

## The Complex Formation between Nickel(II) and 2-Aminoacetamidoxime and Its *N*-Methylated Derivatives

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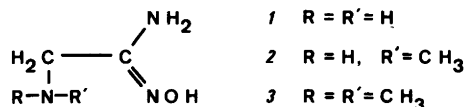
The complex formation equilibria of nickel(II) with 2-aminoacetamidoxime *1*, 2-(methylamino)acetamidoxime *2* and 2-(dimethylamino)acetamidoxime *3* have been studied in 1.0 M Na(ClO<sub>4</sub>) medium at 25 °C by potentiometric titrations with the use of a glass electrode. Experimental data collected from acid, neutral and weakly alkaline solutions were analyzed with respect to the complexes formed and their stability constants using the least-squares computer program MINQUAD. With ligands *1* and *2*, nickel(II) forms octahedral stepwise complexes Ni(HL)<sup>2+</sup>, Ni(HL)<sub>2</sub><sup>2+</sup>, Ni(HL)<sub>3</sub><sup>2+</sup>, and a square-planar complex Ni(HL)L<sup>+</sup> with the intramolecular O...O hydrogen bridge between the oxime oxygen atoms. Data for system *3* can be explained with the octahedral mononuclear binary complexes Ni(HL)<sup>2+</sup>, Ni(HL)<sub>2</sub><sup>2+</sup> together with the hydrolytic ternary species HL<sub>1</sub>Ni(HL)<sub>2</sub><sup>+</sup> and HL<sub>6</sub>Ni<sub>4</sub>(HL)<sub>4</sub><sup>2+</sup>.

The metal complexes of different oxime ligands in the solid state as well as in aqueous solution have been described in several reports from this laboratory. The investigation has now been extended to include the nickel(II) complexes formed with 2-aminoacetamidoxime *1* and with two of its derivatives containing one *2* and two *3* methyl groups on the amine nitrogen.

The amidoxime group is capable of binding metal ions as such or in the form of the amidoximate anion and can behave as bidentate

ligand through the amide nitrogen and oxime oxygen (or nitrogen) atoms. The colour reactions of this grouping with several transition metals were already noted in the early days of coordination chemistry.<sup>1</sup> However, when the amidoxime ligand contains an additional –NRR' donor site allowing a five-membered chelate ring *via* the amine nitrogen to be formed, the second coordinating atom can be either the oxime nitrogen or the amide nitrogen. In both modes of chelation the stabilities of the complexes would be expected to decrease with increasing *N*-methylation. It could also be presumed that coordination through the oxime nitrogen would easily lead to the formation of a bis complex species with the strong intramolecular hydrogen bridge between the oxime oxygen atoms. Such a bond would stabilize the planar dsp<sup>2</sup> hybridization of nickel(II) and thereby limit the maximum number of binding ligands to two.

In this communication we report the results of a potentiometric study on complex formation equilibria of ligands *1*–*3* with divalent nickel in aqueous 1.0 M Na(ClO<sub>4</sub>) medium. During the investigation we also isolated some of these chelates in the solid state and determined their structures by X-ray methods. The details of the X-ray diffraction data will be published in a forthcoming paper. There are apparently no previous reports on the metal complexes formed with these ligand systems.



### EXPERIMENTAL

*Ligand preparations.* 2-Aminoacetamidoxime *1* was prepared by action of hydroxylamine on

2-aminoacetonitrile applying the method first described by Tiemann.<sup>2</sup> To a suspension of hydroxylammonium chloride (1.0 mol) and 2-aminoacetonitrile hydrochloride (0.8 mol) in 200 ml of absolute ethanol was slowly added a sodium ethoxide solution (prepared by dissolving 1.8 mole of sodium to *ca.* 500 ml of absolute ethanol) with vigorous stirring. After completion of the reaction the solid sodium chloride was filtered off and the clear colourless solution was stirred for about 48 hours at room temperature. When anhydrous HCl was passed into the solution cooled to 0 °C, *1* was precipitated as its monohydrochloride; yield *ca.* 60 % of the theoretical.

