Metal Complexes with Mixed Ligands. 25. Complex Formation in the Ag(I) – Tris(hydroxymethyl)aminomethane – OH⁻ System in 3.0 M (Na)ClO₄ Medium

INGER GRANBERG, WILLIS FORSLING and STAFFAN SJÖBERG

Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden

Three-component equilibria between silver(I), tris-(hydroxymethyl)aminomethane ($H_2NC(CH_2OH)_3$, L, THAM) and OH⁻ were studied by means of emf titrations at 25 °C in an ionic medium of 3.0 M (Na)ClO₄. In the measurements, glass as well as Ag,AgCl electrodes were employed. The total concentrations of silver(I), B, and HL^+, C, were varied within the limits $0.002 \le B \le 0.08$ M and $0.005 \le C \le 0.160$ M, respectively, and the ratio C/B between $0.5 \le C/B \le 12$. With $C/B > 4$ data could be explained with the complexes AgL^+ and AgL_2^+ with $\log \beta_1 = 3.406 \pm 0.002$ and $\log \beta_2 = 7.198 \pm 0.002$. At low ratios of C/B, a ternary hydroxy THAM complex, AgOHL with $\log K$ ($Ag^+ + L + H_2O \rightleftharpoons AgOHL + H^+$) $= -6.40 \pm 0.05$, is formed. Data have been analyzed with the least-squares computer program LETAGROPVRID.

The ability of different metal – imidazole complexes to form ternary species with the ligands OH⁻ and Cl⁻ has been demonstrated in preceding papers of this series.[1–5] The results have clearly shown that the ternary $Me^{z+} - L - X^-$ complexes ($Me^{z+} = Co^{2+}$,[1] Ni^{2+}, Cu^{2+},[3] Zn^{2+},[2] Cd^{2+},[4] Hg^{2+},[3] Ag^+,[5] $X^- = OH^-$, Cl^-) are of greater stability than the corresponding $Me^{z+} - X^-$ complexes. These findings indicate that coordinated imidazole ligands enhance the affinity for the anions Cl⁻ and OH⁻. An explanation for this behaviour is given by Sigel,[6] who claims that the high stability of ternary metal complexes with aromatic nitrogen containing ligands is mainly caused by back-donation from the metal ion into the unsaturated π-orbitals of the ligands which lowers the electron concentration near the central ion.

As a test of this hypothesis, Forsling[7] exchanged imidazole for the aliphatic N-ligand tris(hydroxymethyl)aminomethane (TRIS or THAM, L) and complexation in the nickel(II) system was investigated. It was found that THAM forms a proton series of tetrameric hydroxy complexes, viz. $Ni_4(OH)_4(L)_4^{4+}$, $Ni_4(OH)_4(L)_3(H_{-1}L)^{3+}$ and $Ni_4(OH)_4(L)_2(H_{-1}L)_2^{2+}$ as well as the trimer $Ni_3(OH)_3(L)_2^{3+}$. All these ternary species were found to predominate in slightly alkaline solutions (pH 7–9). It was also concluded that THAM as ligand enhances the affinity for OH⁻ as second ligand; however, a direct comparison with the corresponding imidazole system could not be made as no ternary polynuclear hydroxy complex was formed in this system.

The aim of the present investigation is to interpret complexation in the $Ag^+ - THAM - OH^-$ system, with special reference to the formation of probable ternary hydroxy complexes and compare the results with those corresponding to the imidazole system.

EXPERIMENTAL

Chemicals and analysis. Tris(hydroxymethyl)-aminomethane, L, $H_2NC(CH_2OH)_3$ (SIGMA, reagent grade) was used without further purification after drying at 80 °C. Stock solutions of HL^+ were prepared by dissolving a weighed amount of L in excess of standardized $HClO_4$. The total concentrations of HL^+, C, were determined potentiometrically and were found to agree within 0.2 % with the amounts weighed. Stock solutions of *sodium perchlorate* and *silver perchlorate* as well as the dilute *perchloric acid* and the *sodium hydroxide* were prepared and standardized as earlier.[5]

Apparatus. The cell arrangement and the experimental details of the emf measurements have been described earlier.[5]

Electrodes. Ag, AgCl electrodes were prepared and tested as described earlier.[5] Glass electrodes (Ingold type 201-NS) were tested against the hydrogen electrode and were found to give a constant and reproducible potential with $-\log[H^+] \lesssim 9.1$.

