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THE COBALT(II) AND NICKEL(II) THIOCYANATE SYSTEMS: A SPECTROPHOTOMETRIC STUDY

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CONTENTS

A. INTRODUCTION

The stability constants of the cobalt(II) complexes found in aqueous thiocyanate solutions have been studied by several authors [1]. Senice and Perrier [2] determined spectrophotometrically the first stability constant using the near-UV band at 273 nm, and Tribalat and Zeller [3] determined K_1 using the visible band at 520 nm. The latter authors also gave approximate values for the succeeding constants and proved that the highly absorbing blue complex extractable with hexanone-2 is the tetracyanato complex.

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(i) *The stability constants of Zeltmann and Morgan*

Zeltmann and Morgan [4] studied the cobalt(II) thiocyanate solutions using ^{17}O and ^{14}N and the nuclear magnetic resonance (NMR) technique. With this method they were able to obtain information about the structures and relative amounts of the complex species. On this basis, Zeltmann and Morgan calculated the semi-thermodynamic stability constants, K_n ($n = 1$–4)

$$K_n = \frac{[\mathrm{Co(NCS)}_n]\, a_{\mathrm{H_2O}}}{[\mathrm{Co(NCS)}_{n-1}][\mathrm{NCS}^-]\gamma\pm^m} \qquad (1)$$

using molal concentrations and correcting for both the mean activity of the complex-forming salt and the decreasing activity of water in the salt solutions. The stability constants obtained by Zeltmann and Morgan are of a high quality. Their values for the constants in the cobalt(II) chloride system [5] compare well with the values estimated from our spectrophotometric data [6]. Their constants for the cobalt(II) thiocyanate system are used in the present paper in connection with our spectrophotometric measurements.

B. EXPERIMENTAL

The chemicals used were of analytical grade. The stock solution of $Co(NO_3)_2 \cdot 6H_2O$ was analysed by using atomic absorption spectroscopy. The stock solutions of NaSCN were analysed by titration with silver nitrate. The absorption spectra were measured on a Cary 118 spectrophotometer thermostatted at 25 ° C.

C. RESULTS FROM THE SECOND VISIBLE BAND

(i) *Molar absorbances of the octahedral species* $[Co(NCS)(H_2O)_5]^+$ *and* $[Co(NCS)_2(H_2O)_4]^0$

The way in which the absorption spectra of cobalt(II) thiocyanate solutions in the second visible band change with the average ligand number is shown in Fig. 1. For thiocyanate concentrations up to about 1 M, the solutions retain the red colour, while for higher thiocyanate concentrations they turn blue. Water and the N-bonded thiocyanate occupy similar positions in the spectrochemical series. The hexaaquacobalt(II) ion and the successive thiocyanate complexes with octahedral configuration should therefore be expected to have an absorption maximum at nearly the same wavelength. It can be seen from Fig. 1 that the curves up to $\bar{n} \approx 2$ have a maximum at ca. 520 nm. Solutions with $\bar{n} \approx 2$ contain some of the trithiocyanato complex and the absorptions for wavelengths above ca. 580 nm

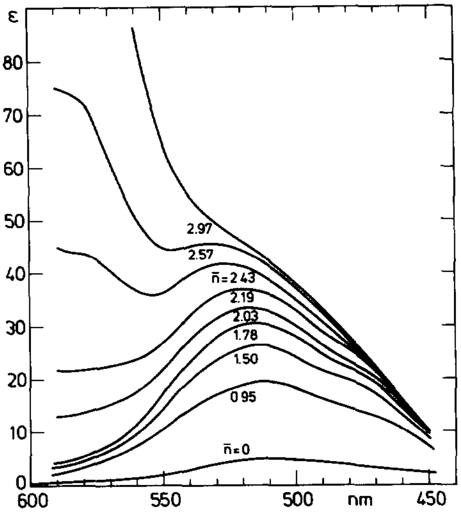

Fig. 1. Absorption curves (ϵ vs. λ) of cobalt(II) thiocyanate solutions. The numerals on the curves show the average ligand number $\bar{n}$ as calculated with the activity constants given by Zeltmann and Morgan [4]. The total NaNCS concentrations corresponding to the curves are 0, 0.195, 0.585, 0.965, 1.544, 1.93, 2.794, 3.49 and 5.24 M. The $Co(NO_3)_2$ concentration is 0.1029 M in the solution without NaNCS and 0.02058 M in all the other solutions.

