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# POLYNUCLEAR COMPLEX FORMATION BETWEEN LEAD(II) AND 2-MERCAPTOETHANOL AND 3-MERCAPTO-1,2-PROPANEDIOL

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The complex formation between Pb(II) and 2-mercaptoethanol (MEL) and 3-mercapto-1,2-propanediol (MPD) was studied by a pH-metrical method at 25°C and in 0.5 $M$ $KNO_3$. The system Pb(II)/MEL can be represented by the formation of five complexes: $B_3A_5$, $B_2A$, $B_3A_4$, $B_2A_2$ and $B_2A_3$. The last two complexes are present only in a small amount. In the system Pb(II)/MPD the same predominant polynuclear complexes, are found, together with some mononuclear species $BA$, $BA_2$ and $BA_3$. The composition and the stability constants of the complexes were determined with the aid of a computerprogram PNUC.

## INTRODUCTION

The Pb(II) complexes of 2-mercaptoethanol (MEL) and 3-mercapto-1,2-propanediol (MPD) have hitherto not been investigated. Complexes of lead with some other, mercapto group containing, ligands are reported. LI and MANNING[1] determined $\log \beta_{1,1}$ for the reaction of Pb(II) with thioglycolic acid, 2-aminoethanethiol and cysteine as respectively 8.5, 11.1 and 12.20. As communicated in previous reports[2-4]: Ni(II), Zn(II) and Cd(II) form polynuclear complexes w[illegible] MEL and MPD.

[illegible]t is interesting to find out whether Pb(II) will also form polynuclear species with these ligands.

## EXPERIMENTAL

### *Reagents*

A stock solution of lead nitrate (Baker) was standardized gravimetrically as $PbCrO_4$.[5] Solutions of both ligands were prepared as indicated in a previous paper.[2] All solutions were made up to an ionic strength of 0.5 with potassium nitrate.

### *Apparatus*

The titration procedure of metalion complexes with thiols has been described before.[2,3] Five different total concentrations of metalion are used: 0.016 $M$, 0.008 $M$, 0.004 $M$, 0.002 $M$ and 0.001 $M$. The total ligand concentration was as usual[2] five times the Pb(II) ion concentration. A digital Radiometer pH $M$ 52, equipped with a glass electrode, type C, and a saturated calomelelectrode, was used for measuring pH values. The electrodes were standardized against a 0.01 $M$ borax buffer according to Bates.[6] A temperature of 25°C ± 0.1°C was maintained.

The calculations were performed with a number of computer-programmes, written in Fortran IV. The programmes were executed on a SIEMENS 4004/150 computer.

## SYMBOLS

As recommended by the IUPAC commission[7] the symbols used in this work are listed below.

$B$ : total concentration of Pb(II) ion.
$b$ : concentration of free Pb(II) ion.
$A$ : total ligand concentration.
$a$ : concentration of free ligand.
$h_ia$ : concentration of protanated ligand $H_iA$.
$h$ : activity of the hydrogen ion.
$K_{Hi}$ : mixed protonation constant of the ligand $H_iA$, defined as $K_{Hi} = h_ia/(h \cdot h_{i-1}a)$.
$N$ : maximum number of hydrogen ions that the ligand can take up.
$C_{base}$ : concentration of base added.
$Z$ : average number of ligand bound per Pb(II) ion.
$B(A_tB)_n$ : core + links representation of a complex.
$t$ : number of ligands in a link.

$n$ : variable integer: number of links in a "core + links" complex.
$\bar{n}$ : average number of links in a "core + links" complex.
$\beta_{q,p}$ : overall stability constant for a complex $B_qA_p$, defined as $\beta_{q,p} = [(B_qA_p)/b^q \cdot a_p]$.
$\log F$ $= \log (B/b)$.
$u$ $= a^t b$.
$y$ $= Z/t$.
$x$ $= t \log a + \log B$.

## RESULTS

The logarithms of the protanation constants $K_{H1}$ for MEL and MPD were determined previously as 9.49 and 9.43 respectively.[2] As mentioned before[4] the formation function $Z(\log a)_B$ can be calculated with a computer programme ZPAF using Eqs. (1) and (2)

$$a = \frac{\mathrm{N} \cdot \mathrm{A} - C_{\mathrm{base}} - (\mathrm{H}^+) + (\mathrm{OH}^-)}{\sum_{n=1}^{N} n \cdot h^n \cdot \prod_{i=1}^{n} K_{Hi}} \qquad (1)$$

$$Z = A - a(1 + \sum_{n=1}^{N} h^n \cdot \prod_{i=1}^{n} K_{Hi})/B \qquad (2)$$

The values of $h$ were obtained pH-metrically.

