

Studies on Metal Carbonate Equilibria.18. Lead(II) Carbonate Complexes in Alkaline Solutions

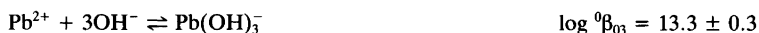
D. Ferri,^a I. Grenthe,^b S. Hietanen^b and F. Salvatore^a

^aDipartimento di Chimica dell'Universita, via Mezzocannone, 4, 80134 Napoli, Italy and ^bThe Royal Institute of Technology, Department of Inorganic Chemistry, S-100 44 Stockholm, Sweden

Ferri, D., Grenthe, I., Hietanen, S. and Salvatore, F., 1987. Studies on Metal Carbonate Equilibria.18. Lead(II) Carbonate Complexes in Alkaline Solutions. - Acta Chem. Scand., Ser. A 41: 349-354.

Potentiometric measurements with a glass electrode and a Pb amalgam electrode at 25 °C have shown that in a 1 M NaClO₄-1 M Na₂CO₃ solution, at acidities ranging from [OH⁻] = 10^{-3.5} M to [OH⁻] = 10^{-0.78} M, and for 10^{-3.398} M ≤ [Pb(II)] ≤ 10^{-2.699} M, the prevailing forms of lead(II) are Pb(CO₃)₂²⁻, PbCO₃OH⁻ and Pb(OH)₃⁻.

The equilibrium constants, expressed on a 3 M NaClO₄ activity scale, have been evaluated for the following reactions



The stoichiometry of the complexes and the magnitude of the equilibrium constants indicate a coordination geometry with Pb(II) at the apex of a square or trigonal pyramid (as found in many solid structures) and with chelate bonded CO₃²⁻.

In a previous study¹ we have examined the chemical equilibria in the Zn(II)-OH⁻-CO₃²⁻ system in 1 M CO₃²⁻. The experimental techniques that might be used to study this system, and the chemical interpretation of the data, are not straightforward. One reason for this is that the low solubilities of ZnCO₃(s) and basic zinc carbonates make it difficult to perform precise potentiometric measurements with metal ion-selective electrodes. We were able to give a reasonable chemical description of the system. Both the nature of the complexes formed, Zn(CO₃)₂²⁻, Zn(OH)₂CO₃²⁻ and Zn(OH)₄²⁻, and their equilibrium constants were in agreement with the known chemical properties of the central ion (four-coordination, presumably in tetrahedral geometry) and the ligand (the formation of chelate complexes as judged by the magnitude of the equilibrium constants).

In the present study we have used the same experimental conditions and the same method to

explore the composition of the complexes formed in the Pb(II)-OH⁻-CO₃²⁻ system. Some previous studies have been made of the Pb(II)-CO₃²⁻ system at lower acidities and carbonate concentrations,²⁻⁸ and a number of different experimental methods have been used, all indicating the formation of PbCO₃ and Pb(CO₃)₂²⁻. The equilibrium constants are in rather good agreement, and are given by the values log β₁₀ ~ 6 and log β₂₀ ~ 9. Under the experimental conditions used by us, one expects the formation of mixed hydroxide/carbonate complexes. We use the composition of these for a discussion of the coordination number and coordination geometry of Pb(II).

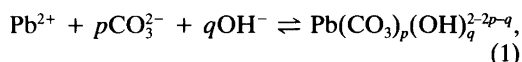
Pb(II) has a stereochemically "active" lone-pair, which often results in pyramidal coordination with Pb(II) at the apex, e.g. in Pb₆O₄(OH)₄, Pb₆O(OH)₆⁴⁺ and Pb₄(OH)₄⁴⁺ (cf. Wells⁹). The stoichiometry of the limiting hydroxide complex Pb(OH)₃⁻ indicates a similar coordination geometry. From a coordination chemical point of view

one might then expect to find the formation of complexes such as $\text{Pb}(\text{OH})\text{CO}_3^-$ and perhaps $\text{Pb}(\text{OH})_2\text{CO}_3^{2-}$, while $\text{Pb}(\text{OH})_3\text{CO}_3^{3-}$ and $\text{Pb}(\text{OH})(\text{CO}_3)_2^-$ are less probable. Carbonate is an excellent bridging ligand, but polynuclear complexes with bridging carbonates do not seem to be formed at high carbonate concentrations.¹⁰⁻¹³

A study of equilibria in the $\text{Pb}(\text{II})\text{-OH}^-\text{-CO}_3^{2-}$ may give additional information on the constitution of mononuclear $\text{Pb}(\text{II})$ complexes.

