

Metal Complexes with Mixed Ligands. 18. A Potentiometric and Spectrophotometric Study of the Systems $\text{Ni}^{2+}-\text{Cl}^-$, $\text{Ni}^{2+}-\text{Imidazole}$ and $\text{Ni}^{2+}-\text{Cl}^--\text{Imidazole}$ in 3.0 M $(\text{Na})\text{ClO}_4, \text{Cl}$ Media

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Equilibria between nickel(II), imidazole ($\text{C}_3\text{H}_4\text{N}_2$), OH^- and Cl^- were studied at 25 °C by means of potentiometric (glass electrode) and spectrophotometric titrations in media consisting of 3.0 M $(\text{Na})\text{ClO}_4$, 3.0 M $(\text{Na})\text{Cl}$ and mixtures of these two with $0 \leq |\text{Cl}^-| \leq 3.0$ M. Besides pure binary species NiL_n^{2+} , $n=1, 2, 3, 4$, and NiCl^+ , data can be explained with the ternary complexes NiLCl^+ , NiL_2Cl^+ , NiL_2Cl_2 and NiL_4Cl_2 , ($\text{L}=\text{C}_3\text{H}_4\text{N}_2$). Formation constants for the ternary chloride species and molar absorption coefficients for the different binary species were evaluated within the wavelength range 350–750 nm. Data were analyzed with the least squares computer program LETA-GROPRID.

In parts 10¹ and 16² of this series equilibria in the system $\text{Ni}^{2+}-\text{OH}^- - \text{C}_3\text{H}_4\text{N}_2$ were studied in the media 3.0 M $(\text{Na})\text{ClO}_4$, 3.0 M $(\text{Na})\text{Cl}$ and 1.0 M $(\text{Na})\text{Cl}$. The results showed that besides the formation of stepwise metal complexes NiL_n^{2+} , $n=1, 2, 3, 4$, also ternary species $\text{Ni}(\text{OH})\text{L}^+$ [3.0 M $(\text{Na})\text{ClO}_4$, 3.0 M $(\text{Na})\text{Cl}$ and 1.0 M $(\text{Na})\text{Cl}$] and $\text{Ni}(\text{OH})\text{L}_3^+$ [1.0 M $(\text{Na})\text{Cl}$] were formed. However, differences in the complexation in the 3.0 M $(\text{Na})\text{ClO}_4$ and 3.0 M $(\text{Na})\text{Cl}$ media indicate the formation of ternary $\text{Ni}^{2+}-\text{C}_3\text{H}_4\text{N}_2-\text{Cl}^-$ species.

The present investigation was made to evaluate the possible formation of ternary $\text{Ni}^{2+}-\text{C}_3\text{H}_4\text{N}_2-\text{Cl}^-$ complexes and the measurements were performed in media consisting of mixtures of 3.0 M $(\text{Na})\text{ClO}_4$ and 3.0 M $(\text{Na})\text{Cl}$ with $0 \leq |\text{Cl}^-| \leq 3.0$ M. To determine the difference in absorbance in the

chloride media due to the formation of ternary species, spectrophotometric titrations were employed in which both $\log [\text{H}^+]$ and absorbance values were measured. This method was also used in an attempt to obtain a value of the constant for the formation of NiCl^+ .

EXPERIMENTAL

Chemicals and analysis. All solutions used were prepared and analyzed as described earlier.¹

Apparatus. The cell arrangement and experimental details of the emf measurements are fully described earlier.¹

The spectrophotometer used was a Heath model 721 single beam instrument with an automatic sample-reference changer and was equipped with an automated potentiometric titrator. A detailed description of the automated potentiometric and spectrophotometric titration system will be given in a forthcoming paper by Ginstrup, Lyhamn and Ingri.³ The sample cells were of flow-through type with path lengths of 1.001 cm (HELLMA, type 05) or 2.000 cm (HELLMA, type 05).

Method. The present study was carried out as a series of titrations in which both emf and absorbance values were measured, as in the system $\text{H}^+ - \text{Ni}^{2+} - \text{C}_3\text{H}_5\text{N}_2^+$ in 3.0 M $(\text{Na})\text{ClO}_4$ and 3.0 M $(\text{Na})\text{Cl}$ media. However, in the investigations of the systems $\text{H}^+ - \text{Ni}^{2+} - \text{C}_3\text{H}_5\text{N}_2^+ - \text{Cl}^-$ and $\text{Ni}^{2+} - \text{Cl}^-$ in the mixed media 3.0 M $(\text{Na})\text{ClO}_4, \text{Cl}$ just emf-values resp. absorbance values were measured.

