - \delta H^+ + B\right\} \frac{K_a}{[H^+]_f} \tag{6}$$

where $[H^+]_i$ = hydrogen ion concentration before addition of the complex.
$[H^+]_f$ = hydrogen ion concentration after addition of the complex.
δH^+ = $[H^+]_f - [H^+]_i$
K_a = acid dissociation constant for the equilibrium represented by Eq. [3].
B = correction for the acidity of the metal complex.
A_i, A_f = initial, final concentration of unassociated anion.
HA_T = total concentration of all carboxylate anionic species.

Ion pair association constants were obtained for the interaction between selected benzenecarboxylate ions and the ions $Co(NH_3)_6^{+3}$, $Co(NH_3)_5Cl^{+2}$, $Cr(MeNH_2)Cl^{+2}$, $Cr(NH_3)_5Br^{+2}$, and $Cr(MeNH_2)_5Cl^{+2}$. The data are given in Tables II–VI.

Discussion

It is usually anticipated that ion pair formation will be a simple function of ion size and ion charge. Thus the ion pair formation constants reported in Tables II–VI are seen to depend upon the cation in a completely expected way. For instance comparison of the entries in Tables II and III shows that for the same anion K_f changes by about a factor of ten when the ion is changed from +3 ($Co(NH_3)_6^{3+}$) to +2 ($Co(NH_3)_5Cl^{2+}$) while maintaining the ion size

TABLE II. Ion Pair Formation Constants (K_f) for $Co(NH_3)_6^{+3}$[a] with Some Benzenecarboxylates at 25 °C.

Benzene carboxylate[b]	pH_i	pH_f	log K_f
1	4.925	4.754	2.45
	4.906	4.735	2.45
135	5.282	4.473	3.61
	5.426	4.642	3.59
124	6.757	5.775	3.87
	6.356	5.361	3.87
1235	6.645	5.478	4.06
	6.753	5.547	4.11
123	6.844	5.608	4.14
	7.158	5.940	4.13

[a] $Co(NH_3)_6^{3+}$ = 2.000 × 10^{-3} *M*. [b] Benzenecarboxylate = 1000 × 10^{-3} *M*.

TABLE III. Ion Pair Formation Constants (K_f) for $Co(NH_3)_5Cl^{+2}$ with Some Benzenecarboxylates at 25 °C.

Benzene carboxylate[d]	pH_i	pH_f	B(m*M*)	log K_f	(log K_f)[e] ave
1[a]	4.503	4.302		2.09	2.04 ± 0.05
135[b]	5.277	5.032	0.026	2.55	2.56 ± 0.01
12[c]	5.848	5.653	0.030	2.63	2.63 ± 0.00
124[c]	6.500	6.164	0.033	2.97	2.96 ± 0.03
1245[c]	6.865	6.428	0.032	3.03	3.04 ± 0.04
123[c]	6.735	6.317	0.032	3.29	3.28 ± 0.02
12345[c]	7.250	6.672	0.029	3.67	3.66 ± 0.02
123456[c]	7.763	7.163	0.031	3.74	3.74 ± 0.03

[a] $Co(NH_3)_5Cl^{2+}$ = 5.000 × 10^{-3} *M*. [b] $Co(NH_3)_5Cl^{2+}$ = 2.000 × 10^{-3} *M*. [c] $Co(NH_3)_5Cl^{2+}$ = 1.000 × 10^{-3} *M*. [d] Benzenecarboxylate = 1.000 × 10^{-3} *M*. [e] Average of the values obtained in three determinations. The uncertainty is the mean deviation from the average value.

TABLE IV. Ion Pair Formation Constants (K_f) for $Cr(NH_3)_5Cl^{+2}$ with Some Benzenecarboxylates at 25 °C.

Benzene carboxylate[c]	pH_i	pH_f	B	log K_f	(log K_f)[d] ave
135[a]	5.356	5.066	0.034	2.57	2.52 ± 0.06
124[b]	6.491	6.127	0.033	3.06	3.07 ± 0.03
1245[b]	6.403	6.047	0.031	3.11	3.06 ± 0.05
1235[b]	6.522	6.182	0.030	3.24	3.23 ± 0.01
123[b]	6.666	6.225	0.030	3.33	3.36 ± 0.03
1234[b]	6.891	6.368	0.032	3.54	3.53 ± 0.02
12345[b]	7.216	6.726		3.67	3.68 ± 0.02
123456[b]	7.546	6.036	0.034	3.69	3.69 ± 0.02

[a] $Cr(NH_3)_5Cl^{2+}$ = 2.000 × 10^{-3} *M*. [b] $Cr(NH_3)_5Cl^{2+}$ = 1.000 × 10^{-3} *M*. [c] Carboxylate = 1.000 × 10^{-3} *M*. [d] Average of three determinations. The uncertainty is the mean variation from the average value.

