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

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The frequency and intensity of the C—N stretching vibration have been measured for the thiocyanate ion and the thiocyanato complexes of cobalt(II) in five different non-aqueous solvents (acetoniitrile, propane-1,2-diolcarbonate, trimethylphosphate, dimethylacetamide, and dimethyl sulfoxide). It has been concluded that the thiocyanate groups are N-bonded and that the first complex has an octahedral configuration [Co(NCS)D₆]⁺ (D is the solvent).

The stability constants of the first complex have also been determined and the results are discussed with regard to the donor properties of the solvents.

The majority of useful solvents in coordination chemistry appears to have donor properties. Therefore, the ligands to be coordinated to a metal ion in such solvents would have to compete with the solvent molecules for the coordination sites. The stability of a metal-ligand complex system would then be dependent on the donor strength of the solvent. Gutmann et al.¹ have made calorimetric measurements on the interactions of a large number of solvent molecules (D) with antimony(V) chloride as reference acceptor in an inert solvent (dichloroethane), and determined the heats of reaction for

\[ D + SbCl₅ \rightleftharpoons D SbCl₅; \quad -\Delta H_{DSbCl₅} \]

For the reactions investigated this quantity is proportional to the logarithm of the formation constant of DSbCl₅ obtained from spectrophotometric¹ and NMR-measurements.²

Gutmann³ suggests that the \(-\Delta H_{DSbCl₅}\) values can be used as representative expressions for the degree of interaction between donor and acceptor and defines the donor number (DN) as the numerical quantity of \(-\Delta H_{DSbCl₅}\)

\[ DN_{SbCl₅} = -\Delta H_{DSbCl₅} \]

The donor numbers of many solvents together with their dielectric constants can be found, e.g. in Ref. 3, p. 69. These values for the solvents studied in this paper are also given in Table 1.

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Table 1. The donor numbers $DN_{\text{SbCl}_3}$ and the dielectric constants $\varepsilon$ of the solvents used.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$DN_{\text{SbCl}_3}$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile (AN)</td>
<td>14.1</td>
<td>38.0</td>
</tr>
<tr>
<td>Propane-1,2-diolcarbonate (PDC)</td>
<td>15.1</td>
<td>69.0</td>
</tr>
<tr>
<td>Water</td>
<td>18.0</td>
<td>81.0</td>
</tr>
<tr>
<td>Trimethylphosphate (TMP)</td>
<td>23.0</td>
<td>20.6</td>
</tr>
<tr>
<td>$N,N$-Dimethylacetamide (DMA)</td>
<td>27.8</td>
<td>38.9</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td>29.8</td>
<td>45.0</td>
</tr>
</tbody>
</table>

Of course, the numerical values of the donor numbers are only valid for SbCl$_3$ as acceptor, but one could expect that their relative order is maintained with other acceptors if the bonding character is not changed too much. Gutmann $^3$ has demonstrated this by studies on the stability of halido and pseudo-halido complexes of Co(II) in various donor solvents. Thus, the molar ratios $X^-/\text{Co}^{2+}$ required to obtain the tetrahedral CoX$_4^{2-}$ for various solvents usually increase with increasing donor number of the solvent but the correlation is not perfect.

The general study of complex formation in non-aqueous solvents has been neglected up to the present time. The best way to describe a complex system is to determine the stability constants by equilibrium analysis. One of the ligands used by Gutmann in his studies of the influence of solvent donor properties on the stability of a complex system is the thiocyanate ion, SCN$^-$. The thiocyanato complexes may, with advantage be studied by infrared spectroscopy $^4$ owing to the distinct absorption band of the C–N stretching vibration.

