

An Infrared Spectroscopic Study on the Thiocyanato Complexes of Nickel(II) in Non-aqueous Solutions

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The nickel(II) thiocyanate systems in acetonitrile, propane-1,2-diolcarbonate, trimethylphosphate, dimethylacetamide, and dimethyl sulfoxide have been investigated using infrared spectroscopic techniques. The stability constants of the four first complexes and the molar absorption coefficients of the C—N stretching vibration of the bonded thiocyanate ion have been determined in all the solvents except propane-1,2-diolcarbonate. From an estimated value of the integrated absorption ($\epsilon \Delta\nu_{1,2}$), it is concluded that there is N-coordination between the metal and the thiocyanate ion.

The order of stability of the nickel(II) thiocyanate system in the various solvents is, with one exception, that presupposed from the donor properties of the solvents.

Recently, Gutmann and Bardy¹ published an investigation on the formation of thiocyanato complexes of nickel(II) in various non-aqueous donor solvents. By using spectrophotometric, conductometric, and potentiometric methods they tried to describe the kind of species existing in solution and their configuration. They also determined how large the excess of ligand to metal has to be to obtain the highest thiocyanate-coordinated form, $\text{Ni}(\text{NCS})_6^{4-}$, quantitatively. The results were then used in discussing the donor properties of solvents.²

However, in the work of Gutmann and Bardy, no quantitative description of the stability of the complexes was made. As in the case of the thiocyanato complexes of cobalt(II),³ we believe that a knowledge of the stability constants would be valuable when the donor properties of the solvents are discussed.

It has long been known that there is in most cases a distinct difference in the infrared spectrum of the thiocyanate ion when it is

coordinated to a metal as compared to that of the free ion. On the other hand, there are, as a rule, no detectable differences in spectra between the consecutively formed complexes $\text{ML}_n^{4,5}$ in solution. Of course it is not possible to exclude a small splitting of the bands but this is not so pronounced that it can be used to distinguish between different complexes. But in most cases infrared spectra can be used to determine stability constants of the complexes from the absorption band of the free ligand.⁵ Furthermore, from the infrared spectra it can be concluded whether the thiocyanate group is coordinated to the metal *via* the nitrogen or the sulfur atom.⁶

METHOD OF INVESTIGATION

The following notations are used in the present paper:

C_M = total concentration of metal.

C_L = » » » ligand.

$[\text{M}]$ = free » » metal.

$[\text{L}]$ = » » » ligand.

\bar{n} = $\frac{C_L - [\text{L}]}{C_M}$ = mean ligand number.

$[\text{ML}_n]$ = concentration of the n -th complex.

β_n = $\frac{[\text{ML}_n]}{[\text{M}][\text{L}]^n}$ = overall stability constant of the n -th complex.

β_0 = 1

K_n = $\frac{[\text{ML}_n]}{[\text{ML}_{n-1}][\text{L}]} = \frac{\beta_n}{\beta_{n-1}}$ = stepwise stability constant of the n -th complex.

X = $\sum_{n=0}^N \beta_n [\text{L}]^n$

$$X_n = \frac{X_{n-1} - \beta_{n-1}}{[L]}$$

$$\alpha_n = \frac{[ML_n]}{C_M} = \frac{\beta_n [L]^n}{X}$$

A_ν = absorbance at the band maximum of wave number ν cm⁻¹.

ϵ_L = molar absorption coefficient of the free ligand.

ϵ_n = molar absorption coefficient of the complex ML_n.

d = the cell thickness.

The method of investigation used in this work is based on the fact that there is a considerable difference between the C-N stretching vibration frequency of the nickel-thiocyanato complexes (about 2100 cm⁻¹) and that of the free ligand (about 2060 cm⁻¹) in all the solvents used. Thus, knowing the molar absorption coefficient of the SCN⁻ ion one can determine the free ligand concentration from the "free ligand peak". For a series of solutions of general composition C_M Ni(ClO₄)₂ and C_L M NaSCN, where C_M is kept constant and C_L varied, it is possible to calculate the mean ligand number, \bar{n} . Then the polynomial X can be obtained as

$$\ln X([L]_j) = \int_0^{[L]_j} \bar{n}/[L] d[L] \quad (1)$$

The integration can be carried out graphically and also the determination of the stability constants from the corresponding values of X and [L]. (For a more detailed treatment of this graphical method see, e.g., Ref. 7). The stability constants can also be calculated numerically from the corresponding \bar{n} and [L] values (see below).