Method. The present investigation has been carried out as a series of titrations in which both $[H^+]$, h and $[Ag^+]$, b were measured using a glass electrode and an Ag,AgCl electrode, respectively.

The total concentrations of Ag^+, B and HL^+, C, were varied within the limits $0.002 \leq B \leq 0.040$ M and $0.005 \leq C \leq 0.160$ M. h and b were varied by adding hydroxide or hydrogen ions. For quotients $C/B \leq 2.5$, the available $-\log h$ range was restricted due to the formation of a precipitate. With $C/B > 2.5$, no precipitates were observed and the titrations could be continued as long as the glass electrode functioned properly ($-\log h < 9.1$). In general, most of the titrations were performed at constant C/B ratio, and the following were studied: 0.5, 1, 1.5, 2, 2.5, 3, 4, 6, 8 and 12.

The reproducibility and reversibility of equilibria were tested by performing both forward (increasing $-\log h$) and backward (decreasing $-\log h$) titrations. As a test of the reversibility, dilution experiments at different C/B ratios and at constant Z values were performed (Z is defined as $(h - H)/B$).

h and b were determined by measuring the emf of the cell (1), where ME denotes the measuring electrode (glass electrode and Ag,AgCl electrode)

$$- RE \| \text{equilibrium solution} | ME + \tag{1}$$
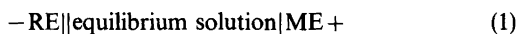
and RE denotes Ag,AgCl|0.01 M Ag^+, 2.99 M Na^+, 3.00 M ClO_4^- ||3.00 M $NaClO_4$.

Assuming the activity coefficients to be constant, the expressions (2a) and (2b) are valid for the measured emf. E_{OH} and E_{OB} are constants determined in acidic (H^+, Ag^+, HL^+) solutions of known composition, where complex formation can be neglected ($-\log h \leq 3$).

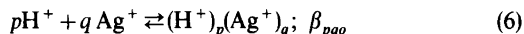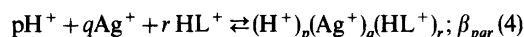$$E_H = E_{OH} + 59.16 \log h + E_j \tag{2a}$$

$$E_B = E_{OB} + 59.16 \log b + E_j \tag{2b}$$

It has been found that E_{OH} is dependent on the Ag^+, b, HL^+, c and L ($k_a ch^{-1}$) contents. Investigations show that the change in E_{OH}, due to changes in b, c and $ck_a h^{-1}$ could be described by the linear function (3), where $\Delta E_{Ag} = 2.0 \pm 0.1$ mV M^{-1}, $\Delta E_{HL}^2 = 5.3$ mV M^{-1} and $\Delta E_L^2 = 8.7$ mV M^{-1}. The magnitude of ΔE_{OH} caused by

concentration changes during the titrations used in the final calculations, was estimated. ΔE_{OH} did not exceed 0.1 mV, which will hardly cause any changes in the equilibrium model.

$$\Delta E_{OH} = \Delta E_{Ag}\Delta b + \Delta E_{HL}\Delta c + \Delta E_L \Delta (ck_a h^{-1}) \tag{3}$$

Data treatment. We will assume the presence of three component equilibria of the general type (4) together with the two component equilibria (5) and (6).

