

# Metal Complexes with Mixed Ligands. 17. An Emf Investigation of the Complex Formation between the Hydroxo Nickel(II) Tetramer and Tris(hydroxymethyl)aminomethane Ligands

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Three component equilibria between nickel(II), tris(hydroxymethyl)aminomethane ( $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3$ , HL, THAM), and  $\text{OH}^-$  were studied by means of emf titrations at 25 °C in an ionic medium of 3.0 M (Na)ClO<sub>4</sub>. The total nickel, *B*, and the total THAM, *C*, were varied within the limits  $0.003 \leq B < 0.227$  M and  $0.005 \leq C < 0.227$  M and the ratios *C/B* between  $1 \leq C/B < 11$ . Data can be explained with the metal complexes  $\text{NiHL}^{2+}$  and  $\text{Ni}(\text{HL})_2^{2+}$  together with a series of tetranuclear ternary hydrolytic species  $\text{Ni}_4(\text{OH})_4(\text{HL})_4^{4+}$ ,  $\text{Ni}_4(\text{OH})_4(\text{HL})_3\text{L}^{3+}$ ,  $\text{Ni}_4(\text{OH})_4(\text{HL})_2\text{L}_2^{2+}$  and the trinuclear ternary complex  $\text{Ni}_3\text{H}_{-3}(\text{HL})_3^{3+}$ . The equilibrium constants with standard deviations ( $3\sigma$ ) are given. Data were analyzed with the least squares computer program LETAGROPVRID.

In earlier papers of this series the three component equilibria in the systems copper(II)–imidazole ( $\text{C}_3\text{H}_4\text{N}_2$ )– $\text{OH}^-$ ,<sup>1</sup> nickel(II)–imidazole– $\text{OH}^-$ ,<sup>2,3</sup> and zinc(II)–imidazole– $\text{OH}^-$ <sup>4</sup> were investigated.<sup>2</sup> In addition to the metal complexes  $\text{Me}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$ , *n* = 1, 2, 3, 4, ternary complexes were also formed. Furthermore, there seems to be a strong connection between the binary metal hydrolysis and the ternary hydrolytic species obtained in the various systems. Thus in the copper system investigated by Sjöberg, data clearly indicated the formation of  $\text{Cu}_2(\text{OH})_2\text{L}_2^{2+}$ ,  $\text{Cu}_2(\text{OH})_2\text{L}_4^{2+}$  and  $\text{CuOHL}^+$  (*L* =  $\text{C}_3\text{H}_4\text{N}_2$ ), while the dominating hydrolytic species are  $\text{Cu}_2(\text{OH})_2^{2+}$  and  $\text{CuOH}^+$ . In the zinc system the main ternary species appeared to be  $\text{ZnOHL}^+$  and  $\text{Zn}_2(\text{OH})\text{L}_2^{3+}$  in 3.0 M (Na)Cl resp.  $\text{Zn}(\text{OH})\text{L}_3^+$

and  $\text{Zn}_2(\text{OH})\text{L}_3^{3+}$  in 3.0 M (Na)ClO<sub>4</sub>, while the binary hydrolytic complexes in the corresponding media are  $\text{Zn}_2\text{OH}^{3+}$  and  $\text{ZnOH}^+$ .

However, in the nickel system only mononuclear ternary species were obtained, *viz.*  $\text{NiOHL}^+$  (3.0 M (Na)Cl, 3.0 M (Na)ClO<sub>4</sub>, 1.0 M (Na)Cl) and  $\text{Ni}(\text{OH})\text{L}_3^+$  (1.0 M (Na)Cl), while the dominating hydrolysis complexes seem to be  $\text{Ni}_4(\text{OH})_4^{4+}$ ,  $\text{Ni}_2\text{OH}^{3+}$  together with  $\text{NiOH}^+$ .<sup>5,6</sup> The reason why no polynuclear ternary species are formed may possibly be that the available pH and solubility ranges in the case of imidazole are too restricted to permit such complexes. Thus it seems worthwhile to exchange imidazole for another amine ligand, which fulfills the demands for solubility and acidity strength to form polynuclear ternary hydrolytic species. According to earlier investigations<sup>7–9</sup> two suitable ligands should be triethanolamine ( $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ ) and tris(hydroxymethyl)aminomethane ( $\text{H}_2\text{NC}(\text{CH}_2\text{OH})_3$ , THAM).

In an investigation of the system nickel(II)–triethanolamine– $\text{OH}^-$  by Cadiot-Smith<sup>7</sup> comprising both potentiometric and spectrophotometric methods, several polynuclear ternary complexes are proposed. The metal complexes  $\text{NiT}^{2+}$  and  $\text{Ni}_2\text{T}^{2+}$  as well as the polynuclear species  $\text{T}_2\text{Ni}_2(\text{OH})_2^{2+}$ ,  $\text{T}_4\text{Ni}_4(\text{OH})_6^{2+}$  and  $\text{T}_3\text{Ni}_2(\text{OH})_4$  and the mononuclear ternary complexes  $\text{TNi}(\text{OH})_2^{2+}$  and  $\text{TNi}(\text{OH})_2$  were reported (*T* =  $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ ).

