Acta Chemica Scandinavica A 31 (1977) 157—162

Hydrolysis of the Tin(II) Ion, Sn^{2+}, in Alkaline Solution

WANDA MARK

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O. Box, S-402 20 Göteborg 5, Sweden

Emf methods have been used to study the complex formation between tin(II) ions and hydroxide ions in 3 M $NaClO_4$ at 25 °C. A fully automatic computer-operated system was used in the investigation which was mainly carried out through titration of strongly alkaline tin(II) solutions with perchloric acid. The experimental data could best be explained by the formation of the complex $Sn(OH)_3^-$ only. The stability constant was obtained graphically and the data were corrected for experimental errors by the program LETAGROP. The value obtained for the equilibrium constant is:

$$Sn^{2+} + 3\,OH^- \rightleftharpoons Sn(OH)_3^-$$

$$\lg \beta_3 \pm 3\sigma = 24.58 \pm 0.04$$

The hydrolysis of tin(II) ions in acid medium has been studied by Tobias,[1] whose data could be explained by the formation of the complexes $Sn_3(OH)_4^{2+}$, $Sn_2(OH)_2^{2+}$ and $SnOH^+$. The only attempt to investigate the complex formation of Sn^{2+} in hydroxide solutions has been made polarographically by Smrž.[2] By assuming that the only complex formed was $Sn(OH)_3^-$ the stability constant for this complex was determined to be $\beta_3 = 4 \times 10^{24}$ M^{-3}. An investigation of the complex formation of lead(II) ions in alkaline solution, by Carell and Olin,[3] gave the following results in 3 M $NaClO_4$ medium

$$Pb^{2+} + 2\,OH^- \rightleftharpoons Pb(OH)_2 \qquad \lg \beta_2 = 10.90 \pm 0.10$$

$$Pb^{2+} + 3\,OH^- \rightleftharpoons Pb(OH)_3^- \qquad \lg \beta_3 = 13.66 \pm 0.05$$

The aim of the present work was to determine whether $Sn(OH)_3^-$ is the only complex formed in alkaline tin(II) solutions or if $Sn(OH)_2$ and possibly $Sn(OH)_4^{2-}$ are also present. A preliminary investigation of this system by the author showed that the complex $Sn(OH)_3^-$ is much stronger than $Pb(OH)_3^-$ and that the constant is of the same magnitude as that determined by Smrž.

Since most recent investigations on hydrolysis systems in solution have been performed in 3 M $NaClO_4$ at 25 °C this medium and temperature were employed in the present investigation.

List of symbols

A	total concentration of OH^-
a	free concentration of OH^-
B	total concentration of Sn(II)
b	free concentration of Sn(II)
Sn-Hg(G)	tin amalgam electrode used to generate Sn^{2+}
Sn-Hg(M)	tin amalgam electrode used to measure Sn^{2+}
RE	reference Ag,AgCl electrode
S	equilibrium solution
E_{Sn}	measured emf
E_{0Sn}	a constant in $E_{Sn} = E_{0Sn} + (RT \ln 10/2F) \lg b + E_j$
E_j	liquid junction potential, $E_j = 8[OH^-]$ mV[4]
Z	average number of OH^- per Sn(II) in complexes
η	lg (B/b)
β_n	formation constant of $Sn(OH)_n^{(n-2)-}$ from Sn^{2+} and OH^-
A_0	the concentration of OH^- before titration
A_T	the concentration of OH^- in the titration solution
H_T	the concentration of H_3O^+ in the titration solution
δA_0	group parameter obtained by refining A_0