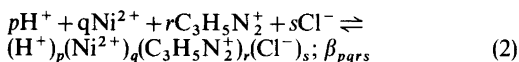
The potentiometric titrations were similar to those described in earlier papers.^{1,4} The equilibrium solutions contained $|\text{ClO}_4^-| + X = 3.0$ M, where X

is the chloride concentration. The general compositions of the solutions were: B mM Ni^{2+} , C mM $\text{C}_3\text{H}_5\text{N}_2^+$, H mM H^+ , X mM Cl^- ($|\text{ClO}_4^-| + X - C - H - 2B$) mM Na^+ and $3000 - X$ mM ClO_4^- . In the titrations the total concentrations of nickel (II), B , and imidazole, C , were varied, while the ratio C/B was always held constant. The total concentration of hydrogen ions, H , was calculated over the zero level, Ni^{2+} , $\text{C}_3\text{H}_5\text{N}_2^+$ and H_2O and the free hydrogen ion concentration, h , was varied by addition of OH^- and measured with a glass electrode. h was determined according to the relation

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$

where E_0 is a constant determined in acid solutions where complex formation could be neglected. The liquid junction potential $E_j = -16.7 h$ mV was used in 3.0 M $(\text{Na})\text{ClO}_4$, 3.0 M $(\text{Na})\text{Cl}$ as well as in mixtures of these two media. It has earlier been shown by Sjöberg⁴ that within the chloride concentration range $0 \leq X \leq 3.0$ M with $|\text{ClO}_4^-| + X = 3.0$ M the concentration scale for H^+ remains constant. No change in E_0 could be found on replacing ClO_4^- by Cl^- or vice versa.

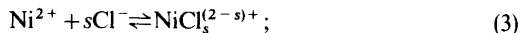
We will assume the presence of four-component equilibria of the general form



It is convenient to write complexes where $-p = r = s$ as $\text{Ni}_q(\text{C}_3\text{H}_4\text{N}_2)_n\text{Cl}_s^{(2q-s)+}$ and the stability constant as β_{nqs} . This terminology is used throughout this paper.

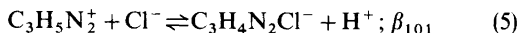
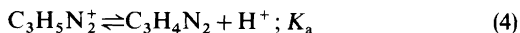
In addition to the four-component equilibria in (2) we have

(i) the complex formation between Ni^{2+} and Cl^-



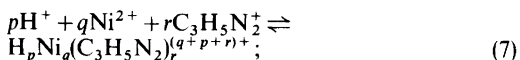
(ii) the imidazole equilibria, which within the concentration range

$$0 \leq X \leq 3.0 \text{ M with } |\text{ClO}_4^-| + X = 3.0 \text{ are}$$



with $\log K_a = -7.940$, $\log \beta_{101} = -8.641$ and $\log \beta_{102} = -9.279$.^{4,5}

(iii) the nickel(II) imidazole equilibria



with equilibrium constants given in Table 1. In the present study the C/B -ratios were kept at high values, where the hydrolytic equilibria of the nickel(II) ion as well as formation of ternary nickel(II)- OH^- - L complexes could be neglected. The species NiOHL^+ is formed only at low C/B -ratios ($C/B \leq 4$) and low B concentrations ($B < 5$ mM).

Equilibria (3)–(7) were determined in separate investigations and are assumed to be known in calculations concerning the four component equilibria.

The measurements using the combined emf and spectrophotometric method were performed in the following way: For each titration point the emf of the glass electrode was measured until equilibrium was obtained and then the transmittance, T , was recorded at a number of different wavelengths ($N\lambda$). As reference a 3.0 M NaClO_4 or 3.0 M NaCl solu-

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 reaction $n\text{L} + q\text{Ni}^{2+} + s\text{Cl}^- \rightleftharpoons \text{L}_n\text{Ni}_q\text{Cl}_s^{(2q-s)+}$, where L stands for $\text{C}_3\text{H}_4\text{N}_2$. When no $3\sigma(\log \beta_{nqs})$ is given, the formation constant has not been varied.

