On the Infrared Spectra of Transition Metal Complexes

of the Thiocyanate Ion in Pyridine

RAGNAR LARSSON and ATIS MIEZIS

Department of Inorganic Chemistry, Chemical Institute, University of Lund, Lund, Sweden

The infrared absorption spectra in the region 2000—2200 K have been recorded for some metal thiocyanate systems in pyridine solutions. It has been concluded that the complexity of the bivalent, first-row transition metal ions is much stronger in pyridine than in water. The absorption intensities have been used to distinguish between M-NCS and M-SCN complexes.

During the past few years much interest has been devoted to the study of infrared spectra of the SCN^- ion in coordination compounds. One of the most striking results is the one reported by Turco and Pecile:[1] Depending on the nature of the other ligand in mixed complexes, the thiocyanate ion can coordinate to the same metal ion either *via* the sulphur atom or *via* the nitrogen one.

Also, the findings of Tramer [2] is of considerable interest. He reports (Ref.2, Fig. 4) that in the series $HgCl_2(SCN)_2^{2-}$, $HgBr_2(SCN)_2^{2-}$, and $HgI_2(SCN)_2^{2-}$ the CN-vibration frequency has the values 2116, 2111, and 2101 K. As an increase of the CN-frequency is most probably a measure of the strength of the metal-ligand bond, and as I^- is more strongly bonded than Br^- and Cl^- are, one can infer that the strength of the Hg-SCN bond is decreased by the action of the partner ligands, and more so the stronger these are bonded.

Burmeister [3] has recently presented evidence that in $[Co(CN)_5SCN]^{3-}$ there is a Co-SCN bond, contrary to what is the case in the complex $[Co(NH_3)_5NCS]^{2-}$ where there is a Co-NCS bond.

In a previous work from this laboratory [4] it was reported that the integrated absorption of the CN-vibration frequency of the SCN^- ion bound to the bivalent first-row transition metals in aqueous solution is for all practical purposes constant and equal to that of the free ligand.

As these complexes have the constitution $M(NCS)_n(OH_2)_m$ it was considered interesting to investigate the spectral properties of complexes of the composition $M(NCS)_nL_m$, where L is a ligand with properties, distinctly different from water. If the type of bonding of the SCN^- ion depends upon the nature

of L (as the above-mentioned works [1-3] and also that of Goodgame *et al.*[5] indicate) a change of the integrated absorption may be expected. If this quantity is greater than that of the free ion it will mean N-coordination, if it is less, S-coordination is indicated.[6]

With these considerations in mind, we have started an investigation on thiocyanate complexes in pyridine solution. The choice of pyridine as the ligand L depends on many things: The easiness to prepare complexes of the type $Mpy_m(NCS)_2$ where $m = 2$ or 4, the comparatively good properties of pyridine as a solvent for infrared spectroscopy, and the possibility of studying — by means of UV, IR, and NMR spectroscopy — the changes of the pyridine ligands also in the above-mentioned complexes. Furthermore, the general study of complex formation in pyridine has been surprisingly neglected up to the present date.

The measurements were performed with a Perkin Elmer 221 G spectrophotometer. Cells with sodium chloride windows and with 0.03, 0.1, and 0.2 mm cell-thickness were used.

As a preliminary investigation we have prepared the following compounds from the prescriptions given in analytical textbooks: $Cd\ py_2(NCS)_2$, $Co\ py_4(NCS)_2$, $Ni\ py_4(NCS)_2$, $Cu\ py_2(NCS)_2$, and $Zn\ py_2(NCS)_2$.

