

Thermodynamics of Metal Complex Formation in Aqueous Solution. VII. Equilibrium and Enthalpy Measurements on the Nickel(II)—Selenocyanate System

LENNART KULLBERG

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund 7, Sweden

The stability constants and the enthalpy changes for the formation of nickel(II)—selenocyanate complexes in aqueous solution have been determined by means of a calorimetric titration method. The value of β_1 has also been determined spectrophotometrically. From the enthalpy changes measured, and the free energy changes computed from the stability constants, the entropy changes have been calculated. All data refer to 25.00 °C and an aqueous sodium perchlorate medium of ionic strength 1.00 M.

The selenocyanate complexes of nickel(II) are formed in more exothermic reactions than the thiocyanate complexes. This is more than compensated by the entropy terms, however, which are more negative for the selenocyanate system. On the balance, the thiocyanate complexes are therefore a little stronger than the selenocyanate ones.

In a previous paper¹ the changes of free energy, enthalpy and entropy accompanying the formation of selenocyanate complexes of zinc and cadmium have been determined and compared with the same quantities for the corresponding thiocyanate complexes. The changes of free energy, ΔG°_j , have been computed from the measured stability constants while the changes of enthalpy, ΔH°_j , have been measured calorimetrically. Finally, the changes of entropy, ΔS°_j , have been obtained from the relation

$$\Delta G^\circ_j = \Delta H^\circ_j - T \Delta S^\circ_j$$

Also the thiocyanate complexes of nickel(II) and copper(II) have been studied before.² It would evidently be of interest to extend the comparison by investigating the selenocyanate complexes of these two metal ions as well.

In this paper a calorimetric and spectrophotometric investigation of the nickel(II)—selenocyanate system is reported. The copper(II) system seems impossible to study as a brown precipitate is formed immediately upon addition of selenocyanate ions to a copper(II) solution. The precipitate most probably consists of a mixture of elemental selenium and copper(I) cyanide compounds.³

The nickel(II)—selenocyanate system has hitherto been little studied, probably because the complexes tend to decompose in aqueous solution. Golub and Skopenko⁴ have spectrophotometrically demonstrated the existence of NiSeCN^+ in aqueous solution, however. They also found that the system is much more stable in non-aqueous solvents like methanol and acetone. The strength of the complexes increased in the sequence $\text{H}_2\text{O} < \text{methanol} < \text{acetone}$.

The disintegration in aqueous solution is rapid at high selenocyanate (and nickel) concentrations. It is presumably catalyzed by light. Thus, in the calorimetric measurements, performed in complete darkness, ligand concentrations, C_L , up to 150 mM could be used without perceptible decomposition while in the spectrophotometric measurements a disturbing decomposition occurred already at a $C_L = 100$ mM, even for moderate values of C_M ($\lesssim 10$ mM). In view of the weak complex formation only the first stability constant can be precisely determined. A reliable method for the determination of β_1 in such cases is the so called M-method,^{5,6} which has been applied here. In this method,

C_M is varied while C_L is kept low and constant which allows the determination of the first complex without interference from the higher ones.

All measurements in this study have been carried out at 25.00 °C in an aqueous medium of an ionic strength $I=1.00$ M with sodium perchlorate as supplementary electrolyte.

CALCULATIONS

Notation. The same notation is used as before.³ For convenience, the most important definitions and formulas are collected below.

A = absorbance

l = sample path length

λ = wavelength

$a = A/l$

$\epsilon_M, \epsilon_L, \epsilon_j$ = the molar absorption coefficients of M and L and the complex ML_j .

$$a_M = \epsilon_M C_M \quad (1)$$

$$a_L = \epsilon_L C_L \quad (2)$$

Calculation from spectrophotometric measurements. Assuming C_L is kept so low that formation of complexes higher than ML can be neglected, the following relation can be deduced^{5,6}

$$\frac{[M]C_L}{a - a_M - a_L} = \frac{1}{(\epsilon_1 - \epsilon_M - \epsilon_L)\beta_1} + \frac{[M]}{(\epsilon_1 - \epsilon_M - \epsilon_L)} \quad (3)$$

As the concentration of the complex ML is small compared to the concentration of the free metal ion it is allowed to put $[M] \approx C_M$ in the first approximation. By plotting the left member of eqn. (3) vs. C_M a first value of β_1 is then obtained. If necessary better values are then arrived at by successive approximations.