The nickel(II)–tris(hydroxymethyl)aminomethane– $\text{OH}^-$  system was studied by Hall *et al.*<sup>8</sup> applying spectrophotometric methods and poten-

tiometric titrations carried out in an ionic medium of 0.5 M NaClO<sub>4</sub>. They proposed the species NiHL<sup>2+</sup>, Ni(HL)<sub>2</sub><sup>2+</sup> and NiL<sup>+</sup> to be formed (HL = H<sub>2</sub>NC(CH<sub>2</sub>OH)<sub>3</sub>). They also established that a polynuclear ternary species is formed with a ratio of nickel(II) ion to reacted hydroxyl ion of 1:1.5.

The same system is investigated by Bai and Martell<sup>9</sup> at 25 °C and at an ionic strength of 0.10 M. They explained data by assuming the species NiHL<sup>2+</sup>, Ni(HL)<sub>2</sub><sup>2+</sup>, Ni<sub>2</sub>L<sub>3</sub><sup>+</sup> and Ni<sub>3</sub>(H<sub>-1</sub>L)<sub>2</sub>L<sup>+</sup> to be formed. Both spectrophotometric and potentiometric methods were used and as the Ni(II)-THAM reaction is very slow, the titrations were performed batchwise using series of bottles.

However, in both investigations the variation ranges in the total concentrations of nickel(II), *B*, were rather small, which makes the determination of the polynuclear complexes quite difficult.

Any of these ligands is probably a suitable choice for our purposes. However, as THAM is commonly used as an acidimetric standard and is easily purified and dried and has low hygroscopicity while triethanolamine lacks all these qualities, the former was chosen. Furthermore as THAM is used extensively as a buffer in the study of chemical kinetics as well as in biological studies even though the THAM-metal ion interaction has not been completely studied, equilibrium data in the Ni<sup>2+</sup> - H<sub>2</sub>NC(CH<sub>2</sub>OH)<sub>3</sub> - OH<sup>-</sup> system should be of great interest.

## EXPERIMENTAL

*Tris(hydroxymethyl)aminomethane*, H<sub>2</sub>NC(CH<sub>2</sub>-OH)<sub>3</sub>, HL (SIGMA, reagent grade) was used without further purification after drying. Stock solutions of H<sub>2</sub>L<sup>+</sup> were prepared by dissolving HL in HClO<sub>4</sub>. Titration solutions were generally prepared by weighing in HL to nickel(II) solutions. Stock solutions of sodium and nickel perchlorate as well as the dilute perchloric acids and sodium hydroxide solutions were prepared and standardized as earlier.<sup>2</sup>

The cell arrangement and experimental details of the emf measurements are fully described earlier.<sup>2</sup>

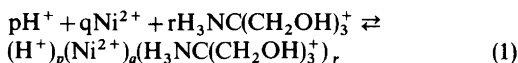
## METHOD

The titration procedures used were similar to those described in earlier papers.<sup>1,2</sup> During the titrations the total concentrations of nickel, *B*,

THAM, *C*, were generally kept constant, but dilution experiments were also carried out. In general each titration was performed at a constant *C/B*-ratio. The free hydrogen ion concentration, *h*, was varied by adding hydroxide ions or hydrogen ions and measured with a glass electrode. To check the reliability two electrodes were often immersed in the same equilibrium solution. The change in the differences between the emf values was not allowed to exceed 0.2 mV. Owing to formation of precipitates and the reduced reliability of the glass electrodes at high  $-\log h$ -levels, the available  $-\log h$ -range was restricted to an upper limit of 7-9. The reproducibility and reversibility of equilibria were tested by performing both forward (increasing  $-\log h$ ) and backward (decreasing  $-\log h$ ) titrations. To check the reversibility, dilution experiments were also carried out at some *C/B*-ratios. Special efforts were made to cover as wide a concentration range as possible. A constant ionic medium of 3.0 M (Na)ClO<sub>4</sub> was used in order to avoid activity coefficient variations. The reactions especially at low quotients *C/B* are extremely slow and stable potentials of the glass electrodes were not attained until 6-8 h after every change in the composition of the equilibrium solution at the  $\log h$ -range of ternary complex formation. When equilibrium was obtained the emf-values remained constant to 0.1 mV for several hours. An ordinary titration lasted 2-3 days, which naturally should influence the accuracy of the measurements. However, as the ternary hydroxyl species are obtained in great amounts, minor changes in, for example, *E*<sub>0</sub> of the glass electrodes owing to the lengthy titration measurements seem to be rather insignificant.

The total concentrations of *B* and *C* were varied within the limits  $0.003 \leq B < 0.227$  M and  $0.005 \leq C < 0.227$  M and the ratios *C/B* between  $1 \leq C/B < 11$ .

Calibrations and assumptions in connection with the use of the glass electrodes were the same as described earlier.<sup>2</sup> We will assume the presence of three component equilibria of the general type



Applying the law of mass action to these equilibria the conditions for the total concentrations then give

$$B = b + \sum_p \sum_q \sum_r q \beta_{pqr} h^p b^q c^r \quad (2)$$

$$C = c + \sum_p \sum_q \sum_r \beta_{pqr} h^p b^q c^r \quad (3)$$

$$H = h - k_a h^{-1} c + \sum_p \sum_q \sum_r p \beta_{pqr} h^p b^q c^r \quad (4)$$

where  $b = [\text{Ni}^{2+}]$  and  $c = [\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3^+]$ .