No. of titr./ no. of points	$\sigma(C-c)$ $\times 1000$	NiCl^+ $\log(\beta_{011})$ $\pm 3\sigma$	NiL^{2+} $\log(\beta_{110})$ $\pm 3\sigma$	NiLCl^+ $\log(\beta_{111})$ $\pm 3\sigma$	NiL_2Cl^+ $\log(\beta_{211})$ $\pm 3\sigma$	NiL_3Cl^+ $\log(\beta_{311})$ $\pm 3\sigma$	NiL_2Cl_2 $\log(\beta_{212})$ $\pm 3\sigma$	NiL_4Cl_2 $\log(\beta_{412})$ $\pm 3\sigma$
19/271	0.28	-0.47	3.37 ^a	3.16 ± 0.03	5.48 ± 0.12	8.29 ± 0.07	5.70 ± 0.03	10.17 ± 0.06
6/39	0.14	-0.53 ± 0.10	3.37 ± 0.01	3.14 ± 0.09				

^a Ref. 1.

tion was used. The absorbance, OD, at a particular wavelength λ is given by the relation

$$\text{OD}_\lambda = \sum \epsilon_i c_i$$

where ϵ_i is the molar absorption coefficient for the absorbing species i at the wavelength λ and c_i the concentration of the same species. Thus the spectrophotometric measurements give data (OD, log h , H , B , C , X)_{Nλ}.

Data treatment. It is possible to reduce the four component system $\text{H}^+ - \text{Ni}^{2+} - \text{C}_3\text{H}_5\text{N}_2^+ - \text{Cl}^-$ to the three component system $\text{C}_3\text{H}_4\text{N}_2 - \text{Ni}^{2+} - \text{Cl}^-$ under the assumption that $-p=r$ in eqn. (2), which means that only complexes of the type $\text{Ni}_q\text{L}_n\text{Cl}_s^{(2q-s)+}$ are formed. With this assumption $|\text{C}_3\text{H}_4\text{N}_2|$ can be calculated according to the relation

$$\frac{|\text{C}_3\text{H}_4\text{N}_2|}{K_a h^{-1}(C - (h - H))} = K_a h^{-1} |\text{C}_3\text{H}_5\text{N}_2^+| \quad (8)$$

where K_a is the acidity constant of $\text{C}_3\text{H}_5\text{N}_2^+$ in 3.0 M (Na)ClO₄. Thus as input to the computer, data in the form (A , log $|\text{C}_3\text{H}_4\text{N}_2|$, B , X)_N, $A = C - c$ are given instead of (H , log h , B , C , X)_N. This was done to save computer time, which is considerably greater with four components.

The mathematical analysis of the emf-data were performed with the least squares computer program LETAGROPVRID⁶ (version ETITR).⁷ On treating the data, the error squares sum $U = \sum (A_{\text{calc}} - A_{\text{exp}})^2$ was minimized, where A denotes $C - c$, i.e. the total imidazole concentration not obtained as $\text{C}_3\text{H}_5\text{N}_2^+$.

In calculations on the combined emf- and spectrophotometric data, the LETAGROP version TITRER-SPEFO⁸ was used and $U = \sum (\text{OD}_{\text{calc}} - \text{OD}_{\text{exp}})^2$ was minimized.

The different standard deviations given, $3\sigma(\log \beta)$ and $\sigma(\epsilon)$ were defined and calculated according to Sillén.⁹ The computation was performed on a CDC3300 and a CYBER 172 computer.

DATA, CALCULATIONS AND RESULTS

Results from earlier measurements concerning the complex formation between nickel(II) and imidazole are given in Ref. 1.

The spectrophotometric measurements were performed to obtain accurate values of the molar absorption coefficients ϵ_{min} for the different nickel(II) species and both log h and absorbance were thereby measured.

Many workers have reported formation of a NiCl^+ complex and even NiCl_2 in aqueous solu-

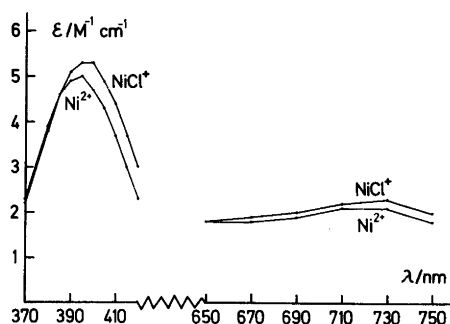


Fig. 1. Molar absorption coefficients, $\epsilon \text{ cm}^{-1} \text{ M}^{-1}$, as a function of the wavelength, $\lambda \text{ nm}$, plotted for the species $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and $\text{NiCl}(\text{H}_2\text{O})_5^+$.

tions.¹⁰ Only the former seems to be of importance at chloride concentration levels up to 3.0 M, but the reported log β_{11} -values for the formation of NiCl^+ are widely spread. An attempt to determine a value of β_{11} valid in the 3.0 M ionic medium was made by performing spectrophotometric titrations at a constant acidity level, where hydrolysis reactions are negligible.