Usually there is no detectable difference in the frequency of this vibration between consecutively formed complexes. But when this frequency of the complexes is compared with that of the "free" ligand there would often be a frequency shift. If the frequency shift is large it is possible to obtain the stability constants from "free" ligand concentration measurements using the "free" ligand band. $^5$ For the Co$^{2+}$–NCS$^-$ systems in this study, however, the consecutively formed complexes do not have the same frequency of the C–N stretching vibration. Furthermore, only the first complex shows a large frequency shift upon coordination whereas the frequencies of the other complexes lie close to that of the "free" ligand. This makes it impossible to use the "free" ligand band for the determination of the stability constants. In its place the first complex band can be used and the method is described below. Of course, only the stability constant of the first complex may be determined in this way but nevertheless any constants would be of value when discussing donor properties of solvents.

The solvents investigated were: acetonitrile ($\text{CH}_3\text{CN}$), propane-1,2-diolcarbonate ($\text{C}_4\text{H}_6\text{O}_3$), trimethylphosphate [$\text{CH}_3\text{O}_3\text{PO}$], $N,N$-dimethylacetamide [$\text{CH}_3\text{CON}(\text{CH}_3/2)$] and dimethyl sulfoxide [($\text{CH}_3\text{SO}$)].

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PRINCIPLE OF INVESTIGATION

The method is thoroughly described in Ref. 5, and therefore only a short presentation will be made here of the actual conditions and the equations used in the calculations.

Notations

\[ C_M = \text{total concentration of metal} \]
\[ C_L = \text{total concentration of ligand} \]
\[ [M] = \text{free concentration of metal} \]
\[ [L] = \text{free concentration of ligand} \]
\[ [ML] = \text{concentration of the first complex} \]
\[ \beta_1 = [ML]/[M][L] = \text{stability constant of the first complex} \]
\[ A_\nu = \text{absorbance at the band maximum of the first complex (at the wave number } \nu) \]
\[ A_\nu^\circ = \text{absorbance when } C_M \rightarrow \infty \]
\[ \varepsilon_1 = \text{molar absorption coefficient of the first complex at the band maximum} \]
\[ \varepsilon_{L\nu} = \text{molar absorption coefficient of the "free" ligand at the wave number } \nu \]
\[ d = \text{the cell thickness} \]

For all experimental series, \( C_L \) was kept constant while \( C_M \) was varied. If \( C_M > C_L \) it may be assumed that ML was the only mononuclear complex of importance. The existence of polynuclear complexes was excluded as it probably would imply an absorption band at somewhat higher frequencies and no such band was found for the actual systems. Then

\[ C_M = [M] + [ML] \tag{1} \]
\[ C_L = [L] + [ML] \tag{2} \]
\[ A_\nu = \varepsilon_1 [ML] d + \varepsilon_{L\nu} [L] \tag{3} \]

In the systems investigated there was always a large difference in frequency between the absorption band maxima of the ligand and the first complex. Therefore, \( \varepsilon_{L\nu} \) would be very small and the last term in eqn. (3) may be neglected. Then, by combining eqns. (1) - (3) (cf. Ref. 5, p. 1437) one can obtain the following relation:

\[ A_\nu = A_\nu^\circ - A_\nu/[\beta_1(C_M - C_L A_\nu/A_\nu^\circ)] \]

Thus, \( A_\nu \) plotted against \( A_\nu/(C_M - C_L A_\nu/A_\nu^\circ) \) should give a straight line with the slope \(-1/\beta_1\). \( A_\nu^\circ \) was not known at first but may as a first approximation be set to \( A_\nu^\circ \approx A_\nu \). That means that first \( A_\nu \) was plotted against \( A_\nu/(C_M - C_L) \) and a new value of \( A_\nu^\circ \) was obtained as the intercept on the ordinate axis. With this value of \( A_\nu^\circ \) inserted a renewed plotting could be done and so on until no perceivable change in the parameters was found.