$$pH^+ + qAg^+ + r HL^+ \rightleftharpoons (H^+)_p(Ag^+)_q(HL^+)_r; \beta_{pqr} \tag{4}$$

$$HL^+ \rightleftharpoons L + H^+; k_a \tag{5}$$

$$pH^+ + q Ag^+ \rightleftharpoons (H^+)_p(Ag^+)_q; \beta_{pqo} \tag{6}$$

For reaction (5) Forsling[7] reported $\log(k_a \pm 3\sigma) = -8.646 \pm 0.002$. For reaction (6) two complexes have been reported. Biedermann and Hietanen[8] found the complex AgOH to predominate at high B (1 M $AgNO_3$) giving $\log \beta_{-110} \lesssim -11.1$. At low B (< 1 mM in 3 M $NaClO_4$) Antikainen and Dyrssen[9] found $Ag(OH)_2^-$ to be the main hydrolytic species with $\log \beta_{-210} = -24.84$.

These results on the two-component equilibria will be considered as known in the following and no attempts will be made to adjust their equilibrium constants.

The search for a model (pqr) and corresponding equilibrium constants β_{pqr} that give the best fit to experimental data was carried out using the least-squares computer program LETAGROPVRID[10] (version ETITR).[11]

The different standard deviations given were defined and calculated according to Sillén.[12] The computations were performed on a CD 6600 computer.

CALCULATIONS AND RESULTS

The analysis of data was started by making $\bar{n}(\log[L])$, $(E_H$-data) and $\eta(\log[L])$, $[(E_B + E_H)$-data] plots which are given in Fig. 1 and Fig. 2, where $\bar{n}$ and η are defined as in Ref. 5. According to these figures, $\bar{n}$ as well as η seem to be independent of B and C for quotients > 4, thus indicating formation of a series of mononuclear complexes AgL_n^+. Data fulfilling these conditions will be denoted Data 1. However, with $C/B \leq 4$ and $B \leq 0.010$ M, systematic deviations from the mononuclear $\bar{n}$ as well as η curves were observed, which implies that additional species are formed. These data will be treated separately and denoted as Data 2. In the
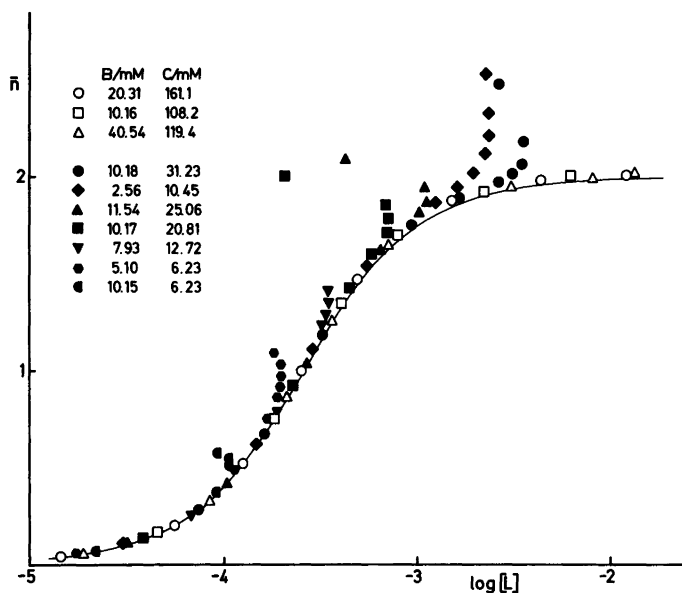
Fig. 1. Experimental data plotted as curves $\bar{n}$ log[L]. In order to make the figure clear, only a few titrations have been plotted. The full drawn curve has been calculated with the proposed constants for AgL^+ and AgL_2^+.

