

Studies on Cobaltamines

IV. A Proton Addition Reaction of Some Thiocyanatocobaltamines

RAGNAR LARSSON

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

When $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ and *trans*- $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ are dissolved in concentrated sulphuric acid, a colour change from red to yellow is observed. The absorption curves in the visible and near ultraviolet region are presented. The colour change is shown to be caused by a proton addition reaction, similar to the additions of Ag^+ and Hg^{2+} . It is assumed from the presented data that the $\text{Co}-\text{NCS}-\text{H}$ bond is essentially of the same character as the $\text{Co}-\text{NCS}-\text{Ag}$ and $\text{Co}-\text{NCS}-\text{Hg}$ bonds. This result is put in relation to the current discussion on the covalent bonds of b-class metals¹.

It has long been recognized² that silver ions have the ability to coordinate to the thiocyanato group in thiocyanato cobalt(III) ammine complexes. In addition mercury(II) ions have the same coordinating ability³. As a result of this reaction the colour of the cobalt complexes shifts from red to yellow^{3,4}. According to Werner² the colour of the compounds obtained are similar "almost to confusion" to that of the luteo salts. Schaeffer⁵ has related this colour shift to the ability of Ag^+ and Hg^{2+} ions to interact with the π electrons of the thiocyanato group.

During investigations on the reactions of thiocyanato cobalt amines it was observed by the present author, that when these compounds were dissolved in concentrated sulphuric acid a similar change in colour occurred. Although this colour change must have been observed many times during ordinary analytical procedures, it has not been found reported in the available literature. Therefore some experiments were performed to investigate this reaction in detail and to relate it to the already known addition reactions of silver and mercury(II) ion.

MEASUREMENTS

The following experiments were performed:

1. In order to estimate the change of the absorption spectra of cobaltamines when the solvent is changed from water to conc. sulphuric acid the

Table 1. Data of the spectrum of $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ dissolved in water and in conc. sulphuric acid.

Solvent	$\lambda_{\text{max}1}$ m μ	$\log \epsilon_{\text{max}1}$	$\lambda_{\text{max}2}$ m μ	$\log \epsilon_{\text{max}2}$
Water	476	1.75	339.5	1.66
Conc. H_2SO_4	479	1.78	339.7	1.69

absorption spectrum of $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ was determined in the two solvents. As seen from Table 1 there is only a very small shift in the wavelengths and extinction coefficients of the maxima.

2. In order to relate the change of the absorption spectra of thiocyanatocobaltamines when dissolved in conc. sulphuric acid to that produced by heavy metals, the spectra of $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ and *trans*- $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ were determined in water, in conc. sulphuric acid and in aqueous solutions containing large quantities of mercury nitrate. The results are given in Figs. 1 and 2 and Table 2. The data for the $\text{Coen}_2(\text{NCS})_2^{2+}$ ion should be compared to the data given by Shimura and Tsuchida⁶ for the *trans*- $\text{Coen}_2(\text{NH}_3)_2^{3+}$ ion, ($\lambda_{\text{max}1} = 467$ m μ , $\log \epsilon_{\text{max}1} = 1.77$; $\lambda_{\text{max}2} = 336$ m μ , $\log \epsilon_{\text{max}2} = 1.73$). The same spectra were obtained for solutions containing 0.1 M and 0.2 M $\text{Hg}(\text{NO}_3)_2$, which indicates the completeness of the reaction.

3. The possibility of a substitution reaction in the inner coordination sphere of the cobalt atom is very unlikely as Co(III) thiocyanato complexes

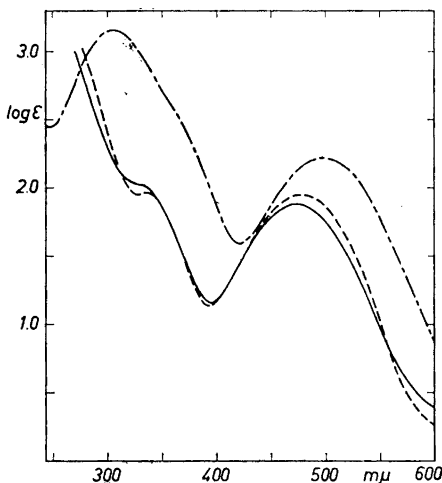


Fig. 1. Spectra of $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ dissolved in water (---), in conc. sulphuric acid (—) and in 0.1 M $\text{Hg}(\text{NO}_3)_2$ (- - -).

