

An Infrared Spectroscopic Investigation of the Silver-Thiocyanato Complex System in Pyridine Solution

RAGNAR LARSSON and ATIS MIEZIS

Divison of Inorganic Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

The silver-thiocyanate system in pyridine solution has been investigated by means of infrared spectroscopic techniques.

As a result of the large frequency shift on complex formation (2059 cm^{-1} to 2089 cm^{-1}) the intensity of the C—N stretching vibration both of the free thiocyanate ion and the S-bonded mononuclear complexes could be measured for silver-thiocyanate solutions of various compositions. Three mononuclear complexes have thereby been established and the stability constants and the molar absorptivities of these determined (Table 4).

It has been found that there are great differences between this system in pyridine and in aqueous solution, especially regarding the greatly different amounts of polynuclear complexes formed in the two solvents (water > pyridine).

The infrared absorption corresponding to the C—N stretching vibration has in recent years been recorded for a large number of thiocyanato complexes.¹⁻⁸ From these studies some regularities can be found. One of these is the following rough relation between the bond types and the difference in the C—N frequency of the complex and that of the free ligand. M—NCS complexes: $\nu_{\text{complex}} - \nu_{\text{ligand}} < 25 \text{ cm}^{-1}$; M—SCN complexes: $15 \text{ cm}^{-1} < \nu_{\text{complex}} - \nu_{\text{ligand}} < 40 \text{ cm}^{-1}$; bridged M—SCN—M complexes: $\nu_{\text{complex}} - \nu_{\text{ligand}} > 30 \text{ cm}^{-1}$. As the overlap is quite obvious this is no good diagnostic tool for the determination of the bond type. As alternatives the absorption intensity of the C—N vibration absorption,^{1,6} or the frequencies of the C—S stretching² or the N—C—S bending vibration³⁻⁵ have been suggested.

In a previous study⁹ we started an infrared spectroscopic investigation on thiocyanato transition metal complexes in pyridine solution. A result of that work was the observation that the silver(I) system showed a considerable difference between the C—N frequency of the complex (or complexes), 2089 cm^{-1} , and the free ligand, 2059 cm^{-1} . This shift has made it possible to perform a determination of the stability constants from ligand concentration measurements. Furthermore, the shift is of such a magnitude that it is reasonable to

characterize the ligands as nonbridging. Whether the complexes are mononuclear or not, does not of course follow from this. On the other hand, it was also reported that at C_{Ag}/C_{SCN} ratios >1 a new absorption peak appeared at a higher frequency (2102 cm^{-1}). From the general trends of the IR spectra of thiocyanato complexes one can infer that this band corresponds to SCN-bridged complexes, at least if it can be shown that the first mentioned complexes are of the S-bonded type, which is most likely from the value of the integrated absorption.

In view of the possibility of polynuclear complex formation we initially investigated the Ag(I) system choosing the conditions such that no polynuclear complexes are formed. Finally the formation of the bridged complexes was studied.

It is well known that investigations of equilibria between ionic species in solution should be carried out at a high and constant ionic strength with the aid of a supporting, inert electrolyte. In this investigation, however, this was not possible as no suitable supporting electrolyte was sufficiently soluble in pyridine. Pyridinium perchlorate was soluble to the extent of about 1.5 M, but such solutions gave rise to a large light absorption in the actual spectral range. Hence the measurements had to be performed on solutions containing sodium thiocyanate and silver perchlorate, the formal ionic strength being that originating from the concentrations of the ionic species in solution.

Notations used in this paper

C_L	= total concentration of ligand
C_M	= » » » metal
$[L]$	= free » » ligand
$[M]$	= » » » metal
$\bar{n} = \frac{C_L - [L]}{C_M}$	= the mean ligand number
$[ML_n]$	= concentration of the n -th mononuclear complex
$\beta_n = \frac{[ML_n]}{[M][L]^n}$	= stability constant of the n -th mononuclear complex
β_0	= 1
X	= $\sum_{n=0}^N \beta_n [L]^n$
α_n	= $\frac{[ML_n]}{C_M} = \frac{\beta_n [L]^n}{X}$
k_1	= $\frac{[M_2L]}{[ML][M]}$; $k_2 = \frac{[M_2L_2]}{[ML]^2}$
A_ν	= absorbancy at the band maximum of wavenumber $\nu\text{ cm}^{-1}$
ϵ_L	= molar absorptivity of the free ligand
ϵ_n	= » » » » complex ML_n
ϵ_{2n}	= » » » » M_2L_n
d	= the cell thickness