EXPERIMENTAL

Chemicals and analyses

Perchloric acid (Merck, *p.a.*) was standardized against thallium carbonate (BDH). *Sodium perchlorate* was prepared from sodium carbonate (Merck, *p.a.*) and perchloric acid, as described by Biedermann.[5] *Sodium hydroxide* solutions were prepared from a 50 % NaOH stock solution and standardized against potassium hydrogen phthalate. *Tin(II) ions* were generated by anodic oxidation of tin in tin amalgam by means of a constant current source. The tin amalgam used for the generation of Sn^{2+} was kept in a teflon dish which was immersed in the equilibrium solution during the electrolysis only, by an automatic lift arrangement (*cf.* Fig. 1). The procedure used was that described by Gobom and Kovács.[6] Iodometric determination of the tin(II) content agreed well with the concentration calculated. *Tin amalgam* was prepared by dissolving 0.8 % tin in mercury in a 0.1 M $HClO_4$ solution. The mixture was stirred violently for several hours and stored in an argon atmosphere.

Apparatus

A tin amalgam electrode was used to measure the concentrations of free Sn^{2+} in the equilibrium solutions. To prevent the platinum wire used for connection from coming into contact with the alkaline solutions the bottom of the titration vessel was drawn out into a U-formed tube into which the amalgam was poured. The platinum wire could then be immersed in the measuring amalgam from the outside of the vessel (*cf.* Fig. 1). A cell of the following type was used for the emf measurements:

$$-\,\mathrm{Sn\text{-}Hg(M)|S|3\ M\ NaClO_4|0.1\ M\ NaCl,}$$
$$\mathrm{2.9\ M\ NaClO_4|RE}+$$

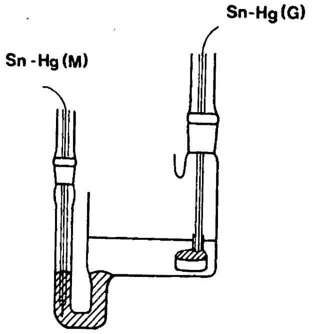

Fig. 1. Schematic representation of the titration vessel used in the experiments. The shaded areas represent tin amalgam.

The composition of the reference half cell used for the generation of tin(II) ions was the same as that for the measuring cell. The vessels used for the salt bridges and the reference electrodes were of the Wilhelm type.[7] The cells were kept in a paraffin oil thermostat at 25.00 ± 0.01 °C in a room thermostated to 25.0 ± 0.1 °C.

The equilibrium solutions and the measuring amalgam in the tube were kept in an inert atmosphere by passing argon gas over the surfaces. The argon gas was taken from cylinders and purified by passage through a column of activated copper and then through four bottles containing 10 % H_2SO_4, 10 % NaOH, 3 M $NaClO_4$ and 3 M $NaClO_4$, respectively.

The emf's of the cell were measured with a digital voltmeter, HP 3450A, which had a sensitivity of 1 μV in the measuring range. The titrations were performed and controlled by a fully automatic computer-operated system developed at this department by Gobom and Kovács.[6]

Emf measurements

Tin(II) ions were generated electrolytically from the tin amalgam by means of a constant current source, using a current of 3.289 mA. This meant that the electrolysis had to proceed for 40 min to achieve a tin(II) ion concentration of 1.0 mM in a solution of 40 ml. When the electrolysis was carried out in alkaline solution it had to be done in steps of a few seconds to prevent precipitation of stannous oxide.

The tin(II) ions were generated stepwise in the alkaline solutions for 5 s in each step to avoid precipitation of stannous oxide around the generating amalgam electrode. This procedure thus took several hours. The alkaline tin(II) solutions were titrated with perchloric acid and attempts were made to reach an OH^- concentration close to the solubility limit of stannous oxide.

After each titration perchloric acid was added to the equilibrium solution in such an amount that $[H_3O^+] \approx 80$ mM. No tin(II) complexes are formed at this hydrogen concentration [1] and the emf's were measured at different tin(II) concentrations to enable the determination of $E_{0\mathrm{Sn}}$. In some titrations the calculated values of $E_{0\mathrm{Sn}}$ were the same for different tin(II) concentrations, but the agreement was mostly not satisfactory and, moreover, the emf's drifted. This was probably due to the fact that the solubility range of stannous oxide had to be passed when the solutions were acidified and some precipitate might remain undissolved.