LETAGROP calculations different data sets were used (*cf.* Table 2). This procedure enabled us to compare results obtained from the different calculations and thus to obtain information about the reliability of the different electrodes as well as of eventual errors in the analytical concentrations.
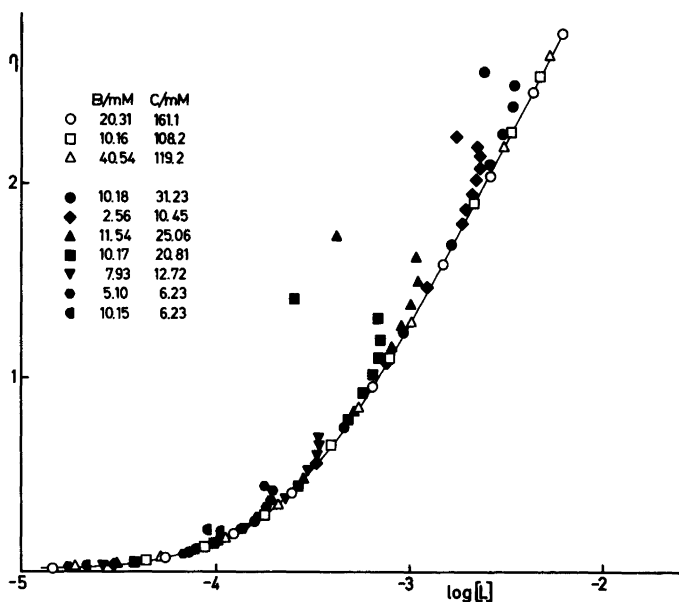

Fig. 2. Experimental data plotted as curves η log[L].

Data 1. A LETAGROP analysis showed that E_H, E_B as well as $E_H + E_B$ data could be well explained with the complexes AgL^+ and AgL_2^+. Details of these calculations are given in Table 1. According to this table the agreement in $\beta_{-1,1,1}$ and $\beta_{-2,1,2}$, independent of data sets or minimizing function, is very good, the spread being less than 0.023 and 0.012 logarithmic units, respectively.

The values, $\log \beta_{-111} = -5.242 \pm 0.002$ and $\log \beta_{-212} = -10.102 \pm 0.002$, obtained from calculations on the combined $E_H + E_B$ data, are considered as the most reliable ones and are final proposals.

Data 2. In the search for the ternary species, it was assumed that the formation constants for the species AgL^+ and AgL_2^+ had the values proposed above. Furthermore, formation constants for the hydrolytic species $AgOH$ and $Ag(OH)_2^-$ were those given by Biedermann and Dyrssen, respectively. The analysis of Data 2 was started with a pqr analysis of the residuals at $C/B < 4$, *i.e.* a systematic trial and error procedure which tests complexes with different composition $(H^+)_p(Ag^+)_q(HL^+)_r$ one by one. The test was carried out with a representative part of data including 16 titrations and 216 experimental points. The result of the analysis is shown in Fig. 3. It is seen from these data that the lowest error squares sum is obtained for the complex $(H^+)_{-2}(Ag^+)_1(HL^+)_1$ with $\log \beta_{-2,1,1} = -15.05 \pm 0.05$ giving $\sigma(E_B)$ is somewhat higher than one could expect from the calculations with Data 1

and depends largely on a systematic deviation at pH 8.5. This deviation did not exceed 0.5 mV and a covariation of β_{-212} with β_{-211} explained the systematic deviations by changing the formation constants for AgL_2^+ by 0.006 in $\log \beta_{-2,1,2}$ (*cf.* Table 1). The formation constant for the complex $(H^+)_{-2}(Ag^+)_1(HL^+)_1$ was found to be $\log \beta_{-2,1,1} = -15.14 \pm 0.06$ giving $\sigma(E_B) = 0.20$ mV. As the ternary complex is formed in slightly alkaline solution ($-\log h \gtrsim 9$) supplementary measurements were performed where the $-\log h$ range was extended to $-\log h \lesssim 10.5$. As the glass electrode provides too uncertain data to be of any use within this range, only E_B data were treated and the result of a calculation on these is also given in Table 1. As can be seen, β_{-211} was in very good agreement with that obtained from $E_H + E_B$ data at a lower $-\log h$ range ($\log \beta_{-211} = -15.07 \pm 0.05$, $\sigma(B) = 0.04$ mM.

Although this ternary complex is formed in small amounts (*cf.* Fig. 4), there is consistency in E_H as well as E_B data, which makes the evaluated equilibrium model trustworthy.