The calculational problem is then to find the model (sets of  $pqr$  and  $\beta_{pqr}$ ) that best can explain the experimental data.

The search for the best model was made by using the least squares computer program LETAGROPVRID<sup>10</sup> (version ETITR).<sup>11</sup> As "best" model or models we will consider those giving the lowest error squares sum

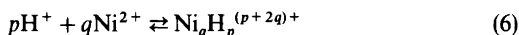
$$U = \sum (Z_{\text{calc}} - Z_{\text{exp}})^2 \text{ where } Z = (h - H)/C.$$

The LETAGROP calculations also give standard deviations  $\sigma(Z_c)$ ,  $\sigma(\beta_{pqr})$  and/or  $\sigma(\log \beta_{pqr})$ , calculated and defined according to Sillén.<sup>12</sup> The computation was performed on a CYBER 172 computer.

Concerning the binary proton THAM equilibrium



we will make use of the results obtained from separate experiments and for the binary hydrolysis



the results obtained by Burkov-Sillén.<sup>5</sup>

For reaction (5)  $\log(K_a \pm 3\sigma)$  was found to be  $-8.646 \pm 0.002$ . For reaction (6) investigations both of Ohtaki-Biedermann<sup>6</sup> (3.0 M (Na)Cl) and Burkov-

Sillén<sup>5</sup> (3.0 M (Na)ClO<sub>4</sub>) clearly show that the main species in a hydrolyzed Ni<sup>2+</sup> solution is a hydroxonickel(II) tetramer, Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> and  $\log \beta_{-44} = -27.37$  was reported in 3.0 M (Na)ClO<sub>4</sub>.

These binary equilibria were assumed to be exactly known and all effects above this level will be treated as being caused by the metal complexes Ni(HL)<sub>n</sub><sup>2+</sup> and ternary species.

## DATA, CALCULATIONS AND RESULTS

The data used to evaluate the binary proton THAM equilibrium comprise 6 titrations with 146 experimental points within the concentration ranges  $0.020 \leq C \leq 0.200$  M. The analysis ended at  $\sigma(Z) = 0.003$  and the  $\log(K_a \pm 3\sigma)$  obtained was  $-8.646 \pm 0.002$ .

The mathematical analysis of the three component data was started by making a Bjerrum plot  $\bar{n}(\log[\text{HL}])$ . The plot is shown in Fig. 1. It is seen that even at the highest quotient  $C/B$  ( $C/B \geq 10$ ) the function  $\bar{n}(\log[\text{HL}])$  seems to be dependent on  $B$  and  $C$  thus indicating formation of ternary species Ni<sub>q</sub>H<sub>-p</sub>(HL)<sub>r</sub><sup>(2q-p)+</sup>. However, at sufficiently low  $\log[\text{HL}]$ -values, all data, even at the lowest  $C/B$ -ratios, fall on a single curve, thus indicating formation of stepwise mononuclear complexes Ni(HL)<sub>n</sub><sup>2+</sup>. By selecting data from all  $C/B$ -ratios fulfilling the condition that  $\bar{n}(\log[\text{HL}])$  is independent of  $B$  and  $C$ , it should be possible to obtain accurate values of the Ni(HL)<sub>n</sub><sup>2+</sup>-species. A LETAGROP analysis of these data including 8 titrations and 54 titration points ended at  $\sigma(Z_c) = 0.0025$  and the actual  $\log \beta_n$ -values obtained according to the reaction

Table 1. Results of the final LETAGROP calculations giving the formation constants for the "best fitting" complexes. The formation constants are related according to the relation  $p\text{H}^+ + q\text{Ni}^{2+} + r\text{H}_2\text{L}^+ \rightleftharpoons (\text{H}^+)_p - (\text{Ni}^{2+})_q (\text{H}_2\text{L}^+)_r$ . The errors are  $3\sigma(\log \beta_{pqr})$ .

Number of titr./ number of points	$p, q, r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p, q, r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p, q, r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p, q, r$	$\log(\beta_{pqr} \pm 3\sigma)$	$\sigma(z)$
6/146	-1,0,1	-8.646 ±0.002							0.003
8/54	-1,1,1	-5.47 ±0.01	-2,1,2	-11.56 ±0.02					0.003
23/328 <sup>a</sup>	-5,3,2	-30.06 ±0.04	-8,4,4	-46.65 ±0.03	-9,4,4	-54.85 ±0.05	-10,4,4	-63.60 ±0.06	0.007

<sup>a</sup>  $\beta_{-111}$  and  $\beta_{-212}$  were not varied.

