Studies on Metal Complexes in Aqueous Solution by Infrared Spectrophotometry

III. Further Investigations on Thiocyanato Complexes

STURE FRONÆUS and RAGNAR LARSSON

Department of Inorganic and Physical Chemistry and Infrared Laboratory, Chemical Institute,
University of Lund, Lund, Sweden

The frequency and intensity of the C—N vibration have been measured for some thiocyanato complexes of widely different metals. The relevant data can be found in Table 4. It is found that the systems can be divided into three classes, depending upon whether the integrated absorption is equal to, greater or less than that quantity for the free thiocyanate ion. It is suggested that these classes correspond to different types of bonding: I. Very small degree of electron exchange between ligand and metal. II. "Lone-pair donation" from the nitrogen atom. III. "Lone-pair donation" from the sulphur atom.

In the case of the cadmium system two absorption peaks are found, which are supposed to correspond to mononuclear and polynuclear complexes, respectively.

In the preceding paper[1] of this series we reported infrared absorption frequencies and intensities for some thiocyanato complexes of the bivalent first-row transition metals. In this paper we report further measurements on some thiocyanato complexes of some typical a- and b-class metals[2].

We have made it our object to correlate changes in absorption frequency and intensity with the structure and bonding characteristics of the complexes. Such measurements have frequently been reported[3-11a] during the last few years. However, with two exceptions[9,11a], all studies have been confined to the solid state. As it has been amply demonstrated by Price, Sherman and Wilkinson[12] that lattice forces can strongly influence the position of the C—N frequency (for the CN^- and OCN^- ions), the value of the information is considerably decreased.

EXPERIMENTAL

The experimental procedure was the same as before.

Chemicals used. Uranyl perchlorate was prepared according to Arhland[13] and $K_3[Cr(NCS)_6]$ and $K_2[Pt(SCN)_6]$ according to the literature. The preparation of
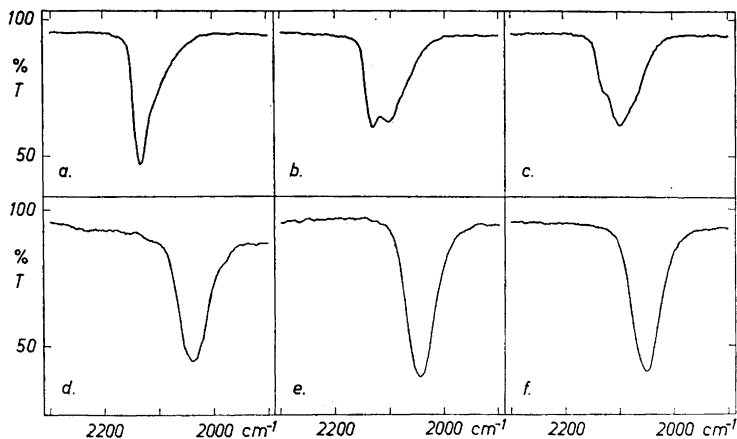
Fig. 1. a.—c. The Cd^{2+}—SCN^- system.

a. C_M = 2.00 M; C_A = 0.30 M
b. C_M = 1.08 M; C_A = 0.30 M
c. C_M = 0.45 M; C_A = 0.30 M

d.—f. The Fe^{3+}—SCN^- system.

d. C_M = 0.84 M; C_A = 0.15 M
e. C_M = 0.56 M; C_A = 0.15 M
f. C_M = 0.28 M; C_A = 0.15 M

[Co(NH₃)₅NCS](ClO₄)₂ is described in a recent paper by one of us [14]. Hg(SCN)₂ was precipitated from dilute solutions of Hg(NO₃)₂ and NaSCN, and washed with water, alcohol and ether. The other salts were perchlorates prepared from reagent quality chlorides.

MEASUREMENTS

The spectra of the following metal-thiocyanato systems were recorded for a constant thiocyanate concentration but a varying metal concentration: Cd^{2+}, UO_2^{2+} and Fe^{3+}. Some representative records for varying composition of the solutions are given in Fig. 1.