for $\bar{n} > 1.78$ are caused by this complex which has a tetrahedral configuration. It can therefore be concluded from the data that the dithiocyanato complex still has octahedral structure. However, this disagrees with the conclusions of Zeltmann and Morgan [4] who assumed that the transformation to a tetrahedral structure occurs already with the uptake of the second thiocyanate ion.

The average ligand numbers in Fig. 1 were calculated using the activity constants given by Zeltmann and Morgan [4]:

$$K_1 = 15 \pm 7, \quad K_2 = 28 \pm 0.2, \quad K_3 = 0.24 \pm 0.03, \quad K_4 = 0.050 \pm 0.006 \quad (2)$$

These constants refer to a molal concentration, and in order to use them in connection with volume concentrations the activity coefficients given by Miller and Sheridan [7] were recalculated using the molar concentrations shown in Table 1. The activity of water was calculated from the osmotic coefficients given by the same authors. The estimated concentrations of free thiocyanate $[NCS^-]$ are shown in Table 2.

D. RESULTS FROM THE FIRST VISIBLE BAND

(i) *The limiting absorption of* $[Co(NCS)_4]^{2-}$ *in concentrated NaNCS solutions*

The ϵ vs. λ absorption spectra of the blue cobalt(II) solutions are shown in Fig. 2. The intensities around 615 nm increase with a high power of the

TABLE 1

Activity data for aqueous NaNCS solutions [a] (calculated from isopiestic measurements at 25 °C) [7]

m	$\gamma\pm^m$	c	$\gamma\pm^c$	a_{H_2O}	$\log\gamma\pm^c$	$\log\gamma\pm^c$ (calc)	$\log\frac{\gamma\pm^c}{a_{H_2O}}$	$\log\frac{\gamma\pm^c}{a_{H_2O}}$ (calc)
0.51	0.714	0.50	0.728	0.983	−0.137	–	−0.130	–
1.042	0.713	1.00	0.743	0.964	−0.129	–	−0.113	–
2.179	0.752	2.00	0.819	0.921	−0.087	–	−0.051	–
3.422	0.845	3.00	0.964	0.869	−0.016	–	+0.045	–
4.787	1.00	4.00	1.197	0.813	+0.078	+0.068	+0.168	–
6.29	1.18	5.00	1.484	0.743	+0.171	+0.180	+0.300	0.300
7.95	1.46	6.00	1.935	0.666	+0.287	+0.292	+0.463	0.473
9.80	1.82	7.00	2.548	0.582	+0.406	+0.404	+0.641	0.646
11.9	2.28	8.00	3.39	0.504	+0.530	+0.516	+0.828	0.819
14.3	2.68	9.00	4.26	0.432	+0.629	+0.628	+0.994	0.992
17.0	3.10	10.00	5.27	0.366	+0.722	+0.740	+1.158	1.165

[a] The following relationships are valid in concentrated NaNCS solutions: $\log\gamma\pm^c = -0.38 + 0.112C_{NaNCS}$ for $C > 4$ M; $\log[(\gamma\pm^c)/(a_{H_2O})] = -0.565 + 0.173C_{NaNCS}$ for $C > 5$ M. m, molal concentration; c, molar concentration.