2-(Methylamino)acetamidoxime *2* and 2-(dimethylamino)acetamidoxime *3* were prepared similarly to *1* using 2-(methylamino)acetonitrile hydrochloride and 2-(dimethylamino)acetonitrile, respectively, as starting reagents. Both compounds were obtained in good yields (70–80 %) in the form of their monohydrochlorides. Recrystallizations from hot ethanol gave all three hydrochlorides as white needle-like crystals. Analyses: C, H, N, Cl. The formula weights of the air dried products as determined by potentiometric titrations were 126.1 (calc. 125.6), 139.4 (calc. 139.6) and 153.6 (calc. 153.6) for ligands *1*, *2* and *3*, respectively.

*Method.* The present investigation was carried out as a series of potentiometric titrations at 25 °C and in a constant 1.0 M Na(ClO<sub>4</sub>) medium. The free hydrogen ion concentration, *h*, was determined by measuring the emf of the cell

–RE | equilibrium solution | GE+

where GE denotes a glass electrode (Beckman, type 40495) and RE=Hg, Hg<sub>2</sub>Cl<sub>2</sub> | 0.01 M Cl<sup>-</sup>, 0.99 M ClO<sub>4</sub><sup>-</sup>, 1.00 M Na<sup>+</sup> | 1.00 M NaClO<sub>4</sub>. Assuming the activity coefficients to be constant, the following expression is valid:

$$E = E_o + 59.157 \log h + E_j \quad (1)$$

For each separate titration the electrode system was calibrated against the background electrolyte by means of  $E_o$ ,  $E_j$ -titration, after which the main run was started. For the liquid junction potential we used  $E_j = j_h h$ ; the values of the coefficient  $j_h$  varied slightly in different runs and the average value was  $-60 \text{ mV M}^{-1}$ . The changes in the values of  $E_o$  caused by the concentration changes during the titrations were considered negligible.

In the binary titrations made to determine acidity constants of the oxime groups it was necessary to obtain potential readings from relatively high  $-\log h$  ranges (values of  $-\log h$  up to *ca.* 11.8 were used). Employment of the glass electrode under such conditions has often been questioned. However, the value of the ionic product of water ( $pK_w = 13.74(1)$ ) obtained during the calculations was found to be in satisfactory agreement with the literature value of  $k_w$  valid in 1 M NaClO<sub>4</sub> ( $pK_w = 13.770$ )<sup>3</sup> and we considered it unnecessary to replace the glass electrode by a hydrogen electrode, especially since the complex formation reactions studied occurred in consider-

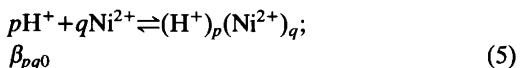
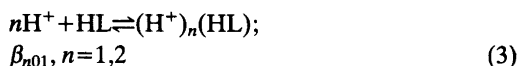
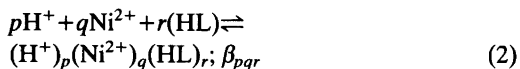
*Table 1.* Initial total concentrations (10<sup>3</sup> mol/l) of metal ( $C_M$ ) and ligand ( $C_L$ ), number of titration points, and rough  $-\log h$  ranges used in the calculations.

Ligand	$C_M$	$C_L$	No. of points	$-\log h$ Range	Ligand	$C_M$	$C_L$	No. of points	$-\log h$ Range	
<i>1</i>		13.65	67	2.36	<i>2</i>	4.931	11.09	36	4.38	
		18.26	72	2.68		4.369	18.46	55	5.13	9.26
		25.00	81	2.44		4.369	22.61	32	5.69	9.38
		33.23	80	2.50		3.218	26.32	39	3.62	8.76
	14.98	15.04	23	2.69		2.434	36.22	32	4.04	8.80
	8.320	16.30	60	2.78		<i>3</i>	10.80	42	2.09	11.66
	4.362	17.18	75	2.75			13.57	56	2.27	11.73
	4.369	23.61	66	2.82			16.41	40	2.01	11.63
	6.399	17.60	35	2.87			20.32	62	1.89	11.73
	<i>2</i>		12.54	60			2.19	10.71	10.84	26
		19.31	71	2.49	2.623		27.34	48	4.32	8.84
		25.38	78	2.25	2.633		17.97	48	4.67	8.82
		27.31	82	2.07	3.404		14.40	42	4.84	8.81
12.59		12.55	24	3.93	4.522		14.08	34	4.70	8.85
9.339		13.98	34	3.90	5.763		11.67	40	4.69	8.86
8.334		17.34	48	3.86	7.388	8.734	21	4.91	7.41	
				8.31						

ably lower  $-\log h$  regions. Thus the inaccuracy in the values of the NOH acidity constants could hardly lead to erroneous selection of the complex models.

