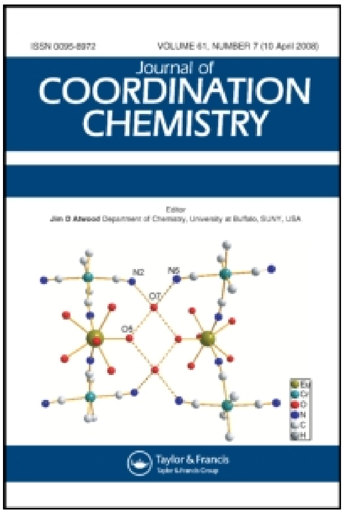

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AMINO-ACIDS AS LIGANDS: THE SYSTEM LEAD(II)-AMINOACETATE[†]

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The equilibria occurring between lead(II) and aminoacetate ion (L) have been investigated in 1 M ionic medium, (Na)ClO$_4$, at 25°C by potentiometric methods using lead stationary amalgam and glass electrodes.

The experimental data are explained by assuming the formation of the complexes PbL ($\log \beta = 4.78$), $PbHL$ ($\log \beta = 10.75$), PbL_2 ($\log \beta = 7.66$), $PbHL_2$ ($\log \beta = 14.7$), and PbH_2L_2 ($\log \beta = 21.15$).

INTRODUCTION

Complex formation between amino-acids and cations represents an object of investigation of our laboratory. Aminoacetate, 2- and 3-aminopropanoate as ligands towards cadmium(II) were reported in previous papers[1-3]. We now present results on the system lead(II)-aminoacetate.

Results obtained by other authors are collected in "Stability Constants".[4]

Mackenzie and Mellor[5] identified the complex PbL_2 with stability constant $\log \beta = 7.7$ (at 25°C and in 0.1 M KNO$_3$) using a glass electrode and $\log \beta = 7.4$ *via* polarographic measurements.

Other workers investigating the system by e.m.f. measurements carried out with a glass electrode but in different conditions of temperature and ionic strength, found evidence for the presence of PbL and PbL_2. Monk[6] found $\log \beta = 5.47$ and $\log \beta = 8.86$ at 25°C and $\mu \rightarrow 0$, Maley and Mellor[7] $\log \beta = 5.53$ and $\log \beta = 9.98$ (25°C and $\mu \simeq 0.01$), and Perkins[8] $\log \beta = 9.3$ (22°C in 0.01 M Pb(NO$_3$)$_2$).

More recently, Rao and Subrahmanya[9] explained their polarographic measurements at 30°C and in 1.0 M KNO$_3$ by assuming the formation of PbL ($\log \beta = 5.11$) and PbL_2 ($\log \beta = 7.08$).

The aim of the present work is to investigate the system lead(II) aminoacetate by means of e.m.f. measurements carried out using glass and stationary amalgam electrodes in a wide range of $-\log[H^+]$ and of the reagent concentrations, in order to establish the presence (or otherwise) of polynuclear or mixed complexes involving protons.

Symbols

B = total concentration of lead(II) corrected for hydrolysis.
b = concentration of free Pb^{2+}.
H = analytical excess of hydrogen ions; h = concentration of free H^+.
A = total concentration of the ligand; a = concentration of free ligand.
$\eta = \log (B/b)$
L = the ligand. Charges are omitted.
k_n = protonation constant of aminoacetate, defined by $[H_nL] = k_n h [H_{n-1}L]$ where $n = 1, 2$
$\beta_{r,p,q}$ = stability constant of the general species $Pb_qH_pL_r$, defined by:

$$[Pb_qH_pL_r] = \beta_{r,p,q} b^q h^p a^r$$

where $q \geqslant 1; p \gtreqless 0; r \geqslant 1$.

The hydrolysis constants $K_{z,w}$ and K_v refer, respectively, to the equilibria:

$$w\,Pb^{2+} + z\,H_2O \rightleftharpoons Pb_w(OH)_z + z\,H^+ \qquad K_{z,w}$$

$$Pb^{2+} + v\,OH^- \rightleftharpoons Pb(OH)_v \qquad K_v$$

METHOD OF INVESTIGATION

The equilibria between lead(II) and aminoacetate were investigated in 1.00 M (Na)ClO$_4$ as constant ionic medium; the activity coefficients may then be assumed to remain constant, according to Biedermann and Sillén[10].