The results obtained in the different investigations are given below.

(i) *Nickel(II) chloride in mixtures of 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl.* Four different titrations were performed yielding 33 titration points and 528 absorbance values at 16 different wavelengths in the range 370–750 nm. The concentration ranges studied were $0.096 \leq B \leq 0.302 \text{ M}$ and $1.25 \leq X \leq 3.0 \text{ M}$ and the titrations were performed at a constant acidity level of $|\text{H}^+| = 0.030 \text{ M}$. The calculations showed that within the concentration ranges investigated, the formation of the complex NiCl^+ could be established with log $K(\text{Ni}^{2+} + \text{Cl}^- \rightleftharpoons \text{NiCl}^+) = -0.47 \pm 0.10$. The standard deviations $\sigma(\text{OD})$ at the different wavelengths were all very small (0.001–0.002) thus indicating a good fit to experimental data (cf. Fig. 1).

(ii) *Nickel(II) imidazole in 3.0 M (Na)ClO₄ medium.* Four different titrations including 197 titration points were performed. 24 different wavelengths ranging from 350 to 750 nm were investigated and thus 4728 measured absorbance values were collected. The following concentration ranges were investigated: $0.018 \leq B \leq 0.062 \text{ M}$, $0.115 \text{ M} \leq C \leq 0.240 \text{ M}$, $1.2 \leq -\log h \leq 7.7$ with $C/B = 2, 4, 5$ and 11. Only mononuclear $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$ species are formed at these concentration ranges and the