During the measurements  $h$  was varied by adding hydroxide or hydrogen ions to the solution. The compositions of the starting solutions, number of the titration points, and the  $-\log h$  ranges used in the calculations are quoted in Table 1. The upper limits of the reactants and the  $-\log h$  ranges in the metal-ligand systems were largely determined by formation of precipitates or by very slow attainment of equilibria.

*Data treatment.* In evaluating the equilibrium constants,  $H^+$ ,  $Ni^{2+}$  and HL (the neutral oxime) were chosen as components. The general three-component equilibrium (2) and the two-component equilibria (3–5) are the following:



For the binary hydrolytic equilibrium (5) we used the results summarized by Baes and Mesmer.<sup>4</sup> Inclusion of the proposed complexes and equilibrium constants (recalculated values valid in 1 M NaClO<sub>4</sub>) in the calculations showed that the  $Ni^{2+}$  hydrolysis was negligible in our conditions. Since the ligands were added to the titration solution as their hydrochlorides the formation of the chloro complexes of nickel had also to be taken into consideration. On the basis of known weakness of these complexes<sup>5</sup> and the low concentrations of  $Cl^-$  in our solutions it can be estimated that no significant amounts of  $(H^+)_p(Ni^{2+})_q(HL)_r(Cl^-)_s$  species were formed.

The calculational problem is to find the sets of  $pqr$  that best explain the experimental data. The search for the best model was made with the least-squares computer program MINQUAD,<sup>6</sup> which minimizes the sum of the squares of residuals,  $U = \sum(\Delta C_M^2 + \Delta C_L^2 + \Delta C_H^2)$ , where  $C_M$ ,  $C_L$  and  $C_H$  are the total molar concentrations of metal, ligand and proton, respectively. The computational work was performed on a Univac 1108 computer.

## CALCULATIONS AND RESULTS

*The  $H^+$ -ligand systems.* In the concentration ranges used in the measurements no association products were found and each of the separate systems could be well explained in terms of the equilibrium constants  $\beta_{101}$ ,  $\beta_{201}$  and  $k_a$ . The results are presented in Table 2. Although the calculated standard deviations even in the constants referring to the oxime dissociations were relatively low, the experimental technique used does not permit accurate measurements in alkaline solutions. Very wide error limits have therefore been estimated for the values given for the constant  $k_a$ . To facilitate comparisons between the different acid functions of the ligands, the stepwise protonation constant  $k_2$  has been included in Table 2. In subsequent calculations all the ligand-proton equilibria were assumed to be exactly known and no attempts were made to adjust the corresponding equilibrium constants.

*The  $H^+ - Ni^{2+}$ -ligand 1 system.* The analysis of the data was begun with construction of the Bjerrum plot,  $\bar{n}(\log[HL])$ , shown in Fig. 1. At sufficiently low  $-\log[HL]$  values the data can reasonably be explained by formation of the stepwise mononuclear complexes  $Ni(HL)_n^{2+}$  with  $n=1-3$ . At higher  $-\log h$  values ( $>5.5$ ), the titration solutions change from pale green to orange with increasing basicity. The data points

Table 2. Values of the proton-ligand equilibrium constants relating to the reactions (3)–(4). The errors  $3\sigma(\log\beta_{n01})$  are given for  $\log\beta_{101}$  and  $\log\beta_{201}$ . The error estimated for  $\log k_a$  corresponds to  $ca. 10\sigma(\log k_a)$ .

	Ligand 1	Ligand 2	Ligand 3
$\log\beta_{101}$	$7.942 \pm 0.004$	$8.260 \pm 0.007$	$7.606 \pm 0.005$
$\log\beta_{201}$	$10.409 \pm 0.006$	$10.372 \pm 0.012$	$9.365 \pm 0.009$
$\log k_a$	$-12.5 \pm 0.1$	$-12.4 \pm 0.1$	$-12.3 \pm 0.1$
* $\log k_2$	2.467	2.112	1.759