The calculation of β_1 has also been made by the least squares computer program "Letagrop Spefo" developed by Sillén and Warnqvist.⁷ The input data are the total concentrations C_M and C_L and the absorption coefficients a of each solution. The error square sum to be minimized is

$$U_{rel} = \sum_i (a_{i,calc} - a_{i,exp})^2 (a_{i,exp})^{-2} \quad (4)$$

The calculation gives the stability constants, β_j , and the molar absorption coefficients of the

species. The molar absorption coefficients ϵ_M and ϵ_L have been determined separately and regarded as known parameters during the calculations.

Calculation from calorimetric measurements. The equilibrium constants and the enthalpy changes have been calculated by the least squares computer program "Kalori".⁸ With this program the computer searches for the set of values of unknown parameters ($\beta_j, \Delta H_j$) which will minimize the error square sum

$$U(\beta_j, \Delta H_j) = \sum_i (Q_{i,calc} - Q_{i,corr})^2 \quad (5)$$

The input data are the corresponding values of Q_{corr} , initial volume, V_0 , added volume, v , and the total concentrations of metal and ligand in the S and T solutions.

EXPERIMENTAL

Chemicals: Nickel perchlorate, sodium selenocyanate and sodium perchlorate were prepared and analyzed as described before.³

The spectrophotometric measurements at constant wavelength were made with a Zeiss PMQ II Spectrophotometer. Suitable wavelengths were selected by means of absorption spectra, recorded with a Hitachi Spectrophotometer. For several reasons, the measurements should preferably be performed at a wavelength where the absorption curve has a horizontal tangent. The complex solution has a relative maximum at about 400 nm (curve B, Fig. 1). Unfortunately, also the hydrated nickel(II) ion absorbs strongly in this region (curve A) which makes a precise determination of β_1 from measurements in this band impossible. At

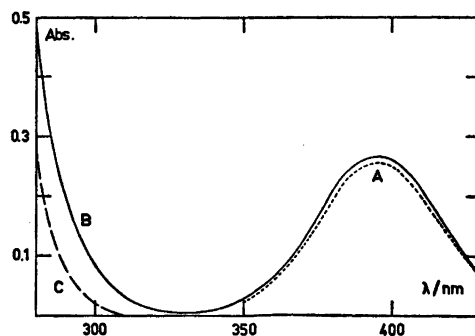


Fig. 1. Absorption curves of free nickel(II) ions, a complex nickel(II) selenocyanate solution and selenocyanate ions at 25 °C and at $I=1.0$ M and a cell thickness of 1.00 cm. A: 50 mM $Ni(ClO_4)_2$. B: 50 mM $Ni(ClO_4)_2 + 10$ mM NaSeCN. C: 10 mM NaSeCN.

lower wavelengths, the complex solution has a strong band starting at ≈ 320 nm while the absorption of the hydrated ion is negligible down to ≈ 250 nm. On the other hand, the absorption of SeCN^- (curve C) is quite strong in this region. In the range $285 < \lambda < 305$ nm, however, the difference between curves B and C is relatively large while the absorption of the complex solution is large enough for a good determination. In this favourable range five different wavelengths *viz.* 285, 290, 295, 300, and 305 nm have been selected.

The solutions were made up in 25 cm³ measuring flasks from stock solutions of nickel(II) perchlorate, sodium selenocyanate, and sodium perchlorate. To minimize disturbances due to disintegration, they were measured immediately upon mixing against a blank containing 1.00 M NaClO_4 .