DISCUSSION

The present investigation of the silver(I) − THAM − OH^- system was carried out by measuring two free concentrations, h and b. In the LETAGROP calculations one of the quantities h, b, H or B was excluded, thus yielding four different types of data
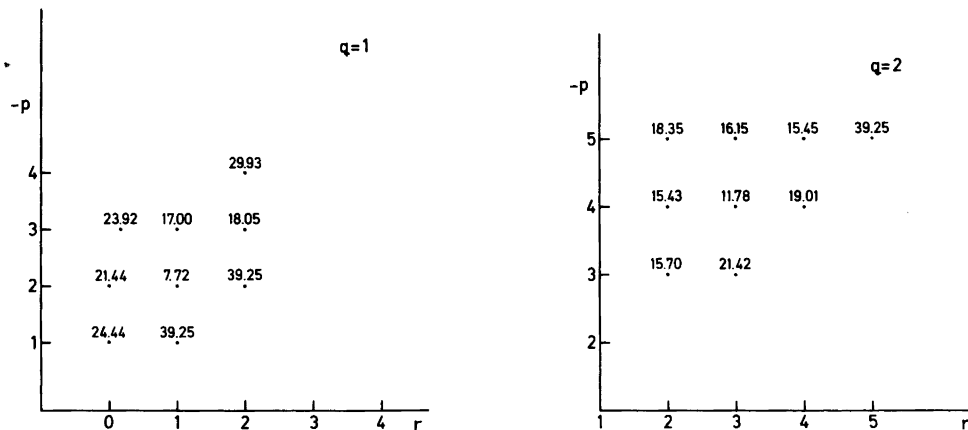

Fig. 3. LETAGROP search for ternary $H_pAg_q(HL)_r^{(p+q+r)+}$ complexes. The diagram gives error square sums $U(pr)_q$, where $U = \Sigma(E_{BCALC} - E_{BEXP})$ assuming only one complex. In the calculation the hydrolytic species and the binary species AgL^+ and AgL_2^+ have been assumed to be known. The calculation is based on 216 experimental points, chosen to cover as great concentration ranges as possible.
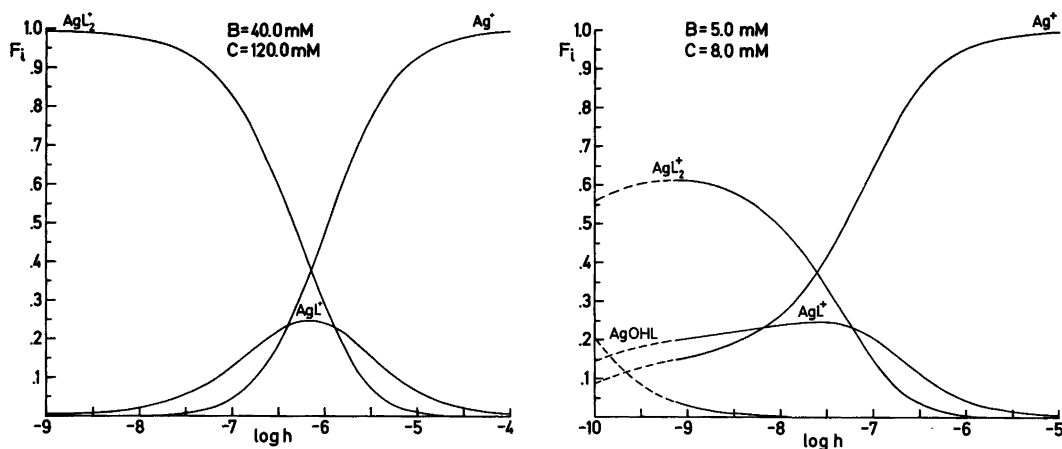
Fig. 4. Distribution diagrams $F_i(\log h)_{BC}$. F_i is defined as the ratio between silver(I) in the species and the total silver(I). The computer program SOLGASWATER [19] was used for the calculations with the set of proposed constants. Broken lines denote ranges where no measurements have been performed due to precipitation (extrapolated range).

sets (*cf.* Table 1).* Results of these calculations have shown that the agreement in the evaluated formation constants was good, which is an indication that systematic or occasional errors in H and B as well as h and b are negligible.