EXPERIMENTAL CONDITIONS

Recording of the spectra. The measurements were made using a Perkin-Elmer 221, and matched cells with windows of NaCl were used in both the sample and reference beam. The solution in the reference cell was pure pyridine. The available cells had the following approximate thicknesses: 0.2, 0.1, and 0.03 mm. The measurements were somewhat complicated by the fact that it was very difficult to produce all the chemicals absolutely dry and also because of the tendency of pyridine to absorb moisture. The moisture present attacked the surfaces of the NaCl windows during the measurements and it was thus necessary to redetermine the cell thicknesses regularly. The wave number readings of the instrument in the spectral region under investigation (2300–1900 cm^{-1}) were checked periodically by measuring the spectra of carbon monoxide in a 10 cm gas cell.

Chemicals used. All chemicals were of analytical grade and used without further purification.

The solutions to be investigated were made from stock solutions, 1 M NaSCN and 0.5 M AgClO_4 in pyridine, with the exception of those of the highest concentrations, which were made up by dissolving weighed amounts of the salts. Silver perchlorate was prepared from silver oxide and perchloric acid, and after recrystallisation the stock solution was prepared, the concentration of which was determined by electrolysis.

Testing of Beer's law. In order to verify the Lambert-Beer's law and to obtain spectral data of the free thiocyanate ion, measurements of NaSCN in pyridine were made. The following values were obtained:

$$\begin{aligned} \nu_{\text{SCN}} &= 2059 \text{ cm}^{-1} \\ \epsilon_{\text{SCN}} &= 1.02 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1} \\ \Delta\nu_{1/2} &= 15 \text{ cm}^{-1} \\ \epsilon \cdot \Delta\nu_{1/2} &= 1.53 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \end{aligned}$$

For the highest SCN^- concentrations a deviation from Beer's law was observed (Fig. 1). The deviation from a straight line, perhaps caused by some type of ion-association or from stray light effects, was such that the calculated values of the molar absorptivity, ϵ , were low. Therefore when analyzing the Ag(1)-thiocyanato system at high $[\text{SCN}^-]$ the free $[\text{SCN}^-]$ was calculated using these lower values of ϵ obtained as accurately as possible from the plot of A versus C_{SCN} reproduced in Fig. 1.

NONBRIDGED COMPLEXES

The method of measurement is based on the determination of the concentration of the free ligand from the relationship:

$$A_{2059} = d \cdot \epsilon_L [\text{L}] \quad (1)$$

For a series of solutions of general composition C_M M AgClO_4 and C_L M NaSCN, where C_M was kept constant and $C_L > C_M$, one can thus determine the mean ligand number:

$$\bar{n} = \frac{C_L - [\text{L}]}{C_M} \quad (2)$$

If only mononuclear complexes are present it should then be possible to obtain the polynomial X by the graphical method developed by Fronæus.¹⁰ It holds that

$$\ln X([\text{L}]_j) = \int_0^{[\text{L}]_j} \bar{n}/[\text{L}] \, d[\text{L}] \quad (3)$$

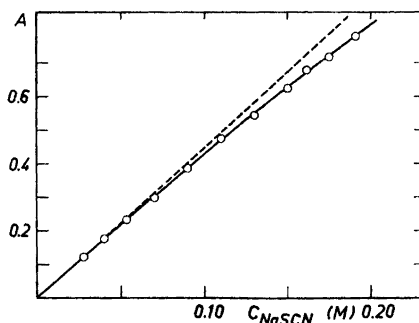


Fig. 1. Optical densities of solutions of NaSCN (Beer-law plot). $d = 4.40 \times 10^{-3}$ cm.

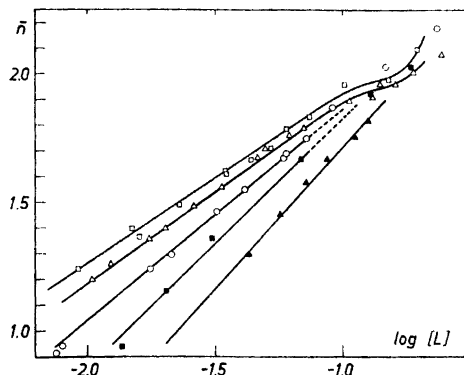


Fig. 2. \bar{n} as a function of $\log [L]$ for different values of C_M . $C_M = 0.025$ M (\square), $C_M = 0.050$ M (\triangle), $C_M = 0.10$ M (\circ), $C_M = 0.20$ M (\blacksquare), and $C_M = 0.40$ M (\blacktriangle).

