The Complex Formation between Cd^{2+} and the Unsubstituted Benzenetricarboxylate Ions

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From potentiometric measurements of $[H^+]$ and $[Cd^{2+}]$ the stability constants of the complexes formed between Cd(II) and the three simple benzenetricarboxylic acids have been determined in 1 M $Na(ClO_4)$ at 25 °C. The species BA, BA_2 and BHA are formed. In the 1,2,3-benzenetricarboxylate system there is also evidence for the existence of a dinuclear complex, B_2A_2.

In a previous paper the stability constants of the Cd(II) and Pb(II) complexes formed with the benzoate, phthalate and isopthalate ions were reported.[1] This study is now extended to include the three unsubstituted benzenetricarboxylate ions. No formation constants have been found for these ligands in the literature. Unfortunately, the solubilities of the lead salts are too low to permit precise measurements with the amalgam electrode. This electrode has been found to work less satisfactorily at total metal ion concentrations of less than 0.2 mM probably due to the presence of small amounts of oxygen. The investigation is therefore restricted to the cadmium complexes. Due to the low solubilities of the NaH_2A salts, it has been possible to study only ligands in the $HA^{2-} - A^{3-}$ buffer system, where A^{3-} is the tricarboxylate ion.

EXPERIMENTAL

The experiments were carried out as potentiometric titrations where the total concentration of the ligand was varied by the addition of $HA^{2-} - A^{3-}$ buffers. The quotient between the total concentration of hydrogen ion and tricarboxylate ion, H/A, was nearly constant at low total metal ion concentrations, B, while greater variation occurred at higher metal ion concentration due to the perchloric acid in the metal stock solution. The concentration of free hydrogen ion, h, and free metal ion, b, was measured by means of the cells

$$-\text{glass}|\text{equilibrium solution S}|\text{ref}+$$
$$E_g = E_{o,g} - 59.16 \text{ (mV) log } (h/M) - E_j$$

$$-\text{Cd(Hg)}|\text{equilibrium solution S}|\text{ref}+$$
$$E_{Cd} = E_{o,Cd} - 29.58 \text{ (mV) log } (b/M) - E_j$$

at 25 °C in a 1 M $Na(ClO_4)$ medium. The liquid junction potential, E_j, which was measured as described in Ref. 2 is given by

$$E_j = kh + l[H_3A] + m[H_2A] + n[HA] + o[A]$$

where k, l, m, n and o are constants. The reference electrode and the test of the glass electrodes (Beckman 40498 and Ingold 201) are described in Ref. 2. The concentration of Cd^{2+} was measured by an amalgam electrode. The readings of the potentials to ± 0.01 mV were done with a digital voltmeter DATA PRECISION 2520.

Chemicals. 1,2,3-Benzenetricarboxylic acid, 1,2,3-BTCA (Fluka, pract.) was purified by recrystallization from water. The acid crystallizes as $H_3A.2H_2O$ and drying at 110 °C over phosphorus pentaoxide is recommended.[3] It was not found possible to completely remove the water without decomposition of the acid, as prolonged drying lowered the formula weight below the theoretical value (210.1). The acid was therefore carefully dried and each solution standardized by alkalimetric titrations. The formula weight was then about 213−214.

1,2,4-Benzenetricarboxylic acid, 1,2,4-BTCA (Merck-Schuchardt, *zur Synthese*). The acid was recrystallized twice from water after treatment with

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charcoal. The formula weight was found to be 210.4 (calc. 210.1).

1,3,5-Benzenetricarboxylic acid, 1,3,5-BTCA (Merck-Schuchardt, *zur Synthese*) was purified as described for 1,2,4-BTCA and the formula weight was 210.3 (calc. 210.1).