\*  $\log k_2 = \log\beta_{201} - \log\beta_{101}$

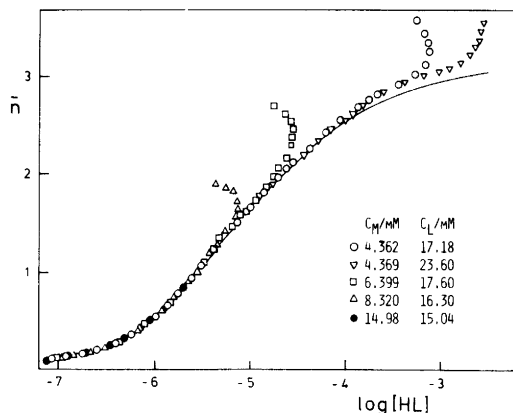


Fig. 1. Experimental data for ligand 1 plotted as curves  $\bar{n}(\log[\text{HL}])$ . In order to make the figure clear only part of the data points used in the calculations have been plotted.

no longer fall on a single curve, indicating the presence of deprotonated or polynuclear complex species. Since the  $\text{Ni}(\text{HL})_n^{2+}$  complexes clearly possessed acidic properties and the formation of planar bis complex was expected, a complex model comprising species  $\text{Ni}(\text{HL})^{2+}$ ,  $\text{Ni}(\text{HL})_2^{2+}$ ,  $\text{Ni}(\text{HL})_3^{2+}$  and  $\text{H}_1\text{Ni}(\text{HL})_2^+$  was tested using the complete data set (Table 1, 259 experimental points). The results are given in Table 3. The low error squares sum indicated a very satisfactory fit. Since the standard deviations in the constants are relatively low [ $3\sigma(\log\beta_{pqr}) \leq 0.02$ ] and all the complexes occur in great amount (Fig. 2), we regard them as well established.

Further analysis showed the detection of any other deprotonated complex species besides  $\text{H}_1\text{Ni}(\text{HL})_2^+$  in the system to be impossible. The same was true for all the polynuclear species tested. We then concluded that the experimental data are describable in terms of the

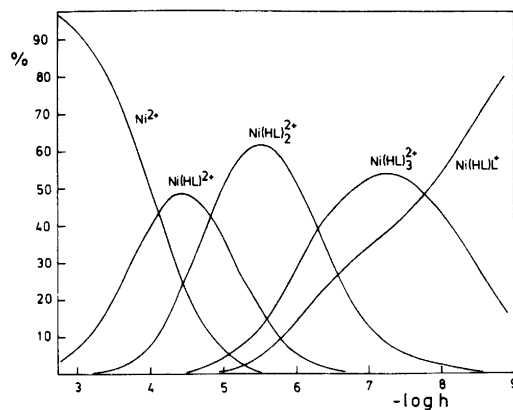


Fig. 2. Percentage distribution of nickel among various species in the  $\text{Ni}^{2+}$ -ligand 1 system with  $C_M=4.362$  mM and  $C_L=17.18$  mM.

complexes  $\text{Ni}(\text{HL})^{2+}$ ,  $\text{Ni}(\text{HL})_2^{2+}$ ,  $\text{Ni}(\text{HL})_3^{2+}$  and  $\text{H}_1\text{Ni}(\text{HL})_2^+$  alone, with the equilibrium constants given in Table 3.

The limiting factor for these complex formation studies was the relatively low solubility of the perchlorate salt of  $\text{H}_1\text{Ni}(\text{HL})_2^+$ , and most of the titrations were ended by the appearance of an orange-coloured  $\text{NiL}_2\text{HClO}_4$  precipitate. Limited concentration ranges had therefore to be used in the measurements.

*The  $\text{H}^+ - \text{Ni}^{2+}$  - ligand 2 system.* The essential features of the complex formation with this ligand are largely the same as with ligand 1. The  $\bar{n}(\log[\text{HL}])$  plot is given in Fig. 3. The MINIQUAD analysis showed that the same complex species as for ligand 1 could explain the 300 data points in Table 1 fairly well.

A representative distribution diagram of the complexes is shown in Fig. 4. In this system  $\text{Ni}(\text{HL})_3^{2+}$  was found only as a minor species in most of our titrations, and even at the highest

Table 3. Final values of the complex formation constants relating to the reaction (2). The errors given are  $3\sigma(\log\beta_{pqr})$ .