Notations

The reacting species, Pb^{2+} and CO_3^{2-} form a series of mononuclear (*vide infra*) complexes, $\text{Pb}(\text{CO}_3)_p(\text{OH})_q^{2-2p-q}$, according to the general reaction:



f_{pq} = activity factor of the species $\text{Pb}(\text{CO}_3)_p(\text{OH})_q^{2-2p-q}$ on the 3 M NaClO_4 activity scale.

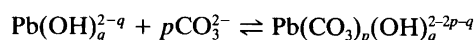
B = analytical concentration of lead(II)

C = analytical concentration of OH^-

c = free concentration of OH^-

β_{pq} and ${}^0\beta_{pq}$ = formation constants for reaction (1) on the 1 M NaClO_4 -1 M Na_2CO_3 and 3 M NaClO_4 activity scales, respectively.

K_{pq} and ${}^0K_{pq}$ = equilibrium constants for the reaction:

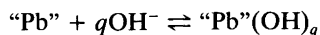


on the 1 M NaClO_4 -1 M Na_2CO_3 and the 3 M NaClO_4 activity scales, respectively.

β_q is the conditional equilibrium constant for the reaction:

Table 1. Survey of the $E_b(\log c)_B$ data. E_b in mV.

$\log B$	$-E_b(-\log c)$
-3.398	798.2 (2.560), 797.7 (2.644), 797.3 (2.714), 797.1 (2.784), 796.9 (2.893), 796.7 (2.974), 796.5 (3.096), 796.2 (3.180), 795.9 (3.245), 795.6 (3.356), 795.3 (3.432), 794.9 (3.491), 794.4 (3.561)
-3.398	802.1 (2.105), 797.7 (2.423), 800.2 (2.222), 803.8 (1.970), 806.9 (1.803), 810.0 (1.669), 812.9 (1.573), 815.5 (1.485), 817.8 (1.424), 822.1 (1.319), 825.7 (1.243), 830.3 (1.147), 835.8 (1.051), 838.6 (1.001)
-3.398	797.3 (2.462), 796.9 (2.525), 796.5 (2.602), 796.3 (2.675), 796.2 (2.734), 796.3 (2.832), 796.2 (3.001), 796.0 (3.091), 795.6 (3.187), 795.4 (3.295), 795.3 (3.365), 795.3 (3.414), 795.6 (3.486)
-3.398	799.6 (2.278), 803.1 (2.001), 804.3 (1.968), 806.4 (1.864), 807.4 (1.801), 810.2 (1.678), 811.7 (1.617), 814.5 (1.525), 816.5 (1.465), 818.6 (1.402), 822.5 (1.307), 825.4 (1.238), 827.2 (1.201), 831.6 (1.111), 834.9 (1.044)
-3.222	848.9 (0.772), 847.4 (0.778), 846.0 (0.792), 844.4 (0.807), 843.3 (0.822), 842.0 (0.842), 839.8 (0.875), 836.8 (0.915), 833.8 (0.963), 831.3 (0.995), 828.2 (1.003), 825.4 (1.088), 823.0 (1.128), 820.2 (1.184), 816.9 (1.251), 813.2 (1.316), 812.2 (1.356)
-3.000	841.4 (0.831), 839.7 (0.836), 838.1 (0.843), 836.7 (0.856), 835.4 (0.871), 834.1 (0.883), 831.7 (0.912), 828.4 (0.951), 827.4 (0.973), 824.6 (1.010), 822.0 (1.042), 820.0 (1.078), 817.8 (1.130), 814.8 (1.189)
-3.000	832.2 (0.956), 830.4 (0.971), 828.6 (0.991), 827.1 (1.015), 825.7 (1.035), 824.2 (1.054), 821.7 (1.099), 818.2 (1.155), 816.6 (1.165), 813.3 (1.220), 811.0 (1.272), 809.4 (1.326), 807.7 (1.395)
-2.699	832.2 (0.837), 832.0 (0.837), 831.3 (0.841), 830.4 (0.849), 829.6 (0.859), 828.8 (0.864), 827.2 (0.880), 825.9 (0.903), 824.6 (0.915), 822.2 (0.949), 819.8 (0.983), 818.9 (0.996), 818.1 (1.012), 817.2 (1.025), 816.3 (1.051), 814.6 (1.074), 813.6 (1.104)

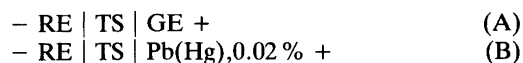


where “Pb” is the sum over p of all the species $\text{Pb}(\text{CO}_3)_q^{2-2p}$, referred to the 1 M NaClO_4 -1 M Na_2CO_3 activity scale.