All measurements were repeated at least three times. The solutions to be measured and the cell compartment of the spectrophotometer were thermostated at 25.0 ± 0.1 °C.

The calorimetric measurements. The calorimeter and the technique of measurement have been described previously.⁹ In each series, the reaction vessel initially contained V_0 cm³ of a solution S and a titrant T was then added. The compositions of the solutions S and T are given in Table 3. In order to determine the corrections for the heats of dilution, series analogous to those of the main measurements were performed except that only one of the two reactants was present simultaneously.

The heat equivalent of the calorimetric system, determined by electrical calibrations, was found to obey $\epsilon_s = 2.317 + 0.0226(V - 100.0)$ for all solutions used.

MEASUREMENT AND RESULTS

Spectrophotometric measurements. The experimental data are collected in Table 1. The molar absorption coefficients for Ni^{2+} , ϵ_M , and for SeCN^- , ϵ_L , have been determined separately. For the wavelengths used ϵ_M is negligible. The values of ϵ_L can easily be obtained from the data given in Table 1. The first approximation, with $[\text{M}] \approx C_M$, results in a mean value of $\beta_1 = 9.4 \text{ M}^{-1}$. With this value better values of $[\text{M}]$ were calculated. The straight lines then obtained yielded final values of $(\epsilon_1 - \epsilon_M - \epsilon_L)$ and β_1 , Table 2. The limit of error in the value of $\beta_1 = (10.0 \pm 0.7) \text{ M}^{-1}$ corresponds to 3σ . At the computer calculation with the least-squares program "Letagrop Spefo" the experimental data from all five wavelengths used could be treated simultaneously. From this calculation a value of $\beta_1 = (9.8 \pm 0.3) \text{ M}^{-1}$ was obtained, the error again corresponding to 3σ . The standard deviation, σ , for the differences between experimental

Table 1. Absorbances (cell length 2.000 cm) for the ligand concentrations $C_L = 10.00$ mM (A_{10}) and $C_L = 5.00$ mM (A_5).

C_M/mM	305 nm		300 nm		295 nm		290 nm		285 nm	
	A_{10}	A_5	A_{10}	A_5	A_{10}	A_5	A_{10}	A_5	A_{10}	A_5
0	0.051	0.026	0.090	0.045	0.165	0.083	0.306	0.153	0.566	0.283
20.0		0.059		0.098		0.163		0.273		0.450
40.0	0.167	0.082	0.275	0.136	0.447	0.223	0.717	0.357	1.126	0.562
60.0	0.202	0.101	0.335	0.168	0.538	0.271	0.847	0.427	1.298	0.654
80.0	0.229	0.115	0.380	0.191	0.610	0.307	0.950	0.479	1.440	0.726
100.0	0.253	0.127	0.420	0.211	0.670	0.337	1.036	0.523	1.544	0.787

Table 2. Constants obtained from the graphical evaluation of the spectrophotometric measurements.

λ/nm	305		300		295		290		285		
	C_L/mM	10	5	10	5	10	5	10	5	10	
$(\epsilon_1 - \epsilon_L)/\text{cm}^{-1} \text{ M}^{-1} \text{ }^a$		19.3	20.6	33.2	35.5	51.6	54.3	73.0	75.9	95.2	101.0
$\beta_1(\epsilon_1 - \epsilon_L)/\text{cm}^{-1} \text{ M}^{-2}$		217	202	343	316	516	489	762	735	1060	1020
β_1/M^{-1}		11.2	9.8	10.3	8.9	10.0	9.0	10.4	9.7	11.1	10.1
$\beta_1(\text{average})/\text{M}^{-1}$		10.0 \pm 0.7									

^a $\epsilon_M = 0$.

Table 3. Determination of the heats of formation for the nickel selenocyanate complexes. For all the series: $V_0 = 100.0 \text{ cm}^3$ and $V = (V_0 + v) \text{ cm}^3$.