Several types of titrations were performed. The first type of measurement, made using lead amalgam, allows determination of the b and h values[1]. B and H

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were kept constant whereas A was gradually increased until $-\log h$ reached the value $\simeq 9$. In the second type, for each experimental point, b values could be determined at constant B and h and by increasing A.

Other titrations were performed in alkaline solutions ($0.050 \leqslant [OH^-] \leqslant 0.2$ M) from which there was no evidence for complex formation

EXPERIMENTAL

Material and Analysis

Sodium perchlorate, perchloric acid, sodium hydroxide, and solutions of the ligands were prepared and used as described previously[11,12].

Lead(II) perchlorate stock solution was prepared by dissolving PbO in a slight excess of dilute $HClO_4$. PbO was prepared by igniting PbC_2O_4 at 750°C. This salt was obtained from $Pb(NO_3)_2$ (Riedel de Haën p.a. product) recrystallized twice from HNO_3 ($\simeq 0.01$ M), and $H_2C_2O_4$ which was recrystallized from water.

The $[Pb(II)]_{tot}$ in the solution was determined as sulphate, according to Winkler[13] and as iodate[14]. The results of several determinations agreed within ± 0.1%. The analytical excess of hydrogen ions ($\sim 10^{-4}$ M) in the stock solution was determined according to Gran[15]. Lead amalgam was prepared by dissolving freshly cut lead metal (Riedel de Haën) in bi-distilled mercury. It was stored under 10^{-2} M $HClO_4$ in a N_2 atmosphere. The concentration of the amalgam was ca. 0.1% (weight).

Nitrogen from cylinders was purified by passing it through two activated copper columns, 10% NaOH, 10% H_2SO_4, water and 1 M $NaClO_4$.

Details of the e.m.f. Measurements

All measurements were carried out at 25.00 ± 0.05°C. The cell arrangement was similar to that described by Forsling, Hietanen and Sillén[16]. Ag, AgCl reference electrodes were prepared according to Brown[17].

The behaviour of the glass electrode, the measurements and their reproducibility were as described in a previous work[2]. Measurements involving the amalgam electrode were performed with a Leeds and Northrup mod. k5 compensator. The amalgam electrode functioned satisfactorily, reaching constant values about 30 minutes after each addition and the reproducibility was within ± 0.1 mV.

DATA AND CALCULATION

In order to calculate the data in the form $\eta(-\log h \leqslant 9)$, the presence of hydrolytic species of lead (II) was taken into consideration. Olin[18,19] and Carell and Olin[20] determined the hydrolysis constants at 25°C but in different media (0.3 M $NaClO_4$, 3M $NaClO_4$, and self medium). The equilibria found in self medium are negligible under our experimental conditions. The values of the other hydrolysis constants at 25°C and 1 M $NaClO_4$ were calculated by linear interpolation from those obtained by Olin and Carell and Olin. We obtained: $\log K_{1,1} = -7.85$; $\log K_{4,4} = -19.73$; $\log K_{4,3} = -23.23$; $\log K_{8,6} = -42.53$; $\log K_2 = 10.49$ and $\log K_3 = 13.38$. This interpolation involves an insignificant loss of accuracy on B ($\leqslant 0.2\%$). We also determined the ionic product of water, k_w with a hydrogen electrode and found the value $-\log k_w = 13.78 \pm 0.02$.

Calculation of a, the Concentration of the Free Ligand

In the first type of measurements (H and B constant) the H values varied from 0.025 to 0.100 M. For each H, comparatively small values of B ($B \leqslant 0.02\, H$) were studied. Under these experimental conditions, the complexes concentration is negligible with respect to H; the material balance for H then becomes:

$$H = h + k_1 ha + 2k_1k_2h^2a \qquad (1)$$

where k_1 and k_2 (protonation constants of the ligand) determined previously[3] are: $\log k_1 = 9.73 \pm 0.03$ and $\log k_1k_2 = 12.22 \pm 0.04$.