If polynuclear complexes are present \bar{n} is a function not only of $[L]$ but also of C_M . In order to avoid this difficulty measurements were performed at several values of the parameter C_M . \bar{n} was plotted against $[L]$ and the curves thus obtained were intercepted at a number of constant values of $[L]$. Using the points of intersection, \bar{n} was plotted against C_M and the curves extrapolated to $C_M = 0$. Thus $[\bar{n}]_{C_M=0}$ and $(\bar{n}/[L])_{C_M=0}$ could be obtained for each value of $[L]$. Consequently eqn. (3) is replaced by

$$\ln X([L]_j) = \int_0^{[L]_j} (\bar{n}/[L])_{C_M=0} d[L] \quad (4)$$

Eqn. (4) thus gives the polynomial X for the mononuclear complexes, whether or not polynuclear complexes are found. It should be noted that this procedure also causes other C_M -depending effects, that may be caused by, *e.g.*, non-constancy of the ionic strength, to vanish. The stability constants can then be calculated graphically by the commonplace procedure of plotting the functions

$$X_n = \frac{X_{n-1} - \beta_{1-n}}{[L]} \text{ versus } [L] \text{ and extrapolating to } [L] = 0.$$

Knowing the stability constants of the mononuclear complexes the molar absorptivities of these complexes can be calculated from the measured absorbancy of the 2089 cm^{-1} absorption band. As we have assumed this band to correspond to nonbridged complexes it is thus the molar absorptivities of the mononuclear, nonbridged complexes that result from such a calculation.

It holds that

$$A_{2089} d^{-1} = \sum_{n=1}^N \epsilon_n [ML_n] \quad (5)$$

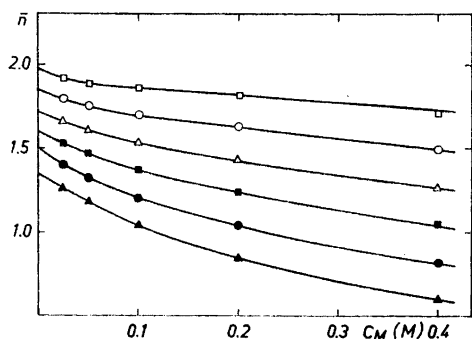


Fig. 3. \bar{n} as a function of C_M for different values of $[L]$. $[L]=0.100$ M (\square), $[L]=0.063$ M (\circ), $[L]=0.040$ M (\triangle), $[L]=0.025$ M (\blacksquare), $[L]=0.016$ M (\bullet), and $[L]=0.010$ M (\blacktriangle).

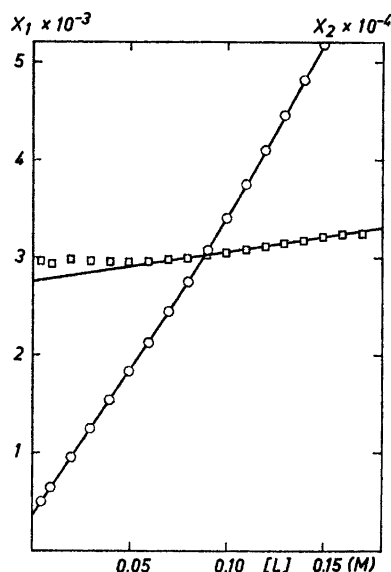


Fig. 4. X_1 (\square) and X_2 (\circ) as a function of $[L]$.

or

$$A_{2089} \cdot d^{-1} \cdot C_M^{-1} = \sum_{n=1}^N \varepsilon_n \alpha_n \quad (6)$$

From this relation ε_1 can be obtained graphically, e.g. by plotting $A_{2089} \cdot d^{-1} \cdot C_M^{-1} \cdot \alpha_1^{-1}$ versus $[L]$ and extrapolating to $[L]=0$. Thereafter the other parameters ε_n can be calculated by a similar technique.

Results. The experimental data and the mean ligand number calculated from these, for five different values of C_M , are given in Tables 1 and 2. In Fig. 2, \bar{n} is represented as a function of $\log [L]$. It is clearly observed that \bar{n} is dependent on C_M . Consequently the extrapolation procedure described above was applied. Fig. 3 shows the extrapolation curves for some different values of $[L]$. By graphical integration X was then obtained and the stability constants could be calculated, also graphically (Fig. 4). They are included in Table 4.