Other chemicals were prepared and purified as earlier described.[2]

CALCULATIONS AND RESULTS

The stability constant for the reaction

$$p\text{H}^+ + q\text{B} + r\text{A} \rightleftharpoons \text{H}_p\text{B}_q\text{A}_r$$
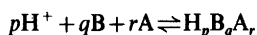
is denoted by

$$\beta_{pqr} = [\text{H}_p\text{B}_q\text{A}_r]h^{-p}b^{-q}a^{-r}$$

The proton-tricarboxylate systems. The protonation constants were found from titrations at low A since the monosodium salt, NaH_2A, has a rather limited solubility. In the 1,2,3- and 1,3,5-BTCA systems it was found necessary to keep A at values around 3 mM to prevent precipitation. Due to the somewhat higher solubility in the 1,2,4-BTCA system the measurements could be carried out at $A = 0.015$ M. This system was also chosen for a more extensive study of medium effects. The expression for E_j (see Ref. 4) found from titrations on buffers with $H/A = 0.1, 0.31, 0.50, 0.80, 1.1, 1.9$ and 2.5 was found to be $E_j = -31.8[\text{A}^{3-}] - 25.2[\text{HA}^{2-}] - 49.1[\text{H}_2\text{A}^-]$. The coefficient for $[\text{A}^{3-}]$ is not far from the value obtained for A^{3-} in excess of OH^-, $k_{\text{A(OH)}} = -38$ mV/M, and the factor for $[\text{HA}^{2-}]$ is almost identical with $k_{\text{A(OH)}}$ for the phthalate ion.[1] For H_2A^- the coefficient is considerably larger than for the benzoate ion, -9.5 mV/M,[1] and indicates dimerisation reactions. Since the concentration of H_2A^- in the investigated solutions is small, no attempt has been made to identify the dimeric species. This will hardly affect the reported stability constants. The results are given in Table 1.

The Cd(II) — tricarboxylate systems. Preliminary sets of stability constants were calculated from $(B/b - 1)/a = f(a)$ graphs at various quotients H/A as described in Ref. 6. The concentration of free ligand was estimated from the equation for the total ligand concentration by successive approximations. The stability constants obtained by the graphical procedure were then used as start values in the Letagrop calculations where $\Sigma(E_{\text{calc}} - E_{\text{exp}})^2$ was minimized.

The Cd(II) — 1,2,3-BTCA system. The system was investigated by titrations at $B = (0.3 - 2.5) \times 10^{-3}$ M with the buffers (H/A, A_{max}); 0.05, 0.016; 0.1, 0.016; 0.2, 0.015; 0.5, 0.012; 0.7, 0.007. A_{max} is the highest value of A reached in the titration. The data from measurements at $B \le 1 \times 10^{-3}$ M could be explained by the formation of the complexes BHA, BA and BA_2 with $\sigma(E_{\text{Cd}}) = 0.06$ mV for 80 experimental points. Experiments at $H/A = 0.05$ with $B = (0.3, 1$ and $2.5) \times 10^{-3}$ M showed a systematic trend and $E_{\text{calc}} - E_{\text{exp}}$ was -0.5 mV at the highest metal ion concentration. By including a B_2A_2 complex, the deviations were removed and $\sigma(E_{\text{Cd}}) = 0.04$ mV for 159 experimental points. The results from the least-squares refinements are given in Table 2.

The Cd(II) — 1,2,4-BTCA system. Titrations were carried out with the buffers (H/A, A_{max}); 0.06, 0.05; 0.10, 0.05; 0.50, 0.05; 0.8, 0.025; 1.1, 0.025; 1.9, 0.013. B was varied in the range $(0.3 - 2.0) \times 10^{-3}$ M. Titrations at $B \le 1 \times 10^{-3}$ M were well explained by the formation of BA, BA_2, BHA and BHA_2 as indicated by $\sigma(E_{\text{Cd}}) = 0.02$ mV. With these constants a systematic trend was again found in $E_{\text{calc}} - E_{\text{exp}}$ when B increased from 0.3×10^{-3} to 2.0×10^{-3} M at $H/A = 0.05$. The difference was 0.3 mV at most. Inclusion of B_2A_2 gave $\sigma(E_{\text{Cd}}) = 0.02$ mV for 150 experimental points. The constants are given in Table 2.