	Ligand 1	Ligand 2	Ligand 3
$\log\beta_{011}$	$5.720 \pm 0.005$	$5.253 \pm 0.004$	$3.979 \pm 0.004$
$\log\beta_{012}$	$10.843 \pm 0.007$	$9.505 \pm 0.007$	$5.52 \pm 0.02$
$\log\beta_{013}$	$14.74 \pm 0.02$	$11.88 \pm 0.08$	
$\log\beta_{-121}$	$4.27 \pm 0.02$	$2.406 \pm 0.006$	$-3.24 \pm 0.05$
$\log\beta_{-644}$			$-26.77 \pm 0.02$

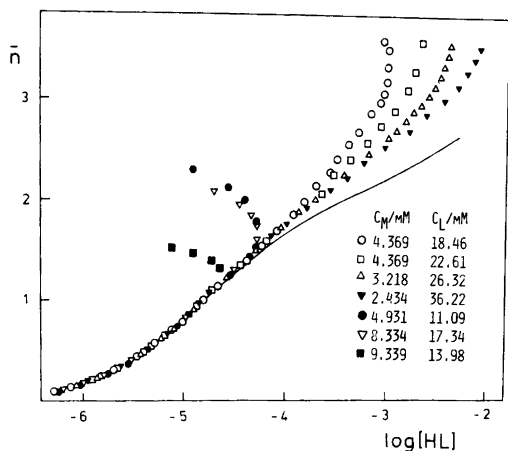


Fig. 3. A part of the experimental data for ligand 2 plotted as curves  $\bar{n}(\log[HL])$ .

ligand–metal ratio (15:1) the maximum concentration of  $Ni(HL)_3^{2+}$  was only 20 % of the total nickel concentration. This is also reflected in the relatively large standard deviation in the value of  $\log\beta_{013}$ .

*The  $H^+ - Ni^{2+}$  - ligand 3 system.* The behaviour of ligand 3 towards nickel ions deviates significantly from that of ligands 1 and 2. This is already noticed in the colour of the solutions which gradually change from green-blue to green-brown, as  $-\log h$  is raised. There is no sign of the

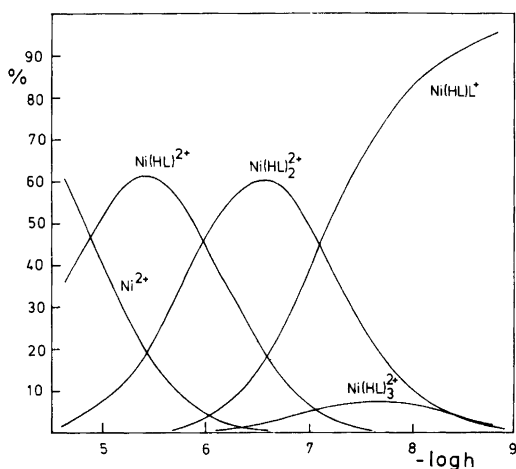


Fig. 4. Percentage distribution of nickel among various species in the  $Ni^{2+}$ -ligand 2 system with  $C_M=4.369$  mM and  $C_L=18.46$  mM.

orange colour found in the previous system. With this ligand the reactions at quotients  $C_L/C_M < 2$  and  $C_H < 0$  (the zero level of the ligand was calculated according to HL) were extremely slow and the achievement of stable potential readings remained uncertain. When such titrations were performed batchwise using a series of bottles, it was found that after a few days the solutions turned cloudy and the corresponding titration points had to be omitted in the calculations.

The Bjerrum plot is shown in Fig. 5. At low values of  $[HL]$  the function  $\bar{n}(\log[HL])$  seems to be independent of  $C_M$  and  $C_L$  and refers to the formation of the mononuclear complexes  $Ni(HL)^{2+}$  and  $Ni(HL)_2^{2+}$ . When the data fulfilling these conditions were treated separately using the MINQUAD analysis gave an entirely satisfactory fit and yielded the following formation constants with their standard deviations ( $3\sigma$ ):  $\log\beta_{011}=3.978\pm 0.003$  and  $\log\beta_{012}=5.595\pm 0.018$ . The values of these constants were assumed to be known during the search for the additional complexes and were not varied until the final calculations.