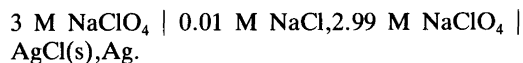
All equilibrium constants are expressed in molar units.

Method

The emfs, E_a and E_b , of the cells:



have been measured at 25°C. RE denotes the reference half cell:

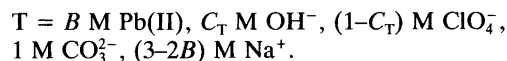


GE is the glass electrode and TS represents the test solution of the following composition:

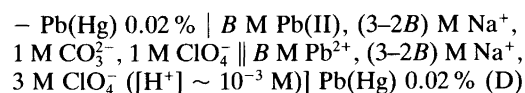


B ranged from $4 \cdot 10^{-4}$ M to $2 \cdot 10^{-3}$ M, and the free hydroxide concentration, c , from $10^{-3.5}$ M to $10^{-0.78}$ M.

The E_b ($\log c$) $_B$ data, reported in Table 1, were collected by measuring the emf of cells (A) and (B) after each addition to TS of the titrant solution, T, of composition:



In addition, the emf, E_d , of the cell:



was measured, at 25°C, for a series of B values in the range investigated.

Experimental

Materials and analysis. A stock solution of $\text{Pb}(\text{ClO}_4)_2$ was prepared by dissolving PbO(s)

(Merck *p.a.*) in perchloric acid (Merck *p.a.*). The lead concentration was determined by complexometric titration with EDTA using Xylenol Orange as indicator, according to the procedure suggested by Schwarzenbach.¹⁴

NaClO_4 stock solutions were prepared and analyzed as described elsewhere.¹⁵ Na_2CO_3 (Merck *p.a.*) was used without further purification. NaOH solutions were prepared and analyzed according to Ref. 10.

Measurements. All the measurements were performed at $25.00 \pm 0.01^\circ\text{C}$ (oil bath). The cell arrangement was similar to that described by Forsling *et al.*¹⁶ The Ag, AgCl electrodes were prepared according to Brown.¹⁷ Metrohm glass electrodes were employed and were calibrated, in the acidity range investigated, versus the hydrogen electrode. A small correction for the sodium error had to be introduced only at the lowest acidities. Lead amalgams were prepared by electrolysis of acidic $\text{Pb}(\text{ClO}_4)_2$ solutions. The electrolysis (at 3 mA constant current) was carried out for the time required to obtain 0.0200% amalgams.

Emf measurements were performed with a precision of 0.1 mV using the apparatus described elsewhere.¹

Calculations

The deduction of the stoichiometric coefficients (p, q) for the predominant complexes is made in the same way as described previously.¹

I. *Determination of q and β_q .* The experimental data, $(E_b - 29.58 \log B)$ vs. $-\log [\text{OH}^-]$, were tested with normalized functions. The only model that gave an acceptable fit included complexes with $q = 1$ and 3. The normalized function (the full-drawn curve in Fig. 1) was

$$Y = 29.58 \log (1+u+Lu^3) \text{ vs } -\log u,$$

where $u = \beta_1 \cdot c$ and $L = \beta_3/\beta_1^3$.

From the position of best fit and the value $L = 0.028$, we obtain

$$\log \beta_1 = 1.98 \pm 0.05$$

$$\log \beta_3 = 4.4 \pm 0.2$$

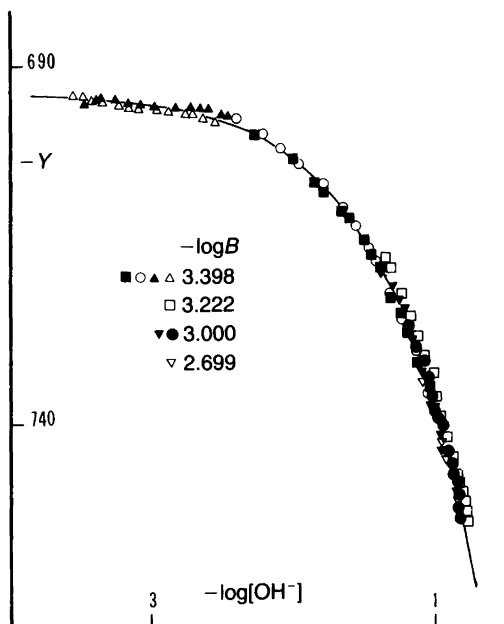


Fig. 1. The symbols represent the experimental function $Y = E_b - 29.58 \log B$ vs. $-\log[\text{OH}^-]$. The model curve has been calculated by assuming $q = 1$ and 3 and using the values of the equilibrium constants reported in the text.

where the errors are graphically estimated maximum errors.