The Cd(II) — 1,3,5-BTCA system. In this system the low solubilities did not allow measurements with $B > 1 \times 10^{-3}$ M and the accessible H/A range was limited to values less than 0.3. The data from

Table 1. Protonation constants of A^{3-}. The figures within parentheses are three times the estimated standard deviations from the least-squares calculations by LETAGROP VRID, version ETITR.[5]

Acid	$\beta_{101} \times 10^{-4}/\text{M}^{-1}$	$\beta_{201} \times 10^{-8}/\text{M}^{-2}$	$\beta_{301} \times 10^{-10}/\text{M}^{-3}$
1,2,3-Benzenetricarboxylic	9.11(0.06)	4.47(0.03)	14.3(0.1)
1,2,4-Benzenetricarboxylic	3.36(0.03)	1.089(0.008)	2.04(0.02)
1,3,5-Benzenetricarboxylic	1.67(0.01)	0.622(0.004)	6.15(0.06)

Table 2. The stability constants, β_{pqr}, of the complexes written as $H_pB_qA_r$. Three times the estimated standard deviations from the least-squares calculations are given within parentheses.

Acid	β_{011}/M^{-1}	$\beta_{012} \times 10^{-2}/M^{-2}$	$\beta_{111} \times 10^{-5}/M^{-2}$	$\beta_{022} \times 10^{-5}/M^{-3}$
1,2,3-Benzenetricarboxylic	244(2)	62.1(1.6)	41.5(1.1)	23.1(1.5)
1,2,4-Benzenetricarboxylic[a]	76.6(0.3)	9.07(0.08)	7.37(0.06)	1.33(0.11)
1,3,5-Benzenetricarboxylic	33.3(1.0)	3.8(0.5)	3.0(0.4)	

[a] $\beta_{112} = (1.96 \pm 0.06) \times 10^7/M^{-3}$.

the buffers $(H/A, A_{max})$; 0.05, 0.025; 0.1, 0.020; 0.33, 0.012 can be explained by the formation of the complexes BA, BA$_2$ and BHA. No indications of dinuclear complexes could be observed. $\sigma(E_{Cd})$ for 60 experimental points was 0.06 mV. The stability constants are given in Table 2.

DISCUSSION

The formation of CdA, CdA$_2$ and CdHA is well established in the systems studied and it is interesting to compare the values of β_{011} and $\beta_{1,0}$, the equilibrium constant for the reaction $B + HA \rightleftharpoons BHA$, with β_{011} for the Cd(II)−benzoate complex (10.2 M^{-1}). In the 1,3,5-BTCA system with separated carboxylate groups the value of β_{011} is about three times the value of β_{011} (Cd−benzoate) while in the 1,2,4-BTCA system the constant is somewhat higher than the value found in the phthalate system (72.2 M^{-1}).[1] In both systems the value of $\beta_{1,0}$ is rather close to $2\beta_{011}$ for the monodentate benzoate ion. The reason why CdHA$_2$ is found only in the 1,2,4-BTCA system is probably the more favourable concentration range accessible in that system.

In the 1,2,3-BTCA system the metal complexes are as expected considerably stronger and there is evidence for the formation of a dinuclear complex Cd$_2$A$_2$. The differences in $E_{calc} - E_{exp}$ of up to −0.5 mV, interpreted as due to the formation of the dimer, were found from measurements on solutions with moderate changes in the ionic medium $(\leq 5\%)$.

The B$_2$A$_2$ complex in the 1,2,4-BTCA system is indicated by even smaller potential differences. It should be pointed out that no significant effects due to changes in B were observed in the phthalate and isophthalate systems (previous measurements[1] have been extended to cover the range $0.3 < [Cd(II)]_{tot} < 2$ mM).

In the dimer the tricarboxylate ions might be joined by a three-coordinated cadmium ion. The

other metal ion would then be attached to the two adjacent uncoordinated carboxylate groups on one of the ligands. From molecular models a sandwich-like structure with two three-coordinated metal ions appears to be another possibility. The equilibrium constant for the reaction $CdA_2 + Cd \rightleftharpoons Cd_2A_2$ is larger than β_{011}, which would better agree with the latter suggestion. A structure with the tricarboxylate ions connected by two two-coordinated cadmium ions is less likely, since then one would expect B$_2$A$_2$ to form with the phthalate ion as ligand.

Lead carboxylate complexes are typically 5−10 times stronger than the corresponding cadmium complexes. Used in conjunction with the value of the stability constant for the Pb(II)−salicylate complex reported by Lee,[7] the results obtained here can be used to estimate the relative importance of polycarboxylate- and salicylate-like sites for binding Pb(II) to humic and fulvic acids. One then finds that about pH 7 to 8, the two sites are of about equal importance. Below pH 7, polycarboxylate sites become increasingly important.

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