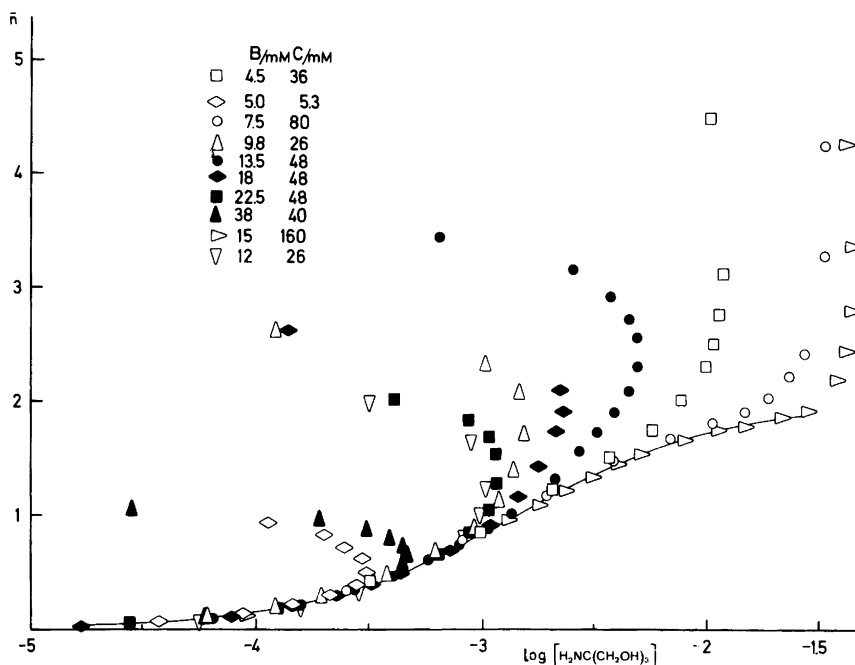
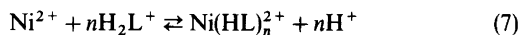


Fig. 1. Experimental data plotted as curves  $\bar{n}(\log[HL])$ . In order to make the figure clear only a few titrations have been plotted. The full curve has been calculated with the formation constants for the metal species  $NiHL^{2+}$  and  $Ni(HL)_2^{2+}$  given in Table 1. A complete list of experimental data is available from the author.



were  $\log(\beta_1 \pm 3\sigma) = -5.47 \pm 0.01$  and  $\log(\beta_2 \pm 3\sigma) = -11.56 \pm 0.02$ .

These equilibrium constants ( $\log K_a$ ,  $\log \beta_1$  and  $\log \beta_2$ ) were then assumed to be exactly known with the values given above and they were not varied until some final calculations. The data used to evaluate the ternary complex model comprises 23 titrations with 328 titration points.

Experimental data fulfilling the condition  $Z_c > 1$  i.e.  $C+H-h < 0$ , cannot be visualized by the  $\bar{n}(\log[HL])$ -function. These data are therefore represented as  $Z_c(\log h)_{B,C}$ -curves (see Fig. 2) and the accomplishment of the condition  $Z_c > 1$  is in itself a demonstration of ternary complex formation.

The search for the ternary species was started with *pqr*-analysis (systematic testing of different *pqr*-complexes) on a representative part of data, comprising 8 titrations with 124 titration points (Table 2). It was soon found that at every *q*-section (corresponding to the number of nickel atoms in the

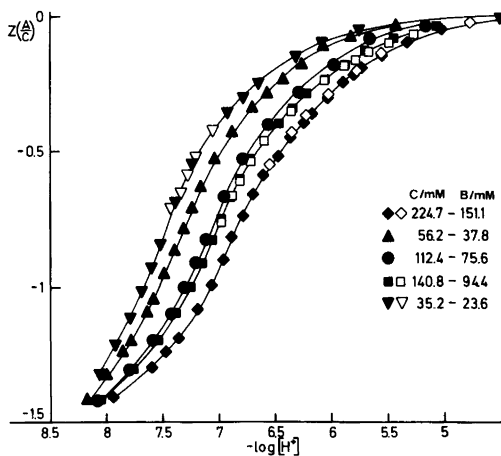


Fig. 2. Experimental data plotted as curves  $Z_c(\log h)_{B,C}$  for the quotient  $C/B=1.5$ . The full curves have been calculated using the formation constants for the binary and ternary species given in Table 1. Open symbols refer to back titrations.

Table 2. Results of some introductory LETAGROP calculations comprising a representative part of experimental data, no variations of the binary constants given in Table 1 have been made. The constants  $\beta_{pqr}$  are defined in Table 1 and the errors are  $3\sigma(\log\beta_{pqr})$ ; Data I.