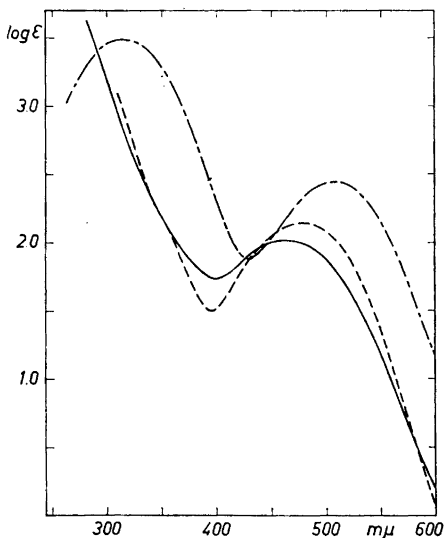


Fig. 2. Spectra of *trans*- $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ dissolved in water (-.-.-), in conc. sulphuric acid (—) and in 0.1 M $\text{Hg}(\text{NO}_3)_2$ (---).

Table 2. Data of observed peaks of spectra of $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ and *trans*- $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ dissolved in water, conc. sulphuric acid and 0.1 M $\text{Hg}(\text{NO}_3)_2$.

Complex	Solvent	λ_{max_1} m μ	log ϵ_{max_1}	λ_{max_2} m μ	log ϵ_{max_2}
$[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$	Water	498	2.22	306	3.16
	conc. H_2SO_4	474	1.89	330 *	2.02
	0.1 M $\text{Hg}(\text{NO}_3)_2$	476	1.95	333	1.96
$[\text{Coen}_2(\text{NCS})_2]^+$	Water	509	2.44	315	3.49
	conc. H_2SO_4	465	2.02	—	—
	0.1 M $\text{Hg}(\text{NO}_3)_2$	479	2.14	—	—

* shoulder

are known to be quite inert⁷ and the reaction is apparently momentary. Nevertheless an experiment was performed to investigate this question. A solution of $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ in conc. H_2SO_4 (17.7 M) was diluted in iccold water and — when the solution had room temperature — diluted so as to give a solution of the complex in 17.7/20 M H_2SO_4 . The spectrum of this solution was compared with that of a solution obtained by dissolving the complex directly in 17.7/20 M H_2SO_4 . The recovery of the original complex was estimated to be 95–97 % indicating that the colour change is not due to an irreversible decomposition reaction.

4. In spite of the results of experiment 1, there still remains the possibility that the colour change under discussion is caused by a "solvent effect" operating primarily on the thiocyanato group. If this is true one should expect a continuous change of the extinction coefficients of the complex for a series of water-sulphuric acid mixtures as solvents. Such measurements for the most simple salt used in this investigation, $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$ are recorded in Fig. 3. It is seen that there is no "continuous" change but rather a very sharp change of the properties of the solution in the narrow concentration region 14–15 M.

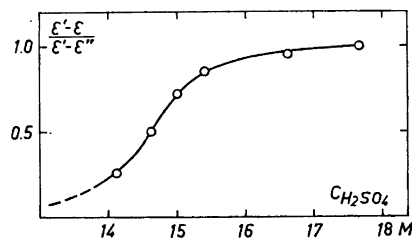


Fig. 3. The function $(\epsilon' - \epsilon)/(\epsilon' - \epsilon'')$ for the $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ complex plotted against the sulphuric acid concentration. The extinction coefficients were read from the curves at 550 m μ .

ϵ' = extinction coefficient of the complex in pure water
 ϵ'' = » » » » » » conc. H_2SO_4
 ϵ = » » » » » » mixed solvents.