In order to determine the molar absorptivities of the three complexes thus established, $A_{2089} \cdot d^{-1} \cdot C_M^{-1} \cdot \alpha_1^{-1}$ was plotted against $[L]$ (Fig. 5). As could be expected this function was also dependent on C_M and an extrapolation to $C_M=0$ was undertaken (Fig. 6). Thereafter ε_2 and ε_3 could be determined from the intercept and slope, respectively, of the entity $(A_{2089} \cdot d^{-1} \cdot C_M^{-1} \cdot \alpha_1^{-1} - \varepsilon_1) \cdot [L]^{-1}$ plotted against $[L]$ (Fig. 7). The results expressed as molar absorptivity per SCN-group are given in Table 4.

Table 1. Experimental values of the absorbance of the ligand and complex absorption peaks together with the experimental values of n .

C_M (M)	C_L (M)	$d \times 10^3$ (cm)	Free ligand			Complex	
			A_{2089}	[L] (M)	\bar{n}	A_{2089}	$\frac{A}{d}$ (cm ⁻¹)
0.0249	0.0401	2.04	0.1938	0.0093	1.236	0.3565	17.5
0.0249	0.0501	2.04	0.3354	0.0161	1.365	0.3938	19.3
0.0249	0.0501	2.07	0.3209	0.0152	1.401	0.4035	19.5
0.0249	0.0601	2.04	0.4789	0.0230	1.490	0.4191	20.5
0.0249	0.0751	0.968	0.3470	0.0351	1.606	0.2083	21.5
0.0250	0.0753	0.947	0.3468	0.0349	1.619	0.2083	21.4
0.0249	0.0853	0.968	0.4318	0.0437	1.666	0.2223	23.0
0.0249	0.0952	0.968	0.5207	0.0527	1.704	0.2283	23.6
0.0249	0.1053	0.968	0.6015	0.0609	1.781	0.2333	24.1
0.0249	0.1201	0.295	0.2161	0.0746	1.829	0.0747	25.3
0.0250	0.1513	0.448	0.4382	0.1023	1.960	0.1148	25.6
0.0250	0.2009	0.448	0.6351	0.1515	1.972	0.1264	28.2
0.0249	0.2493	0.448	0.8000	0.1970	2.100	0.1288	28.7
0.0499	0.0703	0.940	0.1013	0.0106	1.196	0.3193	34.0
0.0499	0.0752	2.04	0.2599	0.0125	1.258	0.6889	33.8
0.0499	0.0852	0.940	0.1691	0.0176	1.356	0.3600	38.3
0.0498	0.0902	0.970	0.2028	0.0205	1.389	0.3765	38.9
0.0498	0.0902	0.440	0.0917	0.0204	1.400	0.1551	35.3
0.0499	0.1004	2.04	0.5447	0.0262	1.487	0.8116	39.8
0.0499	0.1303	0.440	0.2013	0.0468	1.675	0.1871	42.5
0.0498	0.1503	0.940	0.5999	0.0626	1.761	0.4520	48.1
0.0498	0.1601	0.440	0.3063	0.0712	1.786	0.1979	45.0
0.0498	0.2002	0.440	0.4506	0.1060	1.893	0.2155	49.0
0.0498	0.2403	0.440	0.5952	0.1427	1.961	0.2294	52.1
0.0498	0.2601	0.440	0.6701	0.1622	1.963	0.2316	53.0
0.0498	0.2813	0.440	0.7431	0.1812	2.011	0.2374	54.1
0.0499	0.3510	0.322	0.8127	0.2474	2.078	0.2236	69.4
0.1032	0.1015	0.940	0.0738	0.0077	0.909	0.4980	53.0
0.1032	0.1049	0.940	0.0773	0.0081	0.938	0.5057	53.8
0.1030	0.1452	0.940	0.1694	0.0177	1.238	0.6622	70.4
0.0998	0.1506	2.07	0.4547	0.0215	1.293	—	—
0.1028	0.1827	0.940	0.3088	0.0322	1.464	0.7574	80.6
0.1028	0.1996	0.940	0.3922	0.0409	1.544	0.8240	87.7
0.0997	0.2256	0.970	0.5817	0.0589	1.672	0.8721	90.1
0.1026	0.2332	0.940	0.5763	0.0601	1.687	0.8706	92.6
0.1026	0.2514	0.940	0.6911	0.0721	1.748	0.9115	97.0
0.1024	0.2827	0.940	0.8739	0.0911	1.871	0.9675	102.9
0.0998	0.3514	0.299	0.4181	0.1487	2.030	0.3054	102.1
0.0997	0.4512	0.300	0.6383	0.2341	2.177	0.3363	112.1
0.1992	0.2004	2.04	0.2844	0.0137	0.937	—	—
0.1992	0.2505	2.04	0.4254	0.0205	1.155	—	—
0.1994	0.3009	0.430	0.1371	0.0309	1.354	0.5973	139.0
0.1992	0.4008	0.430	0.2937	0.0689	1.666	0.7379	171.6
0.1993	0.5021	0.430	0.5274	0.1189	1.923	0.8464	196.8
0.1995	0.5931	0.430	0.7443	0.1880	2.031	0.8857	206.0

Table 1. Continued.