---

* A complete list of the experimental data is available from this department.

The calculations gave clear evidence for the existence of a ternary complex $H_{-1}AgL$, besides the two binary complexes AgL^+ and AgL_2^+. There was no indication for the existence of any polynuclear species. The ternary complex $H_{-1}AgL$ is formed in small amounts ($\sim 4\%$ of B) at low C/B ratios (≤ 4). It is not possible from the potentiometric data to deduce whether this is a hydroxy complex Ag(OH)L

Table 1. Results of LETAGROP calculations on different data sets. The formation constants β_{pqr} are defined according to the equilibria $p\mathrm{H}^+ + q\,\mathrm{Ag}^+ + r\,\mathrm{HL}^+ \rightleftarrows \mathrm{H}_p\mathrm{Ag}_q(\mathrm{HL})_r^{(p+q+r)+}$. The errors 3σ (log β_{pqr}) are given when the corresponding equilibrium constant has been varied.

Data	Number of titr./number of points	AgL^+ $\log(\beta_{-111}$ $\pm 3\sigma)$	AgL_2^+ $\log(\beta_{-212}$ $\pm 3\sigma)$	$AgOHL$ $\log(\beta_{-211}$ $\pm 3\sigma)$	$\sigma(Y)$	Data set used
E_H	17/226	-5.233 ± 0.004	-10.094 ± 0.002		0.033^a	h, H, B, C
E_B	17/226	-5.256 ± 0.004	-10.106 ± 0.007		0.024^b	b, H, B, C
$E_H + E_B$	17/226	-5.231 ± 0.004	-10.100 ± 0.002		0.037^a	h, b, H, C
$E_H + E_B$	17/226	-5.242 ± 0.002	-10.102 ± 0.002		0.063^c	h, b, B, C
$E_H + E_B$	19/250	-5.242	-10.102	-15.05 ± 0.05	0.24^c	h, b, B, C^d
$E_H + E_B$	19/250	-5.242	-10.096 ± 0.002	-15.14 ± 0.06	0.20^c	h, b, B, C
E_B	20/252	-5.242	-10.111 ± 0.008	-15.07 ± 0.05	0.042^b	b, H, B, C

^{a} $Y = H_{CALC} - H_{EXP}/mM$. ^{b} $Y = B_{CALC} - B_{EXP}/mM$. ^{c} $Y = E_{B\ CALC} - E_{B\ EXP}/mV$. ^{d} Proposed constants.

or a complex where THAM acts as a chelate, $Ag(H_{-1}L)$.

Due to steric reasons the first alternative is most likely. Furthermore, if one of the hydroxy groups in the THAM molecule loses one proton and the ligand acts as a chelate, it must be reflected in the magnitude of the corresponding stability constant. In an investigation of the $Cu^{2+}-THAM-OH^-$ system, Bai and Martell[13] found a series of ternary complexes, *e.g.* $Cu(H_{-1}L)^+$, $Cu(H_{-1}L)L^+$, $Cu(H_{-1}L)_2$ and $Cu_2(H_{-1}L)_2^{2+}$. According to a structure determination[14] of the complex $Cu(H_{-1}L)_2$, L acts as a bidentate chelate through the amino group and one of the OH groups. This behaviour was assumed to be likely for the other ternary species as well. By considering the equilibria

$$CuL^{2+} \rightleftharpoons Cu(H_{-1}L)^+ + H^+$$
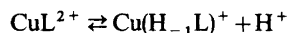
Bai and Martell found log $K_a(CuL^{2+}) = -6.0$, which can be compared with the values log $K_a(Cu^{2+}) = -8.0$[15] and log $K_a(Cu(imidazole)^{2+}) = -7.2$.[3] This means that the chelate complex $Cu(H_{-1}L)^+$ is more stable than the hydroxy species $CuOH^+$ and $Cu(imidazole)OH^+$.