TABLE V. Ion Pair Association Constants (K_f) for $Cr(MeNH_2)_5Cl^{+2}$[a] with Some Benzenecarboxylates at 25 °C.

Benzene carboxylate[b]	pH_i	pH_f	log K_f	(log K_f)[c] ave
12	6.015	5.928	2.41	
123	6.938	6.735	2.95	2.92 ± 0.04
12345	7.443	7.109	3.34	3.35 ± 0.03
123456	7.557	7.128	3.56	3.57 ± 0.01

[a] $Cr(MeNH_2)_5Cl^{2+}$ = 1.000 × 10^{-3} *M*. [b] Benzenecarboxylate = 1.000 × 10^{-3} *M*. [c] Average of three determinations. The uncertainty is the mean deviation from the average.

TABLE VI. Ion Pair Formation Constants (K_f) for $Cr(NH_3)_5Br^{+2}$[a] with Some Benzenecarboxylates at 25 °C.

Benzene carboxylate[b]	pH_i	pH_f	B	log K_f	(log K_f)[c] ave
135	5.024	4.843	0.006	2.71	2.69 ± 0.06
124	6.394	5.944	0.024	3.41	3.36 ± 0.11
1245	6.554	6.102	0.025	3.38	3.37 ± 0.05
1235	6.810	6.288	0.025	3.52	3.48 ± 0.10
123	6.866	6.309	0.024	3.66	3.70 ± 0.04
1234	7.258	6.588	0.030	3.82	3.81 ± 0.01

[a] $Cr(NH_3)_5Br^{++}$ = 1.000 × 10^{-3} *M*. [b] Benzenecarboxylate = 1.000 × 10^{-3} *M*. [c] Average of three determinations. The uncertainty is the mean deviation from the average.

constant. This is about what might have been expected [20]. In Tables III and IV where the comparison is between ions of the same size and charge (+2) but involving different metal atoms (Co^{3+} and Cr^{3+}) the same anions are seen to bind to the metal atoms to the same extent. When the ion charge is maintained constant but the ion size is varied as in Tables IV and V ($Cr(NH_3)_5Cl^{2+}$ vs $Cr(MeHN_2)_5Cl^{2+}$) the larger anion, as expected, binds a common anion less strongly.

In rather marked contrast the binding constants are not strongly dependent upon the *total* charge on the anion. This is perhaps best illustrated by the data in Table III where the *total* anionic charge varies from −1 (benzoate) to −6 (1,2,3,4,5,6-benzenehexacarboxylate) while K_f varies by only a factor of 50. This factor is much smaller than would have been anticipated on the basis of the charge dependence of the cations or of other systems previously commented upon [20]. A fairly obvious corollary of this behavior is that the carboxylate groups that carry the negative charges of the anionic species are acting as independent or nearly independent charge centers. Nevertheless, despite the quantitative (see above) and qualitative (see Table III – for 12 logK_f = 2.63, for 135 logK_f = 2.56) lack of dependence upon anion

TABLE VII. Statistically Corrected Ion Pair Formation Constants for the Interactions between Some Metal Complexes and Some Benzenecarboxylate at 25 °C.

Benzene carboxylate	$\log K_f$				
	$Co(NH_3)_6^{3+}$	$Co(NH_3)_5Cl^{2+}$	$Cr(NH_3)_5Cl^{2+}$	$Cr(MeNH_2)_5Cl^{2+}$	$Cr(NH_3)_5Br^{2+}$
1	2.45	2.04			
135	3.12	2.08	2.04		2.21
12		2.33		2.11	
124	3.39	2.48	2.59		2.88
1245		2.44	2.46		2.77
1235	3.49		2.63		2.88
123	3.66	2.80	2.88	2.44	3.22
1234			2.93		3.21
12345		2.96	2.98	2.65	
123456		2.96	2.91	2.79	

charge there are still some variations of K_f with anion charge that require rationalization. Perhaps the most obvious place to start such rationalization is with the observation that if the carboxylate groups are acting as independent charge centers then the hexacarboxylate is favoured statistically over the monocarboxylate because it has six times as many charge centers. Such a statistical correction is, of course, easily made and the corrected results have been collected in Table VII. It is evident from this tabulation that the statistical correction does not remove the dependence upon cation size and charge discussed above. Furthermore, there remains a dependence of K_f upon some property of the anions. This property would appear to be the basicity of the anions since $\log K_f$ is shown, in Fig. 1, to be a reasonably linear function of the pK_a's for the weakly basic carboxylate anions. This correlation can be cast in the form of Eq. 7

$$\log K_f = m pK_a + b \qquad (7)$$

which was first used by Bjerrum [21] in the form

$$\log K_{ML} = a \log K_{HL} + b \qquad (8)$$

to correlate the stability constant of a metal complex with the dissociation constant of the ligand, where K_{ML} is the stability constant for the complex ML, K_{HL} the dissociation constant of the acid HL and a and b are constants for the system. This equation has appeared in many forms but the analysis by Irving and Rossotti [22] showed they are all fundamentally based upon Eq. 9.