In some cases it is possible to use the "complex peak" to obtain \bar{n} and [L] by the method of "corresponding solutions".^{8,7} The absorbance at the maximum of this band (A_ν) is measured and by definition

$$\frac{A_\nu}{d} = \sum_{n=1}^N \epsilon_n [ML_n] = \frac{C_M}{X} \sum_{n=1}^N \epsilon_n \beta_n [L]^n \quad (2)$$

From this equation one can conclude that A_ν/dC_M is a function of [L] only. Corresponding values of [L] and \bar{n} are now obtained in the following way: On the basis of several

series with constant C_M but varying C_L, A_ν/dC_M can be plotted against C_L with C_M as a parameter. The curves thus obtained are then cut at a number of constant A_ν/dC_M values and from the points of intersection C_L can be plotted against C_M for every constant A_ν/dC_M chosen. The C_L-C_M curves would then be straight lines with the equations

$$C_L = [L]_j + \bar{n}_j C_M \quad (3)$$

By extrapolating these lines to C_M=0 one obtains the [L] values and from the slopes the corresponding \bar{n} . The determination of [L] in this way can, however, be done only if the complexity of the system is not too strong.

Knowing the stability constants of the complexes, the molar absorption coefficients can be calculated from the measured absorbance of the "complex band". Eqn. (2) can be written

$$\frac{A_\nu}{dC_M} = \sum_{n=1}^N \epsilon_n \alpha_n \quad (4)$$

Now if $\epsilon' = A_\nu/dC_M \alpha_1$ is plotted *versus* [L] and the resulting curves extrapolated to [L]=0, ϵ_1 is obtained. Then ϵ_2 (i.e. $\epsilon_2 \beta_2 / \beta_1$) is determined in the same way from a plot of $(\epsilon' - \epsilon_1)/[L]$ *versus* [L], and so on.

Numerical calculations of the stability constants. The stability constants obtained graphically were checked by a numerical method developed by Karlsson.⁹ The method is based on the principles of Deming as they have been reviewed by Guest.¹⁰ The input data to the computer program CURVEFIT⁹ were \bar{n}_i , [L]_i, $\sigma_{\bar{n}_i}$, $\sigma_{[L]_i}$. The standard deviations $\sigma_{\bar{n}_i}$ and $\sigma_{[L]_i}$ were given by the estimated uncertainties in \bar{n}_i and [L]_i. The functional relationship used between \bar{n} and [L] was

$$\bar{n}([L], \beta) = \frac{\sum_{n=1}^4 n \beta_n [L]^n}{\sum_{n=0}^4 \beta_n [L]^n} \quad (5)$$

and the error square sum

$$\text{CHISQ} = \sum_i \left(\frac{\Delta n_i^2}{\sigma_{\bar{n}_i}^2} + \frac{\Delta [L]_i^2}{\sigma_{[L]_i}^2} \right) \quad (6)$$

was minimized by the subroutine STEPIT.¹¹ $\Delta \bar{n}_i = \bar{n} - \bar{n}_i$ and $\Delta [L]_i = [L] - [L]_i$ where (\bar{n}_i , [L]_i) refer to the observed point and (\bar{n} , [L])

to the adjusted point on the least-squares curve. The slope of the line between these points was given by

$$\tan \theta_i = -1 / \left(\frac{\sigma_{[L]_i}^2 d\bar{n}}{\sigma_{\bar{n}_i}^2 d[L]} \right) \quad (7)$$

The errors in the constants were also calculated by STEPIT using the following method: The matrix of the second partial derivatives of the error square sum with respect to the parameters was calculated. Twice the inverse of this matrix would be the covariance matrix assuming that the error square sum is an approximately quadratic function of the parameters over the error range. Then the standard deviations would be given by the square roots of the diagonal elements of this matrix. To check the values of the standard deviation another subroutine was used. Starting from the adjusted values of \bar{n} and $[L]$, all of them were disturbed by a small amount, randomly chosen from a normal distribution with mean zero and the standard deviation $\sigma_{\bar{n}_i}$ or $\sigma_{[L]_i}$. From the new set of points the best set of parameters was found by reminimization. From several sets of parameters obtained in this way the standard deviations could be estimated. No perceptible difference in the results using the two methods could be found.