Due to the long time for generating Sn(II) ions in the alkaline solutions and to the difficulties in obtaining the $E_{0\mathrm{Sn}}$ values another way of performing the titrations was tried. The titrations were started in perchloric acid where the tin(II) ions were generated and the emf's were measured in between the steps of the electrolysis in order to determine the constant $E_{0\mathrm{Sn}}$. The acid solutions were then titrated with sodium hydroxide solutions, but due to difficulties in dissolving the precipitated stannous oxide, it was doubtful if equilibrium was attained during the titrations. This method was therefore abandoned in favour of commencing with an alkaline solution.

Efforts were made to measure the free hydrogen concentration during the titrations but neither a glass electrode nor a hydrogen gas electrode did function in the alkaline equilibrium solutions.

Earlier experiments by the author had shown the main tin(II)-bearing species to be $Sn(OH)_3^-$. To ensure that no polynuclear complexes were formed, titrations were performed in which a was kept constant and B was varied between 0.1 and 1.0 mM. The slope of the straight line obtained by plotting $\lg B = f(\lg b)$ was 0.98 which indicated that only mononuclear species had to be considered. The free OH^- concentrations, a, were calculated assuming $a = A - 3B$, *i.e.* that the ratio OH/Sn was 3:1 in the dominating tin(II) species.

Two series of titrations were performed. In one series the total OH^- concentration, A, ranged from 265 mM to ≈ 80 mM and in the other A ranged from 97 mM to ≈ 30 mM. To avoid variations in the activity factors no measurements were made in more concentrated hydroxide solutions. In each titration the total tin(II) concentration, B, was kept constant by electrolytic generation of tin(II) ions for every addition of perchloric acid. The different total tin(II) concentrations were: $B = 1.00$, 0.50 and 0.25 mM where 0.25 mM was the lowest total tin(II) concentration that led to satisfactory results. Due to the long time of electrolysis required to achieve a concentration of $B = 1.00$ mM it was not considered feasible to perform titrations at higher B.

A great number of titrations had to be carried out because of the practical difficulties encountered during the experiments. In many cases equilibrium was not attained even after 1 to 2 h, due to a slight amount of precipitate formed during the electrolysis. These experiments were rejected and in the titrations used for the calculations equilibrium was established within half an hour and no precipitate was detected during the generation of the tin(II) ions. To make sure that true equilibria were measured back-titrations were carried out in a few cases by addition of sodium hydroxide solution.

The measuring amalgam electrode proved to be unstable in alkaline solutions. Its potential oscillated about an equilibrium value and the deviation could reach ± 0.10 mV. The emf measurements were therefore performed in such a way that 25 readings were made on the digital voltmeter with an interval of 3 s. A mean value was calculated by the computer and printed out. After four such measurements the printed emf's were compared and tested for equilibrium. If no equilibrium had been attained another group of four measurements was made, otherwise the titration was continued. In acid solutions the electrode potential was stable for several hours and oscillated only within ± 0.01 mV. The discrepancy between the behaviour of the electrode in the two different media may be attributable to the Frumkin effect. In 3 M $NaClO_4$ where the concentration of supporting electrolyte is high and kept constant, the ϕ_2-potential of the electrode double layer (the outer Helmholtz plane) should be negative and have the same value in alkaline as in acid solutions.[8,9] According to the expression $(2-j)\phi_2 = RT/F \ln ([SnL_j^{2-j}]/[SnL_j^{2-j}]')$ where j is the number of anionic ligands, $[SnL_j^{2-j}]$ and $[SnL_j^{2-j}]'$ are concentrations in the solution and at the electrode double layer, respectively, the total tin(II) concentration at the electrode double layer will be much lower in alkaline solutions ($B = [Sn(OH)_3^-]$) than in acid solutions ($B = [Sn^{2+}]$). Assuming the ϕ_2-potential to be approximately -60 mV there will be a difference between the total tin(II) concentrations in the two cases with a factor 10^3. The value of the exchange current density at the electrode will therefore most probably be much higher in acid solutions than in alkaline which explains the fact that more stable potentials are established in acid solutions.

