The Complex Formation between Pb^{2+} and Dicarboxylic Acids $(CH_2)_n(COOH)_2$ with $n=1-4$

ABBAS HAMMAM,* ÅKE OLIN and PÄR SVANSTRÖM

Institute of Chemistry, University of Uppsala, P.O.B. 531, S-751 21 Uppsala, Sweden

The complex formation between Pb^{2+} and the malonate, succinate, glutarate, and adipate ions (A) has been studied by potentiometric measurements in 1 M $Na(ClO_4)$ at 25 °C. The presence of $Pb(HA)$, $Pb(HA)_2$, PbA, PbA_2, and $Pb(HA)A$ has been established and the stability constants of the species have been determined. Complexes with three ligands may also be present. It has not been possible to elucidate their compositions with certainty.

In the previous parts of the studies on the complexes formed between Pb^{2+} and dicarboxylate ions the stability constants for the maleate[1] and oxalate[2] systems have been determined. These investigations have now been extended to include the ligands malonate, succinate, glutarate, and adipate. In what follows these ligands will be denoted by A^{2-}. The $Pb^{2+}-A^{2-}$ systems have previously been studied mainly by polarographic measurements. In solutions containing only A^{2-} the complexes PbA, PbA_2, and PbA_3 have been found by Gaur and Palrecha.[3] In addition PbA_4 has been suggested by Maheswari, Jain, Saraswat, and Gaur[4] to exist in the malonate system. From glass electrode measurements the stability constants of the PbA complexes have been reported by Yasuda, Yamasaki, and Ohtaki.[5] Little or no attention has been paid to the formation of protonated complexes. Only Lai and Hsieh[6] have reported on such complexes, viz., PbHA and $Pb(HA)_2$ in the malonate system.

This work presents the results from potentiometric measurements, where particular care

has been taken to ensure broad concentration ranges in the $H_2A-HA^--A^{2-}$ systems.

EXPERIMENTAL

Method. The measurements were carried out as a series of potentiometric titrations. In general the total concentration of Pb(II),B, and the quotient between the total concentration of H^+, H, and the total concentration of dicarboxylate ion, A, were kept constant during a titration. The concentration of free hydrogen ion, h, and the concentration of Pb^{2+}, b, were measured at 25.0 °C with the cells

$$- \text{ glass } | \text{ Equilibrium solution S } | \text{ Ref } + \qquad \text{(I)}$$

$$E_g = E°_g - 59.16 \text{ (mV) } \log(h/M) - E_j \qquad \text{(1)}$$

$$- \text{Pb-Hg } | \text{ Equilibrium solution S } | \text{ Ref} + \qquad \text{(II)}$$

$$E_{Pb} = E°_{Pb} - 29.58 \text{ (mV) } \log(b/M) - E_j \qquad \text{(2)}$$

The ionic medium has been 1 M $Na(ClO_4)$ for all the systems studied. The succinate system has also been investigated in 3 M $Na(ClO_4)$. The liquid junction potential, E_j, including the activity factor for H^+ was determined as described earlier[1] and is given by

$$E_j = k[H^+] + l[H_2A] + m[HA^-] + n[A^{2-}] \qquad \text{(3)}$$

where k, l, m, and n are constants.

Apparatus. The potentiometric titrations were performed with an automatic titrator built in this department. All potentials were measured with a digital voltmeter, Data Precision 2520, to ± 0.01 mV. Details on the preparation and stability of the electrodes can be found in Ref. 1. The equilibration of the malonate buffers with lead malonate (s) was performed in the same equipment as used in the investigation of the oxalate system.[2]

Chemicals and analysis. Malonic acid (Merck zur Synthese) was recrystallized three times

* Present address: Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt.

from an ether-acetone mixture (1:1) and benzene added to the filtrate to lower the solubility. The formula weight as determined by alkalimetric titration was 104.3 (calc. 104.1). Lead malonate crystals for the solubility measurements were prepared by precipitation from homogeneous solution by addition of small portions of urea during several hours.

Succinic acid (Merck zur Analyse) was recrystallized three times from water and the formula weight found was 118.3 (calc. 118.1).

Glutaric acid (Fluka *purum* and Merck "zur Synthese") was purified by repeated recrystallizations from ether-benzene (1:4). The formula weight was 132.3 (calc. 132.1).

Adipic acid (Kebo *purum*) was recrystallized three times from water and the formula weight was found to be 146.3 (calc. 146.1).