0.3993	0.5599	0.940	0.4159	0.0434	1.294		
0.3988	0.6370	0.322	0.1889	0.0575	1.453		
0.3993	0.7018	0.430	0.3072	0.0728	1.575		
0.3988	0.7534	0.430	0.3675	0.0875	1.670		
0.3987	0.8122	0.430	0.4654	0.1126	1.755		
0.3993	0.8529	0.430	0.5217	0.1276	1.816		

SCN-BRIDGED COMPLEXES

As mentioned above the new absorption band appearing at 2102 cm^{-1} when $C_M > C_L$ is probably to be attributed to SCN-bridged complexes. By definition these must contain more than one metal ion. As the accuracy of measurement does not allow a detailed analysis, we have chosen to deal with the least possibly complicated model, *viz.* we assume the existence of a series of complexes M_2L_n where $n \leq 2$. When C_M is large and consequently $[L]$ is small, the only mononuclear, nonbridged complex of any importance is assumed to be ML, an assumption strengthened by the measurements reported above.

The quantity to be measured is then the concentration of ML. As we have already determined ε_1 it follows that

$$[\text{ML}] = A_{2089}/d \varepsilon_1 \quad (7)$$

Our assumptions lead to

$$C_M = [M] + [\text{ML}] + 2[\text{M}_2\text{L}] + 2[\text{M}_2\text{L}_2] \quad (8)$$

Table 2. Experimental values of the halfwidth of the ligand and complex absorption peaks.

C_M	$[L]$ (M)	$\nu_{1/2}$ (L) (cm^{-1})	$\nu_{1/2}$ (ML_n) (cm^{-1})	C_M	$[L]$ (M)	$\nu_{1/2}$ (L) (cm^{-1})	$\nu_{1/2}$ (ML_n) (cm^{-1})
0.025 M	0.0093	17.4	18.9	0.10 M	0.0077	21.2	18.6
	0.0161	16.1	20.5		0.0081	21.2	18.6
	0.0230	15.3	21.4		0.0177	18.3	20.1
	0.0349	15.4	23.8		0.0322	17.1	21.3
	0.1023	15.1	—		0.0409	17.3	21.4
	0.1515	15.4	—		0.0601	17.4	22.6
0.05 M					0.0721	17.3	22.6
	0.0106	17.6	19.5	0.0911	17.6	22.6	
	0.0125	18.5	19.8	0.20 M			
	0.0176	17.0	20.1		0.0309	19.9	21.0
	0.0262	17.5	21.3		0.0689	19.8	22.4
	0.0626	16.1	23.6		0.1189	18.3	23.3
	0.1812	16.4	26.9		0.1880	18.5	25.0
	0.2474	16.5	30.0				

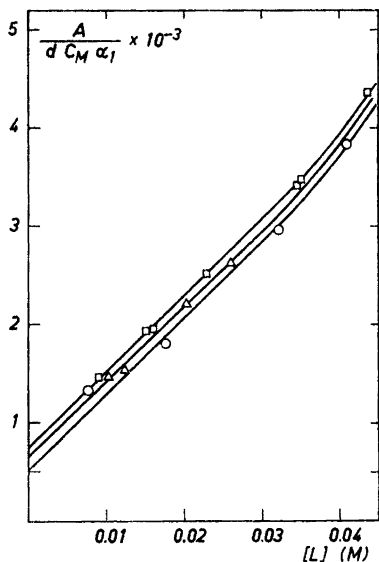


Fig. 5. $A/d \cdot C_M \alpha_1$ as a function of $[L]$ for different values of C_M . $C_M = 0.025$ M (\square), $C_M = 0.050$ M (\triangle), and $C_M = 0.10$ M (\circ).