INTERPRETATION OF DATA

Since the concentration of free ligand, a, is large compared to B and the complexes formed are mononuclear, the formulae given by Leden [10] can be used, *i.e.* $\partial\eta/\partial \lg a = Z$ and $a = A - BZ$. The most probable complexes are $Sn(OH)_2$, $Sn(OH)_3^-$ and $Sn(OH)_4^{2-}$. Since the dominating complex was assumed to be $Sn(OH)_3^-$ the preliminary calculations were performed with $a = A - 3B$. The Z values obtained varied between 3.00 and 3.05. This could indicate the presence of $Sn(OH)_4^{2-}$ in addition to $Sn(OH)_3^-$ and if these two complexes are the only complexes formed, from the expression for the total tin(II) concentration $B = b + \beta_2 ba^2 + \beta_3 ba^3 + \beta_4 ba^4$ the equation $Bb^{-1}a^{-3} = \beta_3 + \beta_4 a$ is obtained. By plotting $Bb^{-1}a^{-3}$ as a function of a, a straight line would result if the hypothesis were valid. As this is not the case for any titration, the presence of $Sn(OH)_4^{2-}$ was considered out of question. Moreover, the lines obtained for $\eta(\lg a)$ did not deviate towards higher values for $\Delta\eta/\Delta \lg a$ at high hydroxide concentrations.

Table 1. Preliminary values of A_0 and $E_{0\mathrm{Sn}}$ compared to δA_0 and $E_{0\mathrm{Sn}}$ calculated by LETAGROP for the best fit of the experimental data listed in Table 2.

$B\times10^3$ M	$A_0\times10^3$ M	$\delta A_0\times10^3$ M	$E_{0\mathrm{Sn}}$ (meas.)	$E_{\mathrm{Sn}0}$ (calc.)
1.00	265.14	−1.04	−429.20	−429.97
1.00	97.52	−1.62	−428.43	−430.44

The presence of the complex $\mathrm{Sn(OH)_2}$ was tested by plotting $Bb^{-1}a^{-2}$ as a function of a, thus assuming that only $\mathrm{Sn(OH)_2}$ and $\mathrm{Sn(OH)_3^-}$ were formed. The graphs obtained were straight lines although the intercepts on the $Bb^{-1}a^{-2}$ axis varied, which was probably due to poor accuracy in the determination of the constants $E_{0\mathrm{Sn}}$.

In most titrations the differences between calculated emf's when only $\mathrm{Sn(OH)_3^-}$ was taken into consideration and the measured emf's drifted, but in a way that could not be explained by the existence of $\mathrm{Sn(OH)_2}$. The best fit of the data was thus obtained for $\mathrm{Sn(OH)_3^-}$ as the only complex formed in the concentration ranges studied.

Data from seven titrations ($B=0.25$, 0.50 and 1.00 mM) for which $E_{0\mathrm{Sn}}$ were determined most accurately were used to calculate the stability constant β_3. For each titration the constant was obtained from the slope of the

Table 2. Emf data for two titrations, $B=1.0$ mM, for tin(II) in alkaline solutions. The five columns give the values for added volume of titrator (ml), E_{Sn} (mV), A (mM), η(calc.), $\Delta E_{\mathrm{Sn}}=E_{\mathrm{Sn}}(\text{calc.})-E_{\mathrm{Sn}}(\text{exp.})$ (mV), respectively. The calculations are based on $\lg\beta_3=24.58$ and the A_0 and $E_{0\mathrm{Sn}}$ values are those obtained by LETAGROP refinement.