TABLE 2

Fractions of the molar absorbances of the measured solutions relative to the limiting molar absorbances at four wavelengths ($\alpha_x = \epsilon/\epsilon_4$)

No.	C_{Co}	C_{NCS^-}	$[NCS^-]$	$\gamma\pm^c$	a_{H_2O}	Wavelength (nm)			
						640	630	620	610
1	0.02058	0.195	0.175	0.76	1.00	0.00155	0.00141	0.00132	0.00164
2	0.02058	0.585	0.56	0.75	0.98	0.00522	0.00496	0.00489	0.0055
3	0.02058	0.965	0.95	0.75	0.96	0.0115	0.0112	0.0114	0.0122
4	0.02058	1.544	1.515	0.805	0.94	0.0312	0.0307	0.0307	0.0318
5	0.02058	1.930	1.89	0.91	0.92	0.0554	0.0541	0.0541	0.0552
6	0.00309	2.895	2.885	0.99	0.87	0.166	0.161	0.158	0.158
7	0.00309	3.86	3.85	1.15	0.83	0.313	0.307	0.303	0.304
8	0.00206	4.825	4.82	1.43	0.755	0.505	0.490	0.475	0.469
9	0.00206	5.79	5.79	1.80	0.685	0.667	0.664	0.659	0.660
10	0.00206	6.75	6.75	2.35	0.605	0.848	0.831	0.810	0.795
11	0.00206	7.72	7.72	3.20	0.525	0.923	0.910	0.898	0.888
12	0.00206	8.88	8.88	4.15	0.445	0.978	0.969	0.969	0.959
13	0.00206	9.264	9.26	4.55	0.42	0.985	0.983	0.997	1.000
14	0.00206	10.55	10.55	5.70	0.33	1.000	1.000	1.000	1.000
						$\epsilon_4 = 315.8$	$\epsilon_4 = 411.0$	$\epsilon_4 = 476.3$	$\epsilon_4 = 476.1$

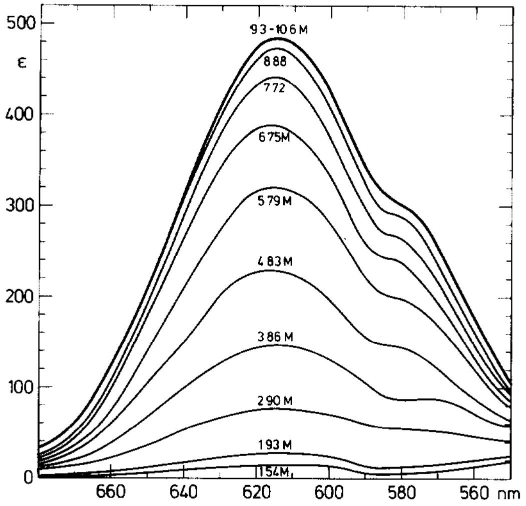

Fig. 2. Absorption spectra (ϵ vs. λ) of cobalt(II) thiocyanate solutions in the first visible band with NaNCS concentrations varying from 1.54 to 10.55 M. The $Co(NO_3)_2$ concentrations are as shown in Table 2.

thiocyanate concentration. This absorption is due to the tetrahedral cobalt(II) complexes which, according to the preceding discussion, can only be due to the anions $[Co(NCS)_3(H_2O)]^-$ and $[Co(NCS)_4]^{2-}$. At high thiocyanate concentrations, the absorption curves converge towards a limiting absorption which can only be ascribed to the tetrathiocyanato complex $[Co(NCS)_4]^{2-}$. The relative values of the molar absorbances $\alpha_x = \epsilon/\epsilon_4$ show (Table 2) a very uniform picture, as expected for a system composed of two coloured species with maximum absorbances at the same wavelength. Besides the values of α_x calculated at four wavelengths, Table 2 contains the tabulated concentrations and the necessary activity data for the measured solutions.

(ii) Molar absorbances of $[Co(NCS)_3H_2O]^-$

The molar absorbances of $[Co(NCS)_3H_2O]^-$ (ϵ_3) can be estimated from the relation

$$\epsilon = \alpha_x\epsilon_4 = \alpha_3\epsilon_3 + \alpha_4\epsilon_4 \tag{3}$$

as the monothiocyanato and dithiocyanato complexes have effectively no absorbance in the wavelength range considered. The molar absorbances of $[Co(NCS)_4]^{2-}$ (ϵ_4) are many times higher than those for ϵ_3, and for this reason, ϵ_3 values are best determined where the fractions of the fourth complex are still small compared with those of the third complex. The results of the calculations for solutions 1–6 in Table 2 are shown in Table 3.