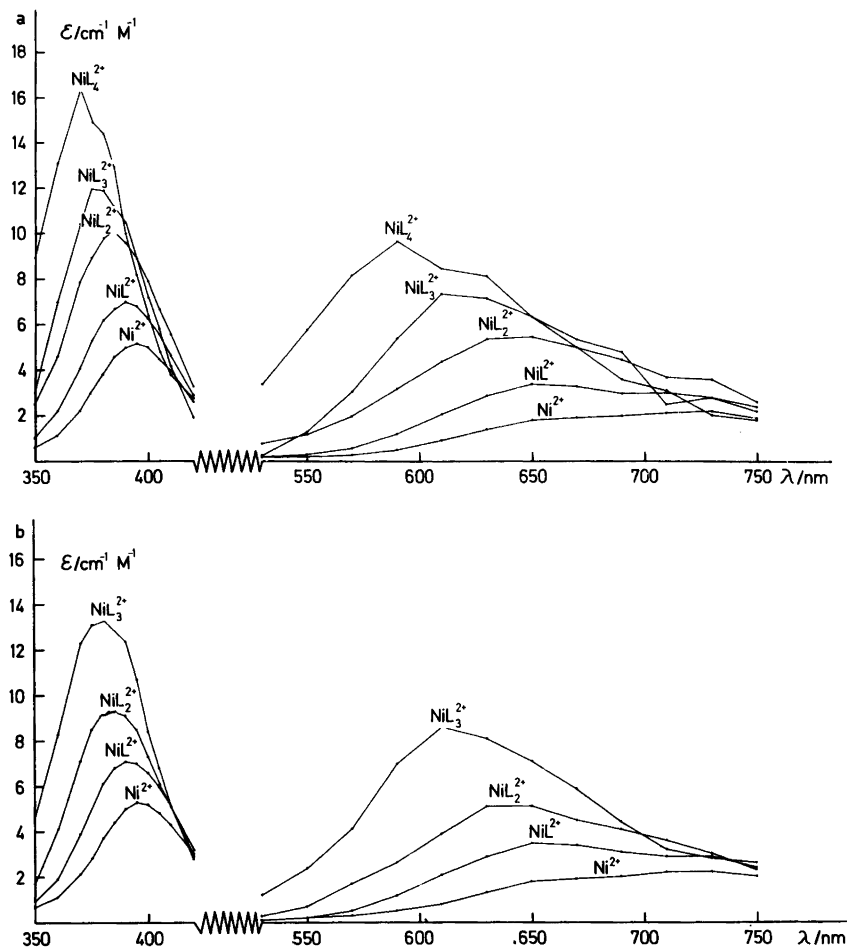


Fig. 2. Molar absorption coefficients, $\epsilon \text{ cm}^{-1} \text{ M}^{-1}$, as a function of the wavelength, $\lambda \text{ nm}$, plotted for the mononuclear species $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_n^{2+}$, $n=0, 1, 2, 3$ and 4. (a) 3.0 M (Na)ClO₄ and (b) 3.0 M (Na)Cl medium. L stands for $\text{C}_3\text{H}_4\text{N}_2$. The errors $\sigma(\epsilon)$ for the different species are ≤ 0.01 (Ni^{2+}), 0.02–0.07 (NiL^{2+}), 0.02–0.10 (NiL_2^{2+}), 0.05–0.3 (NiL_3^{2+}) and ≤ 0.5 (NiL_4^{2+}), with the errors $\sigma(\text{OD})=0.001-0.005$. A complete list of the molar absorption coefficients obtained at different wavelengths is available upon request.

molar absorption coefficients ϵ_{-n1n} for each of the different nickel(II) species were calculated at the wavelengths studied. The formation constants for the complexes were taken from Ref. 1 and a satisfactory fit to experimental data was obtained. Owing to the small absorption of the complexes no attempt to determine the formation constants β_{-n1n} from spectrophotometric data was made. The molar absorption coefficients ϵ_{-111} and ϵ_{-212} were determined in the range $0 \leq \bar{n} \leq 1.8$ and ϵ_{-313}

and ϵ_{-414} in the range $1.8 \leq \bar{n} \leq 2.8$, where the first two were kept constant. Molar absorption coefficients (with standard deviations) of the different NiL_n^{2+} -species are given in Fig. 2.

(iii) *Nickel(II) imidazoles in 3.0 M (Na)Cl medium.* Four different titrations yielding 122 titration points were performed and the same wavelengths as in (ii) were covered, thus giving 2928 absorbance values. The following concentration ranges were investigated: $0.029 \leq B \leq 0.058 \text{ M}$,

$0.086 \leq C \leq 0.353$ M, $0.85 \leq -\log h \leq 7.6$ with $C/B = 1.2, 5, 6$ and 12 . As in 3.0 M $(\text{Na})\text{ClO}_4$ only mononuclear NiL_n^{2+} species are formed and no attempt to determine the β_{-n1n} values was made. The calculation of the molar absorption coefficients was performed as in (ii), but since precipitation appeared at $n \sim 2.5$ the value of ϵ_{-414} was not determined. As chloride ions are coordinated in the different species, the formation constants and molar absorption coefficients in 3.0 M $(\text{Na})\text{Cl}$ must be considered as conditional. However, only very small shifts to higher wavelengths are obtained for the different species and thus it seems to be impossible to evaluate the ternary $\text{Ni}^{2+} - \text{C}_3\text{H}_4\text{N}_2 - \text{Cl}^-$ complexes from spectrophotometric data. Molar absorption coefficients with standard deviations are given in Fig. 2.

(iv) *Nickel(II) imidazoles in mixtures of 3.0 M (Na)ClO₄ and 3.0 M (Na)Cl.* To evaluate the formation of the ternary $\text{Ni}^{2+} - \text{C}_3\text{H}_4\text{N}_2 - \text{Cl}^-$ complexes measurements were performed in the four-component system $\text{H}^+ - \text{Ni}^{2+} - \text{C}_3\text{H}_4\text{N}_2 - \text{Cl}^-$. The total nickel, B , the total imidazole, C , and the total chloride, X , were varied within the limits $0.0043 \leq B \leq 0.090$ M, $0.020 \leq C \leq 0.201$ M, $0 \leq X \leq$

3.0 M and the ratios C/B between $1.4 \leq C/B \leq 40$. The titrations were performed at different constant Z -values ($Z = 0.4, 0.6, 0.9, 1.1, 1.4, 1.7, 2, 2.3, 2.5, 2.6$ and 3.2) $Z = (h - H)/B$ and X was varied by the addition of 3.0 M NaCl medium to a solution with $|\text{ClO}_4^-| = 3.0$ M or *vice versa*. The formation constants of the binary species NiL_n^{2+} , $n = 1, 2, 3, 4$, obtained in the 3.0 M $(\text{Na})\text{ClO}_4$ medium and NiCl^+ obtained from (i) were supposed to be exactly known and they were not varied until some final calculations. Owing to the small difference in absorbance between the ternary nickel(II) complexes no attempt to evaluate formation constants and molar absorption coefficients of these species from spectrophotometric data were made.