EXPERIMENTAL CONDITIONS

The nickel(II)-thiocyanate system was investigated in five different solvents. They were acetonitrile (AN), propane-1,2-diolcarbonate (PDC), trimethylphosphate (TMP), *N,N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO). The solutions used were made from stock solutions of anhydrous nickel(II) perchlorate and sodium thiocyanate in these solvents. The experimental procedures have been described in detail in a previous paper.³ As in that work the measurements had to be performed in solutions with uncontrolled ionic strengths because of the low solubilities of supporting electrolytes in these solvents. However, the results of the measurements on silver-thiocyanato complexes in another organic donor solvent, *i.e.* pyridine,^{5,12} indicate that the stability constants would hardly be influenced significantly by the change of the activity coefficients that would be caused by the varying ionic strength. The infrared spectra are recorded using a Perkin-Elmer 521 grating spectrophotometer.³ As could be seen in, *e.g.*, Fig. 1

there is usually some overlap between the "free ligand band" and the "complex band", although not very large. Because of this fact there would be some difficulties in the determination of the baseline, especially for the less intense band. By using both bands in the calculation of the stability constants one can concentrate the absorbance readings to the most intense band. To that end the method of "corresponding solutions" is used at low free ligand concentrations in some systems.

RESULTS *

Measurements on NaSCN

In order to use the "free ligand peak" for free ligand concentration determinations the molar absorption coefficients for the thiocyanate ion in the various solvents must be known. Therefore, measurements on the C-N stretching vibration of NaSCN were made and the results can be seen in Table 1. The wave numbers of the bands and the integrated absorptions are also included in this table.

Measurements on the nickel(II) thiocyanate systems

TMP. Only two bands could be observed in the C-N stretching region of the spectra, one at 2 059 cm⁻¹ and the other at 2 102 cm⁻¹. The former was assigned as the vibration of the "free" ion and the latter corresponds to the C-N stretching vibration of the thiocyanate groups coordinated to the metal. From the "free ligand band" the free ligand concentration was obtained and the stability constants determined according to the methods described above. Four complexes could be established and their stability constants are included in Table 2. The "complex band" gave the data needed for the calculation of the molar absorption coefficients and the results can be found in Table 1.

DMSO. Two bands were found at 2056 cm⁻¹ and 2092 cm⁻¹. As for TMP, the former was used in the determination of the stability

* The experimental material of this work is very comprehensive and a complete presentation of it would be very space-demanding. According to the editorial rules of Acta Chemica Scandinavica these data could not be included in the paper. A reader, specially interested in the details of this work, is therefore recommended to apply directly to the author for a copy of the experimental data.

Table 1. Infrared spectral data for NaSCN and the thiocyanato complexes of Ni(II) in various solvents. The values of ϵ_n are calculated per SCN group.

Solvent	NaSCN ν (cm^{-1})	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\epsilon \Delta\nu_{1/2} \times 10^{-4}$ ($\text{M}^{-1} \text{cm}^{-2}$)	$\text{Ni}(\text{NCS})_n$ ν (cm^{-1})	ϵ_1 ($\text{M}^{-1} \text{cm}^{-1}$)	ϵ_2	ϵ_3	ϵ_4	$\epsilon_1 \Delta\nu_{1/2} \times 10^{-4}$ $\text{M}^{-1} \text{cm}^{-2}$
AN	2062	701	1.3	2097	1000 ± 300	850 ± 400	970 ± 400	750 ± 400	2.0 ^b
TMP	2059	525	0.8	2102	1280 ± 150	870 ± 200	650 ± 400	1100 ± 400	2.3
DMA	2058	913	1.1	2094	880 ± 100	770 ± 120	780 ± 150		2.6
DMSO	2056	850	1.1	2092		620 ± 200			2.6
PDC	2057	571	1.3	2089					
H ₂ O ^a	2066	537	2.0	2119	640				2.1

^a Values taken from Ref. 6. ^b $\epsilon_2 \Delta\nu_{1/2} \times 10^{-4}$.