Other chemicals were prepared and analysed as described earlier.[1]

CALCULATIONS AND RESULTS

Since both HA^- and A^{2-} can act as ligands the complexes $Pb_q(HA)_m$, Pb_qA_n, and $Pb_q(HA)_mA_n$ will be assumed to form. Due to the small solubility of the lead dicarboxylates the upper limit of the concentration range for Pb(II) was about 1×10^{-3} M. Experiments with different total metal ion concentrations showed that $q = 1$. The stability constant for the reaction

$$B(=Pb^{2+}) + mHA + nA \rightleftharpoons B(HA)_mA_n$$
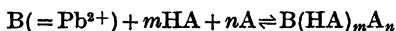
is denoted by

$$\beta_{m,n} = [B(HA)_mA_n]b^{-1}[HA]^{-m}a^{-n} \qquad (4)$$

and for the reaction written as

$$pH + qB + rA \rightleftharpoons H_pB_qA_r$$
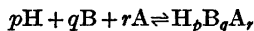
by

$$\beta_{pqr} = [H_pB_qA_r]h^{-p}b^{-q}a^{-r} \quad (q = 0 \text{ or } 1) \qquad (5)$$

The total concentration of Pb^{2+} is

$$B = b + \sum_m \sum_n \beta_{m,n}b[HA]^m a^n \qquad (6)$$

and the buffer quotient ϕ is defined by $\phi = [HA]/a$. The analysis of the measurements was carried out in two steps. Data from solutions with less than 10 % of the perchlorate ions exchanged for the ligands were used in the first step. On the assumption that only complexes with $m+n \leqslant 2$ are formed eqn. (6) can be written

$$y_1 = (B/b - 1)a^{-1} = \beta_{0,1} + \beta_{1,0}\phi + \beta_{0,2}a + \beta_{1,1}\phi a + \beta_{2,0}\phi^2 a \qquad (7)$$

A representative example of the use of eqn. (7) is given in Figs. 1−3 with data from the succinate system. In Fig. 1 y_1 is plotted as a function of a at constant ϕ. Straight lines are obtained indicating that complexes with $m+n \leqslant 2$ predominate. The intercepts $y_2 = (\beta_{0,1} + \beta_{1,0}\phi)$ and the slopes $y_3 = (\beta_{0,2} + \beta_{1,1}\phi + \beta_{2,0} \phi^2)$ of these lines are plotted as functions of ϕ in Figs. 2 and 3. From these plots, which suggested the existence of Pb(HA), Pb(HA)$_2$, PbA, PbA$_2$, and Pb(HA)A in all the systems
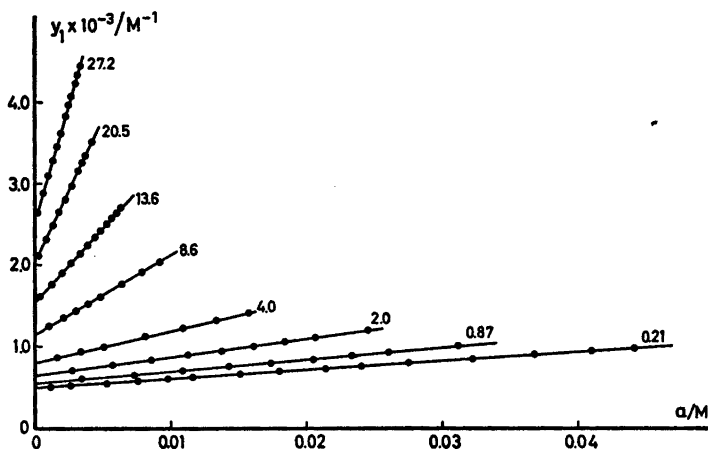

Fig. 1. $y_1 = (B/b - 1)a^{-1}$ plotted as a function of a (see eqn. (7)). Each line refers to a constant value of the buffer quotient $\phi = [HA]a^{-1}$. This value is given in the graph. Only data from solutions where less than 10 % of the perchlorate ions have been exchanged are included.
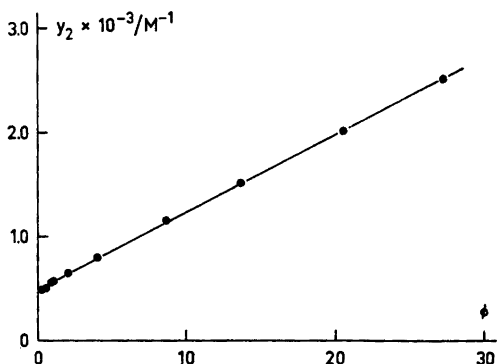
Fig. 2. The y_1-intercepts, $y_2 = \beta_{0,1} + \beta_{1,0}\phi$, of the lines in Fig. 1 plotted as a function of ϕ. Results for a few buffer quotients not shown in Fig. 1 for clarity are also included.

studied, preliminary values of the stability constants were calculated. These were next refined by the least-squares program Letagrop Vrid, version Etitr,[7] from $150-200$ experimental points.