Bjerrum plots $\bar{n}(\log |\text{C}_3\text{H}_4\text{N}_2|)$ are calculated using the acidity constant valid in 3.0 M $(\text{Na})\text{ClO}_4$. This \bar{n} is given by

$$\bar{n} = (h - H - [\text{L}] - [\text{LCl}^-] - [\text{LCl}_2^{2-}])/B =$$

$$\left(h - H - (C + H - h)h^{-1} \{K_a - X(\beta_{101} + X\beta_{102})\} \right) / B$$

and thus correction for the complexes $\text{C}_3\text{H}_4\text{N}_2\text{Cl}^-$ and $\text{C}_3\text{H}_4\text{N}_2\text{Cl}_2^{2-}$ in the mixed chloride media is

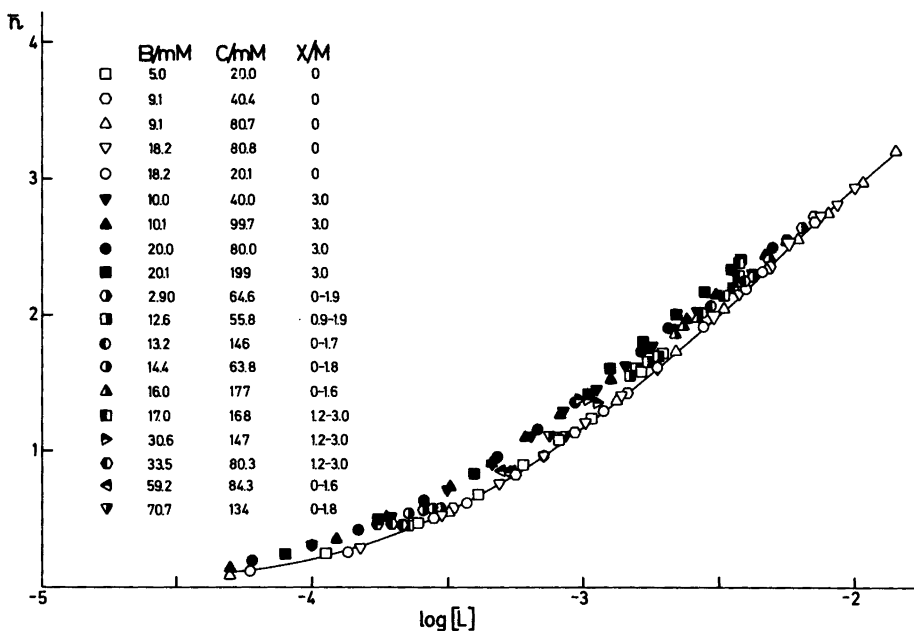


Fig. 3. Experimental data plotted as curves $\bar{n}(\log |\text{C}_3\text{H}_4\text{N}_2|)$. Open symbols refer to titrations in 3.0 M $(\text{Na})\text{ClO}_4$ and filled symbols to 3.0 M $(\text{Na})\text{Cl}$. Half-filled symbols are obtained in mixtures of the two media. A complete list of experimental data is available upon request.

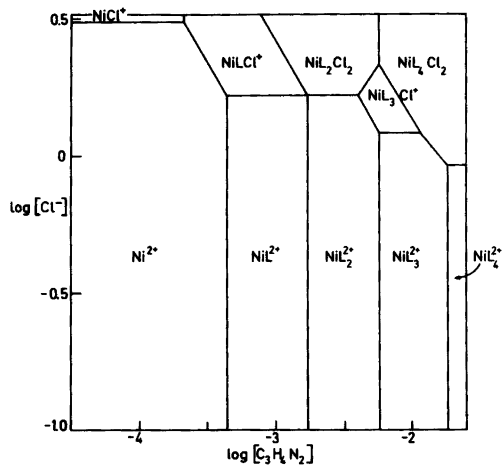


Fig. 4. Predominance area diagram for the different nickel(II) imidazole complexes. (The dominating species at every fixed $\lg[\text{Cl}^-] - \lg[\text{L}]$ level is given.) The computer program SOLGASWATER¹⁷ was used in the calculations.