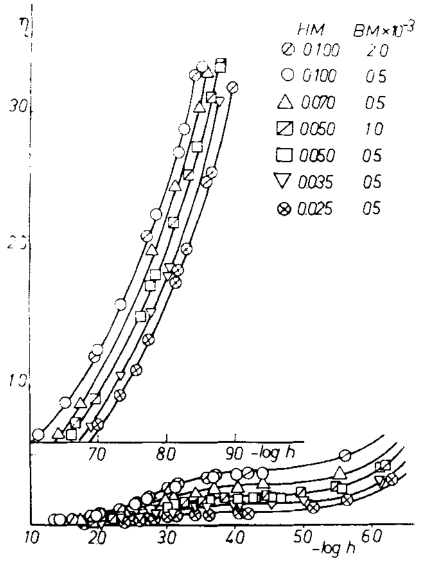

FIGURE 1 Experimental data $\eta(-\log h)$ at different B and H values. The curves, calculated with the proposed values of the constants, correspond to $B = 5 \times 10^{-4}$ M.

The experimental data obtained from these measurements are plotted in Figure 1 in the form $\eta(-\log h)_{H,B}$. The a values could be calculated from Eq. (1).

For the measurements carried out at constant $-\log h$, the a values were calculated from the material balance for A:

$$A = a + k_1ha + k_1k_2h^2a + (B - b) \qquad (2)$$

No significant loss of accuracy was involved, because it was assumed that when A was small complexes with $r = 1$ prevailed, whereas at higher A the complexes concentration could be neglected because in these measurements $B = 0.25 \times 10^{-3}$ M, hence $B \ll A$.

The Prevailing r, p and q Values

From Figure 1 it can be deduced that no polynuclear complexes are present, because points obtained at constant H and for different B fall on the same curve, hence η is independent of b and $q = 1$.

In order to verify the presence of mixed complexes with the participation of protons, some of experimental data were plotted in Figure 2 in the form $\eta(-\log a)$. As points obtained at different H fall on different curves, mixed complexes are present. Furthermore, η is an increasing function of H and consequently the complexes are formed with the taking up of protons, i.e. $p \geqslant 0$.

η is a function of h and a and its dependence on these parameters was studied by the method proposed by Sillén[21]. This method consists in deriving from three-variables data, such as $\eta(h, a)$, relationships between two variables at a constant value of the third; successively, the dependence on the third variable is studied.

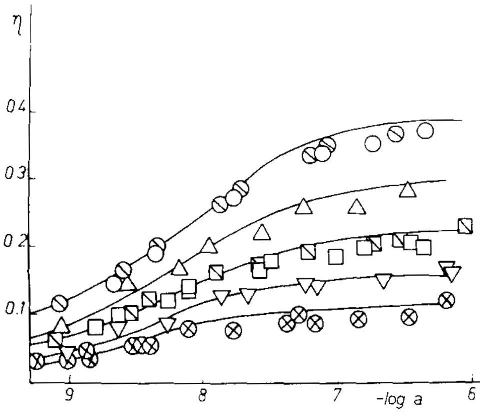

FIGURE 2 η as a function of $-\log a$. A part of the data is reported. The symbols are the same as in Figure 1.

TABLE I

(1) Survey of γ_1 and γ_2 values obtained from the data $\eta(-\log h)$
$-\log h(\log\gamma_1, \log\gamma_2)$: 2.75(7.90 ± 0.05, 15.97 ± 0.12); 3.25(7.42 ± 0.05, 14.80 ± 0.10); 3.75(6.96 ± 0.05, 13.63 ± 0.10); 4.50(6.22 ± 0.05, 12.13 ± 0.10); 5.50(5.43 ± 0.05, 9.85 ± 0.10); 6.50(4.90 ± 0.05, 8.64 ± 0.10); 7.50(4.85 ± 0.05, 7.63 ± 0.10); 8.25(4.87 ± 0.05, 7.61 ± 0.10); 8.75(4.94 ± 0.05, 7.64 ± 0.10).
(2) Survey of γ_1 and γ_2 values obtained from the measurements carried out at $-\log h$ constant.
$-\log h(\log\gamma_1, \log\gamma_2)$: 2.50(8.35 ± 0.05, ——); 3.00(7.67 ± 0.03, 15.33 ± 0.07); 4.00(6.71 ± 0.03, 13.13 ± 0.07); 5.00(5.80 ± 0.03, 11.30 ± 0.07); 6.00(5.20 ± 0.03, 9.41 ± 0.07); 7.00(4.88 ± 0.05, 7.83 ± 0.07); 8.00(4.94 ± 0.05, 7.59 ± 0.07).