The data at greater ligand concentrations, corresponding to an exchange of at most $20-25\%$ of the perchlorate ions for A^{2-} and HA^-, could not be fully explained by the complexes with $m+n \leqslant 2$. $E_{calc} - E_{exp}$ reached about 1 mV at the highest ligand concentrations. Since the effect on the activity coefficients of an exchange of ClO_4^- against A^{2-} is not known and difficult to establish, one is prompted to proceed
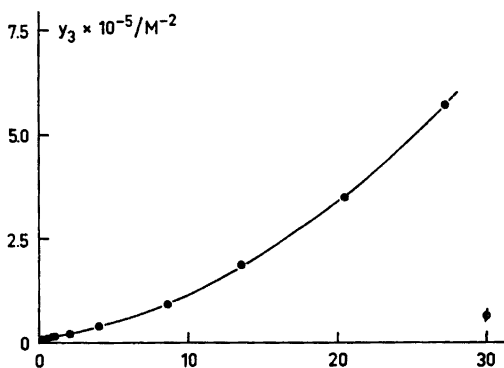

Fig. 3. The slopes, $y_3 = \beta_{0,2} + \beta_{1,1}\phi + \beta_{2,0}\phi^2$, of the lines in Fig. 1 plotted as a function of ϕ. The drawn curve is the polynomial of the second degree fitted to the experimental points by least-squares calculations.

using one of the following hypotheses. Either the deviations are considered to be caused by changes in the activity coefficients or these assumed to be constant and the data explained by inclusion of complexes with $m+n=3$. The truth may well lie between the two assumptions. An attempt has been made to explain the data according to the last mentioned (2nd) hypothesis by inclusion of $Pb(HA)_3$, PbA_3, $Pb(HA)_2A$, and $Pb(HA)A_2$. With all nine complexes present in the model the refinements failed, however. This is not unexpected since the concentrations of the complexes with $m+n=3$ obviously must be small.

As a guidance for further computations the stability constants of the complexes with $m+n=3$ were estimated as follows. $\beta_{0,3}$ and $\beta_{3,0}$ were calculated assuming an invariant ratio between the stepwise stability constants. The constants for the mixed complexes were then estimated on the assumption that the equilibrium constants for the reactions

$$2Pb(HA)_3 + PbA_3 \rightleftharpoons 3Pb(HA)_2A$$

and

$$Pb(HA)_3 + 2PbA_3 \rightleftharpoons 3Pb(HA)A$$
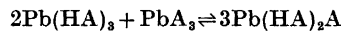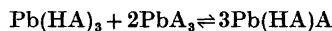
have the statistical value of 27 valid for closely related ligands. With these constants approximate distribution curves were calculated, which for the malonate and succinate systems indicated that PbA_3 and to a lesser extent $Pb(HA)A_2$ could be present in the solutions. In the glutarate and adipate systems the concentrations of PbA_3, $Pb(HA)_2A$, and $Pb(HA)A_2$ were approximately equal.

The $H^+ - A^{2-}$ *systems.* β_{101} and β_{201} were determined from titrations carried out with $A = 0.010$ and 0.025 M. The results are presented in Table 1. The β-values for malonic and succinic acid are in good agreement with those reported by Dellien and Malmström[8] and by Schwarzenbach and Szilard.[9] For the other two acids no constants are available in 1 M $NaClO_4$. The stepwise protonation constants of A^{2-}, K_1 and K_2, have been included in Table 1 to facilitate a comparison with their values in pure water, $K_1{}^\circ$ and $K_2{}^\circ$. Log K_2 shows the same increase with the number of CH_2-groups as does log $K_2{}^\circ$. The series of log $K_1{}^\circ$ values on the other hand exhibits a maximum at malonic

Table 1. Cumulative and stepwise protonation constants of A^{2-}. The values in pure water, $K°$, have been taken from Ref. 10. The figures within parentheses are three times the estimated standard deviations from the least-squares calculations.