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EXPERIMENTAL CONDITIONS

Chemicals used. All the chemicals used were of analytical grade. The solutions to be titrated were made from anhydrous stock solutions of cobalt(II) perchlorate and sodium thiocyanate in five different solvents. They were: Acetonitrile, purified by repeated distillations over \( \text{P}_2\text{O}_5 \), until this no longer became brown-coloured, and then once over \( \text{CaCO}_3 \). Propane-1,2-diolcarbonate, distilled before use. Trimethylphosphite, boiled over CaO and then distilled over dried \( \text{Na}_2\text{CO}_3 \). N,N-Dimethyacetamide, purified according to Gutmann et al. Dimethyl sulfoxide, purified as described by Schläfer and Schaffernicht. Anhydrous cobalt(II) perchlorate was prepared by resolution of the hexahydrated salt. This was dissolved in the respective solvent (except acetonitrile) and the solution was evaporated to near dryness. Then the residue was redissolved and the procedure repeated twice. After that a stock solution could readily be made by filling up solvent to the required volume. The solutions of cobalt(II) perchlorate in acetonitrile were prepared in another way. The hexahydrated salt dissolved in acetonitrile was stirred several times with \( \text{P}_2\text{O}_5 \) and then refluxed for 2 h with an additional portion of \( \text{P}_2\text{O}_5 \). When the mixture was filtered into anhydrous ethyl ether there was a precipitation of a compound which analysis showed to be \( \text{Co}(\text{CH}_3\text{CN})_4(\text{ClO}_4)_4 \) (cf. Ref. 11). From this the stock solutions could be prepared.

No special examinations of the purity of the solutions have been made. A water content would be observable in the infrared spectra of the solutions but no such absorptions have been noticed.

Unfortunately, the measurements had to be performed in solutions with uncontrolled ionic strengths because the solubilities of possible supporting electrolytes were low. Thus, the formal ionic strength is that originating from the concentrations of the ionic species in solution. For aqueous solutions, however, the stability constants obtained in this way seem to be rather independent of the total salt concentration and it is reasonable to presume that this could be valid also for the solutions used here.

Recording of the spectra. The measurements were made using a Perkin-Elmer 521 grating spectrophotometer. Matched cells with windows of CaF\(_2\) were used in both the sample and reference beam. The content of the reference cell was pure solvent. The cells were of the semi-permanent type which can be completely dismantled for path-length alterations. The maximum thicknesses of the spacers that could be used were about 0.5 mm for acetonitrile and 0.2 for the other solutions because of solvent absorption in the spectral region. The exact thicknesses of the cells were determined using the usual interference fringe technique. The spectra were run with an expanded wave number scale and the spectral slit width of the instrument was about 1.5 cm\(^{-1}\). The wave number readings in the spectral region under investigation were checked periodically by measuring the spectra of carbon monoxide in a 10 cm gas cell.

RESULTS

Measurements on NaSCN. In order to verify Lambert-Beer's law and to obtain spectral data of the "free" thiocyanate ion, measurements on the C–N stretching vibration of NaSCN were made. When the absorbance at the band maximum were plotted against the concentration good straight lines were obtained. Examples of these are given in Fig. 1. From the slopes of the lines the molar absorption coefficients could be calculated. They are summarized in Table 2 together with the wave numbers, band half-widths (\( \Delta \nu_{1/2} \)) and integrated absorptions (\( \varepsilon \times \Delta \nu_{1/2} \)).

Measurements on the cobalt(II) thiocyanate systems. All the systems show the same essential features and as representative examples of the spectra those of the system Co\(^{2+}\)–NCS–TMP have been chosen (Fig. 2). When the ratio \( \text{C}_{\text{SCN}}/\text{C}_{\text{Co}} \) is small there is a shift of the C–N stretching band to a frequency 25–35 cm\(^{-1}\) higher than that of the "free" thiocyanate ion (see

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Table 2. Infrared spectral data for NaSCN and the thiocyanato complexes of Co(II) in various solvents together with the stability constants of the first complex.