Number of titr./ number of points	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$\sigma(z)$	$U \times 10^{-3}$
8/124	-9,4,4	-53.99 ± 0.09			0.0265	86.1
8/124	-11,5,5	-64.90 ± 0.11			0.0266	86.8
8/124	-8,4,4	-46.25 ± 0.07	-10,4,4	-63.33 ± 0.14	0.0182	40.1
8/124	-9,3,4	-56.78 ± 0.14	-9,5,4	-52.37 ± 0.11	0.0310	112
8/124	-10,5,5	-57.26 ± 0.13	-12,5,5	-73.98 ± 0.25	0.0252	77.3
8/124	-11,4,5	-67.36 ± 0.15	-11,6,5	-63.40 ± 0.24	0.0254	78.7

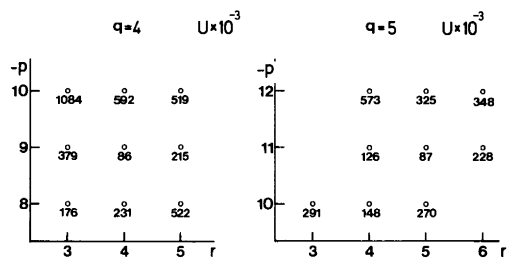


Fig. 3. LETAGROP-search for ternary species. The diagrams give error squares sums  $U(pr)_q \times 10^{-3}$ ,  $q=4, 5$ , assuming only one complex.

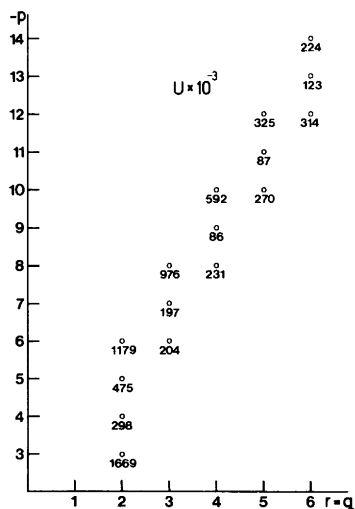


Fig. 4. LETAGROP-search for ternary species. A summary of the error squares sums  $U(pr)_q \times 10^{-3}$  concerning the  $q$ -sections  $2 \leq q \leq 6$ , and assuming  $r=q$ . Only one complex is supposed to be formed.

complexes) the lowest error squares sum was obtained when  $r=q$ , i.e. the numbers of nickel(II) and THAM in the complexes are the same.

A good illustration of this statement is given by the results of the calculations for  $q=4$  and  $q=5$  in Fig. 3. Thus the calculations can be summarized in one figure, where the error squares sums for the species, fulfilling the condition  $r=q$ , are given for the different  $q$ -sections,  $z \leq q \leq 6$ ; Fig. 4.

It is seen that the lowest error squares sums are obtained for the complexes  $\text{Ni}_4\text{H}_{-5}(\text{HL})_4^{3+}$  and  $\text{Ni}_5\text{H}_{-6}(\text{HL})_5^{4+}$ . However, remaining effects indicate the formation of two or more ternary species and the tetranuclear model appeared to give a better fit to experimental data assuming either two or three complexes to be formed. Results of some calculations including probable combinations of tetranuclear and pentanuclear complexes are given in Table 2, calculation denoted Data I. As seen from this table, the best model assuming two complexes seems to include the species  $\text{Ni}_4\text{H}_{-4}(\text{HL})_4^{4+}$  and  $\text{Ni}_4\text{H}_{-6}(\text{HL})_4^{2+}$ .

Thus the following conclusions may be drawn from the introductory  $pqr$ -analysis:

(i) polynuclear and most probably tetranuclear ternary complexes are formed.

(ii) the condition  $q=r$  seems to be fulfilled, e.g., complexes of the type  $(\text{NiHL})_{q=r}\text{H}_{-p}^{(2q-p)+}$  seem to be dominating at least on the average,

(iii) the average number of  $\text{OH}^-$  bound per nickel in the complexes is  $\sim 2.25$  calculated over the level  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{NC}(\text{CH}_2\text{OH})_3^+$  and  $\text{Ni}^{2+}$ .

The condition  $p=r$  indicates that titration experiments at low quotients  $C/B$  should be especially favourable for determining the ternary  $\text{Ni}_q\text{H}_{-p}(\text{HL})_r$  species. Owing to the low solubility of the complexes at the ratio  $C/B=1$ , leading to precipitation of nickel(II) hydroxide, comparative titration ex-

Table 3. Results of LETAGROP calculations for some different assumptions concerning the ternary complexes formed. The constants  $\beta_{pqr}$  are defined in Table 1 and the errors are  $3\sigma(\log \beta_{pqr})$ . If no  $3\sigma$  is given the corresponding constant has not been varied.  $1 \leq C/B < 11$ .