Acid	$\beta_{101} \times 10^{-5}/M^{-1}$	$\beta_{201} \times 10^{-7}/M^{-2}$	$\log K_2$	$\log K_1$	$\log K_2°$	$\log K_1°$
Oxalic	0.0367 (0.0004)	0.00376 (0.00005)	1.01	3.56	1.271	4.266
Malonic	1.161 (0.003)	4.49 (0.02)	2.59	5.06	2.855	5.696
Succinic	1.317 (0.002)	129.6 (0.3)	3.99	5.12	4.207	5.638
Succinic (3 M NaClO$_4$)	3.057 (0.007)	643.0 (1.7)	4.32	5.49		
Glutaric	0.845 (0.004)	132.0 (0.6)	4.19	4.93	4.343	5.272
Adipic	0.878 (0.003)	175.6 (0.1)	4.30	4.94	4.430	5.277

and succinic acid. This maximum also shows up in 1 M NaClO$_4$.

The malonate system. The measurements were carried out with $B = 5 \times 10^{-4}$ M and the buffers (H/A, A_{max}/M); 0.17, 0.12; 0.57, 0.23; 0.81, 0.10; 1.47, 0.20. A_{max} is the highest value of A reached in the titration. The data obtained in the range where ⩽10 % of the ionic medium has been changed could be explained by the formation of PbHA, Pb(HA)$_2$, PbA, PbA$_2$, Pb(HA)A and $\sigma(E_{Pb})$ was 0.04 mV. This set of complexes does not satisfactorily account for the data at high ligand concentrations. Inclusion of PbA$_3$ and Pb(HA)A$_2$ removes systematic trends in $E_{calc} - E_{exp}$ and $\sigma(E_{Pb})$ is 0.03 mV. Addition of only one of these complexes leads to systematic deviations and $\sigma(E_{Pb})$ is 0.08 mV with only PbA$_3$ added. The low solubility of lead malonate limits the accessible concentration ranges and many titrations were interrupted by seemingly unpredictable precipitations. The solubility product of lead malonate, K_s, was therefore determined by equilibrating buffers with A^{2-} in the concentration range $a = (0.6 - 43) \times 10^{-3}$ M with lead malonate (s) and measuring b by the amalgam electrode. From 8 measurements K_s was found to be $(8.57 \pm 0.10) \times 10^{-8}$ M^{-2}. This value shows that the emf measurements have been carried out on supersaturated solutions. This could also

be the case for the other systems investigated but no further determinations of solubility products have been made. The result from the final least-squares refinement is found in Table 2.

The succinate system. The measurements were carried out with $B = 0.5$ and 1.0×10^{-3} M and the buffers; (H/A, A_{max}/M); 0.17, 0.13; 0.35, 0.17; 0.50, 0.13; 0.79, 0.17; 1.0, 0.20; 1.29, 0.28. This system has been studied more comprehensively than the others, since here the problems associated with the solubilities of the ligand and its lead compounds are less pronounced. The data at low ligand concentrations can be accounted for by the set of complexes with $m + n \leqslant 2$ and $\sigma(E_{Pb})$ was 0.04 mV. Inclusion of the data at high ligand concentrations necessitated the addition of PbA$_3$ and Pb(HA)A$_2$. $\sigma(E_{Pb})$ was 0.04 with both complexes added. With only one of them included, $\sigma(E_{Pb}) > 0.07$ mV.

The evidence for the presence of PbA$_3$ and Pb(HA)A$_2$ mainly comes from measurements where a substantial change in the medium has been made. The measurements were therefore repeated in 3 M Na(ClO$_4$). As in 1 M Na(ClO$_4$) the data could not be satisfactory explained with the complexes having $m + n \leqslant 2$ only. With the whole set of complexes found in 1 M Na(ClO$_4$) $\sigma(E_{Pb})$ was 0.11 mV. Addition of Pb(HA)$_2$A to the set lowered $\sigma(E_{Pb})$ to 0.06