<table>
<thead>
<tr>
<th>Solvent, D</th>
<th>ν (cm⁻¹)</th>
<th>ε SCN⁻</th>
<th>Δν₁/₂ (cm⁻¹)</th>
<th>ε SCN⁻Δν₁/₂ × 10⁻⁴</th>
<th>ν (cm⁻¹)</th>
<th>ε₁</th>
<th>Δν₁/₂ (cm⁻¹)</th>
<th>ε₁Δν₁/₂ × 10⁻⁴</th>
<th>β₁ (M⁻¹ cm²)</th>
<th>ν (cm⁻¹)</th>
<th>ε Δν₁/₂ × 10⁻⁴ (M⁻¹ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>2062</td>
<td>701</td>
<td>18.5</td>
<td>1.3</td>
<td>2090</td>
<td>1050</td>
<td>22</td>
<td>2.3</td>
<td>730±150</td>
<td>2070</td>
<td>3.9</td>
</tr>
<tr>
<td>PDC</td>
<td>2057</td>
<td>571</td>
<td>22</td>
<td>1.3</td>
<td>2092</td>
<td>650</td>
<td>26</td>
<td>1.7</td>
<td></td>
<td>2068</td>
<td>2.7</td>
</tr>
<tr>
<td>IMP</td>
<td>2059</td>
<td>525</td>
<td>15</td>
<td>0.8</td>
<td>2083</td>
<td>1110</td>
<td>18</td>
<td>2.0</td>
<td>500±100</td>
<td>2072</td>
<td>3.6</td>
</tr>
<tr>
<td>DMA</td>
<td>2058</td>
<td>913</td>
<td>12</td>
<td>1.1</td>
<td>2082</td>
<td>1030</td>
<td>25</td>
<td>2.4</td>
<td>490±100</td>
<td>2070</td>
<td>4.1</td>
</tr>
<tr>
<td>DMSO</td>
<td>2066</td>
<td>850</td>
<td>13</td>
<td>1.1</td>
<td>2083</td>
<td>840</td>
<td>25</td>
<td>2.1</td>
<td>150±30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O⁹</td>
<td>2066</td>
<td>537</td>
<td>37</td>
<td>2.0</td>
<td>1312</td>
<td>700</td>
<td>29</td>
<td>2.0</td>
<td>8.9</td>
<td>2075</td>
<td>4.9</td>
</tr>
</tbody>
</table>

⁹ Values taken from Refs. 5 and 15. Calculated per SCN group.

Fig. 2a; the frequency of the “free” ligand is indicated by an arrow). However, when the ratio is increased the main absorption band is moved to around 2070 (Fig. 2b) and for a large ratio also the band of the “free” ion can be distinguished (Fig. 2c). Usually consecutively formed complexes M(NCS)ₙ or M(SCN)ₙ show no detectable difference between the C—N stretching frequencies of the thiocyanate groups,⁵,¹⁴ so the explanation in this case must be that some of the species have either different types of bonding or different configurations. By experience one would expect all these complexes to be N-bonded and this is also supported by the measured integrated absorptions in this work. The possibility of different configurations is more plausible, especially as there is a distinct change in colour of the solutions from reddish to bright blue when the ratio $C_{SCN^-}/C_{Co^{3+}}$ is increased. Fronæus and Larsson¹⁵ have proposed

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that there would be a much stronger electron exchange between ligand and metal for tetrahedral than for octahedral complexes. Such an electron exchange would decrease the bond order of the C–N bond of the thiocyanate group and thus probably the frequency of the C–N stretching vibration. The effect on the integrated absorption would be an increase when going from octahedral to tetrahedral complexes and such an increase is also found (see Table 2). As a matter of fact also Gutmann and Bohunowsky \(^{16}\) have suggested that the first thiocyanato complex would be a somewhat distorted octahedral [Co(NCS)\(D\)]\(^+\) where D is the donor solvent, while the higher ones would be tetrahedral, e.g. Co(NCS)\(_4\)\(^2\).