$$\log K^T_{ML} = \log K^T_{HL} + \frac{1}{2.3\ RT}(\bar{G}^o_{HL} - \bar{G}^o_{ML}) - (\bar{G}^o_H - \bar{G}^o_M) \qquad (9)$$

where K^T_{ML} and K^T_{HL} are the thermodynamic equilibrium constants and the $\bar{G}^o$ terms are the partial molar free energies corresponding to the species indicated. On this basis it can be seen that log

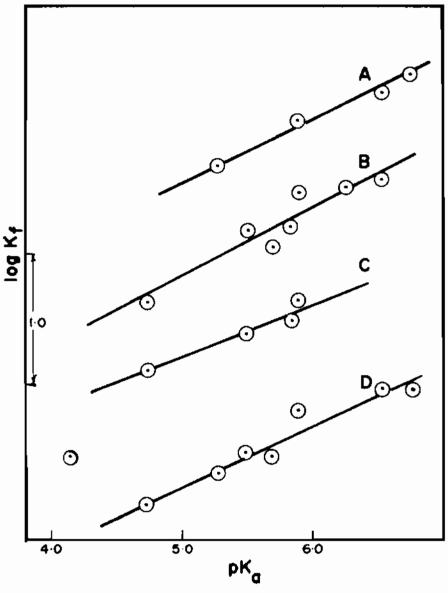

Figure 1. Correlation between the acid dissociation constants for the benzenepolycarboxylates (pK_a) and the association constants for ion pair formation between the carboxylates and a series of metal complexes. A) $Cr(MeNH_2)_5Cl^{2+}$, B) $Cr(NH_3)_5Cl^{2+}$, C) $Co(NH_3)_6^{3+}$, D) $Co(NH_3)_5Cl^{2+}$.

K_{ML} can be a linear function of $\log K_{HL}$ only under those circumstances where the combined molar free energy terms are either negligible, constant or a linear function of $\log K_{HL}$. When a series of ligands is being compared using the same metal the term $(\bar{G}^o_H - \bar{G}^o_M)$ is constant. The term $(\bar{G}^o_{HL} - \bar{G}^o_{ML})$ is unlikely to be zero so for the linear relation to hold it must be either constant or a linear function of $\log K_{HL}$. If it is constant the plot of $\log K_{ML}$ against $\log K_{HL}$ will have unit slope. The variation in the slopes of the lines is small and may well not be significant but in all cases the slope is much less than unity. This suggests a dependence upon the partial molar free energy difference $(\bar{G}^o_{HL} - \bar{G}^o_{ML})$ which places progressively more weight on the hydrogen bound ligand compared to the metal bound ligand as the ligand basicity increases or as the charge density on the metal ion decreases. This is just the kind of behavior that might be expected for ion-paired systems. The variation in ion pair formation constants as the anion basicity changes suggests the involvement of hydrogen bonding as a second order effect in the outer sphere interaction between these anions of weak acids and the complex cations.

The K_f values for the interactions involving the bromopentamminechromium(III) ion have not been extensively employed in developing these correlations. This is because it is thought that the unexpectedly large values for the K_f's in this system are a consequence of the increased lability of the bromocomplex. Thus, it was observed that the measurements involving bromo were complicated by exhibiting a time dependent decrease of the final pH which correlated with the rate hydrolysis of bromopentamminechromium(III) [13]. Apparently then the increase of K_f with time is due to the appearance in solution of the hydrolytically generated +3 cation (aquopentamminechromium(III)). The effect of such a time dependent change is easily corrected for by following the pH as a function of time and extrapolating back to zero time. The data recorded in Table VI were obtained by this extrapolation procedure. Nevertheless the values given are higher than expected on the basis of the charge and size argument. It may well be that the parent compound contains a small amount of the aquo complex produced during preparation and recrystallization. Certainly the measured ion pair formation constant could be minimized by recrystallizing the bromocomplex under conditions that would minimize hydrolysis. The results in Table VI were obtained with the bromopentammine sample that gave minimum values for K_f. However, the important thing here is not the absolute values for K_f but the fact that they follow the trend observed with the other complexes.

The study of this series of anions suggests that when the inner coordination sheath of a metal atom remains intact ion pair formation may show a two term dependence. The major contributor to stability is, as expected, ion charge and ion size. However, hydrogen bonding interactions between the anion and protons on the ligands that form the inner coordination sphere of the metal ion may also play a role. In this way some previously unrecognized fine structure may be introduced into ion–ion interactions.

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