In the case of the cadmium system, Fig. 1 a—c, two new peaks are found at 2098 and 2132 cm⁻¹, respectively, the first one dissappearing, the other one increasing in intensity when the metal ion concentration is increased. We suggest that the 2098 cm⁻¹ peak corresponds to a mononuclear complex and that the 2132 cm⁻¹ peak corresponds to a polynuclear, SCN-bridged complex.

The iron(III)-system exhibits a quite different picture from the systems previously investigated[1]. First of all, the frequency of the new peak (2045 cm⁻¹) is lower than that of the free thiocyanate ion. Furthermore, when the iron concentration is increased the appearance of at least one new absorption peak (present as a shoulder at 2020 cm⁻¹ at the highest iron concentration) is evident. The main peak is under the same conditions shifted to 2040 cm⁻¹. We suggest
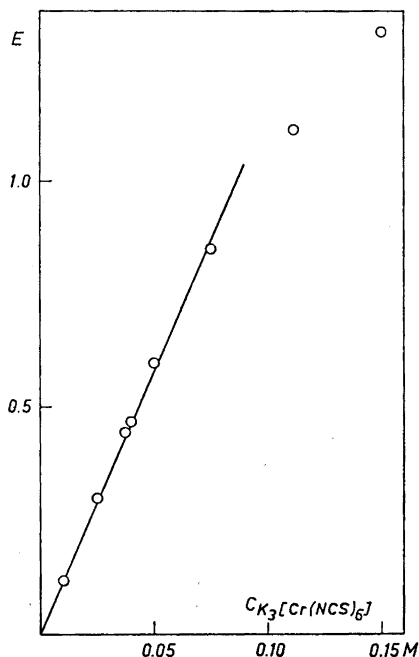
Fig. 2. Total optical density of the absorption peak corresponding to the ion [Cr(NCS)$_6$]$^{3-}$, The deviation from linearity for very large optical densities is clearly seen (*cf.* Ref.[1] p. 1434).

that the 2045 cm^{-1} peak corresponds to a mononuclear complex, and that a series of polynuclear complexes exists in solution giving rise to the other peaks observed. They are most probably not of the SCN-bridged type.

Also in the case of the uranyl system we must expect the formation of hydrolytic polynuclear complexes. Even though the pH of the solution was kept very low, the high metal concentration must certainly cause a large degree of polymerization.

Because of the complicated nature of these three systems no attempt was made to undertake a calculation of the complexity constants. Only the extinction coefficient of the first thiocyanato complex was determined by extrapolation of the absorbance to $1/(C_M - C_A) = 0$ (*vide* Ref.[1]). The results together with the half-width of the complex peak are reported in Table 3. As the uranyl complex peak was superimposed on the peak of the free ligand, the half-width was determined only from the spectra of the two largest metal : ligand ratios.

Furthermore, the spectra of some inert thiocyanato complex ions have been recorded, *viz.* [Co(NH$_3$)$_5$NCS]$^{2+}$, [Cr(NCS)$_6$]$^{3-}$ and [Pt(SCN)$_6$]$^{2-}$. In Fig. 2 is given a plot of the optical density of the [Cr(NCS)$_6$]$^{3-}$ ion *versus* concentration. Due to the low solubility of K$_2$[Pt(SCN)$_6$] and [Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$, the instrument was used with ordinate expansion 4 $\times$ and 10 $\times$ respectively, when recording these complexes. The extinction coefficient of the cobalt complex could not be measured with any great accuracy.