Neither the low-frequency absorption band of the coordinated thiocyanate ion nor that of the “free” ion may be used for a quantitative equilibrium analysis because they are too close together and difficult to resolve. It is possible to obtain the stability constant of the first complex, however, from the high-frequency band found for small ratios \(C'_{SCN^-}/C_{Co^{2+}}\) according to the method described above. The experimental data are collected in Tables 3–6. After

\[ \text{Acta Chem. Scand. 27 (1973) No. 10} \]
Table 3. The Co$^{2+}$ – NCS$^-$ system in AN. Constant $C_L = 0.0051$ M. Cell thickness 0.564 mm. $A_{2000} = 0.303$.

<table>
<thead>
<tr>
<th>$C_M$ (M)</th>
<th>$A_{2000}$</th>
<th>$\frac{A_{2000}}{C_M - C_L}$ (M$^{-1}$)</th>
<th>$\frac{A_{2000}}{C_M - C_L A_{2000}/A_{2000}^2}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1212</td>
<td>0.3005</td>
<td>2.588</td>
<td>2.588</td>
</tr>
<tr>
<td>0.1010</td>
<td>0.2988</td>
<td>3.116</td>
<td>3.113</td>
</tr>
<tr>
<td>0.0808</td>
<td>0.2967</td>
<td>3.919</td>
<td>3.914</td>
</tr>
<tr>
<td>0.0606</td>
<td>0.2903</td>
<td>5.393</td>
<td>5.387</td>
</tr>
<tr>
<td>0.0505</td>
<td>0.2923</td>
<td>6.438</td>
<td>6.413</td>
</tr>
<tr>
<td>0.0404</td>
<td>0.2919</td>
<td>8.269</td>
<td>8.225</td>
</tr>
<tr>
<td>0.0303</td>
<td>0.2876</td>
<td>11.41</td>
<td>11.39</td>
</tr>
<tr>
<td>0.0253</td>
<td>0.2796</td>
<td>13.84</td>
<td>13.58</td>
</tr>
</tbody>
</table>

Table 4. The Co$^{2+}$ – NCS$^-$ system in TMP. Constant $C_L = 0.0302$ M. Cell thickness 0.0150 mm. $A_{2002} = 0.353$.

<table>
<thead>
<tr>
<th>$C_M$ (M)</th>
<th>$A_{2002}$</th>
<th>$\frac{A_{2002}}{C_M - C_L}$ (M$^{-1}$)</th>
<th>$\frac{A_{2002}}{C_M - C_L A_{2002}/A_{2002}^2}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2406</td>
<td>0.3495</td>
<td>1.661</td>
<td>1.660</td>
</tr>
<tr>
<td>0.1805</td>
<td>0.3476</td>
<td>2.314</td>
<td>2.307</td>
</tr>
<tr>
<td>0.1504</td>
<td>0.3474</td>
<td>2.891</td>
<td>2.881</td>
</tr>
<tr>
<td>0.1203</td>
<td>0.3494</td>
<td>3.879</td>
<td>3.865</td>
</tr>
<tr>
<td>0.0995</td>
<td>0.3430</td>
<td>4.950</td>
<td>4.893</td>
</tr>
<tr>
<td>0.0902</td>
<td>0.3368</td>
<td>5.613</td>
<td>5.494</td>
</tr>
<tr>
<td>0.0753</td>
<td>0.3396</td>
<td>7.530</td>
<td>7.351</td>
</tr>
<tr>
<td>0.0666</td>
<td>0.3348</td>
<td>9.221</td>
<td>8.834</td>
</tr>
<tr>
<td>0.0602</td>
<td>0.3321</td>
<td>11.10</td>
<td>10.48</td>
</tr>
</tbody>
</table>

Table 5. The Co$^{2+}$ – NCS$^-$ system in DMA. Constant $C_L = 0.0153$ M. Cell thickness 0.2165 mm.