Table 2. The stability constants of the thiocyanato complexes in various solvents.

Solvent	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})	K_2 (M^{-1})	K_3 (M^{-1})	K_4 (M^{-1})	$\frac{K_1}{K_2}$	$\frac{K_2}{K_3}$	$\frac{K_3}{K_4}$
Graphically determined constants.										
AN	$(5 \pm 5) \times 10^3$	$(1.2 \pm 0.4) \times 10^8$	$(2.8 \pm 1.0) \times 10^{10}$	$(3.0 \pm 1.0) \times 10^{11}$	$(24\ 000)$	230	11	(0.2)	(100)	21
TMP	$(2.3 \pm 0.5) \times 10^3$	$(2.0 \pm 0.4) \times 10^8$	$(6.0 \pm 1.5) \times 10^9$	$(1.1 \pm 0.3) \times 10^9$	87	3.0	1.8	26	29	1.7
DMA	$(2.9 \pm 0.3) \times 10^3$	$(1.8 \pm 0.2) \times 10^8$	$(1.3 \pm 0.2) \times 10^8$	$(1.3 \pm 0.3) \times 10^8$	620	72	10	4.7	8.6	7.2
DMSO	$(4.3 \pm 0.3) \times 10^2$	$(4.6 \pm 0.6) \times 10^3$	$(1.2 \pm 1.0) \times 10^4$	$(1.8 \pm 1.0) \times 10^5$	11	2.6	15	39	4.2	0.2
H ₂ O ^a	15 ± 0.5	44 ± 4	65 ± 10		2.9	1.5		5.1	1.9	
Numerically determined constants										
TMP	$(1.9 \pm 0.4) \times 10^3$	$(1.8 \pm 0.3) \times 10^8$	$(4.4 \pm 1.4) \times 10^9$	$(1.1 \pm 0.3) \times 10^9$	95	2.4	2.5	20	40	1.0
DMA	$(2.8 \pm 0.4) \times 10^3$	$(2.0 \pm 0.3) \times 10^8$	$(1.3 \pm 0.2) \times 10^8$	$(1.3 \pm 0.2) \times 10^8$	710	65	10	3.9	11	6.5
DMSO	$(4.5 \pm 0.2) \times 10^2$	$(4.7 \pm 0.4) \times 10^3$	$(7 \pm 60) \times 10^2$	$(2.6 \pm 0.3) \times 10^5$	10	(0.1)	(370)	45	(100)	—
I	0	0.6×10^8	1.3×10^{10}	1.4×10^{11}						
AN II	5.0×10^3	1.1×10^8	2.8×10^{10}	2.9×10^{11}	22 000	250	10	0.2	88	25
III	1.0×10^4	1.7×10^8	4.4×10^{10}	4.4×10^{11}						

^a The values in H₂O are taken from Ref. 13 and are determined in solutions with constant ionic strength = 1 M.