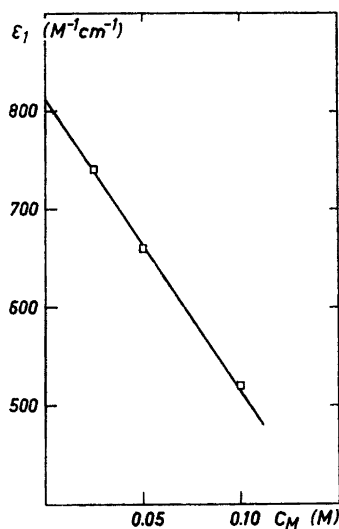


Fig. 6. ϵ_1 as a function of C_M .

and

$$C_L = [ML] + [M_2L] + 2[M_2L_2] + [L] \quad (9)$$

Neglecting the last term in eqn. (9), this eqn. can be written as

$$\frac{C_L - [ML]}{[ML]^2} = k_1 \frac{[M]}{[ML]} + 2k_2 \quad (10)$$

Combining eqns. (8) and (9) one obtains ($[L]$ still neglected)

$$[M](1 + k_1[ML]) = C_M - C_L \quad (11)$$

Introducing eqn. (11) into (10) the final expression obtained is

$$\frac{C_L - [ML]}{[ML]^2} = k_1 \frac{C_M - C_L}{(1 + k_1[ML])[ML]} + 2k_2 \quad (12)$$

The constants k_1 and k_2 were solved by a series of successive approximations. First, the last term of eqn. (12) was neglected, *i.e.* $[M_2L_2]$ was considered small, and an approximate value of k_1 was determined for each experimental value of C_M and C_L ($[ML]$ given by eqn. (7)). Using these approximate values of k_1 $(C_L - [ML])/[ML]^2$ was plotted against $(C_M - C_L)/((1 + k_1[ML]) \cdot [ML])$. From the slope and intercept of the resulting approximately straight line new values of k_2 and k_1 could be determined, and this procedure was then repeated until no further change in the values of the constants was found.

Table 3. Variation of the absorption data of the complex peak for $C_M > C_L$.

C_M (M)	C_L (M)	$d \times 10^3$ (cm)	A_{2089}	$\frac{A}{d}$ (cm ⁻¹)	$\Delta\nu_{1/2}$ (cm ⁻¹)
0.0998	0.1004	0.970	0.4815	49.6	18.3
0.1744	0.1002	0.973	0.4689	48.2	18.9
0.1997	0.1004	0.976	0.4663	47.8	19.1
0.2243	0.1003	0.979	0.4563	46.6	20.0
0.2490	0.1002	1.005	0.4613	45.9	20.1
0.2740	0.1002	1.001	0.4464	44.6	21.1
0.2993	0.1003	0.997	0.4412	44.3	21.5
0.3238	0.1002	0.994	0.4321	43.5	22.4
0.3490	0.1003	0.991	0.4229	42.7	22.6
0.3733	0.1001	0.988	0.4186	42.4	23.4
0.3981	0.1001	0.985	0.4183	42.5	23.6
0.4231	0.1001	0.982	0.4045	41.2	24.4

The molar absorptivities of the two complexes M_2L and M_2L_2 were then determined by resolving the two bands with absorption maxima at 2089 cm⁻¹ and 2102 cm⁻¹. This is easily done if it is assumed that the band at 2089 cm⁻¹ is symmetric about the maximum. For the resulting absorbancy at 2102 cm⁻¹ the following must be true

$$\frac{A/d C_M \alpha_1 - \epsilon_l}{[L]} \times 10^{-4}$$

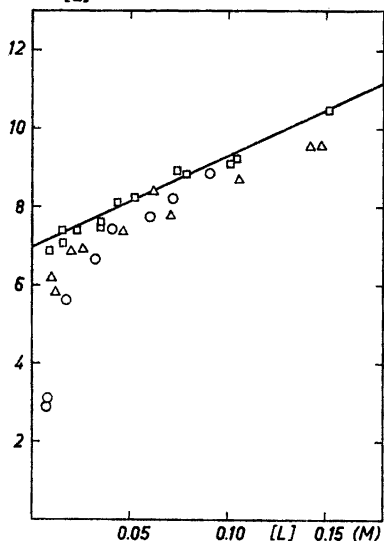


Fig. 7. $(A \cdot d^{-1} \cdot C_M^{-1} \cdot \alpha_1^{-1} - \epsilon_l) / [L]$ as a function of $[L]$ for different values of C_M . $C_M = 0.025$ M (\square), $C_M = 0.050$ M (Δ), and $C_M = 0.10$ M (\circ).