II. Estimation of the predominant values of p .
From eqn. (6) in Ref. 1 we have

$$\beta_q = {}^0\beta_{0q} \cdot f_{\text{Pb}^{2+}} \cdot f_{\text{OH}^-}^{-1} \cdot f_q^{-1} \cdot \left(1 + \sum_{p=1} K_{pq} [\text{CO}_3^{2-}]^p\right) / \left(1 + \sum_{p=1} \beta_{p0} [\text{CO}_3^{2-}]^p\right)$$

where the activity coefficients f_i in the 1 M NaClO_4 -1 M Na_2CO_3 solutions are referred to the 3 M NaClO_4 scale. According to the specific ion interaction theory (SIT) the activity coefficients of all species with a negative charge are expected to be equal to unity (cf. Ref. 1).

A value of

$$\log f_{\text{Pb}^{2+}} / \left(1 + \sum_{p=1} \beta_{p0} [\text{CO}_3^{2-}]^p\right) = -8.9 \pm 0.1$$

was obtained from the measured emf of cell (D). The error was mainly due to the uncertainty in the diffusion potential E_j , which we estimate to be less than 3 mV.

From eqn. (6) in Ref. 1 we have

$$\log \beta_q = \log {}^0\beta_{0q} + \log \left(1 + \sum_{p=1} K_{pq} [\text{CO}_3^{2-}]^p\right) - \log \left[\left(1 + \sum_{p=1} \beta_{p0} [\text{CO}_3^{2-}]^p\right) / f_{\text{Pb}^{2+}} \right]$$

The mononuclear hydrolysis constants $\log {}^0\beta_{01} = 6.3 \pm 0.1$, $\log {}^0\beta_{02} = 10.9 \pm 0.1$ and $\log {}^0\beta_{03} = 13.66 \pm 0.05$ were taken from Olin and Carell¹⁸ and Olin.¹⁹

From the SIT^{1,20} one can easily deduce that $f_{\text{Pb}^{2+}} = \beta_{p0} / {}^0\beta_{p0}$. Hence, we have in 1 M CO_3^{2-}

$$\log \left(\left[1 + \sum_{p=1} \beta_{p0}\right] / f_{\text{Pb}^{2+}} \right) = \log \left(1 + \sum_{p=1} {}^0\beta_{p0}\right) = 8.9 \pm 0.1.$$

From previous equilibrium information we can safely assume that the limiting binary lead(II) carbonate complex in 1 M CO_3^{2-} is $\text{Pb}(\text{CO}_3)_2^{2-}$. The equilibrium constant is then

$$\log {}^0\beta_{20} = 8.9 \pm 0.1$$

This value is in good agreement with the results of previous investigators.

We can now continue and estimate the composition and the equilibrium constants of the ternary complexes $\text{Pb}(\text{OH})_q(\text{CO}_3)_p$.

For $q = 3$ we have $f_{\text{Pb}(\text{OH})_3^-} = 1$, hence:

$$\log \beta_3 = 4.4 = \log {}^0\beta_{03} + \log \left(1 + \sum_{p=1} {}^0K_{p3}\right) - 8.9$$

$$\log \left(1 + \sum_{p=1} {}^0K_{p3}\right) = -0.36 \pm 0.4$$

i.e. $\Sigma {}^0K_{p3}$ is not significantly different from zero. This indicates that no mixed complexes such as

Table 2. Summary of the results on the 3 M NaClO₄ activity scale.