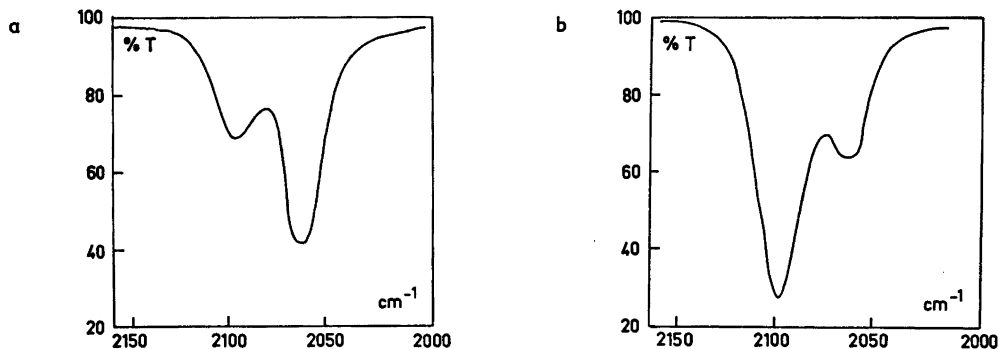


Fig. 1. Spectra of the Ni^{2+} - NCS^- system in AN.
 a. $C_{\text{Ni}^{2+}} = 0.01012 \text{ M}$, $C_{\text{SCN}^-} = 0.1399 \text{ M}$, $d = 0.0508 \text{ mm}$.
 b. $C_{\text{Ni}^{2+}} = 0.01012 \text{ M}$, $C_{\text{SCN}^-} = 0.0401 \text{ M}$, $d = 0.2167 \text{ mm}$.

constants and the latter in the determination of the molar absorption coefficients. The resulting constants can be found in Tables 2 and 1.

AN. In AN the two bands were found at 2062 cm^{-1} and 2097 cm^{-1} . Fig. 1 shows two representative examples of the spectra of solutions with different compositions. Both absorption bands were used in the determination of the stability constants according to the methods described above. The overlap of the \bar{n} , [L] values as determined from the two absorption bands can be seen in Fig. 2. At the graphical determination of the stability constants in this system the extrapolation of X_1 was somewhat hazardous because of the lack of data for small mean ligand numbers. There-

fore the existence of the first complex is uncertain and the stability constants of the following ones inaccurate. The molar absorption coefficient ϵ_1 could not be determined according to eqn. (4) because of the uncertainty of α_1 . But from, e.g. Fig. 4a it could be concluded that $\alpha_1 \approx 0$ at least for $[\text{SCN}^-] > 0.001 \text{ M}$. Then ϵ_2 could be obtained from the extrapolation of $A_{2097}/dC_{\text{Ni}^{2+}}$ versus [L] and after that ϵ_3 and ϵ_4 in the usual way.

DMA. Here the two bands appeared at 2058 cm^{-1} and 2094 cm^{-1} . As in AN, both bands were used in the determination of the stability constants in this solvent. The overlap of the \bar{n} , [L] values obtained from the two bands is illustrated in Fig. 3.

PDC. In PDC there was a precipitate, probably of $\text{Ni}(\text{NCS})_2$, in solutions with

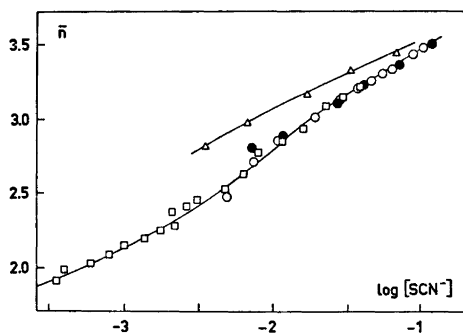


Fig. 2. \bar{n} as a function of $\log [\text{SCN}^-]$ for AN (lower curve) and PDC (upper curve). The values in AN are obtained from the 2062 cm^{-1} band with constant $C_{\text{Ni}} = 0.01012 \text{ M}$ (O) and $C_{\text{Ni}} = 0.02024 \text{ M}$ (●) and from the 2097 cm^{-1} band (□). (See text!) The values in PDC (Δ) are calculated from the 2057 cm^{-1} band.

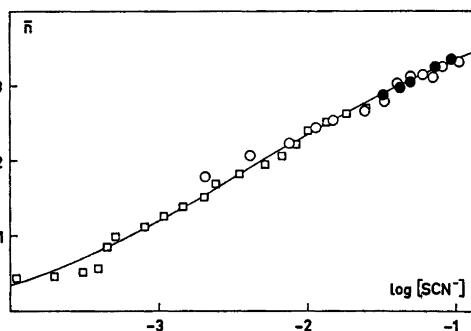


Fig. 3. \bar{n} as a function of $\log [\text{SCN}^-]$ in DMA. The values are obtained from the 2058 cm^{-1} band with constant $C_{\text{Ni}} = 0.01010 \text{ M}$ (O) and $C_{\text{Ni}} = 0.02020 \text{ M}$ (●) and from the 2094 cm^{-1} band (□).