The constant and unknown shift of our pH-values due to our method of standardization, will not affect the $Z$ and $a$ values since our protonation constants are obtained in the same way. For determination of the concentration of hydrogen ions ($\mathrm{H}^+$) a proportionality factor, reported by Goeminne[8] was used. The term ($\mathrm{OH}^-$) could be neglected since the pH never exceeds 9.

In Figure 1 the formation function of the system $\mathrm{Pb}^{2+}$/MEL is shown. As can be seen on this figure the formation curves are not completely equidistant. At low and high values of $Z$, deviations are observed. By plotting $\log B$ versus $-\log a$, an average value of 2.5 was obtained for $t$. All complexes should be represented by the formula $B(A_{2.5}B)_n$. the $y$–$x$ curve calculated with this $t$ value is shown in Figure 2. As could be expected the $y$–$x$ curves do not cover each other at low and high $y$ values. From this $y$–$x$ curve the average number of links $\bar{n}$ was calculated.

These values are given in Table I. As can be seen from this table $\bar{n}$ varies between one and two. Since in the complex $B_qA_p$ $p$ and $q$ must be integer values

TABLE I
The average number of links in function of $y$

| $\bar{y}$ | $\bar{n}$ | $\bar{y}$ | $\bar{n}$ |
|---|---|---|---|
| 0.03 | 1.091 | 0.580 | 1.477 |
| 0.16 | 0.928 | 0.595 | 1.499 |
| 0.325 | 1.035 | 0.610 | 1.583 |
| 0.46 | 1.185 | 0.620 | 1.646 |
| 0.50 | 1.231 | 0.630 | 1.714 |
| 0.53 | 1.282 | 0.645 | 1.824 |
| 0.55 | 1.321 | 0.665 | 1.989 |

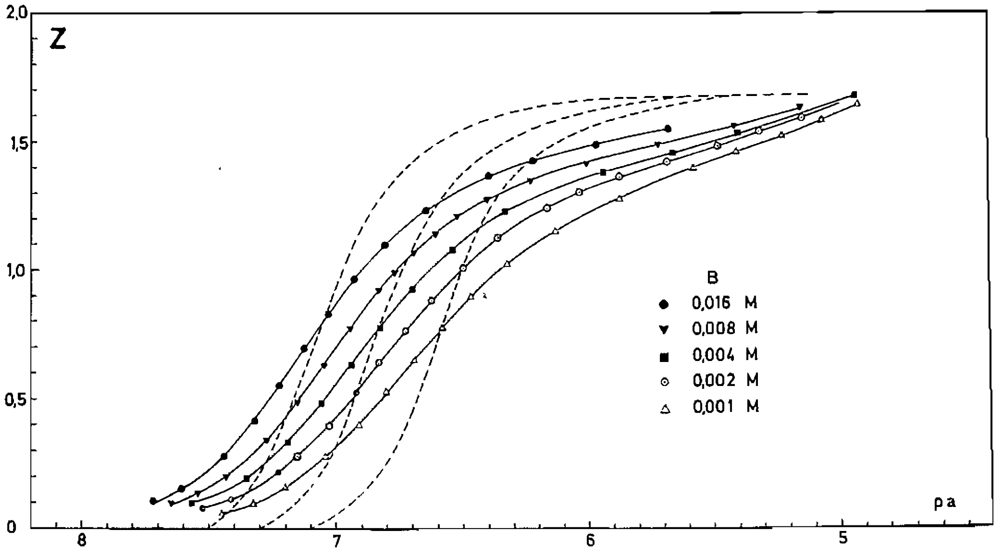

FIGURE 1 The formation curves of the system lead(II) and 2-mercaptoethanol. In dotted lines: theoretical curves for a complex $B_3A_5$ ($B$ = 0.016; 0.004; 0.001).

only the complex $B_3A_5$ could be present in solution.

This is in contradiction with Sillén's theory. Indeed: a single complex always defines a "core + links" series and the observed formation curves should be perfectly equidistant. The shape of the formation curves for a single complex $B_qA_p$ is only determined by the $p$ and $q$ value and a change in stability constant results in a shift along the $pa$ axis. With the aid of a computer programme ALTH[9] the theoretical formation curves or a complex $B_3A_5$ were calculated and plotted. They are shown in dotted lines in Figure 1. It was found that the theoretical and experimental curves have a different shape. The theoretical curves are much steeper than the experimental ones. At intermediate $Z$ values the spacing of experimental and theoretical curves is in agreement with each other. From this we can conclude that, together with a predominant complex $B_3A_5$, other species must be present. All the complexes present in solution are not related to each other as in a "core + links" series.