Also some records were made under conditions suitable for the study of the ions Hg(SCN)$_4^{2-}$ and Co(NCS)$_4^{2-}$. In the first case Hg(SCN)$_2$ was dissolved

Table 1. The Hg^{2+} — SCN^- system. $d = 20.0\ \mu$. $\varepsilon = \dfrac{E}{\bar{n}\ C_M\ d}$

C_M M	C_A M	$\bar{n}$	E	$\dfrac{\varepsilon}{M^{-1}cm^{-1}}$	$\dfrac{\varDelta\nu_{\frac{1}{2}}}{cm^{-1}}$
0.200	3.00	3.91	0.638	409	27
0.100	1.50	3.81	0.333	437	27
0.067	1.00	3.78	0.208	411	25
0.133	2.00	3.85	0.435	425	29
			Mean	420	27

in a great excess of NaSCN; from the known stability constants [15] the average number of ligands bound to the metal could be calculated and thus the extinction coefficient (Table 1). In the latter case NaSCN and $Co(ClO_4)_2$ in mole proportions 5:1 were dissolved in water mixed with a succesively increasing amount of methyl-ethyl-ketone (MEK). The spectra are given in Fig. 3. The solutions containing more than 20 % by volume of ketone were bright blue, indicating the presence of the tetrahedral complex $Co(NCS)_4^{2-}$. The optical densities of the peaks are given in Table 2 together with a calculation of ε for each SCN^- group in the complex. It was noted that the exchange of the solvent from water to a water-ketone mixture changed the absorption parameters of the free thiocyanate ion. Thus $\varepsilon = 671\ M^{-1}cm^{-1}$ and $\nu = 2070\ cm^{-1}$ and $\varDelta\nu_{\frac{1}{2}} = 41\ cm^{-1}$. Although this change is significant and indicates a thiocyanate-ketone interaction, it is not of the order of magnitude to disturb the interpretation of the $Co(NCS)_4^{2-}$ spectrum.

The extinction coefficient calculated from the values in Table 2 were obtained from the expression

$$\varepsilon = \frac{E - \frac{1}{5}C_A \cdot \varepsilon_{A\ 2075} \cdot d}{4/5\ C_A d} \tag{1}$$

where $\varepsilon_{A,\ 2075}$ denotes the extinction coefficient of the free thiocyanate ion in 60 % MEK.
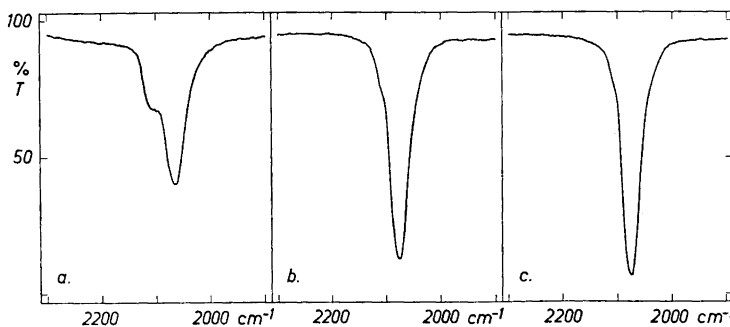

Fig. 3. The Co^{2+} — SCN^- system in water methyl-ethyl-ketone mixtures. a. 0 % MEK, b. 40 % MEK, c. 60 % MEK.

Table 2. Calculation of ε_{SCN^-} of the complex $Co(NCS)_4{}^{2-}$. MEK = methylethylketone. $C_M = 0.075$ M; $C_A = 0.375$ M.

% MEK	40	60	80
E_{2075}	0.864	1.14	1.26
Mean		1.20	

$\varepsilon_{A,\,2075} = 406$ M^{-1}cm^{-1}

$$\varepsilon = \frac{1.20 - 0.06}{0.3 \times 20} \times 10^4 = 1900 \text{ M}^{-1}\text{cm}^{-1}$$

D. Collation of the data for the various systems

The data obtained by the measurements described in this and the preceding paper [1] are collected in Table 3.

As an approximate measure of the integrated absorption the product between the extinction coefficient and the half-width of the band is reported.

It is clearly seen from Table 3 that the systems investigated can be divided into three different classes. For the first one, comprising the bivalent first-row transition metals, it holds that the integrated absorption is constant and — moreover — identical with the same quantity for the free thiocyanate ion.