·To find r and p values, three different approaches were used.

Approach I

From the B material balance, as polynuclear complexes are not present, we can write:

$$\eta = \log\left(1 + \sum_r \sum_p \beta_{r,p,1} h^p a^r\right) \qquad (3)$$

which can be rearranged to give:

$$\varphi_h = (10^\eta - 1)a^{-1} = \sum_r \gamma_r a^{r-1}$$

where $\gamma_r = \Sigma_p \beta_{r,p,1} h^p$ is constant at h constant. The φ_h functions were obtained by interpolation of the $\eta(-\log h)$ data at selected h values. The plots φ_h *versus* a showed that, to good approximation, φ_h can be expressed as a linear function of a in the whole h range; this means that r can assume the values 1 or 2. The intercept and the slope allowed calculations of the values γ_1 and γ_2, respectively (Table I). Other γ_1 and γ_2 values, also reported in Table I, were obtained from the measurements performed at $-\log h$ constant, without interpolation, but by simply plotting $(10^\eta - 1)a^{-1}$ *versus* a.

All γ_r data reported in Table I depend on h. Plotting the $\log\gamma_1$ values *versus* $-\log h$ and the $\log\gamma_2$ values *versus* $-\log h$, gave good agreement between the γ_r values obtained from two different experimental procedures. As an example, the function $\log\gamma_2(-\log h)$ is reported in Figure 3. In order to obtain the p values and the equilibrium constants the normalized curves method was applied[22] to the plots $\log\gamma_1$, and $\log\gamma_2$, *versus* $-\log h$.

By this method, the species PbL, PbHL, PbL_2, PbHL_2 and PbH$_2L_2$ were identified; their stability constants are collected in Table III, approach I.

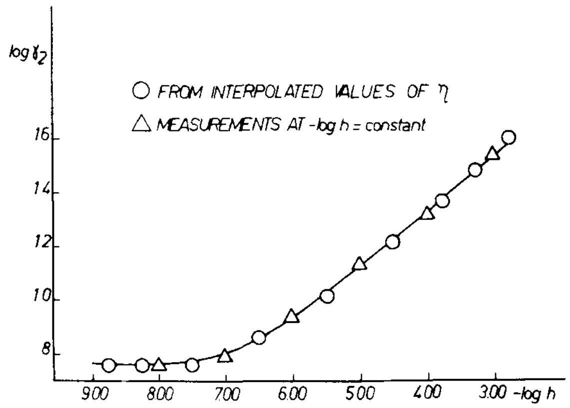

FIGURE 3 γ_2 as a function of $-\log h$. The curve is the normalized one in the position of best fit.

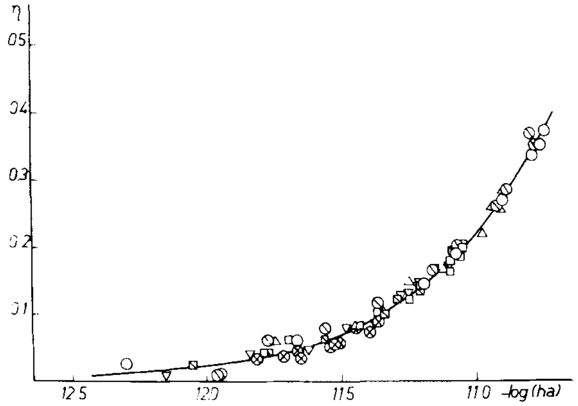

FIGURE 4 η as a function of $-\log(ha)$. The curve is the normalized one in the position of best fit. The symbols are the same as in Figure 1.

Approach II

Inspection of the experimental data shows that at $-\log h \geqslant 5$, for each H, the values $-\log(ha)$ remain constant within ± 0.01.