In order to determine the amount, composition and stability constants of the complexes a computer programme PNUC was designed. This programme is based on the ideas of Sillén, expressed in his programme LETAGROP.[10,11]

The stability constants of a set complexes $B_qA_p$ are determined by minimization of the "square-error sum" $U$, given by Eq. (3).

$$U = \Sigma(Z_{\mathrm{exp}} - Z_{\mathrm{calc}})^2 \tag{3}$$

$Z_{\mathrm{exp}}$ is the experimentally obtained value of the formation function. $Z_{\mathrm{calc}}$ is calculated from $a$, $B$, and estimated values of $\beta_{q,p}$ by means of Eq. 4.

$$Z_{\mathrm{calc}} = \frac{\sum_q\sum_p P\beta_{qp}b^q a^p}{B} \tag{4}$$

Since $b$ is unknown, this value is calculated from Eq. (5).

$$B - b - \sum_q\sum_p q\beta_{qp}b^q a^p = 0 \tag{5}$$

$U_{\mathrm{MIN}}$, the minimum value of $U$, is found with a minimization subroutine based on the "variable metric method" from Davidon.[12] At this minimum the standard deviation $\sigma^2(Z)$ is given by:

$$\sigma^2(Z) = U_{\mathrm{MIN}}/(n_{\mathrm{exp}} - n_{\mathrm{par}}) \tag{6}$$

$n_{\mathrm{exp}}$ is the number of experimental points and $n_{\mathrm{par}}$ is the number of stability constants.

The search for the amount and the composition of the complexes is based on the following principles. If all combinations of all possible complexes will be treated in the previous way, the set of present complexes, called the "best" set, will give the lowest $U_{\mathrm{MIN}}$ and $\sigma^2(Z)$ value. In this work the following strategy was chosen. Since $B_3A_5$ is predominant, complexes with $q$=2, 3 and 4 will be probable. For a combination of each of this complexes with $B_3A_5$ the function $U$ was minimized. The complex is accepted if the $U$ value is lower than $U_{\mathrm{MIN}}$, obtained with a single complex $B_3A_5$. Complexes are rejected if the $U$ value is not lowered or if their contribution to the formation function is small. This contribution, $\alpha_{q,p}$, is given by Eq. (7):

$$\alpha_{q,p} = \frac{q\beta_{qp}b^q a^p}{B} \tag{7}$$

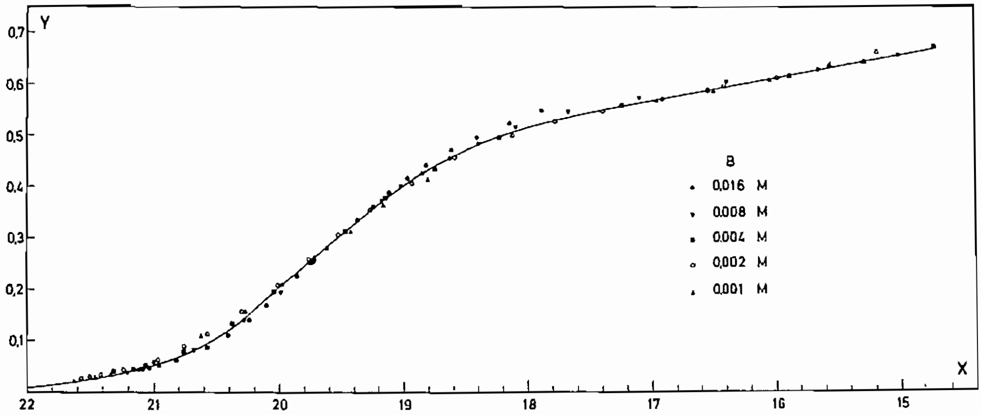

FIGURE 2 The $y$–$x$ curves of the system lead(II) and 2-mercaptoethanol.

Nine complexes were accepted. The total set was minimized in the same way. The results are given in Table II.