$\underline{B}$ = 1.0 mM $\underline{A}_o$ = 264.1 mM

$\underline{H}_T$ = 260.0 mM $\underline{E}_{oSn}$ = -429.97 mV $\underline{V}_o$ = 40 ml

0.0	-1191.94	264.10	22.832	-0.00
0.50	-1191.03	257.63	22.800	0.00
1.00	-1190.11	251.31	22.767	-0.00
1.50	-1189.18	245.15	22.734	-0.01
2.00	-1188.28	239.14	22.702	0.01
2.50	-1187.35	233.27	22.669	0.00
3.00	-1186.42	227.53	22.636	-0.00
3.50	-1185.49	221.93	22.603	-0.00
4.00	-1184.55	216.45	22.570	-0.01
4.50	-1183.60	211.10	22.537	-0.03
5.00	-1182.67	205.86	22.504	-0.02
5.50	-1181.75	200.74	22.470	0.01
6.00	-1180.82	195.74	22.437	0.03
6.50	-1179.86	190.84	22.403	0.02
7.00	-1178.90	186.04	22.370	0.02
7.50	-1177.94	181.34	22.336	0.02
8.00	-1176.98	176.75	22.302	0.03
8.50	-1176.00	172.24	22.268	0.03
9.00	-1175.01	167.83	22.233	0.02
9.50	-1174.03	163.51	22.199	0.03
10.00	-1173.03	159.28	22.164	0.03
10.50	-1172.03	155.13	22.129	0.03
11.00	-1171.01	151.06	22.093	0.02
11.50	-1170.00	147.07	22.058	0.03
12.00	-1168.96	143.15	22.022	0.02
12.50	-1167.92	139.31	21.986	0.02
13.00	-1166.86	135.54	21.949	0.01
13.50	-1165.80	131.85	21.912	0.01
14.00	-1164.75	128.22	21.875	0.04
14.50	-1163.65	124.66	21.838	0.02
15.00	-1162.53	121.16	21.800	-0.00
15.50	-1161.39	117.73	21.761	-0.04
16.00	-1160.27	114.35	21.722	-0.03
16.50	-1159.13	111.04	21.683	-0.04
17.00	-1157.99	107.79	21.643	-0.02
17.50	-1156.82	104.59	21.603	-0.02
18.00	-1155.63	101.45	21.562	-0.03
18.50	-1154.42	98.36	21.520	-0.03
19.00	-1153.18	95.32	21.478	-0.05
19.50	-1151.93	92.33	21.435	-0.06
20.00	-1150.66	89.40	21.392	-0.06

$\underline{B}$ = 1.0 mM $\underline{A}_o$ = 95.90 mM

$\underline{H}_T$ = 106.0 mM $\underline{E}_{oSn}$ = -430.44 mV $\underline{V}_o$ = 40 ml

2.50	-1148.84	84.02	21.308	0.08
3.00	-1147.69	81.81	21.272	-0.02
3.50	-1146.65	79.65	21.236	-0.00
4.00	-1145.60	77.54	21.199	0.00
4.50	-1144.49	75.48	21.163	-0.04
5.00	-1143.43	73.46	21.126	-0.03
5.50	-1142.34	71.49	21.089	-0.04
6.00	-1141.24	69.56	21.052	-0.06
6.50	-1140.24	67.67	21.014	0.04
7.00	-1139.14	65.82	20.976	0.04
7.50	-1138.00	64.02	20.938	0.01
8.00	-1136.92	62.24	20.900	0.05
8.50	-1135.77	60.51	20.861	0.03
9.00	-1134.59	58.81	20.822	-0.01
9.50	-1133.51	57.15	20.783	0.07
10.00	-1132.18	55.51	20.743	-0.10
10.50	-1131.14	53.92	20.703	0.04
11.00	-1129.89	52.35	20.662	-0.01
11.50	-1128.69	50.81	20.621	-0.01
12.00	-1127.44	49.30	20.579	-0.03
12.50	-1126.21	47.82	20.537	-0.03
13.00	-1125.01	46.37	20.494	0.03
13.50	-1123.68	44.95	20.450	-0.02
14.00	-1122.47	43.55	20.406	0.06
14.50	-1121.15	42.18	20.361	0.06
15.00	-1119.83	40.83	20.316	0.07
15.50	-1118.38	39.51	20.269	-0.02
16.00	-1117.02	38.21	20.222	0.01
16.50	-1115.65	36.93	20.174	0.05
17.00	-1114.10	35.68	20.125	-0.06
17.50	-1112.60	34.45	20.075	-0.09
18.00	-1111.12	33.24	20.024	-0.06
18.50	-1109.64	32.05	19.971	-0.01
19.00	-1108.11	30.88	19.918	0.04