$\bar{n} < 2.8$. This means that the stability constants could not be determined because the extrapolation to $[\text{SCN}^-] = 0$ was difficult to make. From the complex formation curve for $\bar{n} > 2.8$, which is drawn in Fig. 2, together with the same curve in AN, it can be inferred that complexes in PDC are slightly more stable than those in AN. In PDC the "complex peak" was found at 2089 cm^{-1} and the "free ligand peak" at 2057 cm^{-1} .

A comparison between the graphically and the numerically determined stability constants

The numerically calculated constants are in most cases in good agreement with the graphical ones. For the AN-system, when using four parameters in the calculations, no chemically acceptable β -values could be obtained. The consecutive constants K_3 and K_4 were, however, very similar to those obtained graphically. As mentioned above the graphical determinations of β are very uncertain depending on the lack of data for small mean ligand numbers. Thus, the existence of the first complex is questionable but if it exists the graphical

method indicates that β_1 should be $< 10^4$. The constants for this system given in Table 2 are therefore obtained from calculations with some fixed values of the parameters β_1 (between 0 and 10^4 M^{-1}). For the DMSO-system β_3 was very uncertain when determined graphically and this uncertainty is even more accentuated in the numerical calculations. The existence of the complex might be questioned.

DISCUSSION

In the same way as for the cobalt(II) thiocyanate systems,³ the increased integrated absorption ($\epsilon \Delta \nu_{1/2}$) of the C–N vibration of the thiocyanate ion upon coordination with the nickel(II) ion (Table 1) indicates that the thiocyanate ion is N-bonded in these solvents. Furthermore, it can be concluded that there is a definite electron exchange between ligand and metal when the complexes are formed. No such electron exchange can be found in aqueous solution,⁶ which probably means that the metal-thiocyanate bond in aqueous solution is merely electrostatic. This should be remembered

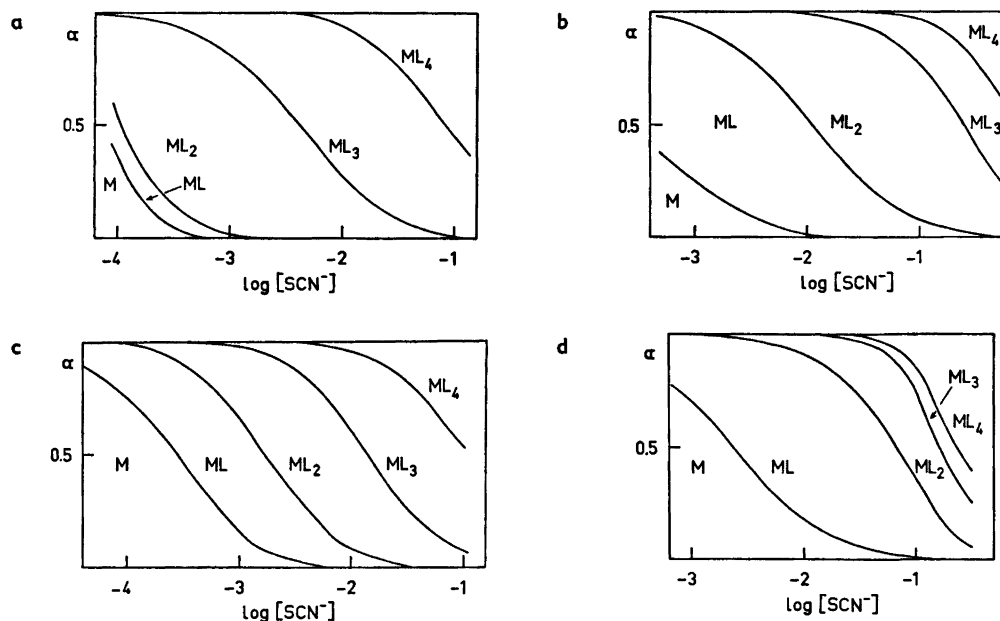


Fig. 4. The distribution of the nickel(II) ion between the mononuclear complexes with varying $[\text{SCN}^-]$ in a, AN; b, TMP; c, DMA; d, DMSO.

when the stability of the complexes in different solvents is discussed.