TABLE II

| complex | log $\beta_{q,p}$ | $\alpha_{q,p}$ MAX | present |
|---|---|---|---|
| $B_3A_5$ | 38.496 | 82 | + |
| $B_2A_1$ | 9.071 | 33 | + |
| $B_2A_2$ | 15.769 | 9 | ±? |
| $B_2A_3$ | 22.037 | 8 | ±? |
| $B_3A_2$ | 17.287 | 2 | – |
| $B_3A_3$ | 24.361 | 2 | – |
| $B_3A_4$ | 32.740 | 69 | + |
| $B_4A_3$ | 26.708 | 3 | – |
| $B_4A_5$ | 41.012 | 5 | – |

$\alpha_{q,p}$MAX is the maximum value of $\alpha_{q,p}$, given in percent, for a complex $B_qA_p$ in the set of experimental points. From this table it can be seen that three complexes must be accepted, two complexes are possible and the four others are probably absent. The model formed by the complexes $B_3A_5$, $B_2A$ and $B_3A_4$ will be a good representation for the system Pb$^{2+}$/MEL. In order to improve this model the other complexes were successively added to it and $U$ was minimized again. The results are given in Table III. It was found that the complexes $B_2A_2$ and $B_2A_3$, did improve the minimum for a small amount. So, the with *marked model in Table III is the best representation for the system Pb$^{2+}$/MEL.

The complexes formed between Pb$^{2+}$ and MPD were determined in the same way. In Figure 3 the formation curves for this system are shown. As these complexes are more soluble the formation curves can be obtained over a wider concentration range. The cross-over point found is a strong indication for a mixture between polynuclear and mononuclear complexes.[9,13] The results obtained with the progra[illegible]e PNUC are given in Table IV.

## DISCUSSION

As seen above the following complexes are formed between 2-mercaptoethanol (MEL) and Pb(II): $B_3A_5$, $B_2A$, $B_3A_4$, $B_2A_2$ and $B_2A_3$. With 3-mercapto-1, 2-propanediol (MPD), Pb(II) forms the polynuclear complexes $B_3A_5$, $B_2A$, $B_3A_4$ and the mononuclear species $BA$, $BA_2$ and $BA_3$. With MEL precipitation of yellow crystals occurred at $Z$=1.6 and no mononuclear species could be detected.

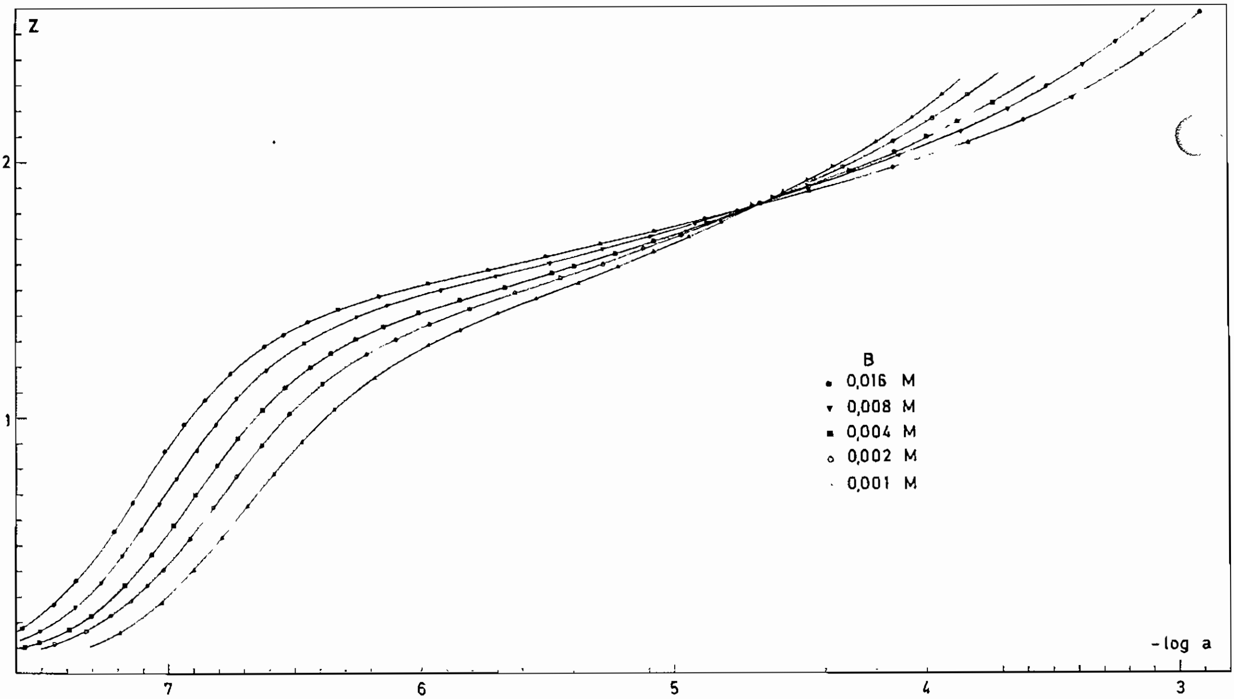

FIGURE 3 The formation curves of the system lead(II) and 3-mercapto-1,2-propanediol.