By putting $t = p - r$ and $\delta_t = \Sigma_r \Sigma_p \beta_{r,p,1} (ha)^r$, Eq. (3) can be expressed as:

$$\eta = \log\left(1 + \sum_t \delta_t h^t\right)$$

$\mathrm{Log}(10^\eta - 1)$ was plotted *versus* $-\log h$ and the plot compared with a family of normalized curves of equation:

$$y = \log(1 + \alpha u + u^2)$$

where $\log(10^\eta - 1) - y = \log \delta_0$; $u = h^{-1} \delta_{-2} \delta_0^{-1}$ and $\alpha = \delta_{-1}/(\delta_0 \delta_{-2})^{1/2}$. The two plots were moved parallel along the two axes to the best fit position; this gave the values of δ_0, δ_{-1} and δ_{-2} reported in Table II. These values now depend on the product ha. The plots $\delta_0 (ha)^{-1}$ and $\delta_{-1} (ha)^{-1}$ *versus ha* could be approximated by straight lines. From the former, the values of $\beta_{1,1,1}$ and $\beta_{2,2,1}$ (intercept and slope) and from the latter those of $\beta_{1,0,1}$ and $\beta_{2,1,1}$ (intercept and slope) were obtained.

TABLE II
Survey of δ_t values

H	$-\log(ha)$	$\log \delta_0$	$\log \delta_{-1}$	$\log \delta_{-2}$
0.100	10.73 ± 0.01	0.30 ± 0.08	−5.83 ± 0.10	−13.84 ± 0.08
0.070	10.88 ± 0.01	0.10 ± 0.05	−6.02 ± 0.08	−14.14 ± 0.05
0.050	11.03 ± 0.01	−0.08 ± 0.05	−6.26 ± 0.08	−14.36 ± 0.05
0.035	11.19 ± 0.01	−0.20 ± 0.08	−6.39 ± 0.10	−14.68 ± 0.05
0.025	11.33 ± 0.01	−0.30 ± 0.1	−6.57 ± 0.10	−14.94 ± 0.08

The parameters $\delta_{-2}(ha)^{-2}$ gave constant values and their average represents the $\beta_{2,0,1}$ value.

This approach provided evidence for the species $\mathrm{Pb}L$, $\mathrm{PbH}L$, $\mathrm{Pb}L_2$, $\mathrm{PbH}L_2$ and $\mathrm{PbH_2}L_2$ with the stability constants reported in Table III, approach II.

Approach III

In this approach we considered only the data obtained at $-\log h \leqslant 5$, where the ligand is present in the form $\mathrm{H}L$, i.e. we assume that η is a function of ha. Since the points fall on the same curve (Figure 4), this assumption is confirmed, and Eq. (3) reduces to

$$\eta = \log\left(1 + \sum_s \beta_{r,p,1} (ha)^s\right)$$

where $s = p = r$. Applying Sillén's normalized curve method[22] leads to the $\beta_{1,1,1}$ and $\beta_{2,2,1}$ values reported in Table III, approach III. The good agreement between experimental points and normalized curve is shown in Figure 4.

Proposed Values for the Equilibrium Constants

The $\beta_{r,p,1}$ values obtained by the different approaches are collected in Table III. In approach III only the species $\mathrm{PbH}L$ and $\mathrm{PbH_2}L_2$ are found, because of the low $-\log h$ range. The species found by approach I are the same as those found by approach II. The values of the constants are comparable. In order to refine the constants, theoretical curves were calculated with different sets of parameters, varying within the limits of those found from the different approaches.

The proposed values give the theoretical curves that agree better with the data, as shown in Figure 1.

TABLE III
Values of $\beta_{r,p,q}$

	Approach I	Approach II	Approach III	Proposed values
$\log \beta_{1,0,1}$	4.80 ± 0.05	4.74 ± 0.05	–	4.78 ± 0.05
$\log \beta_{1,1,1}$	10.75 ± 0.08	10.9 ± 0.3	10.74 ± 0.08	10.75 ± 0.10
$\log \beta_{2,0,1}$	7.65 ± 0.05	7.67 ± 0.05	–	7.66 ± 0.05
$\log \beta_{2,1,1}$	14.7 ± 0.15	15.0 ± 0.3	–	14.7 ± 0.2
$\log \beta_{2,2,1}$	21.2 ± 0.1	21.1 ± 0.15	21.12 ± 0.08	21.15 ± 0.15

By the proposed constants distribution curves of the complexes as a function of $-\log h$ at two A, were calculated, as shown in Figure 5. The species $PbHL$ and PbH_2L_2 prevail at $-\log h \leqslant 5$ and complexes with $r = 2$ are favoured at $A = 0.100$ M more than $A = 0.025$ M, as expected.