The shape of the titration curves indicated that the system must contain hydrolytic complex species. A noticeable inflection point which appeared on each of the titration curves when  $C_H/C_M$  approached  $-1.5$  further indicated that these complexes cannot be mononuclear. This

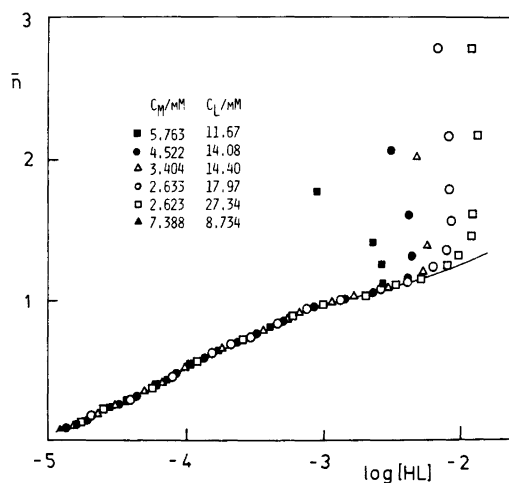


Fig. 5. A part of the experimental data for ligand 3 plotted as curves  $\bar{n}(\log[HL])$ .

was confirmed in the calculations, in which hydrolysis of  $\text{Ni}(\text{HL})^{2+}$  to  $\text{H}_1\text{Ni}(\text{HL})^+$  or  $\text{Ni}(\text{HL})_2^{2+}$  to  $\text{H}_1\text{Ni}(\text{HL})_2^+$  could not be traced.

The following search for the best complexes to describe the remaining experimental data was started with the simple hypothesis that in addition to  $\text{Ni}(\text{HL})^{2+}$  and  $\text{Ni}(\text{HL})_2^{2+}$  only one predominant complex was present. The error squares sum  $U$  was taken as the criterion for the best explanation. It was soon found that by far the best fit of the experimental data was obtained if the complex formed up to the inflection point mentioned had the stoichiometric relation  $\text{H}^+:\text{Ni}^{2+}$  equal to  $-3:2$ . The calculations fulfilling this condition are summarized in Fig. 6, and it is found that the lowest value of  $U$  is obtained for the tetranuclear complex  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$ . All the data in Table 1, in fact, proved to be quite satisfactorily described by assuming the complex species  $\text{Ni}(\text{HL})^{2+}$ ,  $\text{Ni}(\text{HL})_2^{2+}$  and  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  alone. There were, however, systematic drifts in the magnitudes of the residuals  $\Delta C_H$  and  $\Delta C_L$  in the regions where  $C_H$  approaches zero and the  $\chi^2$ -statistics<sup>6</sup> were unsatisfactory. This clearly pointed to the presence of one or more additional complexes. Using a systematic trial and error procedure we found that the best single complex was  $\text{H}_1\text{Ni}(\text{HL})_2^+$ . Although the maximum pre-

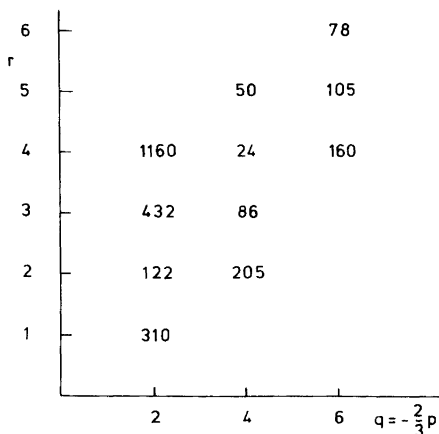


Fig. 6. Search for the ternary  $\text{H}_p\text{Ni}_q(\text{HL})_r^{p+2q}$  complex with  $\text{HL}=3$  assuming  $q = -\frac{2}{3}p$ . The diagram gives the error square sum  $U(qr)_p \times 10^{-8}$  assuming one new complex. The calculations are based on 214 points chosen to cover as great a concentration range as possible. The nickel(II) hydrolysis and the complexes  $\text{Ni}(\text{HL})^{2+}$  and  $\text{Ni}(\text{HL})_2^{2+}$  are supposed to be known.