TABLE III

| model | log $\beta_{q,p}$ | $\alpha_{q,p}$ MAX | present | $U_{\text{MIN}}$ | $\sigma^2\ (Z)$ |
|---|---|---|---|---|---|
| $B_3A_5$ | 38.484 | 85 | + | 0.8449 $10^{-1}$ | 0.162 $10^{-2}$ |
| $B_2A_1$ | 9.066 | 36 | + | | |
| $B_3A_4$ | 32.780 | 78 | + | | |
| $B_3A_5$ | 38.513 | 88 | + | 0.7798 $10^{-1}$ | 0.153 $10^{-2}$ |
| $B_2A_1$ | 8.925 | 28 | + | | |
| $B_3A_4$ | 36.692 | 70 | + | | |
| $B_2A_2$ | 15.771 | 12 | + | | |
| $B_3A_5$ | 38.500* | 84 | + | 0.7583 $10^{-1}$ | 0.152 $10^{-2}$ |
| $B_2A_1$ | 8.937 | 28 | + | | |
| $B_3A_4$ | 32.654 | 66 | + | | |
| $B_2A_2$ | 15.769 | 11 | + | | |
| $B_2A_3$ | 22.034 | 9 | + | | |
| $B_3A_5$ | 38.495 | 88 | + | 0.7951 $10^{-1}$ | 0.159 $10^{-2}$ |
| $B_2A_1$ | 8.874 | 25 | + | | |
| $B_3A_4$ | 32.685 | 70 | + | | |
| $B_2A_2$ | 15.745 | 11 | + | | |
| $B_3A_2$ | 17.274 | 3 | – | | |
| $B_3A_5$ | 38.493 | 88 | + | 0.8090 $10^{-1}$ | 0.162 $10^{-2}$ |
| $B_2A_1$ | 8.877 | 26 | + | | |
| $B_3A_4$ | 32.673 | 70 | + | | |
| $B_2A_2$ | 15.743 | 11 | + | | |
| $B_3A_3$ | 24.359 | 2 | – | | |
| $B_3A_5$ | 38.494 | 88 | + | 0.8069 $10^{-1}$ | 0.161 $10^{-2}$ |
| $B_2A_1$ | 8.874 | 25 | + | | |
| $B_2A_4$ | 32.683 | 70 | + | | |
| $B_2A_2$ | 15.745 | 11 | + | | |
| $B_4A_3$ | 26.707 | 4 | – | | |
| $B_3A_5$ | 38.492 | 88 | + | 0.8322 $10^{-1}$ | 0.166 $10^{-2}$ |
| $B_2A_1$ | 8.886 | 26 | + | | |
| $B_3A_4$ | 32.659 | 66 | + | | |
| $B_2A_2$ | 15.744 | 11 | + | | |
| $B_4A_5$ | 41.008 | 6 | – | | |

The complexes found cannot be classified under a "core + links" series $B(A_tB)_n$. Concerning this aspect the $Pb^{2+}$ complexes are an exception in the series of metal ions studied with these ligand hitherto. Indeed, the $Zn^{2+}$ complexes[3] can be represented by a "core + links" system $B(A_3B)_n$ with $n_{\max} = 5$. $Ni^{2+}$ forms[2] with MEL and MPD complexes $B(A_2B)_n$ with $n$ great. $Cd^{2+}$ was found[4] to form polymeric complexes $B(A_5B_3)_n$.

Proposing a structure for the $Pb^{2+}$ complexes would be no more than a speculation. The coordination number of $Pb^{2+}$ is sometimes called a chemical camelion and indications are found that the $s$ electrons sometimes get a $p$ character. A direct Pb–Pb bound seems not to be impossible.

TABLE IV

| complex | log $\beta_{q,p}$ | complex | log $\beta_{q,p}$ |
|---|---|---|---|
| $B_3A_5$ | 38.088 | $BA$ | 6.634 |
| $B_2A_1$ | 7.87 | $BA_2$ | 12.495 |
| $B_3A_4$ | 32.415 | $BA_3$ | 15.901 |

Other investigations of the complexation of $Pb^{2+}$ with sulfur containing ligands will be necessary for a better knowledge of the (Pb–S) bound.

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