The spectra were recorded for these compounds in pyridine and in pyridine-chloroform solution. The results together with those for NaSCN in pyridine are presented in Table 1. For each of the compounds only one absorption peak in the C—N vibration range could be observed. (The C—S vibration frequency could not be determined as both pyridine and chloroform absorb too heavily in that part of the spectrum). A peak corresponding to free SCN^- (at 2059 K) was not noticeably present in the spectra of the complexes. This must mean that the compounds do not dissociate to any appreciable extent in pyridine. Contrary to this, one finds when, *e.g.*, dissolving $Ni(NCS)_2$ in water that a dissociation occurs to such a degree that a peak characteristic of free ligands is clearly observed, *cf.* Fig. 3 d of Ref. 4.

Thus in spite of the fact [7] that pyridine is a stronger complexing agent for these metals than water is, the thiocyanate groups are bound much stronger in pyridine than in water.

The comparative constancy of the integrated absorption in the pyridine-chloroform solutions also indicates the existence of only one molecular species in these solutions. The variations of these quantities and of the frequencies are probably caused by the change in the dielectric constant of the solutions.

In the case of the zinc system, however, a new peak — or rather a shoulder — appears at 2090 K in the solution of the lowest pyridine content. We cannot tell the nature of the complex corresponding to this peak for certain. As the frequency is higher than that of the main peak, it is possible that an isomerisation takes place: Zn-NCS → Zn-SCN. However, an equally probable explanation is that the equilibrium $Zn\ py_4(NCS)_2 \rightleftharpoons Zn\ py_2(NCS)_2 + 2py$ is driven towards the right side.

The large value of the halfwidth of the peak of the Cu^{2+}-system is noteworthy but difficult to explain.

For all the metal complexes and all compositions of the solvent a perfect adherence to Beer's law was found (Fig. 1). This fact, too, gives support to

Table 1. Spectral data for some compounds of the type $Mpy_m(NCS)_2$ and of NaSCN in pyridine and pyridine-chloroform solutions. The extinction coefficients are calculated per SCN group. The values for NaSCN are calculated from the most dilute solutions ($C = 0.05 - 0.1$ M).

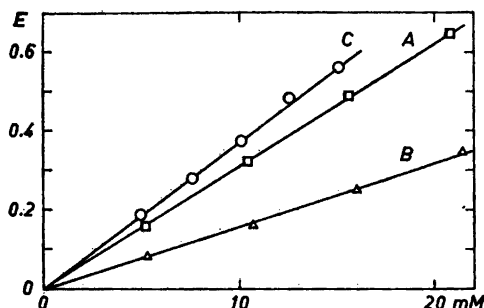|	100 % pyridine				29 % pyridine 71 % chloroform				17 % pyridine 83 % chloroform				5 % pyridine 95 % chloroform			
	ν K	$\varepsilon \times 10^{-3}$ $M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$ K	$\varepsilon \cdot \Delta\nu_{1/2} \times 10^{-4}$	ν K	$\varepsilon \times 10^{-3}$ $M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$ K	$\varepsilon \cdot \Delta\nu_{1/2} \times 10^{-4}$	ν K	$\varepsilon \times 10^{-3}$ $M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$ K	$\varepsilon \cdot \Delta\nu_{1/2} \times 10^{-4}$	ν K	$\varepsilon \times 10^{-3}$ $M^{-1}cm^{-1}$	$\Delta\nu_{1/2}$ K	$\varepsilon \cdot \Delta\nu_{1/2} \times 10^{-4}$
Co py$_4$(NCS)$_2$	2064	1.68	18	3.02	2069	1.31	23	3.01	2071	1.29	23	2.97	2074	1.29	22.5	2.90
Ni py$_4$(NCS)$_2$	2074	1.37	20	2.74	2081	1.15	24	2.76	2083	1.13	24	2.71	2084	1.12	23	2.58
Cu py$_2$(NCS)$_2$	2073	0.99	32	3.17	2076	0.90	35.5	3.20	2078	0.94	35	3.29	2079	0.95	35	3.33
Zn py$_2$(NCS)$_2$	2065	1.28	22.5	2.88	2070	1.22	26	3.17	2072	1.15	28.5	3.28	2071	1.10	34.5	3.80
Cd py$_2$(NCS)$_2$	2052	0.84	23	1.93	2056	0.78	28.5	2.22	2058	0.75	29	2.18	2061	0.75	29	2.18
NaSCN	2059	1.02	15	1.53					2162 ± 3							