TABLE 3

Estimates of the molar absorbance (ϵ_3) of the aquatrithiocyanatocobalt(II) complex [a]

No.	α_3	α_4	$\bar{n}$	ϵ_3 (630 nm)	ϵ_3 (630 nm)	ϵ_3 (620 nm)
1	0.00637	0.000042	0.95	74	88	95
2	0.053	0.000117	1.50	30	38	43
3	0.105	0.000394	1.78	23	28	34
4	0.192	0.0125	2.03	31	39	45
5	0.266	0.0248	2.19	36	45	52
6	0.383	0.0615	2.41	86	106	119
Average				47	57	65

[a] Concentrations are as in Table 2.

The fractions of $[Co(NCS)_3H_2O]^-$ (α_3) and of $[Co(NCS)_4]^{2-}$ (α_4) were calculated using Zeltmann and Morgan's activity constants [4] (see eqns. (1) and (2)). The values of ϵ_3 from solution 1 are somewhat uncertain as the absorbances used are too small ($\epsilon < 1$). The values of ϵ_3 from solution 6, and especially when calculated from the following solutions, are much too high. The reason seems to be that the value used for K_4 and therefore also for $\alpha_4\epsilon_4$ in eqn. (3) is too small.

E. ESTIMATIONS OF THE FOURTH STABILITY CONSTANT

(i) From $\alpha_4 = [Co(NCS)_4^{2-}]/C_{Co(II)}$

At sufficiently high thiocyanate concentrations where the presence of the monothiocyanato and dithiocyanato complexes is negligible, $\alpha_3 \approx 1 - \alpha_4$; therefore from eqn. (3) it follows that

$$\alpha_4 = \frac{\epsilon - \epsilon_3}{\epsilon_4 - \epsilon_3} \tag{4}$$

The values of α_4 and K_4 calculated using eqn. (4) from solutions 9–11 in Table 2 with $\epsilon_3 = 65$ at 620 nm are shown in Table 4.

(ii) From $d \log \alpha_n / d[NCS^-]$

In an earlier paper [8] the author derived the expression

$$\frac{d \log \alpha_n}{d[L]} = \left(\frac{0.4343}{[L]} + B\right)(n - \bar{n}) \tag{5}$$

which is valid for the case where the activity coefficient expression, F, for the system is described by the relationship

$$\log F = A + B[L]$$

TABLE 4

Estimation of the fourth activity constant from α_4: $K_4 = \alpha_4 a_{H_2O}/(1-\alpha_4)[NCS^-]\gamma\pm^c$

No.	$[NCS^-]$	$\gamma\pm^c$	a_{H_2O}	α_4 (620 nm)	K_4
9	5.79	1.80	0.685	0.606	0.101
10	6.75	2.35	0.605	0.780	0.135
11	7.72	3.20	0.525	0.882	0.159
				Average	0.13

TABLE 5

Estimation of K_4 from the slope, δ, and eqn. (5) [a]

No.	$[NCS^-]$	δ	$(a+0.173)$	$4-\bar{n}$	$\bar{n}$	K_4
9	5.79	0.145	0.248	0.585	3.415	–
10	6.75	0.077	0.237	0.324	3.676	0.080
11	7.72	0.0365	0.229	0.159	3.841	0.112
12	8.88	0.0210	0.222	0.095	3.905	0.115
					Average	0.102

[a] $\delta = \dfrac{d \log \alpha_4}{d[NCS^-]}$; $a = \dfrac{0.4343}{[NCS^-]}$; $K_4 = \dfrac{(\bar{n}-3)a_{H_2O}}{\{1-(\bar{n}-3)\}[NCS^-]\gamma\pm^c}$.