EXPERIMENTAL

The measurements were made with a Beckman DK-1 Recording Spectrophotometer with quartz cells. The concentrations of the metal complexes were chosen so as to give an optical density of the maxima in all cases of the magnitude 0.5–0.8.

Chemicals used. $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$ and *trans*- $[\text{Coen}_2(\text{NCS})_2]\text{ClO}_4$ were prepared as before^{8,9}. $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_3$ was prepared according to the method described by Werner¹⁰ with the additional precipitation of the perchlorate by perchloric acid and final recrystallisation. Cobalt content: calc. 14.69 %; found 14.67 %.

DISCUSSION

It is one of the main theorems of the crystal-field theory¹¹ that the splitting of the energy levels of the metal ion is strongly dependent upon the distance between the metal ion and the ligand (point-charge or dipole). As it is most probable that in the complexes under discussion, crystal-field effects are the most important ones in determining the visible spectra of the complexes, we can conclude that the electron density around the nitrogen atom in the thiocyanato group is almost the same whether an Hg^{2+} , Ag^+ or H^+ ion coordinates to the sulphur atom. Indeed, the similarity of the spectra of these association products and of the luteo ions give us the information that the electron density corresponds almost exactly to that of the NH_3 -nitrogen atoms in the luteo ions.

The fact that the same electron density is found around the nitrogen atom whether an Hg^{2+} or an H^+ ion is the association partner casts some light upon the discussion on the division of metals into two classes, characterised by their different coordination ability: From the above data we are forced to conclude that the $\text{Hg}-\text{S}$ and the $\text{H}-\text{S}$ bonding cause almost the same degree of rehybridization of the thiocyanato group and thus the $\text{Hg}-\text{S}$ and $\text{H}-\text{S}$ bonds are of essentially the same character in regard to electronic distribution.

It has been proposed¹ that Hg^{2+} and the other b-group ions owe their strong coordination ability towards sulphur to a d–d π bonding. Because of the above-mentioned similarity between $\text{Hg}-\text{S}$ and $\text{H}-\text{S}$ bonds, however, this explanation can be ruled out in the present case as the hydrogen atom cannot participate in any such bonding, nor in any d–p π bonding involving the π -orbitals of the thiocyanate ligand. It seems more likely then, that the explanation given by Williams¹² (see also Ref.¹³) is more appropriate here. This implies that the small and often highly charged ions of the b-group exert a strong polarizing action upon ligands such as sulphur. This polarizing effect is said to be strengthened by the strongly directional orientation of the filled d-orbitals of the b-group metals.

The above-mentioned rehybridization of the thiocyanate group does also manifest itself by a shift of the high intensity peak at about 300 m μ . This peak has been ascribed to an intra-ligand transition (*cf.* Ref.¹⁴, p. 271). Especially in the case of the $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ ion (Fig. 1) is this shift easily observed, as here the peak in question and the second "crystal-field peak" (${}^1A_{1g} \rightarrow {}^1T_{2g}$ -transition) are almost resolved. As the spectra were not recorded in the far ultraviolet, we cannot say anything definite about this shift, but it seems to

be of the same order of magnitude in the case of the Co—NCS—Hg system as in the case of the Co—NCS—H one.

Another point of great interest of the present investigation is the close similarity to the findings of Schilt^{15,16} on the proton complexes of the [Fephen₂(CN)₂] molecule. However the bonding mechanism proposed by Schilt¹⁶, implying a direct H—Fe interaction, cannot be applied to the present case as the Ag⁺ and Hg²⁺ ions are certainly too large to be situated close to the cobalt nucleus. Rather, it has been concluded recently by Hamer and Orgel¹⁷ that the explanation offered by Schilt is probably not true, as they¹⁷ could prepare a compound [Fephen₂(CN—CH₃)₂] with a very similar spectrum compared to [Fephen₂(CN—H)₂]²⁺.

This fact, in its turn, gives increased support to our interpretation of the σ -bond character of the S—Hg and S—H bonds in the thiocyanatocobaltamines studied in this paper.

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