Fig. 1. Illustration of the adherence to Beer's law. Optical densities for: Cu py$_2$(NCS)$_2$ in 29 % pyridine + 71 % chloroform, $d = 0.2$ mm (O); Co py$_4$(NCS)$_2$ in pyridine, $d = 0.1$ mm ($\square$); Cd py$_2$(NCS)$_2$ in pyridine, $d = 0.1$ mm ($\triangle$).

the existence of only one complex or possibly a mixture of isomeric complexes (the Zn^{2+}-system), the relative amounts of which depending only upon the pyridine concentration. The only exception to this rule was the Na$^+$—SCN$^-$ system, for which we found somewhat smaller extinction coefficients at large C_{NaSCN}.

Probably all of the above-mentioned compounds, at least the Cu,[8] Ni, and Co [9] ones, have the thiocyanate ligand coordinated to the metal *via* the nitrogen atom. It is therefore noteworthy that the integrated absorption per ligand is greater in these systems than that of the free ligand.

This situation may be contrasted with the one for the same systems in water.[6] According to the classification made in our earlier work,[6] the pyridine-thiocyanate-complexes should be placed in group II, *i.e.* complexes with N-coordination and a distinct charge transfer bonding. This is in line with the above-mentioned greater stability of the thiocyanate complexes in pyridine than in water. It is to be expected [6] that the force constant of the N—C stretching vibration should be diminished for Group II-systems. In fact, this is the case for the Cd^{2+} system, where one can observe the C—N peak at a lower frequency than for the "free" SCN$^-$ ion.

For all the other systems an increase of this frequency is observed (Table 1). The shift follows the order Co < Ni $\approx$ Cu > Zn, *i.e.* the same trend that was found [4] earlier for those systems that can be compared. We believe [6] that this effect is related to the frequency shifts found for polyatomic ions that are held tight in ionic matrices. This may seem strange, as it is assumed that it is *via* the nitrogen atom that bonding is effected.

However, from the approximate proportions between the different canonical structures of the SCN$^-$ ion given by Jones,[10] it follows that the centre of negative charge should be somewhere between the C-atom and the S-atom. Hence, by mere electrostatic attraction, the SCN$^-$ ion will be kept tight to the metal ion in such a way that the N—C vibration is hindered. The fact that the C—N bond length is about 1.2 Å and the C—S bond length is about 1.6 Å still allows for "electrostatic" complexes to be formed *via* the nitrogen atom.

As the frequency-shifts discussed above were only about half the shifts found in water, one can ask whether the same holds also for complexes of the M—SCN type. We therefore measured the spectrum of an inert complex,

Table 2. Spectral data for some b-metal thiocyanato complexes. The extinction coefficients are calculated per SCN group and are accurate within 10 %.

	ν K	ε $\mathrm{M^{-1}\,cm^{-1}}$	$\Delta\nu_{1/2}$ K	$\varepsilon \times \Delta\nu_{1/2}$ $\times 10^{-4}$
AgSCN	2089	700	19	1.33
Ag(SCN)$_2$	2089	475	26	1.24
Ag$_2$(SCN)	2102	330	*	
Ag$_2$(SCN)$_2$	2102	190	*	
Hg(SCN)$_2$	2119	290	19	0.55
Pt(SCN)$_6{}^{2-}$	2122	250**	11	0.3

  * Halfwidth difficult to estimate
 ** Rough estimate

viz. K_4 [Pt(SCN)$_6$], dissolved in pyridine. The results (Table 2) show almost the same shift as in water [6] (63 K compared to 60 K). The integrated absorption has decreased compared to what was found in water, in fact in almost the same proportion as the corresponding quantity of the "free" SCN$^-$ ion has.