(a) ○ S: $C_M = 0.1000 \text{ M}$, $C_{\text{NaClO}_4} = 0.700 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 6.135, 6.301, -0.112; 2.000, 5.841, 5.997, -0.065; 3.000, 5.555, 5.703, -0.019; 5.000, 10.306, 10.629, 0.037; 7.000, 9.462, 9.774, 0.026; 9.000, 8.724, 9.027, -0.008; 12.000, 11.812, 12.275, -0.040; 15.000, 10.417, 10.847, 0.043; 18.000, 9.302, 9.703, 0.038;

(b) □ S: $C_M = 0.0790 \text{ M}$, $C_{\text{NaClO}_4} = 0.763 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 5.200, 5.366, 0.064; 2.000, 4.960, 5.116, 0.045; 3.000, 4.718, 4.865, 0.042; 5.000, 8.794, 9.117, -0.006; 7.000, 7.970, 8.281, -0.012; 9.000, 7.260, 7.563, -0.033; 12.000, 9.679, 10.142, -0.036; 15.000, 8.502, 8.932, -0.035; 18.000, 7.505, 7.905, -0.020;

(c) △ S: $C_M = 0.0500 \text{ M}$, $C_{\text{NaClO}_4} = 0.850 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 3.895, 4.061, -0.009; 2.000, 3.623, 3.779, 0.009; 3.000, 3.353, 3.501, 0.047; 5.000, 6.082, 6.405, 0.058; 7.000, 5.405, 5.717, 0.025; 9.000, 4.816, 5.118, 0.022; 12.000, 6.304, 6.767, 0.014; 15.000, 5.402, 5.833, 0.036; 18.000, 4.663, 5.064, 0.061;

(d) ● S: $C_M = 0.0400 \text{ M}$, $C_{\text{NaClO}_4} = 0.880 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 3.264, 3.430, 0.024; 2.000, 3.035, 3.191, 0.013; 3.000, 2.807, 2.955, 0.026;

(e) ■ S: $C_M = 0.0300 \text{ M}$, $C_{\text{NaClO}_4} = 0.910 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 2.588, 2.754, 0.017; 2.000, 2.388, 2.544, 0.003; 3.000, 2.182, 2.330, 0.021; 5.000, 3.888, 4.211, -0.001; 7.000, 3.361, 3.673, -0.001; 9.000, 2.989, 3.291, -0.049; 12.000, 3.810, 4.273, -0.053; 15.000, 3.235, 3.665, -0.062; 18.000, 2.729, 3.130, -0.020;

(f) ▲ S: $C_M = 0.0200 \text{ M}$, $C_{\text{NaClO}_4} = 0.940 \text{ M}$.
T: $C_L = 1.000 \text{ M}$.

v/cm^3 , Q_{exp}/J , Q_{corr}/J , $\Delta Q_{\text{corr}}/J$: 1.000, 1.898, 2.064, -0.079; 2.000, 1.724, 1.880, -0.076; 3.000, 1.541, 1.689, -0.038;

and calculated values of a was found to be 0.0022 which indicates a high precision in the measurements.

Calorimetric measurements. Six different titration series have been carried out, Table 3. In all of these, ligand has been added to a solution of the metal ion. In order to suppress the hydrolysis of nickel(II)¹⁰ and to prevent the disintegration of the selenocyanate ion,¹ pH has to be carefully adjusted. The pH of the metal solutions was about 4.5 and that of the ligand solution 8–9. A value of $C_L = 140 \text{ mM}$ can be reached before decomposition is noticed. If, on the other hand, a nickel solution (of $C_M = 80 \text{ mM}$) is added to a ligand solution (of $C_L = 100 \text{ mM}$) a precipitation of selenium occurs already at the first addition.

It has been tried to fit the data to both two and three complexes. The β_j -values obtained in the two cases are listed in Table 4. As seen from the error square sum, U , a much better fit is achieved with three complexes than with two. As the concentration of the third complex will never amount to more than a few per cent of C_M only a very approximate value of β_3 emerges, implying that the determination of ΔH°_3 becomes very hazardous.