<table>
<thead>
<tr>
<th>$C_M$ (M)</th>
<th>$A_{2002}$</th>
<th>$\frac{A_{2002}}{C_M - C_L}$ (M$^{-1}$)$^a$</th>
<th>$\frac{A_{2002}}{C_M - C_L A_{2002}/A_{2002}^2}$ (M$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2006</td>
<td>0.3349</td>
<td>1.807</td>
<td>1.805</td>
</tr>
<tr>
<td>0.1605</td>
<td>0.3351</td>
<td>2.308</td>
<td>2.305</td>
</tr>
<tr>
<td>0.1204</td>
<td>0.3346</td>
<td>3.184</td>
<td>3.178</td>
</tr>
<tr>
<td>0.1003</td>
<td>0.3314</td>
<td>3.899</td>
<td>3.885</td>
</tr>
<tr>
<td>0.0802</td>
<td>0.3284</td>
<td>5.060</td>
<td>5.021</td>
</tr>
<tr>
<td>0.0702</td>
<td>0.3288</td>
<td>5.989</td>
<td>5.935</td>
</tr>
<tr>
<td>0.0602</td>
<td>0.3257</td>
<td>7.254</td>
<td>7.158</td>
</tr>
<tr>
<td>0.0502</td>
<td>0.3185</td>
<td>9.126</td>
<td>8.897</td>
</tr>
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</table>

$^a A_{2002} = 0.339$.  $^b A_{2002} = 0.340$.

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Table 6. The $\text{Co}^{2+} - \text{NCS}^-$ system in DMSO. Constant $C_L = 0.0301$ M. Cell thickness 0.1050 mm.

<table>
<thead>
<tr>
<th>$C_M$ (M)</th>
<th>$A_{2083}$</th>
<th>$A_{2083}^{2083}$</th>
<th>$A_{2083}^{2083}/A_{2083}^{2083}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2500</td>
<td>0.2595</td>
<td>1.180</td>
<td>1.176</td>
</tr>
<tr>
<td>0.2000</td>
<td>0.2552</td>
<td>1.502</td>
<td>1.492</td>
</tr>
<tr>
<td>0.1750</td>
<td>0.2544</td>
<td>1.756</td>
<td>1.740</td>
</tr>
<tr>
<td>0.1500</td>
<td>0.2510</td>
<td>2.093</td>
<td>2.066</td>
</tr>
<tr>
<td>0.1250</td>
<td>0.2483</td>
<td>2.616</td>
<td>2.565</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.2435</td>
<td>3.484</td>
<td>3.363</td>
</tr>
</tbody>
</table>

$A_{2083}^{2083} = 0.265$. $A_{2083}^{2083} = 0.266$.

the second plotting (A* against $A_s/C_M - C_L A_s/A_s^o$) no further changes in $A_s^o$ and $\beta_1$ could be observed and the values so obtained are those in Table 2. $\varepsilon_1$ is calculated from $A_s^o$ using the relation $A_s^o = \varepsilon_1 d C_L$.

The method described is not applicable to very stable systems, because the slope of the straight lines ($-1/\beta$) would be then very small. For the $\text{Co}^{2+} - \text{NCS}^-$ system in PDC the slope was approximately zero when the plotting of $A_s$ against $A_s/C_M - C_L$ was made. This would imply a larger $\beta_1$ value for the system in PDC than in the other solvents, that is $\beta_1$(PDC) $> 730$ M$^{-1}$.

In Table 2 also some values of the frequencies and integrated absorptions of $\text{Co(NCS)}_4^{2-}$ are given. These values should be considered as rough estimates. They are obtained from spectra similar to that in Fig. 2c by resolving the two bands. The ratios $C_{\text{SCN}^-}/C_{\text{Co}^{2+}}$ of the solutions used for this are large enough$^{14}$ to make it probable that $\text{Co(NCS)}_4^{2-}$ is the only complex present. Nevertheless, as could be seen in Fig. 2c, there are traces of shoulders on the high frequency side of the main absorption band. If this is a remainder of the band of an octahedral complex or some other effect cannot be accounted for at present. No values of frequency and integrated absorption are given in Table 2 for $\text{Co(NCS)}_5^{2-}$ in DMSO since complete formation of this complex would require such a large excess of ligand ($C_{\text{SCN}^-}/C_{\text{Co}^{2+}} > 200$)$^{16}$ that it is not possible to resolve the complex band from the "free" ligand band.