The great shift of the b-group metals, thus established, has made it possible to perform some detailed investigations of thiocyanate complexes in pyridine for labile b-metal systems.

Some of the results of the work on the silver system, the full account of which will soon be published,[11] are included in Table 2 together with some preliminary data of the mercury system. Regarding the silver system, it was possible to prove the existence of two, possibly three, mononuclear complexes in solutions with $C_A > C_M$ and the two binuclear complexes M_2A and M_2A_2 when
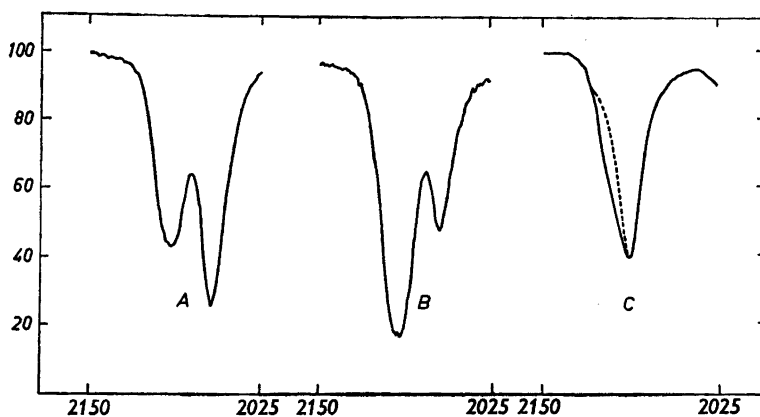

Fig. 2. Spectra of the Ag$^+$—SCN$^-$ system.
A. 0.102 M AgClO$_4$ + 0.401 M NaSCN, d = 0.032 mm;
B. 0.103 M AgClO$_4$ + 0.183 M NaSCN d = 0.10 mm;
C. 0.42 M AgClO$_4$ + 0.10 M NaSCN d = 0.20 mm.

$C_M > C_A$. This situation stands in a strange and striking contrast to the one in aqueous solutions,[12] where a series of polynuclear complexes are formed even when $C_A > C_M$.

Some typical spectra are given in Fig. 2. It is obvious that one obtains well identifiable peaks or at least shoulders and not the broad, diffuse bands obtained by Kinell and Strandberg [13] on aqueous samples. This must be related to the greatly different amount of polynuclear complexes formed in the two solvents. The full discussion of this effect will be postponed until later.[11]

From the integrated absorptions it is evident that in the silver complexes and in the mercury ones the thiocyanate ions are bonded *via* the sulphur atom.

REFERENCES

1. Turco, A. and Pecile, C. *Nature* **191** (1961) 66.
2. Tramer, A. *J. Chim. Phys.* **59** (1962) 232.
3. Burmeister, J. L. *Inorg. Chem.* **3** (1964) 919.
4. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1433.
5. Cotton, F. A., Goodgame, D. M. L., Goodgame, M. and Sacco, A. *J. Am. Chem. Soc.* **83** (1961) 4157.
6. Fronæus, S. and Larsson, R. *Acta Chem. Scand.* **16** (1962) 1447.
7. Bjerrum, J. *Chem. Rev.* **46** (1950) 381.
8. Porai-Koshits, M. A. and Tishchenko, G. N. *Soviet Phys.-Cryst. (English Transl.)* **4** (1959) 216.
9. Porai-Koshits, M. A. and Antsyshkina, A. S. *Kristallografiya* **3** (1958) 686.
10. Jones, L. H. *J. Chem. Phys.* **25** (1956) 1069.
11. Larsson, R. and Miezis, A. *Acta Chem. Scand.* To be published.
12. Leden, I. and Nilsson, R. *Z. Naturforsch.* **10a** (1955) 67.
13. Kinell, P. O. and Strandberg, B. *Acta Chem. Scand.* **13** (1959) 1607.