Number of titr./ number of points	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$p,q,r$	$\log(\beta_{pqr} \pm 3\sigma)$	$\sigma(z)$
7/101 <sup>a</sup>	-8,4,4	-46.55 ±0.03	-9,4,4	-54.86 ±0.09	-10,4,4	-63.60 ±0.05			0.0051
23/328	-8,4,4	-46.44 ±0.03	-9,4,4	-54.86 ±0.12	-10,4,4	-63.55 ±0.12			0.0160
23/328	-8,4,4	-46.63 ±0.04	-9,4,4	-54.86 ±0.12	-10,4,4	-63.60 ±0.12	-4,2,2	-24.55 ±0.05	0.0110
23/328 <sup>b</sup>	-6,3,3	-35.34 ±0.02	-9,4,4	-55.12 ±0.15	-10,4,4	-63.46 ±0.07			0.0107
23/328 <sup>c</sup>	-8,4,4	-46.65 ±0.03	-9,4,4	-54.85 ±0.05	-10,4,4	-63.60 ±0.06	-5,3,2	-30.06 ±0.04	0.0073
23/328 <sup>d,e</sup>	-1,1,1	-5.46 ±0.008	-2,1,2	-11.57 ±0.02	-5,3,2	-30.04 ±0.03			0.0071
23/328 <sup>e</sup>	-8,4,4	-46.55 ±0.03	-9,4,4	-54.90 ±0.06	-5,3,2	-30.12 ±0.04	-6,3,2	-38.66 ±0.21	0.0070
23/328 <sup>e</sup>	-8,4,4	-46.65	-9,4,4	-54.85	-5,3,2	-30.11 ±0.05	-2,1,1	-14.58 ±0.25	0.0071
23/328 <sup>e</sup>	-8,4,4	-46.65	-9,4,4	-54.85	-5,3,2	-30.10 ±0.04	-4,2,1	-28.21 ±0.30	0.0070
23/328 <sup>e</sup>	-8,4,4	-46.65	-9,4,4	-54.85	-5,3,2	-30.07 ±0.03	-3,1,1	-23.24 ±0.25	0.0071

<sup>a</sup>  $2 < C/B < 11$ . <sup>b</sup>  $\beta_{-623} < 0$  and  $\beta_{-535} < 0$ . <sup>c</sup>  $\beta_{-432} < 0$  and  $\beta_{-633} < 0$ . <sup>d</sup>  $\beta_{-844}$  and  $\beta_{-944}$  were not varied. <sup>e</sup>  $\beta_{-10,4,4}$  was not varied.

periments were performed at  $C/B = 1.5$ .

In the evaluation of the ternary complex model experimental data were divided in two or in some calculations three parts consisting of the quotients  $C/B = 1, 1.5$  resp.  $2 - 11$ . The different parts of data, each consisting of 7–10 titrations with 100–150 experimental points, were treated separately but conclusions from one part were applied to the others.

Experimental data comprising titrations with quotients  $C/B > 2$  were very well explained assuming the series  $\text{Ni}_4\text{H}_{-4}(\text{HL})_4^{4+}$ ,  $\text{Ni}_4\text{H}_{-5}(\text{HL})_4^{3+}$  and  $\text{Ni}_4\text{H}_{-6}(\text{HL})_4^{2+}$  to be formed. A data material consisting of 7 titrations with 101 titration points yielded the following formation constants  $\log(\beta_{pqr} \pm 3\sigma)$  related to eqn. 1:

$$\begin{aligned} \log \beta_{-8,4,4} &= -46.55 \pm 0.03 \\ \log \beta_{-9,4,4} &= -54.86 \pm 0.09 \\ \log \beta_{-10,4,4} &= -63.60 \pm 0.05 \end{aligned}$$

with the standard deviation in  $\Delta Z_c$  ( $\Delta Z_c = Z_{\text{calc}} - Z_{\text{exp}}$ ),  $\sigma(Z) = 0.005$  indicating a good fit.

However, at lower quotients  $C/B$  ( $C/B \leq 1.5$ ) this complex model exhibits a much poorer fit to experimental data leaving considerable deviations in  $\Delta Z_c = Z_{\text{calc}} - Z_{\text{exp}}$ . This behaviour demonstrates that either additional ternary complexes exist or at worst that a more or less new complex model has to be determined. A great number of combinations is possible, but we decided to test complexes fulfilling the condition  $r=q$  in the first instance, e.g.  $(\text{NiHL})_2\text{H}^{(4-n)+}$ ,  $(\text{NiHL})_3\text{H}^{(6-m)+}$  and so on. Addition of the species  $\text{Ni}_2\text{H}_{-2}(\text{HL})_2^{2+}$  to the complex model made the error squares sum considerably lower, but a still better fit was obtained by exchanging the species  $\text{Ni}_4\text{H}_{-4}(\text{HL})_4^{4+}$  for  $\text{Ni}_3\text{H}_{-3}(\text{HL})_3^{3+}$ .

Thus this set of complexes  $\text{Ni}_3\text{H}_{-3}(\text{HL})_3^{3+}$ ,  $\text{Ni}_4\text{H}_{-5}(\text{HL})_4^{3+}$  and  $\text{Ni}_4\text{H}_{-6}(\text{HL})_4^{2+}$  provides a good explanation of data at low quotients  $C/B$  ( $C/B \leq 1.5$ ), but upon introducing this complex model to the whole data material negative deviations in  $\Delta Z_c$  appeared in the highest quotients  $C/B$  ( $C/B > 2$ ) indicating a poorer fit to experimental data at these concentration ranges.