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

Acid	β_{111}/M^{-2}	β_{212}/M^{-4}	β_{011}/M^{-1}	β_{012}/M^{-2}	β_{013}/M^{-3}	β_{112}/M^{-3}	β_{113}/M^{-4}
Oxalic [a]	9.7×10^4 (0.9)		1.46×10^4 (0.02)	2.12×10^6 (0.02)			
Malonic	1.60×10^6 (0.03)	3.49×10^{11} (0.19)	6.10×10^2 (0.01)	1.580×10^4 (0.003)	1.45×10^4 (0.04)	1.89×10^8 (0.04)	1.07×10^9 (0.06)
Succinic	9.59×10^6 (0.07)	1.01×10^{13} (0.02)	4.77×10^2 (0.02)	9.76×10^3 (0.12)	7.8×10^3 (1.6)	6.91×10^8 (0.14)	1.57×10^9 (0.26)
Succinic [b] (3 M NaClO$_4$)	3.52×10^7 (0.05)	1.46×10^{14} (0.03)	9.12×10^2 (0.08)	2.75×10^4 (0.06)	3.4×10^4 (0.7)	3.54×10^9 (0.10)	9.4×10^9 (1.9)
Glutaric	8.44×10^6 (0.08)	8.24×10^{12} (0.26)	3.21×10^2 (0.04)	5.83×10^3 (0.17)		5.24×10^8 (0.17)	
Adipic	9.78×10^6 (0.03)	1.13×10^{13} (0.01)	2.981×10^2 (0.007)	5.94×10^3 (0.03)		5.71×10^8 (0.05)	

[a] Ref. 2. [b] $\beta_{213} = (1.3 \pm 0.2) \times 10^{15}/M^{-5}$.

mV. No evidence for this complex could be found from the data in 1 M Na(ClO$_4$). Calculations with an estimated value of β_{213} showed that the amount of Pb(HA)$_2$A is less in 1 M than in 3 M Na(ClO$_4$) which could be the reason why it is not detected there. The final stability constants are found in Table 2.

The glutarate system. The measurements were carried out with $B = 5 \times 10^{-4}$ M and the buffers; $(H/A, A_{max}/M)$; 0.19, 0.12; 0.62, 0.20; 1.25, 0.40; 1.69, 0.37; 1.82, 0.12. Again the data at 10 % exchange of ClO$_4^-$ could be explained by the set of complexes with $m+n \leqslant 2$ and $\sigma(E_{Pb})$ was 0.08 mV. At higher ligand concentrations complexes with $m+n = 3$ were indicated. It was, however, not possible to establish their compositions. More than one of these complexes must be present since inclusion of only one additional complex in the calculations always resulted in a less satisfactory fit. With two complexes included $\sigma(E_{Pb})$ was always < 0.1 mV and any systematic trend in $E_{calc} - E_{exp}$ was less than 0.2 mV. This situation apparently arises because the affinity between Pb^{2+} and A^{2-} decreases as the chain length increases and at the same time the complexing properties of A^{2-} and HA$^-$ become more alike. This make the concentrations of complexes with $m+n = 3$ small

and much the same. Calculations based on estimated β-values indicate that the relative amount on any of these complexes does not exceed 5 %. The constants for $m+n \leqslant 2$ determined from measurements on solutions with < 10 % of the ClO$_4^-$ ions exchanged are entered in Table 2.

The adipate system. The measurements were carried out with $B = 5 \times 10^{-4}$ M and the buffers; $(H/A, A_{max})$; 0.18, 0.13; 0.64, 0.06; 0.78, 0.26; 1.29, 0.22; 1.57, 0.06. The data for less than 10 % exchange of ClO$_4^-$ can be explained by the constants in Table 2. $\sigma(E_{Pb})$ was 0.02 mV. In the adipate system the same situation arose as in the glutarate system when the data at high ligand concentrations were analysed. Several combinations of complexes yielded approximately the same $\sigma(E_{Pb}) \approx 0.03 - 0.04$ mV and no definite conclusions could be drawn. In addition there are few data at high ligand concentrations due to restrictions caused by the solubility of adipic acid.

DISCUSSION

In all systems the complexes Pb(HA), Pb(HA)$_2$, PbA, PbA$_2$, and Pb(HA)A are well established. The compositions of the complexes with $m+n = 3$ are uncertain in the glutarate and

Table 3. The stability constants, $\beta_{m,n}$, of protonated complexes written as $Pb(HA)_m(A)_n$.

Acid	$\beta_{1,0}/M^{-1}$	$\beta_{2,0}/M^{-2}$	$\beta_{1,1}/M^{-2}$	$\beta_{1,2}/M^{-3}$
Oxalic	26.5			
Malonic	13.8	26	1.63×10^3	9.22×10^3
Succinic	72.8	582	5.25×10^3	1.19×10^4
Succinic (3 M NaClO$_4$)	115	1560	1.16×10^4	3.07×10^4
Glutaric	99.9	1150	6.20×10^3	
Adipic	111	1470	6.50×10^3	

adipate systems. Hence no stability constants for such complexes have been entered in Table 2 for these systems. From a practical point of view this is of minor importance since the concentrations of the complexes are small. The procedure proposed in an earlier section to estimate these constants apparently yields fairly good results. The values obtained from the least-squares refinements are quite close to these estimates. It may at this point be apt to restate, that all conclusions regarding complexes with three ligands are based on the loosely-founded assumption of constant activity coefficients even for large changes in the salt background.