$[PbHL_2]$ is very small for both A, which explains the uncertainty in this constant.

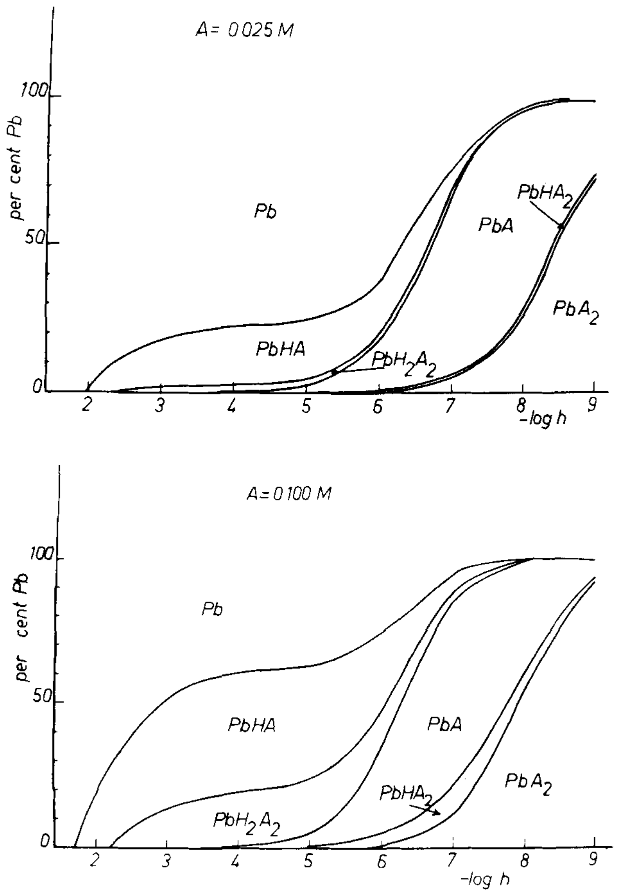

FIGURE 5 Distribution of complexes as a function of $-\log h$ for $B = 0.5 \times 10^{-3}$ M. (a) $A = 0.025$ M and (b) $A = 0.100$ M.

TABLE IV
Comparison between η_s (from amalgam electrode measurements) and η_t (calculated with the constants proposed in Table IV)

$H = 0.100$ M; $B = 0.050$ M
$\eta_s(\eta_t)$: 0.069(0.052); 0.094(0.083); 0.124(0.120); 0.162(0.165); 0.205(0.210); 0.233(0.241); 0.259(0.263); 0.272(0.275); 0.275(0.281); 0.302(0.298); 0.337(0.329).

The correctness of our conclusions is supported by a special series of measurements performed at $H = 0.100$ M and $B = 0.050$ M. The η values obtained directly from the measurements of lead amalgam and those calculated from the proposed constants agree very well, as shown in Table IV.

CONCLUSIONS

The main conclusion of this paper is that protonated complexes are formed between lead(II) and aminoacetate. On the other hand, there is no evidence for complexes involving take-up of OH^-.

The $\beta_{2,0,1}$ value agrees with that proposed by Mackenzie and Mellor, but not with those proposed by others. The proposed $\beta_{1,0,1}$ value is close to that obtained by Rao and Subrahmanya, if the different experimental conditions are taken into account.

By comparing the results obtained for lead(II) with those previously found by cadmium(II)[3], it can be seen that lead(II) bonds one or two L, while cadmium(II) also forms CdL_3. Furthermore, lead(II) forms PbH_2L_2 and $PbHL_2$, not present for cadmium(II). It is reasonable to suppose that in the case of Cd^{II} the formation of a 5-membered chelate ring is favoured by the higher affinity for aminic nitrogen.

Both $PbHL$ and $CdHL$ are present in the acidic range ($-\log h \leqslant 5$), and hence the chelate ring is opened by take-up of H^+. $PbHL$ is more stable than $CdHL$. These considerations suggest that protonation of the $-NH_2$ group is more probable than that of $-COO^-$.

It is of interest to study the behaviour of Pb^{II} towards other amino-acids as ligands and the formation of complexes between amino-acids and other cations. This will be the subject of further works.

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