The spectrophotometric and the calorimetric measurements give consistent β_1 -values, Table 4. The spectrophotometric measurements are somewhat more precise and a value of $\beta_1 = 9.7 \text{ M}^{-1}$ should therefore be a reasonable choice. By keeping $\beta_1 = 9.7 \text{ M}^{-1}$ as a constant parameter values of β_2 , β_3 , and ΔH°_j have been recalculated from the calorimetric data by the program "Kalori". The values obtained, Table 4, are in line with those found previously. A set of β_j -values considered to be the 'best' one is proposed in Table 4. With this set, a final set of ΔH°_j has been computed by the program "Kalori". The low value of $\sigma_{Q_{\text{corr}}} = 0.042 \text{ J}$ indicates a very good fit. The final values of β_j and the functions ΔG°_j , ΔH°_j , and ΔS°_j , are collected in Table 5. In view of the large uncertainty of β_3 the thermodynamic functions of the third step are not given. It may be mentioned that with $\beta_3 = 70 \text{ M}^{-1}$ a value of $\Delta H^\circ_3 \approx 0$ is obtained. In Fig. 2, Δh_v is plotted versus \bar{n} . The series coincide within the experimental errors which shows that no polynuclear complexes are formed. The full drawn curve is calculated from the final values of β_j and ΔH°_j .

Table 4. Stability constants obtained from spectrophotometric and calorimetric measurements. The errors correspond to three standard deviations or to estimated errors.

Method	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}	U
Spectr., graphically	10.0 ± 0.7			
Spectr., by computer	9.8 ± 0.3			
Calorim., two complexes	9.1 ± 1.8	19 ± 9		0.318
Calorim., three complexes	9.4 ± 1.2	18 ± 12	~ 70	0.070
Calorim., β_1 fixed	(9.7)	16 ± 5	~ 80	0.071
Proposed values	9.7 ± 0.4	18 ± 5	70	0.073

Table 5. The stability constants and the values of ΔG°_j , ΔH°_j and ΔS°_j for the stepwise reactions of the thiocyanate and selenocyanate systems of nickel(II). The data for the thiocyanate system are taken from Ref. 2. The errors given correspond to three standard deviations or to estimated errors.

Ligand		SCN ⁻	SeCN ⁻
β_j/M^{-j}	$j=1$	13.8 ± 0.5	9.7 ± 0.4
	2	38 ± 4	18 ± 5
	3	40 ± 15	
$-\Delta G^{\circ}_j$ kJ mol ⁻¹	1	6.51 ± 0.10	5.63 ± 0.10
	2	2.51 ± 0.30	1.5 ± 0.8
	3	0.1 ± 0.9	
$-\Delta H^{\circ}_j$ kJ mol ⁻¹	1	12.02 ± 0.15	12.8 ± 0.3
	2	8.9 ± 1.0	12 ± 3
	3	8.2 ± 4.0	
ΔS°_j J mol ⁻¹ K ⁻¹	1	-18.5 ± 0.6	-24.1 ± 1.0
	2	-21.5 ± 3.5	-35 ± 11
	3	-27 ± 13	

DISCUSSION

For comparison, the values of ΔG°_j , ΔH°_j , and ΔS°_j for the nickel(II)–thiocyanate system² are also included in Table 5. The selenocyanate complexes are somewhat weaker than the thiocyanate ones. The ratio $K_1/K_2=5$ between the first and second stepwise stability constant is about the same for both systems.

The thiocyanate ion may coordinate either *via* sulfur or nitrogen, the selenocyanate ion either *via* selenium or nitrogen. Hard acceptors are coordinated *via* the harder nitrogen atom. Nickel(II) can be classified as a mildly hard acceptor¹¹ and its complexes are certainly in all cases N-bonded. A large difference in the strength of the thiocyanate and selenocyanate complexes of nickel(II) is therefore not to be expected. The small difference actually observed may be due to the influence of the non-bonding ends of the ligands.