where A and B are constants and [L] is the ligand-ion concentration. From the data in Table 1, it appears that $\log(\gamma\pm^c/a_{H_2O})$ for $[NCS^-] > 5$ M follows such a relation with $B = 0.173$. Equation (5) with $n = 4$ was used to

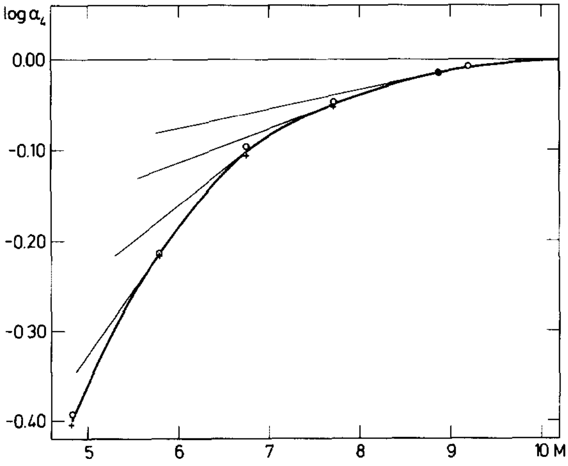

Fig. 3. Graph of log α_4 vs. $[NCS^-]$. Log α_4 is for solutions 8–13 in Table 2 calculated at two wavelengths: +, 620 nm with $\epsilon_3 = 65$; O, 630 nm with $\epsilon_3 = 57$.

calculate $\bar{n}$ and K_4 (Table 5). The slope δ is obtained with sufficient precision from the slope of the tangent to the curve as shown in Fig. 3.

(iii) From three absorption curves

A system of three absorption curves (I–III) which fulfills the condition of being isosbestic is sufficient for the calculation of the equilibrium constant, in the present case K_4. If the molar absorbances decrease in the order $\mathrm{I} < \mathrm{II} < \mathrm{III}$, K_4 can be calculated from eqn. (6) [9]:

$$\frac{(a_\mathrm{L})_\mathrm{III} - (a_\mathrm{L})_\mathrm{II} + \{(a_\mathrm{L})_\mathrm{III}(a_\mathrm{L})_\mathrm{I} - (a_\mathrm{L})_\mathrm{II}(a_\mathrm{L})_\mathrm{I}\}K_4}{(a_\mathrm{L})_\mathrm{III} - (a_\mathrm{L})_\mathrm{I} + \{(a_\mathrm{L})_\mathrm{III}(a_\mathrm{L})_\mathrm{II} - (a_\mathrm{L})_\mathrm{II}(a_\mathrm{L})_\mathrm{I}\}K_4} = \frac{\epsilon_\mathrm{III} - \epsilon_\mathrm{II}}{\epsilon_\mathrm{III} - \epsilon_\mathrm{I}} \tag{6}$$

The results of calculations with $a_\mathrm{L} = [\mathrm{NCS}^-]\gamma \pm {}^c/a_{\mathrm{H_2O}}$, and with the molar absorbances of solutions 10, 11, 12 and 14 in the wavelength range 610–640 nm are shown in Table 6.

The estimates made of the activity constant show that the value of K_4 must be close to 0.10 which may be compared with the value 0.05 given by Zeltmann and Morgan [4]. In solution 14 with $[\mathrm{NCS}^-] = 10.6$ M the ligand number must, according to our measurements, be close to four, whereas when calculated using Zeltmann and Morgan's constants it is only 3.90. Calculated with the same constants, but with $K_4 = 0.10$ instead of 0.05, it is 3.95, a value which is still somewhat too small.

F. THE TETRAHEDRAL BLUE COBALT(II) COMPLEX IN KETONIC SOLVENTS

Tribalat and Zeller [3] showed that the blue tetracyanato complex is extracted from aqueous alkali metal thiocyanate solutions into ketonic solvents. Under the present experimental conditions it was extracted as $\mathrm{Na_2Co(NCS)_4}$ or, in the case of acid solutions, as $\mathrm{H_2Co(NCS)_4}$.