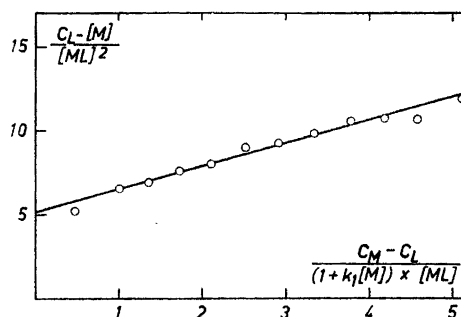


Fig. 8. $(C_L - [ML]) / [ML]^2$ as a function of $(C_M - C_L) / (1 + k_1[M]) \cdot [ML]$.

$$A/d = \epsilon_{21} [M_2L] + \epsilon_{22} [M_2L_2]$$

or

$$\frac{A}{d[M_2L]} = \epsilon_{21} + \epsilon_{22} \frac{[M_2L_2]}{[M_2L]}$$

Thus by plotting $A \cdot d^{-1} [M_2L]^{-1}$ against $[M_2L_2] \cdot [M_2L]^{-1}$ the molar absorptivities can be determined from a straight line.

Results. The absorbancy of the ML band at its maximum (2089 cm^{-1}) is given in Table 3 for a series of C_M values at a constant value of C_L ($C_M > C_L$). This table also shows the halfwidth of the band. Note that $\Delta\nu_{1/2}$ is the overall halfwidth of the mononuclear complex band and the overlapping SCN-bridged complex band with a maximum at 2102 cm^{-1} . These bands could not be resolved by the apparatus. (See Fig. 2 c in Ref. 9).

Following the procedure outlined above, initial approximate values of k_1 were determined for each C_M . k_1 turned out to decrease with increasing C_M , varying from *ca.* 10 to 2.5 M^{-1} within the experimental range of concentration. In the next approximation the values $k_1 = 1.32 \text{ M}^{-1}$ and $k_2 = 2.9 \text{ M}^{-1}$ emerged. Introducing this latter value of k_1 resulted in $k_1 = 1.36 \text{ M}^{-1}$ and $k_2 = 2.6 \text{ M}^{-1}$ (Fig. 8). Further repetitions did not result in any variation from these values. The constants k_1 and k_2 are included in Table 4 together with the values of the molar absorptivities of the two complexes.

DISCUSSION

Some principal difficulties inherent in the present type of investigation are mainly caused by the absence of a supporting electrolyte. The first is that we cannot test the adherence to Beer's law of the complex species present. Since a deviation is found at high concentrations of the free ligand it is also possible that such deviations occur for other species. This of course affects the accuracy of the value of ϵ of the nonbridged complexes. This is especially serious in the case of ϵ_1 since this value is used in the calculation of k_1 and k_2 of the SCN-bridged complexes. However, in these measurements A_{2089} is not changing very much and a false value of ϵ_1 can give at most a false value for the constants, not a false number of the existing species.

Table 4. Spectral parameters and stability constants of the investigated complexes.

Complex	$\nu_{\text{CN}} \text{ cm}^{-1}$	Stability constants	Molar absorptivity (per SCN ⁻ -group) ($\text{M}^{-1} \text{ cm}^{-1}$)
AgSCN	2089	$\beta_1 = (3.55 \pm 0.20) \times 10^2 \text{ (M}^{-1}\text{)}$	$\epsilon_1 = 810 \pm 50$
Ag(SCN) ₂	2089	$\beta_2 = (2.75 \pm 0.25) \times 10^4 \text{ (M}^{-2}\text{)}$	$\epsilon_2 = 450 \pm 75$
Ag(SCN) ₃	2089	$\beta_3 = (3.1 \pm 1.0) \times 10^4 \text{ (M}^{-3}\text{)}$	$\epsilon_3 = 870 \pm 200$
Ag ₂ SCN	2102	$k_1 = 1.4 \pm 0.2 \text{ (M}^{-1}\text{)}$	$\epsilon_{21} = 330 \pm 100$
Ag ₂ (SCN) ₂	2102	$k_2 = 2.6 \pm 0.5 \text{ (M}^{-1}\text{)}$	$\epsilon_{22} = 190 \pm 50$

Secondly, the numerical value of β_2 and especially of β_3 is affected by the variation of the activity factors. However, as \bar{n} for high values of C_L is larger than 2, the existence of the third complex seems to be beyond doubt.

The occurrence of variations in the activity coefficients of the different species is drastically illustrated by the variation of $\bar{n}/[L]$ with C_M (Fig. 3). One observes that the slope is negative. Had the existence of polynuclear complexes — of any kind, not necessarily SCN-bridged ones — been the cause of this variation, the slope would have been positive (*cf.* Fronæus, Ref. 10). The probable explanation of this effect is that changes in the activity coefficients are caused by the varying ionic strength of the solutions. Another equally reasonable explanation is that small amounts of water originating from the silver perchlorate preparation could cause the effect in question.