A reasonable explanation seems to be that the species  $\text{Ni}_3\text{H}_{-3}(\text{HL})_3^{3+}$  actually is a kind of an average complex of two or more other species. A number of combinations were therefore tested and the best explanation of experimental data comprising all quotients  $C/B$ ,  $1 \leq C/B < 11$ , was obtained assuming the species  $\text{Ni}_3\text{H}_{-3}(\text{HL})_2^{3+}$ ,  $\text{Ni}_4\text{H}_{-4}(\text{HL})_4^{4+}$ ,  $\text{Ni}_4\text{H}_{-5}(\text{HL})_3^{3+}$  and  $\text{Ni}_4\text{H}_{-6}(\text{HL})_4^{2+}$  to be formed. The formation constants with standard deviations ( $3\sigma$ ) are given in Table 3 and the analysis ended at  $\sigma(Z)=0.007$ . The complex model suggested by Bai-Martell comprising the species  $\text{Ni}_2\text{L}_3^+$  and  $\text{Ni}_3(\text{H}_{-2}\text{L})_2(\text{H}_{-1}\text{L})$  were also tested, but the formation constants were obtained either with negative values ( $\beta_{-6,2,3} < 0$ ) or with large standard deviations ( $\log(\beta_{-8,3,3} \pm 3\sigma) = -52.5 \pm 0.3$ ) indicating a poor fit to experimental data.

In connection with the evaluation of the ternary complex model the computer program SOLGASWATER<sup>13</sup> equipped with plotting procedures has been very useful. The theoretical  $Z_c(\log h)$ -plots calculated by the program were performed in a scale adjusted to the same "plots" of experimental data. In that way a concise picture of the fit to experimental data of several complex models was immediately obtained.

The SOLGASWATER-program was also used to calculate distribution diagrams and predominance area diagrams in order to visualize the amounts of the different species (see Fig. 5, 6).

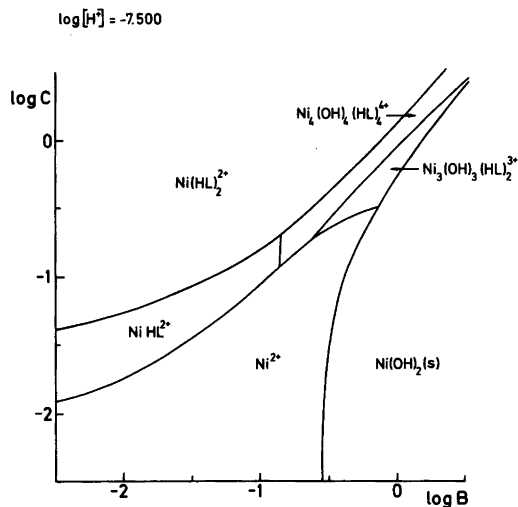


Fig. 5. Predominance area diagrams for the different nickel(II) THAM species. The dominating species at every fixed  $\log B - \log C$  level is given. The solubility product of  $\text{Ni}(\text{OH})_2(\text{s})$ , used in the calculations, is a kind of an average value taken from *Stability Constants*.<sup>16</sup> The computer program SOLGASWATER<sup>13</sup> equipped with plotting procedures was used.

DISCUSSION

The present investigation has given further evidence for the compositional connection between the binary metal hydrolysis and the ternary hydrolytic species. The tetranuclear ternary species  $\text{Ni}_4\text{H}_{-4}(\text{HL})_4^{4+}$ ,  $\text{Ni}_4\text{H}_{-5}(\text{HL})_3^{3+}$  and  $\text{Ni}_4\text{H}_{-6}$

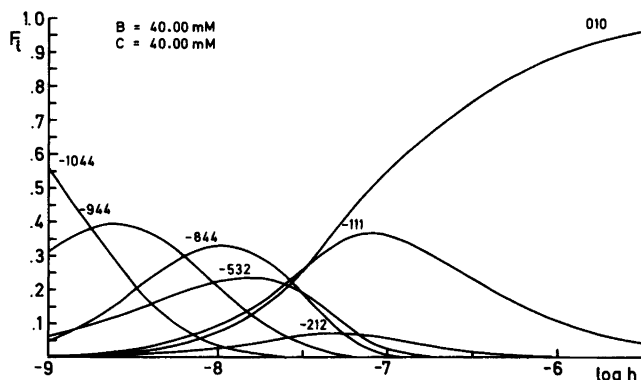
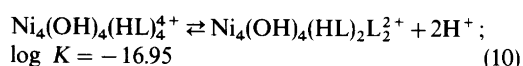
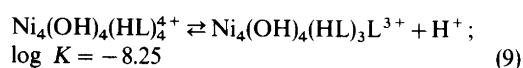
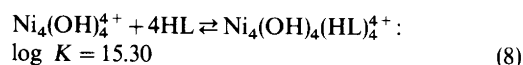


Fig. 6. Distribution diagram  $F_i(\log[H^+])_{B,C}$  of the binary and ternary nickel(II) species in the system  $\text{H}^+ - \text{Ni}^{2+} - (\text{CH}_2\text{OH})_3\text{CNH}_3^+$  in 3.0 M  $(\text{Na})\text{ClO}_4$ .  $F_i$  is defined as the ratio between nickel(II) in the species and total nickel(II). The computer program SOLGASWATER<sup>13</sup> was used in the calculations.