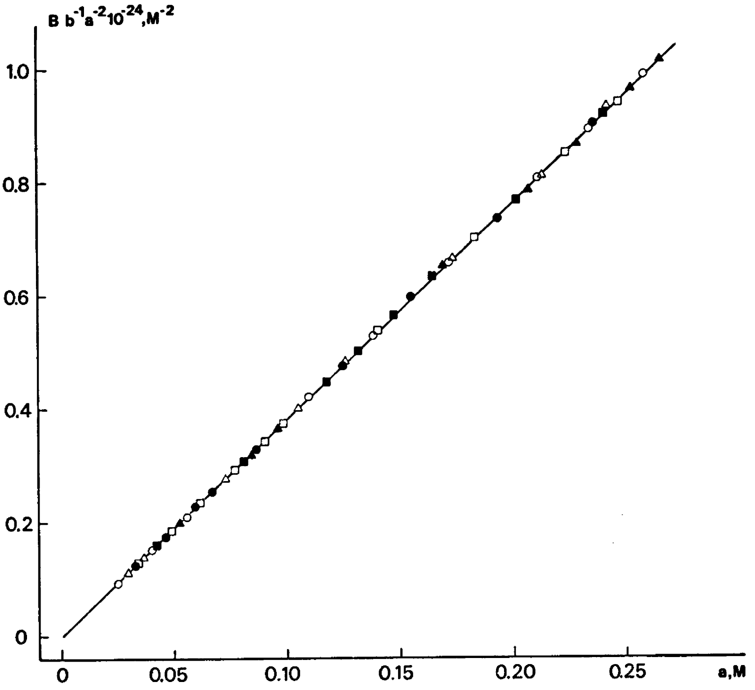

Fig. 2. Randomly chosen experimental data $Bb^{-1}a^{-2} = f(a)$ for titrations in strongly alkaline solutions as well as at lower hydroxide concentrations. The symbols denote the following total tin(II) concentrations: 2.5 mM (▲, △); 0.5 mM (■, □); and 1.0 mM (●, ○).

line $Bb^{-1}a^{-2} = f(a)$. For all these titrations the plotted lines passed through the origin and a mean value was calculated, giving lg $\beta_3 \pm 3\sigma = 24.58 \pm 0.04$ where σ is the standard deviation in β_3. In order to obtain a better fit of the data, the least squares program LETAGROP[11] was used in calculations based on lg $\beta_3 = 24.58$. If the constant lg β_3 was set to 24.58 the constants $E_{0\text{Sn}}$ could be refined and also an allowance for analytical errors in A_0 could be made in each titration. The perchloric acid concentrations H_T, were kept constant, assuming that the experimental errors in determining the concentration of hydroxide solutions are larger than those in determining the acid concentrations.

The calculations were performed with two titrations for each B value in the two series. Since the accuracy of the data was not satisfactory for $B = 0.1$ mM these data were deleted.