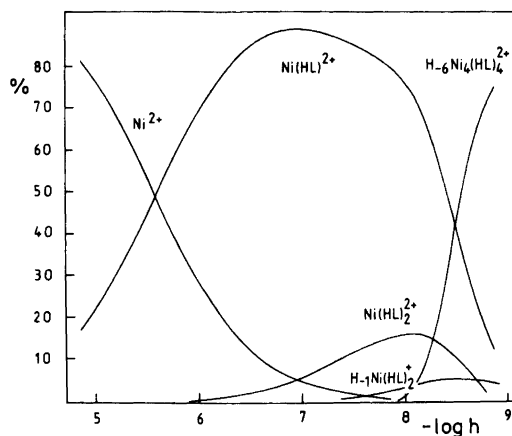


Fig. 7. Percentage distribution of nickel among various species in the  $\text{Ni}^{2+}$ -ligand 3 system with  $C_M=3.404$  mM and  $C_L=14.40$  mM.

sence of this new species was only 13 % relative to the total nickel concentration, its inclusion in the complex model resulted in an error squares sum 66 % lower than with only three complexes present. At the same time  $\chi^2$  improved dramatically from 216 to 19. This implies that there are no obvious systematic errors left in the data. Since the remaining effects seemed to be too small to justify a more detailed analysis, we propose, for inclusion in the final complex model, the species  $\text{Ni}(\text{HL})^{2+}$ ,  $\text{Ni}(\text{HL})_2^{2+}$ ,  $\text{H}_1\text{Ni}(\text{HL})_2^+$  and  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  with the formation constants given in Table 3. A distribution diagram of the complexes in one of the titrations is shown in Fig. 7.

## DISCUSSION

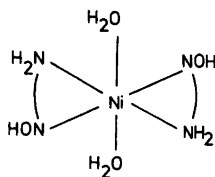
The values of the stepwise protonation constants in Table 2 show that the ligands are moderately strong bases as regards the addition of the first proton to HL, while the species  $\text{H}_2\text{L}^+$  show no significant basicity. The obvious resonance of the oxime group with the adjacent amide group makes it clear that the values  $\beta_{101}$  refer to the protonation of the amine nitrogens and the values of  $k_2$  to the protonation of the amide nitrogens.

Examination of the effects of *N*-substitution on the different protonation reactions shows that the basic strengths of the ligands do not strictly follow the number of the methyl groups: the

order of ligands with increasing  $k_2$  is  $3 < 2 < 1$  while the order with increasing  $\beta_{101}$  is  $3 < 1 < 2$ . These trends are also found for the corresponding ethylenediamine compounds,<sup>7</sup> and can be attributed mainly to the inductive effect (+I) of the alkyl substituents and to reduction of hydrogen bonding.<sup>8</sup>

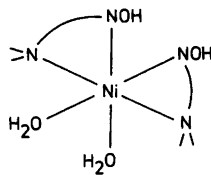
From the complex formation data the existence of the species  $\text{Ni}(\text{HL})_2^{2+}$  and  $\text{Ni}(\text{HL})_3^{2+}$  was established for all three ligands studied. The species  $\text{Ni}(\text{HL})_3^{2+}$  was also found in systems 1 and 2 but not in 3. The decrease of the complex stabilities of these successive complexes with increasing *N*-substitution is clearly seen in the values of the formation constants in Table 3. It can be judged that with ligand 1 all three complexes are readily formed, with 2 formation of the tris complex is considerably hindered, and with 3 the tris complex is not formed at all and the bis complex only with great difficulty. These substituent effects are somewhat greater than those found for *N*-methylated ethylenediamines<sup>7</sup> but they clearly demonstrate the participation of the amine nitrogen atoms in the coordination.

The potentiometric data do not directly indicate which of the remaining nitrogen atoms is involved in the coordination. The more negative character of the oxime group would nevertheless suggest that the oxime nitrogen has the preference. Strong support of this hypothesis is provided by the solid state complexes. During the investigation we isolated the  $\text{Ni}(\text{HL})_2^{2+}$  complexes of ligands 1 and 3 as chlorides in the crystalline state and determined their structures by X-ray methods. For ligand 1 the compound analysed was  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  and the following centrosymmetric *trans*-octahedral coordination was found:



The same chelating groups are also present in the structure of  $[\text{Ni}(\text{HL})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$  formed by 3 but here the coordination about nickel proved to be *cis*-octahedral.

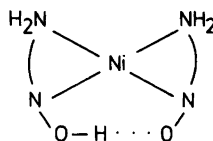
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In summary, we find it credible that the aqueous  $\text{Ni}(\text{HL})_n^{2+}$  complexes are all octahedral and coordination is through the oxime nitrogen and amine nitrogen atoms.