(HL)<sub>4</sub><sup>2+</sup> are obtained in great amounts. The composition of these species is reflected in the composition of the dominating binary hydroxo nickel species Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, and then the tetranuclear ternary series should preferably be written Ni<sub>4</sub>(OH)<sub>4</sub>(HL)<sub>4</sub><sup>4+</sup>, Ni<sub>4</sub>(OH)<sub>4</sub>(HL)<sub>3</sub>L<sup>3+</sup> and Ni<sub>4</sub>(OH)<sub>4</sub>(HL)<sub>2</sub>L<sub>2</sub><sup>2+</sup>. The complexes Ni<sub>4</sub>(OH)<sub>4</sub>(HL)<sub>3</sub>L<sup>3+</sup> and Ni<sub>4</sub>(OH)<sub>4</sub>(HL)<sub>2</sub>L<sub>2</sub><sup>2+</sup> are probably formed by the removal of protons from the hydroxyl groups in the THAM ligand. It is then possible to establish the following equilibria



It is not possible to establish the structure of the ternary species from emf data. Thus an OH<sup>-</sup> group together with an H<sub>2</sub>NC(CH<sub>2</sub>OH)<sub>3</sub> molecule may equally well be regarded as for example H<sub>2</sub>NC(CH<sub>2</sub>OH)<sub>2</sub>CH<sub>2</sub>O<sup>-</sup> and the complexes proposed could also be Ni<sub>4</sub>L<sub>4</sub><sup>4+</sup>, Ni<sub>4</sub>(H<sub>-1</sub>L)<sub>3</sub>L<sup>3+</sup> and Ni<sub>4</sub>(H<sub>-1</sub>L)<sub>2</sub>L<sub>2</sub><sup>2+</sup>. Such displacements of the alcoholic protons are suggested in the present system by Hall *et al.*<sup>8</sup> and Bai-Martell.<sup>9</sup> However, the strong connection between the binary hydrolysis and the ternary hydrolytic species in this and other metal systems<sup>1-4</sup> makes the presence of hydroxide groups more probable.

The Ni<sup>2+</sup> and OH<sup>-</sup> ions in the tetramer, Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, are supposed to form a distorted cube where the nickel and oxygen atoms are arranged tetrahedrally.<sup>14</sup> This structure permits each nickel to interact with three oxygen atoms and *vice versa*.

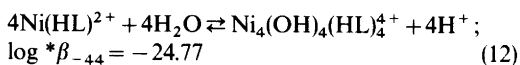
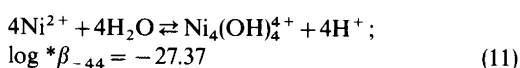
Quite recently a crystal structure of the compound Ni<sub>4</sub>(OH)<sub>4</sub>[C<sub>6</sub>H<sub>9</sub>(NH<sub>2</sub>)<sub>3</sub>]<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>7</sub><sup>15</sup> was presented containing Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup> clusters similar to those described above. The three NH<sub>2</sub> groups in the ligand (1,3,5-triamino(*aaa*)cyclohexane denoted "tach") form an equilateral triangle and they are all coordinated to the same nickel ion. Thus three coordination positions at the octahedral nickel ion are left to be occupied by, for example, OH<sup>-</sup> ions.

The tetranuclear species obtained in the present system should have a similar structure with the NH<sub>2</sub> group and two hydroxyl groups from the

THAM ligand and three OH<sup>-</sup> ions coordinated to each nickel ion.

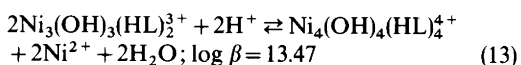
The nickel tetramer built up in this way seems to be very rigid and excess ligand is left quite uncomplexed at high  $-\log h$ -ranges. As the total amounts of the tetranuclear ternary species are great, large angle X-ray scattering (LAXS) measurements should give valuable information of the structure of these complexes and investigations in this direction are in progress.

It is also possible to compare the acidity strength (tendency to hydrolyze) between the hydrated nickel(II) ion (Ni(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>) and the mononuclear species Ni(HL)<sup>2+</sup>. According to the equilibria



it seems that the introduction of a THAM ligand increases the acidity strength of the nickel(II) ion. This behaviour was also found in the nickel(II)-imidazole system.<sup>2,3</sup>

In addition to the tetranuclear series a trinuclear ternary species Ni<sub>3</sub>H<sub>-3</sub>(HL)<sub>2</sub><sup>3+</sup> was also established. The composition of this complex exhibits no direct relation to the binary hydrolysis species Ni<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, Ni<sub>2</sub>OH<sup>3+</sup> and NiOH<sup>+</sup>, but a possible relation between the trinuclear and tetranuclear ternary species is obtained by the equilibria



The formation, as well as the decomposition, of the trinuclear ternary species are probably rather slow reactions since the longest waiting periods to obtain stable potentials were obtained at low *C/B*-quotients, where the amounts of this complex are high.

The available  $-\log h$ -range can be extended to higher values by exchanging the glass electrodes for a hydrogen electrode and/or by performing spectrophotometric titrations. Some preliminary spectrophotometric measurements have been carried out and further experiments are planned. As the reactions of formation and decomposition of the ternary species are slow, kinetic experiments using the stopped-flow technique may be practicable and such studies are planned. In cooperation with



Dr Gun Ivarsson crystal growth experiments have been carried out in order to relate the structures of the species in solution to those formed in the solid state.

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