The concentrations and group parameters for two titrations are given in Table 1. Fig. 2 shows the graphs $Bb^{-1}a^{-2} = f(a)$ for twelve titrations representing the two different titration series. The measured emfs are listed in Table 2 for the two titrations given in Table 1 together with concentrations and differences between the measured emfs and those calculated for lg $\beta_3 = 24.58$.

DISCUSSION

According to Latimer & Hildebrand[12] tin(II) ions disproportionate in alkaline media. However, since the analyses of tin(II) were in good agreement with the tin(II) concentrations calculated from the generations of tin(II) ions, such a disproportionation tendency could not be detected.

The only complex found in the concentration ranges investigated was $Sn(OH)_3^-$. This is in contrast to the $Pb^{2+} - OH^-$ system where both $Pb(OH)_3^-$ and $Pb(OH)_2$ could be detected. To test whether $Sn(OH)_2$ is present at low hydroxide concentrations which were not investigated due to practical difficulties, the solubility data for SnO(s) in alkaline and acid solutions obtained by Garrett and Heiks[13] were used. The solubility product, K_{s0}, was calculated for stannous oxide dissolved in alkaline solutions, assuming that only $Sn(OH)_3^-$ is present even at very low hydroxide concentrations. The complex formation constants reported by Tobias[1] were used for the same calculations in the acid solutions. Mean values were calculated and the results thus obtained were:

$SnO(s) + H_2O \rightleftharpoons Sn^{2+} + 2OH^-$

$\lg K_{s0} = -25.43$ (SnO dissolved in hydroxide)

$\lg K_{s0} = -25.4$ (SnO dissolved in acid)

Solubility products for SnO determined by polarographic measurements are reported by Smrž[2] and Kovalenko[14] to be $\lg K_{s0} = -27.85$ and $\lg K_{s0} = 28.1$, respectively. Emf measurements were used by Prytz[15] to determine K_{s0} in various ionic media and values of $\lg K_{s0}$ between -25.70 and -24.97 were obtained.

Acknowledgements. I wish to thank Professor Nils Ingri, University of Umeå, for introducing me to the problem and Professor Sture Fronæus, University of Lund, for valuable discussions. I am greatly indebted to Ing. Eva Lundqvist for skilful performance of the experiments, to Dr. Sylvia Gobom for placing the titration equipment at my disposal and to Dr. Susan Jagner for revising the English text. The work was supported by a grant from the Swedish Natural Science Research Council (Contract No. 2318) which is gratefully acknowledged.

REFERENCES

1. Tobias, R. S. *Acta Chem. Scand. 12* (1958) 198.
2. Smrž, S. J. *Recl. Trav. Chim. Pays-Bas 44* (1925) 580.
3. Carell, B. and Olin, Å. *Acta Chem. Scand. 14* (1960) 1999.
4. Ingri, N., Lagerström, G., Frydman, M. and Sillén, L. G. *Acta Chem. Scand. 11* (1957) 1034.
5. Biedermann, G. *Ark. Kemi 9* (1956) 277.
6. Gobom, S. and Kovács, J. *Chem. Scr. 2* (1972) 103.
7. Forsling, W., Hietanen, S. and Sillén, L. G. *Acta Chem. Scand. 6* (1952) 901.
8. Fronæus, S., Johansson, R. and Östman, C.-O. *Chem. Scr. 1* (1971) 52.
9. Fronæus, S. and Johansson, C. L. *Electroanal. Chem. Interfacial Electrochem. 60* (1975) 29.
10. Leden, I. *Thesis*, Lund 1943, p. 14.
11. Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi 31* (1969) 365.
12. Latimer and Hildebrand, *Reference Book of Inorganic Chemistry*, Macmillan, New York.
13. Garrett, A. B. and Heiks, R. E. *J. Am. Chem.* Soc. *63* (1941) 562.
14. Kovalenko, P. N. *Zh. Neorg. Khim. 3* (1958) 1065.
15. Prytz, M. *Z. Anorg. Chem. 174* (1928) 355.

Received October 22, 1976.