TABLE 6

Estimation of K_4 by use of three absorption curves

Fraction	Calculated for K_4
$\frac{\epsilon_{14} - \epsilon_{11}}{\epsilon_{14} - \epsilon_{10}} = 0.538 \pm 0.015$	0.128 ± 0.040
$\frac{\epsilon_{12} - \epsilon_{11}}{\epsilon_{12} - \epsilon_{10}} = 0.437 \pm 0.015$	0.050 ± 0.013
	Average 0.09 ±0.03

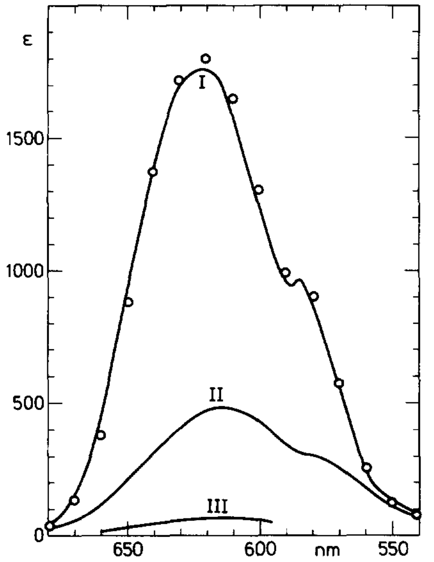

Fig. 4. Curve I, absorption spectrum (ϵ vs. λ) of $H_2Co(NCS)_4$ in 2-octanone ($C_{Co(II)} = 0.000412$) prepared by extraction from a 5 M NaNCS, 0.05 M acid cobalt(II) solution. The open circles indicate the nearly identical spectrum probably of $Na_2Co(NCS)_4$, in 2-hexanone ($C_{Co(II)} = 0.000249$ M) prepared by extraction from a similar $Co(NO_3)_2$–NaNCS solution but without added HNO_3. Curve II, spectrum of $[Co(NCS)_4]^{2-}$ in 10.6 M aqueous NaNCS. Curve III, estimated spectrum of $[Co(NCS)_3H_2O]^-$ in aqueous solution.

The spectrum of the cobalt complex was measured in both 2-hexanone and 2-octanone and is shown in Fig. 4. The cobalt complex is very easily soluble in the organic solvents, and the ketonic solutions of the blue complex were prepared by extraction from aqueous solutions for which the concentrations of HNO_3, $Co(NO_3)_2$ and NaNCS could be varied within wide limits without any influence on the spectrum.

G. THE EQUILIBRIUM BETWEEN TETRAHEDRAL AND OCTAHEDRAL COBALT(II) COMPLEXES IN AQUEOUS SOLUTION

The absorption band of the tetrathiocyanato complex in the ketonic solvents has a maximum at about the same wavelength as the tetracyanato complex in concentrated aqueous NaNCS, but an explanation is required for the fact that the molar absorbances in the ketonic solvents are more than three times higher than those in aqueous solution. From earlier studies [10] it is known that ligand field spectra of well-defined complexes have the same absorption, usually within 5–10%, in water and various organic solvents. The only possible explanation for the very different absorptions of the blue complex in the two solvents must therefore be that in the aqueous solutions there is an equilibrium between the strongly absorbing tetrahedral complex and a red more weakly absorbing octahedral complex $[Co(NCS)_4(H_2O)_2]^{2-}$. Although expected, no measurable absorption in the wavelength range 550–450 nm is shown by the blue cobalt complex in the ketonic solvents, contrary to its presence in the case of the octahedral complexes. The equilibrium constant

$$K_0 = \frac{\left[Co(NCS)_4^{2-}\right]}{\left[Co(NCS)_4(H_2O)_2^{2-}\right]} = \frac{495}{1770} = 0.28 \tag{7}$$