The species  $\text{H}_1\text{Ni}(\text{HL})_2^+$  was found in all the present systems. With ligands 1 and 2 it is orange coloured, occurs in great amounts and usually represents the final product in the alkalimetric measurements. In system 3, in contrast,  $\text{H}_1\text{Ni}(\text{HL})_2^+$  is of uncertain colour and only a minor species. Thus even its real existence can be questioned.

It is evident that the complex  $\text{H}_1\text{Ni}(\text{HL})_2^+$  with  $\text{HL}=1$  and 2 is square-planar with the following structure:



The proof for this complex moiety was obtained from X-ray analysis of solid  $[\text{Ni}(\text{HL})\text{L}]\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ , where HL is 1. This orange complex was obtained from a neutral solution where  $\text{H}_1\text{Ni}(\text{HL})_2^+$  was known to be the predominant species. The same characteristic colour of the complex in the solid state strongly argues for the presence of a like coordination of nickel in the liquid and solid states.

In the structure of  $\text{Ni}(\text{HL})\text{L}^+$  there is still one dissociable proton left, and one could assume the existence of the species  $\text{NiL}_2$  in solution of sufficient alkalinity. Under the conditions used in our measurements no such complexes were found, however. This is probably because the intramolecular hydrogen bond formed between the oxime oxygen atoms is very strong ( $\text{O} \cdots \text{O}$  distances usually below 2.5 Å),<sup>9</sup> with the result that the acidities of the  $\text{Ni}(\text{HL})\text{L}^+$  complexes must be very weak.

It is of interest to note that the formation of square-planar bis complexes does not prevent the co-existence of octahedral tris complexes in

suitable solutions. Figures 2 and 4 show that, as  $-\log h$  is raised, the sequence of the complex formation can be different: in system 1 the species  $\text{Ni}(\text{HL})\text{L}^+$  starts to form after the formation of the tris complex, whereas in system 2, where  $\text{Ni}(\text{HL})\text{L}^+$  is considerably lower in stability, the situation is the reverse.

For ligand 3 two ternary complexes of composition  $\text{H}_1\text{Ni}(\text{HL})_2^+$  and  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  are proposed. Possibly the structure of the minor complex  $\text{H}_1\text{Ni}(\text{HL})_2^+$  is not the same as for ligands 1 and 2. This is already suggested by the acidity constants calculated from Table 3 for the different  $\text{Ni}(\text{HL})_2^{2+}$  complexes: the  $\text{p}K_a$ -value with ligand 3 (8.76) is considerably higher than with ligands 1 (6.57) and 2 (7.10).

A look at the molecular models of the complexes shows that the spatial requirements of the two adjacent  $(\text{CH}_3)_2\text{N}$  groups of 3 make it impossible, without considerable strain in the molecule, to construct a planar  $\text{Ni}(\text{HL})\text{L}^+$  complex containing the intramolecular  $\text{O}\cdots\text{O}$  hydrogen bond. Evidently complex  $\text{H}_1\text{Ni}(\text{HL})_2^+$  with ligand 3 is still octahedral. In the same way the tendency of 3 toward polymerization reactions could be understood to originate from steric factors.

The low standard deviation in the value of the formation constant of the dominating ternary species  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  ( $3\sigma(\log\beta_{-644})=0.02$ ) allows it to be regarded as well established. We cannot, however, suggest any plausible scheme for its formation from simple components and, in principle, it is possible that  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  represents only a kind of one-parameter approximation of a more complicated system. The uncertainty is mainly due to the necessary omission of titration points at low  $C_L/C_M$  ratios from the calculations and thus the limited amount of experimental data.

Since we have not been successful in our attempts to prepare a suitable crystal of the tetranuclear compound for X-ray analysis, suggestions for the actual structure of  $\text{H}_6\text{Ni}_4(\text{HL})_4^{2+}$  will be highly speculative. The often found connection between the compositions of the ternary hydrolytic complexes and binary hydroxo species of the metal<sup>10-15</sup> would suggest the formula  $\text{Ni}_4(\text{OH})_4(\text{HL})_2\text{L}_2^{2+}$ , but an equally plausible formula is  $\text{Ni}_4\text{L}_2(\text{L}-\text{H})_2^{2+}$  which would denote that two of the amidoxime  $\text{NH}_2$  groups are deprotonated and involved in the coordina-

tion in the form of the negative  $-\text{NH}^-$  anion. Such a coordination has recently been found in a solid tetrameric copper(II) complex formed by 3.<sup>16</sup>

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