**DISCUSSION**

All the solvents used in this investigation could be classed as dipolar aprotic.$^{17}$ They are highly polar but have no hydrogen atoms which could be involved in hydrogen bonding. They are all capable of donating a free electron pair situated on the oxygen (nitrogen in acetonitrile) into empty orbitals of a metal ion. The binding effect originating from such an electron donation as well as possible dipole-ion attractions would be expressed by the donor numbers of Gutmann$^{3}$ (Table 1). It is reasonable to assume that cobalt(II) ion is fully solvated in such solvents and that the formation of thiocyanato complexes could be represented as ligand exchange reactions, e.g.

$$\text{CoD}_6^{2+} + \text{NCS}^- \rightleftharpoons [\text{Co(NCS)}D_3]^{2+} + \text{D}$$

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The stability of this complex in the various solvents is expressed by the $\beta_1$ values, and as the ligand exchange will be dependent on the relative donor properties of the solvent molecules as compared to that of the thiocyanate ion, one would expect a relation between the $\beta_1$ values and the donor numbers. As a matter of fact, such a relation is found between the $\beta_1$ values determined in this work (Table 2) and the $DN_{SbCh}$ values of Gutmann (Table 1). However, $\beta_1$ in PDC, which could not be determined, is probably larger than in AN and $\beta_1$ in aqueous solution is much smaller than would be expected from the donor number of water. Thus, it is quite evident that in this case the coordination can not be described in the simple terms of donor numbers. Water is a protic solvent and in such solvents anions are solvated not only by ion-dipole interactions but also by strong hydrogen bonding. This anion solvation together with the high dielectric constant of water could be responsible for the weak coordinating ability of the thiocyanate ion in aqueous solvents. Gutmann has also called attention to the steric factors, because the water molecule is much smaller than the other solvent molecules and would be of a more "suitable" shape for solvent coordination. Steric requirements could also be responsible for a greater stability of the thiocyanato complexes in PDC than in AN although PDC has a larger donor number than AN.

It has been mentioned above that all the thiocyanato complexes of cobalt(II) would be N-bonded in the non-aqueous solvents used. This is concluded from the large values of the integrated absorption for the C–N vibration of the coordinated thiocyanate group, as compared to that of "free" ligand. Furthermore, these values indicate that the M–NCS bond, even in the octahedral complexes, would have a distinct covalent character in these solvents. In water, however, the integrated absorption of the first thiocyanato complex is the same as that of the "free" ion. This invariance tells us that there would be very little electron exchange between ligand and metal, and the bond must be regarded as essentially electrostatic in water. When discussing this electron exchange, it seems that bulk physical properties of the solvent such as the dielectric constant would be more useful than the donor number. Thus, a rather good correlation is found between the relative integrated absorption

![Graph](image_url)

*Fig. 3. The dependence of the relative integrated absorption ($\varepsilon_1, du_1/2 - \varepsilon_{SNC} - du_{1/2}$) on the dielectric constant $\varepsilon$. The line is drawn only to emphasise the trend. ○ AN, ● PDC, △ TMP, ▲ DMA, □ DMSO and ■ H2O.*

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in each solvent, \((\varepsilon_1 \Delta \nu_{i} - \varepsilon_{\text{SCN}} \Delta \nu_{i})/\varepsilon_{\text{SCN}} \Delta \nu_{i}\), and the dielectric constant (Fig. 3).

It must be fully understood that a distinction between the effects of the donor strength and the polarity of a solvent on the complex formation is usually difficult to make. Nevertheless, this investigation shows that the donor numbers of Gutmann may be of use when the relative stabilities of complexes in different solvents are discussed.

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