can therefore be calculated directly from the values of the absorption maxima in the two solvents (1770 in the ketonic and 495 in the aqueous solution). According to this result, the solution in 10.6 M aqueous NaNCS contains 28% of the tetrahedral complex and 72% of the octahedral complex $[Co(NCS)_4(H_2O)_2]^{2-}$. A solution with $C_{Co} = 0.02058$ M, $C_{NaNCS} = 8.55$ and $\bar{n} = 3.83$ (nearly saturated with blue crystals of $Na_2Co(NCS)_4 \cdot 8H_2O$) [11] was measured and found to have practically the same absorption in the wavelength range 520–450 nm as the solution in Fig. 1 with $\bar{n} = 2.97$. Quantitative information cannot be drawn from this fact, but it shows that a higher percentage of the cobalt is transformed to the tetrahedral complex in the solution with $\bar{n} = 3.83$ than in the solution with $\bar{n} = 2.97$. Furthermore, the octahedral monothiocyanato and dithiocyanato complexes must be assumed to be in equilibrium with minimal concentrations of the corresponding tetrahedral complexes. Thus Swaddle and Fabes [12] showed that at high temperature and pressure there exists, even for the hexaaquacobalt(II) ion, an equilibrium with the tetraaqua ion. According to their calculation at room temperature, less than 0.1% is present as the tetraaqua ion.

H. ON THE USE OF SEMI-THERMODYNAMIC STABILITY CONSTANTS

Reasonable results for weak complex formation at high salt concentrations have been obtained [9,13–15] simply by substituting the ligand-ion concentration in the concentration mass action expression:

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \tag{8}$$

with the mean activity $\gamma \pm [L]$ of the complex-forming salt. As the uptake of ligands is accompanied with loss of water molecules, it is theoretically more correct to introduce a correction for the rather considerable changes in the water activity in aqueous solutions at high salt concentrations. This correction was introduced by Zeltmann and Morgan [4] and also by the present author. However, it must not be forgotten that the constants obtained in this way are only "semi" thermodynamic. However, they are more reliable than the concentration constants obtained by maintaining a high constant ionic strength by addition of an inert salt such as $NaClO_4$, as has been discussed recently [16]. As activity constants, they are supposed to have the same values when either molal or molar concentrations are applied.

I. A COMPARISON WITH THE NICKEL(II) THIOCYANATE SYSTEM

The absorption spectra of nickel(II) thiocyanate solutions have recently been studied in aqueous NaNCS solution [15] and the fourth stability constant has been calculated from four isosbestic absorption curves using the expression

$$K_4 = \frac{[\mathrm{Ni(NCS)}_4^{2-}]}{[\mathrm{Ni(NCS)}_3^{-}][\mathrm{NCS}^{-}]\gamma \pm^{c}} \tag{9}$$

The average value is 0.12 ± 0.04. If a correction for the change in the water activity is introduced, then K_4 becomes 0.07 ± 0.02. This change in the value of K_4 has only a small influence on the calculated spectrum of the tetrathiocyanato complex (curve II in Fig. 5).

(i) A blue tetrahedral nickel(II) complex in hexanone

The aqueous Ni(II)–thiocyanato complexes with their relatively small molar absorbances and their maxima at the same wavelength as those of the hexaaqua ion, all have an octahedral configuration. The tetrathiocyanato complex must therefore have the constitution $[Ni(NCS)_4(H_2O)_2]^{2-}$, and the apparent cessation of the increase in the absorption after the uptake of four thiocyanate ions can only mean that the successive stability constants, K_5 and K_6, are too small to cause further complex formation in saturated aqueous solutions. In this connection, Rosenheim and Cohn [11] have reported a salt of the composition $K_4Ni(NCS)_6 \cdot 4H_2O$.