$\text{Pb}^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{Pb}(\text{CO}_3)_2^{2-}$	$\log^0 \beta_{20} = 8.9 \pm 0.1$
$\text{Pb}^{2+} + \text{CO}_3^{2-} + \text{OH}^- \rightleftharpoons \text{PbCO}_3\text{OH}^-$	$\log^0 \beta_{11} = 10.9 \pm 0.3$
$\text{Pb}^{2+} + 3\text{OH}^- \rightleftharpoons \text{Pb}(\text{OH})_3^-$	$\log^0 \beta_{03} = 13.3 \pm 0.3$

$\text{Pb}(\text{OH})_3\text{CO}_3^{3-}$ are formed, or at least that the equilibrium constants for the addition of CO_3^{2-} to $\text{Pb}(\text{OH})_3^-$ are very small.

For $q = 1$ we have

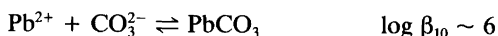
$$\log \beta_1 = 1.98 = \log^0 \beta_{01}$$

$$+ \log \left(1 + \sum_{p=1} K_{p1} \right) / f_{\text{PbOH}^+} - 8.9$$

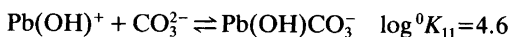
$$= 6.3 + \log \left(1 + \sum_{p=1} {}^0 K_{p1} \right) - 8.9 ;$$

$$\log \left(1 + \sum_{p=1} {}^0 K_{p1} \right) = 4.6 \pm 0.2_5$$

The previous data indicate that the maximum coordination number in the $\text{Pb}(\text{II})\text{-OH}^-\text{-CO}_3^{2-}$ system is ≤ 4 . Hence, we assume that only one mixed species, $\text{Pb}(\text{OH})\text{CO}_3^-$ is formed. A comparison of the equilibrium constants for the reactions



and



supports this assumption.

A summary of the reactions proposed, and of their corresponding equilibrium constants, is given in Table 2.

Conclusions and discussion

The experimental values of $\log \beta_{20}$, found by different investigators using different experimental methods and different ionic media, are reasonably consistent as judged by the data given in Table 3. The values of $\log^0 \beta_{20}$ refer to $I = 0$, and have been calculated using the SIT-method. The interaction coefficients $\epsilon_{\text{Pb}^{2+}, \text{ClO}_4^-}$, $\epsilon_{\text{Pb}^{2+}, \text{NO}_3^-}$ and $\epsilon_{\text{CO}_3^{2-}, \text{Na}^+}$ were taken from Ciavatta,²¹ while $\epsilon_{\text{Pb}(\text{CO}_3)_2^{2-}, \text{Na}^+} \sim -0.1$ was estimated from the charge of the complex and comparison with the interaction coefficients of other species of charge -2 .

The results obtained in this study strongly indicate the formation of a set of mononuclear binary and ternary complexes in the $\text{Pb}(\text{II})\text{-OH}^-\text{-CO}_3^{2-}$ system at $[\text{CO}_3^{2-}] = 1$ M. A distribution diagram is shown in Fig. 2.

The ratio β_{10}^2/β_{20} involving the stepwise constants for the formation of PbCO_3^0 and $\text{Pb}(\text{CO}_3)_2^{2-}$ taken from the data of Bilinski and Schindler⁸ is around 10^3 . This indicates that the chelate formed by the second carbonate is noticeably weaker than that formed by the first. This, in turn, might indicate a preference for three-coordination, as indicated by the stoichiometries

Table 3. Logarithm of the formation constant of $\text{Pb}(\text{CO}_3)_2^{2-}$ in different ionic media (column I). In column II the values of column I are extrapolated to $I = 0$, using the SIT-method, to facilitate comparisons.

Method	Medium	I	II	Ref.
A.s.v. ^a	0.1 M KNO ₃	9.8	10.6	7
D.p.p. ^b	0.1 M KNO ₃	9.1	9.9	7
Solubility	0.3 M NaClO ₄	8.9 ± 0.1	10.1	8
Solubility	1 M NaClO ₄	9.0	10.5	3
Emf	3 M NaClO ₄	8.9 ± 0.1	10.4	This work

^aAnodic stripping voltammetry. ^bDifferential pulse polarography.