The second class, tetrahedral Co^{2+}, $UO_2{}^{2+}$, Fe^{3+} and Cr^{3+}, is characterized by a definite increase in the integrated absorption, whereas the third one, Pt^{4+} and Hg^{2+}, shows a decrease in the said quantity.

Also it is seen that whereas class I and class III gives frequencies higher than that of the free thiocyanate ion, the class II systems show lower (Fe^{3+}),

Table 3. Spectral parameters of the investigated complexes.

	ν cm^{-1}	ε M^{-1}cm^{-1}	$\Delta\nu_{\frac{1}{2}}$ cm^{-1}	$\varepsilon \cdot \Delta\nu_{\frac{1}{2}}$ $\times 10^{-4}$
SCN$^-$	2066	537	37	1.99
Mn^{2+}-SCN$^-$	2093	655	31	2.03
Fe^{2+}-SCN$^-$	2099			
Co^{2+}-SCN$^-$	2112	696	29	2.02
Ni^{2+}-SCN$^-$	2119	640	32	2.05
Zn^{2+}-SCN$^-$	2109	685	34	2.32
[Co(NH$_3$)$_5$NCS]$^{2+}$	2123			
[Co(NCS)$_4$]$^{2-}$	2075	1900	29	4.9
UO$_2$$^{2+}$-SCN$^-$	2066	1100	40	4.4
Fe^{3+}-SCN$^-$	2045	1310	49	6.4
[Cr(NCS)$_6$]$^{3-}$	2088	937	39	3.7
Cd^{2+}-SCN$^-$	2132	635	24	1.5
	2098			
[Pt(SCN)$_6$]$^{2-}$	2126	246	15	0.4
[Hg(SCN)$_4$]$^{2-}$	2112	420	27	1.1

identical (UO_2^{2+}), or at least a trend towards lower frequencies (cf. Co^{2+}, octa-hedral, class I, and Co^{2+}, tetrahedral, class II).

It is also obvious that the high frequency peak of the cadmium system exhibits a striking resemblance to the class III systems.

<div align="center">DISCUSSION</div>

The most noteworthy result of this investigation is the classification of the metals in Table 3. To understand the origin of this effect let us first consider classes II and III. These two classes are characterizied by a distinct change of the integrated absorption, the one towards higher, the other towards lower values compared to the free ligand. Keeping in mind that the metal-ligand bond in all cases is much weaker than the bonds in the SCN group, we can consider the effects as a perturbation of the vibration levels in the SCN group, in this case the v_1 vibration. X-Ray data (for a compilation of existent data, see Ref.[5]) give a clear indication that class II metals coordinate the SCN group via the nitrogen atom whereas class III metals coordinate via the sulphur atom. — We can then rationalize our findings thus: The class II and III metals are those that form "covalent" bonds with the SCN-group, a lone-pair of the ligand being donated into empty orbitals of the metal; the class II metals interacting with a nitrogen lone-pair, the class III ones interacting with a sulphur lone-pair.

On the basis of this rationalization let us try to understand how such a lone-pair donation will affect IR absorption intensities and frequencies:

From his careful analysis of IR-spectra of the thiocyanate ion Jones[16] suggests the following approximate distribution between the resonance structures:

$$\alpha \quad N{\equiv}C{-}S^- \qquad 71 \%$$
$$\beta \quad {}^-N{=}C{=}S \qquad 12 \%$$
$$\gamma \quad {}^{-2}N{-}C{\equiv}S^+ \qquad 17 \%$$

Now a lone-pair donation from the nitrogen atom giving rise to a M—N σ bond, will benefit from the existense of the β and — above all — the γ canonical structures. In other words, the relative amount of structures β and γ will increase with nitrogen-lone-pair coordination. This means a greater dipole moment over the C—N bond, most probably also implying an increased value of the derivative of dipole moment and thus of the absorption intensity (vide, e.g., Ref.[17], p. 190). This is actually found. Furthermore, the increase of the relative amount of structures β and γ will mean a decrease of bond order of the C—N bond, that is a shift of the absorption frequency towards lower values. This is actually found — at least a trend in that direction is observed (vide supra p. 1451).