Within the range of concentration investigated, four mononuclear complexes are found in all the systems. All the complexes except $\text{Ni}(\text{NCS})^+$ in AN and $\text{Ni}(\text{NCS})_3^-$ in DMSO seem to be well established by this investigation (see Fig. 4). Quantitatively this is demonstrated by the values found for the quotients K_n/K_{n+1} (Table 2). With these results in mind it is confusing that Gutmann and Bardy¹ from conductometric measurements have found that generally only $\text{Ni}(\text{NCS})_2$ [in DMA $\text{Ni}(\text{NCS})^+$], $\text{Ni}(\text{NCS})_4^{2-}$, and $\text{Ni}(\text{NCS})_6^{4-}$ appear in these solutions.

The relative stabilities of the consecutive complexes are, however, very different in most of the investigated solutions. Usually abrupt changes in K_n/K_{n+1} may indicate differences, e.g. in stereochemistry or in the kind of bonding between metal ion and ligand for the stepwise formed complexes.¹⁴ Thus, transitions from, e.g., tetrahedral to octahedral configuration¹ may cause such changes. However, in the infrared spectra of the thiocyanato complexes of nickel(II) only one band is found in the range of the C-N stretching vibration. The frequency of this band is about 10 cm^{-1} higher than that of the octahedral cobalt(II) complex in each solvent. This is a normal shift between nickel and cobalt as found in pyridine and pyridine-chloroform solutions.¹⁵ As the integrated absorptions of the nickel complexes are also nearly the same as those of the octahedral cobalt complexes, one would suggest that all the complexes have the same configuration, viz. octahedral. Another possible cause of the changes in K_n/K_{n+1} may be the various steric requirements of the surrounding solvent molecules at the competition for the coordination sites of the metal. How such a steric effect is working in detail is, however, difficult to describe.

The stability of the thiocyanato complexes of nickel(II) may be related to the "donor numbers"² of the solvents used (Fig. 5). β_2 is chosen because of the uncertainty of the first stability constant in AN. The expected decrease in stability with increasing "donor number" of the solvent, if the complex formation is regarded as ligand exchange reactions of a solvated metal ion, can be found for all

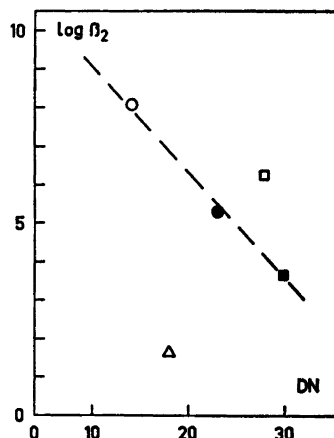


Fig. 5. The dependence of $\log \beta_2$ on the "donor number" of Gutmann.² The line is drawn only to emphasize the trend. \circ -AN, \bullet -TMP, \square -DMA, \blacksquare -DMSO, and \triangle - H_2O .

solvents investigated except DMA. Thus, the complexes in DMA are more stable than those in TMP, which is in contrast to the situation in the cobalt(II) system in the same solvents.³ Also when the β_2 value for the thiocyanato complex in water is introduced in Fig. 5 it can be seen that the conformity with the trend shown by the other solvents is not good. This situation was also found for cobalt(II) and is not unexpected. As mentioned above the metal-thiocyanate bonds should be merely electrostatic in aqueous solution and such bonds are influenced strongly also by the dielectric properties of the solvent.

In summary, the concept of donor numbers seems to be rather reliable when predicting the stability of thiocyanato complexes in aprotic solvents. The donor number of a solvent may, however, never become the exclusive factor determining the stability of complexes formed in all kinds of solvents. Especially in highly polar protic solvents, e.g. water, it is probable that also factors such as the dielectric constant and the hydrogen bonding ability of the solvent have to be considered.

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