made. The plot is given in Fig. 3. The total data material comprised 19 titrations with 271 titration points. The best explanation of experimental data was obtained with the species NiLCl^+ , NiL_2Cl^+ , NiL_3Cl^+ , NiL_2Cl_2 and NiL_4Cl_2 . The complexes NiLCl_2 , NiL_3Cl_2 and NiL_4Cl^+ were rejected by the computer in a covariation with the other species. The final calculation ended at $\sigma(A)=0.28$ and the result is shown in Table 1.

In a data set consisting of six titrations with 39 titration points where $Z < 0.5$ the formation constant of NiCl^+ was varied together with the species NiL^{2+} and NiLCl^+ . This calculation gave a value of the formation constant of NiCl^+ in an indirect way and this value was in a good agreement with the

separately determined one. The results are given in Table 1. In order to visualize the amounts of the ternary species, we have made a predominance area diagram, which is shown in Fig. 4. It is seen from the diagram that the ternary nickel(II)-chloroimidazole species are generally obtained in great amounts, at high chloride concentration levels ($[\text{Cl}^-] > 1.5 \text{ M}$).

DISCUSSION

The present investigation has confirmed the existence of ternary nickel(II)-imidazole- Cl^- complexes. Besides the series NiL_nCl^+ , $n=1, 2, 3$, the complexes NiL_2Cl_2 and NiL_4Cl_2 are obtained in rather large amounts.

The NiL_nCl^+ series can be considered as stepwise reactions in which imidazole molecules are successively coordinated to an NiCl^+ core or alternatively as chloride ions coordinated to NiL_n^{2+} cores with $n=1, 2, 3$. Stepwise constants of these reactions are given in Table 2. The similarities between this and the corresponding copper(II)-⁴ and zinc(II)-imidazole- Cl^- ⁵ systems are remarkable. Thus the species MeLCl^+ , MeL_2Cl^+ , MeL_3Cl^+ and MeL_2Cl_2 are obtained in all systems and the even coordination numbers 2, 4, 6 are usually favoured compared with the odd numbers 1, 3, 5.

The crystal and molecular structures of the crystalline phases in the nickel(II) imidazole system investigated by X-ray diffraction techniques are all octahedral of the form NiL_6^{2+} . However, several other compounds containing nickel(II)- Cl^- -imidazole or substituted imidazole have been prepared and characterized by analytical data, spectral and conductivity measurements,¹¹⁻¹³ differential thermal analysis (DTA), thermogravimetry (TG) and X-ray powder diffraction technique.¹⁴

Table 2. Some stepwise reactions with constants calculated by means of formation constants given in Ref. 1 and Table 5. The different reactions define the stepwise uptake of the ligands $\text{C}_3\text{H}_4\text{N}_2$ (L) and Cl^- are to be read horizontally. ($\text{NiL}_2\text{Cl}^+ \rightleftharpoons \text{NiL}_3\text{Cl}^+ + \text{L} \rightleftharpoons \text{NiL}_3\text{Cl}^+$ with $\log K = 2.82$.)

	log K		log K		log K		log K	
Ni^{2+}	3.37	NiL^{2+}	2.77	NiL_2^{2+}	2.25	NiL_3^{2+}	1.73	NiL_4^{2+}
NiCl^+	3.65	NiLCl^+	1.82	NiL_2Cl^+	2.82	NiL_3Cl^+		
Ni^{2+}	-0.5	NiCl^+						
NiL^{2+}	-0.21	NiLCl^+						
NiL_2^{2+}	-0.66	NiL_2Cl^+	0.22	NiL_2Cl_2				
NiL_3^{2+}	-0.10	NiL_3Cl^+						

Thus the compounds NiL_4Cl_2 (L=imidazole, 1-vinyl-imidazole, 2-methyl-imidazole), $\text{NiL}_4(\text{H}_2\text{O})_2\text{Cl}_2$ (L=imidazole), $\text{NiL}_2(\text{H}_2\text{O})_2\text{Cl}_2$ (L=imidazole), $[\text{NiL}_2\text{Cl}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ (L=1-vinyl-2-methyl-imidazole) and NiLCl_2 (L=imidazole, 1-vinyl-imidazole) have been prepared and characterized. The arrangement around nickel seems to be octahedral in all these cases with the chlorine atoms generally coordinated to the nickel atom. Thus the complexes $\text{NiL}_2\text{Cl}_2(\text{H}_2\text{O})_2$ and NiL_4Cl_2 are obtained both in the solid state and in solution while the compound NiLCl_2 , which has a polymeric structure with chlorine atoms acting as bridges between the nickel atoms, is probably obtained as NiLCl^+ in solution.