As pointed out earlier⁹ the coordination between silver and thiocyanate ions in pyridine stands in contrast to that in aqueous solution. Leden and Nilsson¹¹ have found that in aqueous solution formation of a series of polynuclear complexes $Ag_m(SCN)_{m+2}^{(m+2)-}$, $m \geq 2$, is considerable at high concentrations of thiocyanate and not as in pyridine only when $C_M > C_L$. This difference may be caused by the stronger complexing power of pyridine compared with that of water. Pyridine competes with the thiocyanate ions for the seats of coordination on the silver ions and partly block these for the bridging SCN-groups. It is perhaps for the same reason also that the mononuclear complexes are much stronger in aqueous solution than in pyridine. In aqueous solutions β_2 values between 10^8 and $10^{10} M^{-2}$ and β_3 values between 10^{10} and $10^{11} M^{-3}$ have been reported,¹² whereas we have found $\beta_2 = 2.8 \times 10^4 M^{-2}$ and $\beta_3 = 3.1 \times 10^4 M^{-3}$ in pyridine solution. Note that this is in accordance with the findings of Tramer¹³ on the S-bonding complexes $Hg(SCN)_2L_2^{2-}$, $L = Cl, Br, \text{ or } I$, where it is apparent that the stronger the $Hg-L$ bond the weaker the $Hg-SCN$ bond. However, when the thiocyanate ions are bound *via* nitrogen (*cf.* the bivalent first-row transition metals in Ref. 9) the thiocyanate complexes are much stronger in pyridine than in water. A reasonable explanation as to this behaviour could be the following: While the $M-NCS$ bond can be described as a σ bond the $M-SCN$ in addition would have a π bonding contribution caused by a backdonation of electrons from the filled nonbonding d -orbitals of the metal to vacant orbitals located on the sulphur atom. When pyridine coordinates to the metal there would be a withdrawal of electrons, although not very strong, by the pyridine ring from the metal and the $M-SCN$ π bond would be reduced, resulting in weaker S-bonded thiocyanate complexes in pyridine than in water. The σ bonding $M-NCS$ on the other hand would be enhanced by this effect, giving stronger complexes in pyridine than in water.

Another difference between the two systems is shown by the work of Kinell and Strandberg.¹⁴ When recording Raman spectra of silver-thiocyanate complexes in aqueous solutions they obtained broad diffuse bands at the C-N stretching frequency and not the fairly well identifiable peaks we have found in the IR-investigation in pyridine. This behaviour may also be attributed to the degree of bridging polynuclear complexes in aqueous solution. The C-N stretching vibrations of the various mononuclear complexes in solution seem to have the same frequency, whereas the bridging SCN-groups have a

somewhat higher C—N frequency. In the cases where polynuclear complexes are present, each contributes with its own absorption band, resulting in a broad and diffuse band.

The financial support of the *Swedish Natural Science Research Council* and the *Faculty of Science, Lund*, is gratefully acknowledged.

REFERENCES

1. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1447.
2. Burmeister, J. L. and Basolo, F. *Inorg. Chem.* **3** (1964) 1587.
3. Sabatini, A. and Bertini, I. *Inorg. Chem.* **4** (1965) 959.
4. Sabatini, A. and Bertini, I. *Inorg. Chem.* **4** (1965) 1665.
5. Bertini, I. and Sabatini, A. *Inorg. Chem.* **5** (1966) 1025.
6. Pecile, C. *Inorg. Chem.* **5** (1966) 210.
7. Bennett, M. A., Clark, R. J. H. and Goodwin, A. D. J. *Inorg. Chem.* **6** (1967) 1625.
8. Clark, R. J. H. and Williams, C. S. *Spectrochim. Acta* **22** (1966) 1081.
9. Larsson, R. and Mieziš, A. *Acta Chem. Scand.* **19** (1965) 47.
10. Fronæus, S. *Determinations of Formation Constants of Complexes*, In Jonassen, A. B. and Weinberger, A. *Techniques of Inorganic Chemistry*, Interscience, New York and London 1963, Vol. 1, Chapt. 1.
11. Leden, I. and Nilsson, R. *Z. Naturforsch.* **10a** (1955) 67.
12. *Stability Constants*, The Chemical Society, London, 1964.
13. Tramer, A. *J. Chim. Phys.* **59** (1962) 232.
14. Kinell, P. O. and Strandberg, B. *Acta Chem. Scand.* **13** (1959) 1607.

Received May 22, 1968.