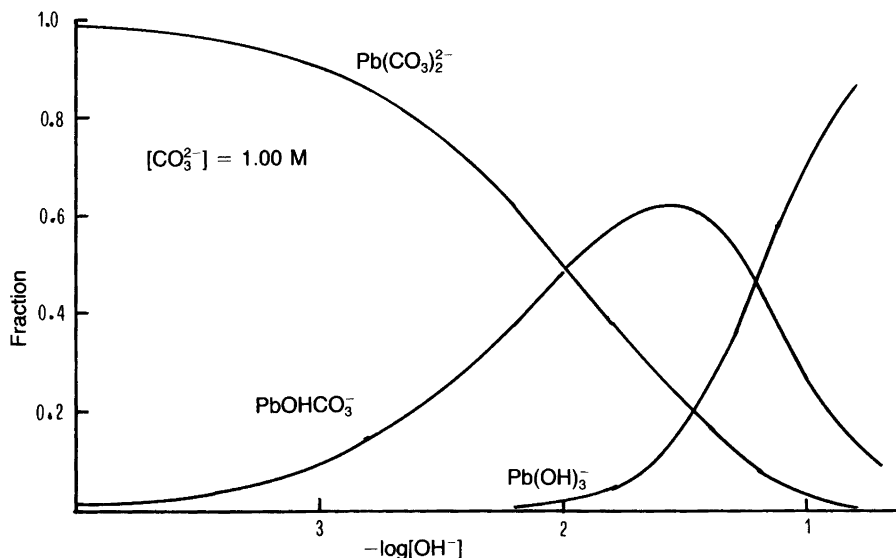


Fig. 2. Distribution of lead(II) between $\text{Pb}(\text{CO}_3)_2^{2-}$, PbOHCO_3^- and $\text{Pb}(\text{OH})_3^-$ at the 1.00 M CO_3^{2-} level.

$\text{Pb}(\text{OH})\text{CO}_3^-$ and $\text{Pb}(\text{OH})_3^-$. The stoichiometry of the species $\text{Pb}(\text{CO}_3)_2^{2-}$, $\text{Pb}(\text{OH})\text{CO}_3^-$ and $\text{Pb}(\text{OH})_3^-$ strongly indicates a coordination geometry with the Pb(II) at the apex of square or trigonal pyramids. This is in fact the coordination geometry found in several solid Pb(II) compounds, as indicated in the introduction.

Acknowledgement. This work has been supported by a grant from the Swedish Natural Science Research Council (NFR).

References

1. Ferri, D., Grenthe, I., Hietanen, S. and Salvatore, F. *Acta Chem. Scand., Ser. A* 41 (1987) 190.
2. Faucherre, J. and Bonnaire, J. *C. R. Seances Acad. Sci., Ser. 2*, 248 (1959) 3705.
3. Baranova, N. N. *Russ. J. Inorg. Chem.* 14 (1969) 1717.
4. Baranova, N. N. *Geokhimiya* (1968) 17.
5. Zirino, A. and Yamamoto, S., *Limnol. Oceanogr.* 17 (1972) 661.
6. Ernst, R., Allen, H. E. and Mancy K. H. *Water Res.* 9 (1975) 969.
7. Bilinski, H., Huston, R. and Stumm, W. *Anal. Chim. Acta* 84 (1976) 157.
8. Bilinski, H. and Schindler, H. *Geochim. Cosmochim. Acta* 46 (1982) 921.
9. Wells, A. F. *Structural Inorganic Chemistry*, 4th ed., Clarendon Press, Oxford 1975, p. 517; *Ibid.* 936.
10. Ciavatta, L., Ferri, D., Grenthe, I. and Salvatore, F. *Inorg. Chem.* 20 (1981) 463.
11. Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, F. and Spahiu, K. *Inorg. Chem.* 22 (1983) 2088.
12. Bruno, J. and Grenthe, I. *J. Chem. Soc., Dalton Trans.* *In press.*
13. Bruno, J. and Grenthe, I. *J. Chem. Soc., Dalton Trans.* *In press.*
14. Schwarzenbach, G. and Flascha, N. *Complexometric Titrations*, Methuen and Co. Ltd, London 1969.
15. Biedermann, G. *Arkiv Kemi* 9 (1956) 277.
16. Forsling, W., Hietanen, S. and Sillen, L. G. *Acta Chem. Scand.* 6 (1952) 901.
17. Brown, A. S. *J. Am. Chem. Soc.* 56 (1934) 646.
18. Carell, B. and Olin, Å. *Acta Chem. Scand.* 14 (1960) 1999.
19. Olin, Å. *Acta Chem. Scand.* 14 (1960) 126.
20. Biedermann, G., Bruno, J., Ferri, D., Grenthe, I., Salvatore, F. and Spahiu, K. *Mater. Res. Soc. Symp. Proc.* 12 (1982) 791.
21. Ciavatta, L. *Ann. Chim. (Rome)* (1980) 551.

Received May 4, 1987.