Furthermore, the crystal and molecular structure of tetrakispyrazolenickel chloride, $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_4\text{Cl}_2$ has been determined by X-ray diffraction techniques.¹⁵ It was found that the $\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_4\text{Cl}_2$ molecule is centrosymmetric, with the nickel atom at the center of an octahedron formed by two chlorine atoms, and a nitrogen atom from each of the four pyrazole molecules. The corresponding imidazole complex should have a similar configuration.

The crystal structure of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ has been determined by neutron diffraction¹⁶ and it was found that the nickel atom is octahedrally coordinated to four oxygen and two chlorine atoms. The two chlorines are located on the two normals to the oxygen plane which is formed by the water molecules with the nickel at the center. By exchanging the water molecules around nickel with two respectively four imidazole molecules the complexes $\text{NiL}_2\text{Cl}_2(\text{H}_2\text{O})_2$ respectively NiL_4Cl_2 are obtained.

In accordance with the spectrochemical series the strength of the ligand field increases within the series $\text{Cl}^- < \text{H}_2\text{O} < \text{C}_3\text{H}_4\text{N}_2$. However, the differences are very small and the possibility to evaluate the ternary $\text{Ni}^{2+} - \text{C}_3\text{H}_4\text{N}_2 - \text{Cl}^-$ species from spectrophotometric data seems to be very limited. In the binary system $\text{Ni}^{2+} - \text{Cl}^-$ the different ϵ -values $\epsilon_{\text{Ni}^{2+}}$ and ϵ_{NiCl^+} , could be sufficiently separated to permit calculation of the formation constant of NiCl^+ . The log K -value obtained, -0.47 ± 0.10 is a rather good mean value of several earlier investigations.¹⁰ The corresponding constant determined from potentiometric data in an indirect way is of the same order (log $K = -0.53 \pm 0.10$) and the agreement is quite satisfactory.

Concerning the binary NiL_n^{2+} species it is seen

Table 3. The wavelengths, λ_{max} , with corresponding molar absorption maxima, ϵ_{max} , for the nickel(II) species.

Complex	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{\text{max}}/\text{cm}^{-1} \text{M}^{-1}$
Ni^{2+}	$\left\{ \begin{array}{l} 395 \\ 730 \end{array} \right.$	$\left\{ \begin{array}{l} 5.0 - 5.2 \\ 2.1 - 2.2 \end{array} \right.$
NiCl^+	$\left\{ \begin{array}{l} 395 - 400 \\ 730 \end{array} \right.$	$\left\{ \begin{array}{l} 5.3 \\ 2.3 \end{array} \right.$
NiL^{2+}	$\left\{ \begin{array}{l} 390 \\ 650 \end{array} \right.$	$\left\{ \begin{array}{l} 7.0 \\ 3.4 \end{array} \right.$
NiL_2^{2+}	$\left\{ \begin{array}{l} 385 \\ 630 - 650 \end{array} \right.$	$\left\{ \begin{array}{l} 10.1 \\ 5.4 - 5.5 \end{array} \right.$
NiL_3^{2+}	$\left\{ \begin{array}{l} 375 - 380 \\ 610 \end{array} \right.$	$\left\{ \begin{array}{l} 11.9 - 12.0 \\ 7.4 \end{array} \right.$
NiL_4^{2+}	$\left\{ \begin{array}{l} 370 \\ 590 \end{array} \right.$	$\left\{ \begin{array}{l} 16.4 \\ 9.7 \end{array} \right.$

from the figures that the strength of the ligand field increases with the number of the coordinated $\text{C}_3\text{H}_4\text{N}_2$ -molecules, (λ_{max} decreases) and ϵ_{max} also increases with n . These findings are in conformity with the corresponding Cu(II)-system,⁴ and are summarized in Table 3.

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