A lone-pair-donation from the sulphur atom, on the other hand, will give rise to a M—S σ bond. With an analogous argument this might be expected to result in an increase of the relative amount of structure α. This means a decreased polarity of the C—N bond, resulting in a lowered absorption intensity, and an increased bond order, resulting in a shift of the absorption frequency towards higher values. Both these effects are actually found.

We now turn our attention to the invariance of the integrated absorption of the thiocyanate ion when coordinated to metals belonging to class I. We suggest that this means that in these complexes there is very little electron exchange between ligand and metal. However, the observed shifts ($\Delta \nu$) of absorption frequencies and the linear dependence of this quantity on log β_1 (Ref.[1]) are still to be explained.

We consider it probable that the increase of the vibration frequency is of a similar origin as the variation of frequency found for polyatomic ions trapped in ionic matrices [12,18].

The invariance of the integrated absorption tells us that in the cases considered coordination of the thiocyanate ion causes no change in the proportions between the three canonical structures α, β and γ given by Jones [16]. Therefore, the increase of the force constant observed must originate from a repulsion from the electron cloud of the metal acting upon the electron cloud of the nitrogen atom. Qualitatively, it seems plausible that the stronger the metal-ligand bond the closer must the nitrogen atom be to the electron cloud of the metal and thus the greater will be the increase of the force constant. However, we fail to arrive at an explanation of the quantitative connection between $\Delta \nu$ and log β_1.

The effects classified here as characterizing classes I, II and III are most probably additive. Thus the unusual large frequency shift found for SCN-bridged polynuclear complexes (the cadmium system investigated here, and the platinum complexes investigated by Chatt and Duncanson [3]) may arise from a great contribution of class I and class III effects dominating over a less important class II contribution.

Also the position of the absorption peaks of the class II complexes might arise from a superposition of a definite shift towards lower frequencies on a class I effect.

If we compare the classification of the octahedral and tetrahedral Co(II) complexes, we find that the first is a class I complex, i.e., with a very low degree of electron exchange between ligand and metal, whereas the last one is a class II complex, i.e., with a definite "covalent" σ-bonding. This is in striking agreement with the theory for the intensities of electronic spectra, demanding a much stronger electron exchange for tetrahedral than for octahedral complexes. (cf., e.g., Ballhausen [19]).

One more observation may be worthy of comment. It is seen from Table 3 that at least for classes I and III it holds that $\Delta \nu_{\frac{1}{2}}$ is always smaller than the same quantity for the free ligand. This follows, of course, from the more effective shielding of the thiocyanate ion from outer disturbances in the complexes than in the free state.

That the iron(III) system exhibits a very broad peak (cf. Table 3) is quite understandable, if as assumed in our discussion above (p. 1449) polynuclear complexes are formed, each contributing with its own absorption peak. The measured half-width is then only a formal quantity. It is most probable that the same holds true also for the uranyl system. However, even if the peaks observed should be composed of several components, the main conclusions drawn from the values of ε_1 and $\Delta \nu_{\frac{1}{2}}$ reported in Table 8 must still hold true.

The measured quantity ε_1 is then smaller than ε would be for a single peak, but as on the other hand $\Delta\nu_{\frac{1}{2}}$ is obviously larger than it would be for a single peak the product may still be of the same order of magnitude as it should be for a single peak.

When this manuscript was close to completion, the paper of Lewis, Nyholm and Smith [11a] appeared. These authors measure the C—N and C—S frequencies of a considerable number of saturated thiocyanato complexes both in the solid state and in solution (acetophenone). They note the difference between the results obtained in these two ways. They also carry on a discussion on the change of bonding in the ligand following upon coordination, which is almost identical to that given here. These authors did not measure the intensity of absorption, and so they must confine their discussion to the change of frequency. As is also reported by Turco and Pecile [11] they find it easier to interpret the change of the C—S frequency than that of the C—N one. This is certainly due to the interference of the electron-repulsion effect discussed above for the class I ions.

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