Table 3 has been constructed in order to facilitate a discussion of the stabilities of the complexes formed by HA$^-$. The relation between log $\beta_{1,0}$ and log K_2 is linear. $\beta_{1,0}$ for the hydrogen maleate complex also falls on this line. An extrapolation of the line to log K_2 for oxalic acid suggests that $\beta_{1,0}$ for $Pb(HC_2O_4)^+$ should be about 2 M^{-1}. The reported value [2] is 26.5 M^{-1}, which might indicate that the $-CO(OH)$ group is partially engaged in the bonding to the metal. The values of $\beta_{011} = \beta_{0,1}$ show the normal decrease and levelling off as the chain length of a bidentate ligand increases. The glutarate and adipate ions probably act as monodentate ligands. The log $\beta_{1,0}$ *vs.* log K_2 graph suggests that a monodentate ligand with a proton affinity corresponding to log $K = 5$ would form a 1:1 complex with a stability constant around
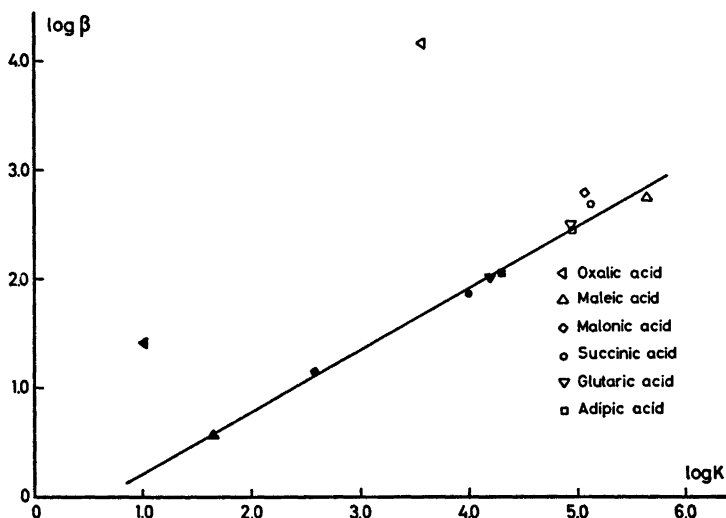

Fig. 4. Log β plotted as a function of log K (log $\beta_{1,0}$ *vs.* log K_2 filled and log $\beta_{0,1}$ *vs.* log K_1 open symbols). The log K_1 value for malonic acid and values for oxalic acid have been excluded in the calculations of the drawn line.

300 M^{-1}. The observed values are about 300 M^{-1}. It is interesting to note that, with the exception of the oxalate system and $\beta_{0,1}$ for the malonate system, the equation $\log \beta = -0.36 + 0.57 \log K$ predicts to 0.1 logarithmic unit the values of $\log \beta_{1,0}$ and $\log \beta_{0,1}$. See Fig. 4. In the equation $\log K_2$ is used for estimating $\log \beta_{1,0}$ and $\log K_1$ for estimating $\log \beta_{0,1}$. It might be argued that the use of $\log K_1$ overestimates $\beta_{0,1}$ for A^{2-} acting as a monodentate ligand. On account of the symmetry of A^{2-} another reasonable estimate would be $\beta_{0,1}$ (monodentate) $\approx 2\beta_{1,0}$. This estimate also suggests that A^{2-} is largely bound as a monodentate ligand.

Pb(HA)$^+$ is a stronger acid than HA$^-$ as expected. The exceptional stability of Pb(C_2O_4) makes Pb(HC_2O_4)$^+$ an even stronger acid than $H_2C_2O_4$. The equilibrium constant for Pb(HA)$_2$ + PbA$_2 \rightleftharpoons$ 2Pb(HA)A varies irregularly between 6.5 and 5 and is thus not far removed from the statistical value for two similar ligands. Using the value 6, $\beta_{1,1}$ for the maleate system becomes 5.6×10^{-2} M^{-1} and explains why a mixed complex could not be detected in that system.

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