If a similar interpretation is made in the $Ag^+-THAM-OH^-$ system, log $K_a(AgL^+) = -9.88$ indicates that this complex is a mixed hydroxy species, as log $k_a(Ag\ imidazole^+)\ -8.11$ and log $K_a(Ag^+) \lesssim -11.1$.

If we compare the acidity constants for the ternary complexes with AgL^+ and OH^- we find that all complexes between silver and an aliphatic nitrogen compound give an acidity constant somewhat stronger than the corresponding value for the hydrated silver ion. This is valid for the complex AgL^+, where L stands for THAM, ethylenediamine,[16] 1,2-propanediamine,[16] 1,3-propanediamine[17] and 1,4-butanediamine[17] with the acidity constants log $k_a = -9.9$, -10.0, -9.6, -10.1 and -10.8 respectively. The corresponding complex with an aromatic amine such as imidazole[4] differs from those mentioned above with log $k_a = -8.11$, which confirms the hypothesis that mixed hydroxy complexes with aromatic N-ligands are more stable than corresponding species with aliphatic N-ligands. Furthermore, the presence of an aliphatic N-ligand seems to enhance the affinity for OH^- compared with the hydrated silver ion. Forsling found similar behaviour for polynuclear mixed complexes in the $Ni^{2+}-THAM-OH^-$ system, while Sigel[18] reported the opposite

tendency for $M-THAM-ATP$ where M stands for $(Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+})$ and ATP stands for Adenosine 5'-Tri-phosphate). This is an indication that the size of the oxygen donor is important for the formation of ternary mixed complexes, due to steric hindrance.

The present investigation has also given further evidence for the compositional connection between the binary metal hydrolysis and the ternary hydrolytic species *(cf.* AgOH and AgOHL).

REFERENCES

1. Forsling, W., Granberg, I. and Sjöberg, S. *Acta Chem. Scand. A* 35 (1981) 473.
2. Forsling, W. *Thesis*, Umeå, Sweden 1978.
3. Sjöberg, S. *Thesis*, Umeå, Sweden 1976.
4. Granberg, I. and Sjöberg, S. *Acta Chem. Scand. A* 35 (1981) 193.
5. Granberg, I. and Sjöberg, S. *Acta Chem. Scand. A* 33 (1979) 531.
6. Sigel, H. *Inorg. Chem.* 19 (1980) 1411.
7. Forsling, W. *Acta Chem. Scand. A* 32 (1978) 857.
8. Biederman, G. and Hietanen, S. *Acta Chem. Scand.* 14 (1960) 711.
9. Antikainen, P. J. and Dyrssen, D. *Acta Chem. Scand.* 14 (1960) 86.
10. Ingri, N. and Sillén, L. G. *Ark. Kemi* 23 (1964) 97.
11. Arnek, R., Sillén, L. G. and Wahlberg, O. *Ark. Kemi* 31 (1969) 353; Brauner, P., Sillén, L. G. and Whiteker, R. *Ark. Kemi* 31 (1969) 365.
12. Sillén, L. G. *Acta Chem. Scand.* 16 (1962) 159; Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 341.
13. Bai, K. S. and Martell, A. E. *J. Inorg. Nucl. Chem.* 31 (1969) 1697.
14. Ivarsson, G. *To be published.*
15. Berecki-Biedermann, C. *Ark. Kemi* 9 (1956) 175.
16. Ohtaki, H. and Ito, Y. *J. Coord. Chem.* 3 (1973) 131.
17. Ohtaki, H. and Cho, K. *Bull. Chem. Soc. Jpn.* 50 (1977) 2764.
18. Fischer, B. E., Häring, U. K., Tribolet, R. and Sigel, H. *Eur. J. Biochem.* 94 (1979) 523.
19. Eriksson, G. *Anal. Chim. Acta* 112 (1979) 375.