If coordination takes place *via* N, the strength of the metal-ligand bonds should be much the same for thiocyanate and selenocyanate and about the same values of ΔH°_j are therefore to be expected. This is in fact also found, Table 5.

For both thiocyanate and selenocyanate the charge density on the non-bonding end decreases upon coordinating. Calculations¹² have shown that upon coordination *via* the N-atoms the decrease of charge is larger on the sulfur atom than on the selenium atom. Thus if an acceptor is coordination *via* the N-atoms, more water should be liberated from the S atom in thiocyanate than from the Se atom in selenocyanate. Consequently the entropy term should be more positive or less negative for the thiocyanate reaction than for the selenocyanate

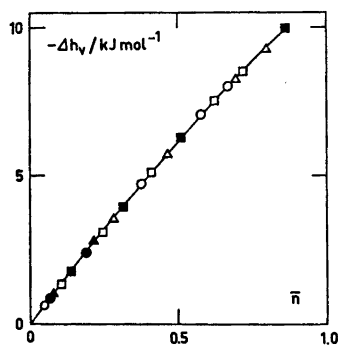


Fig. 2. The total molar enthalpy change, Δh_v , as a function of \bar{n} , for the nickel(II)–selenocyanate system, cf. Table 3.

reaction. If coordination, on the other hand, occurs through the S or Se atoms, the same amount of water should be set free from the non-bonding N atom for both ligands. In this case the entropy terms for the two reactions should be about the same.

As seen from Table 5, ΔS°_1 for the formation of the thiocyanate complex is less negative than ΔS°_1 for the formation of the selenocyanate complex, the difference amounting to $\approx 6 \text{ J mol}^{-1}\text{K}^{-1}$. In a previous study¹ the same difference was found in the case of Zn^{2+} . In the reactions with Cd^{2+} , on the other hand, the two ligands give about the same value of ΔS°_1 . This indicates bonding *via* N in the case of Ni^{2+} and Zn^{2+} , while Cd^{2+} seems to favour S and Se. These conclusions agree with those arrived at *via* infrared spectroscopy¹³ even if the latter method does not exclude the possibility of partial N-bonding in the case of Cd^{2+} .

For the nickel(II)–selenocyanate system ΔS°_2 is more negative than ΔS°_1 . This trend of ΔS°_j is expected if no change of coordination figure occurs.¹⁴

Acknowledgements. I am most grateful to Professor Sten Ahrland for useful discussions and many valuable suggestions. I also wish to thank Professor Sture Fronæus for his kind interest and for facilities provided.

REFERENCES

1. Ahrland, S., Avsar, E. and Kullberg, L. *Acta Chem. Scand. A* 28 (1974) 855.
2. Kullberg, L. *Acta Chem. Scand. A* 28 (1974) 829.
3. Toropova, V. F. *Zh. Neorg. Khim.* 1 (1956) 243.
4. Golub, A. M. and Skopenko, V. V. *Russ. J. Inorg. Chem.* 7 (1962) 653.
5. Evans, M. G. and Nancollas, G. H. *Trans. Faraday Soc.* 49 (1953) 363.
6. McConnell, H. and Davidson, N. *J. Amer. Chem. Soc.* 72 (1950) 3164.
7. Sillén, L. G. and Warnqvist, B. *Ark. Kemi* 31 (1969) 377.
8. Karlsson, R. and Kullberg, L. *To be published.*
9. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* 25 (1971) 3471.
10. Burkov, K. A., Lilič, L. S. and Sillén, L. G. *Acta Chem. Scand.* 19 (1965) 14.
11. Ahrland, S. *Struct. Bonding* 5 (1968) 118.
12. Wagner, E. L. *J. Chem. Phys.* 43 (1965) 2728.
13. Bailey, R. A., Kozak, S. L., Michelsen, T. W. and Mills, W. N. *Coord. Chem. Rev.* 6 (1971) 407.
14. Ahrland, S. *Struct. Bonding* 15 (1973) 167.

Received April 9, 1974.