When a solution which is dilute in nickel(II) ions but concentrated in NaNCS was shaken with 2-hexanone, I found to my surprise that a blue strongly absorbing nickel(II) complex was extracted into the organic phase. This shows that also in octahedral nickel(II) systems, small concentrations of tetrahedral species must be in equilibrium with the octahedral complexes. When an aqueous solution of 0.02 M nickel(II) and 8.55 M NaNCS was shaken with an equal volume of hexanone, 11% of the nickel ions were extracted into the organic phase. The spectrum of the blue tetrathiocyanato complex is shown in Fig. 5. Tetrahedral nickel(II) complexes are Jahn–Teller

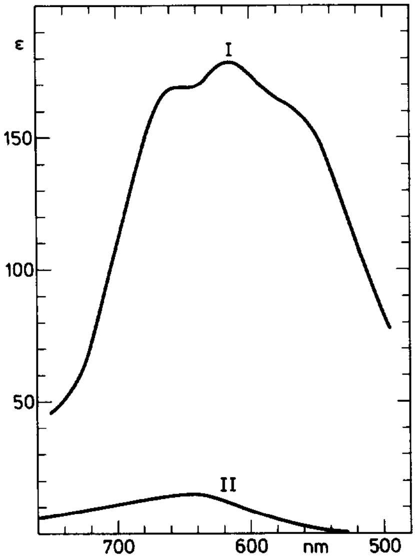

Fig. 5. Curve I, absorption spectrum (ϵ vs. λ) of $Na_2Ni(NCS)_4$ in 2-hexanone ($C_{Ni(II)}$ = 0.00215 M). Curve II, calculated spectrum of $[Ni(NCS)_4(H_2O)_2]^{2-}$ in aqueous NaNCS solutions [15].

destabilized. The isolated blue complex must therefore have a quasi-tetrahedral configuration, as opposed to the blue cobalt(II) complex which has a regular tetrahedral configuration.

J. CONCLUSIONS AND RESULTS

The spectra of the monothiocyanatocobalt(II) and dithiocyanatocobalt(II) complexes show that both these complexes have an octahedral configuration with N-bonded thiocyanate. Zeltmann and Morgan postulated from NMR measurements that the dithiocyanato complex changes to a tetrahedral configuration. This does not agree with the fact that the new band at 615 nm begins first to increase in intensity on formation of the trithiocyanato complex. The absorption band at ca. 615 nm increases in intensity with the thiocyanate concentration up to a limiting absorption of the tetrathiocyanato complex with $\epsilon_4(\max) = 495$. The molar absorption of the tetracyanato complex in ketonic solvents ($\epsilon_4(\max) = 1770$) was found to be much higher than that in aqueous solution. This leads to the conclusion that in aqueous solution there is equilibrium between the blue tetrahedral complex and an octahedral complex $[Co(NCS)_4(H_2O)_2]^{2-}$ with only 28% of the blue complex being present at equilibrium.

The fourth stability constant in its semi-thermodynamic form

$$K_4 = \frac{\left[\mathrm{Co(NCS)_4^{2-}}\right] a_{\mathrm{H_2O}}}{\left[\mathrm{Co(NCS)_3^-}\right]\left[\mathrm{NCS^-}\right] \gamma \pm^{c}} \qquad (10)$$

was estimated in various ways from the spectrophotometric measurements to have the value 0.10 ± 0.01 l mol^{-1} compared with Zeltmann and Morgan's value of 0.050 ± 0.06 for the same constant determined from NMR measurements. The nickel(II) thiocyanate system has been studied recently [15] and the fourth stability constant was recalculated using eqn. (10) as 0.07 ± 0.02 l mol^{-1}.

The Ni(II)–thiocyanato complexes all have octahedral configurations and the fourth complex formed in concentrated NaNCS solutions has $\epsilon_4(\mathrm{max}) = 15$. In the present study, it was shown that it is possible from such solutions to extract with hexanone a strongly absorbing blue complex with $\epsilon_4(\mathrm{max}) = 178$. This proves that octahedral complexes such as $[\mathrm{Ni(NCS)_4(H_2O)_2}]^{2-}$ must also be in equilibrium with minimal concentrations of a tetrahedral complex.

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