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STUDY OF THE SELENOCYANATE COMPLEXES OF COBALT AND NICKEL

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The selenocyanates of cobalt and nickel have so far scarcely been studied ([1]). In the literature there are only the results of Spacu' s preparative studies ([2,3]) on ammine complexes of these metals with $SeCN^-$ ions in the outer sphere. We set ourselves the aim of studying the formation of selenocyanate complexes of cobalt and nickel as a function of the nature of the solvent, of synthesizing simple selenocyanates of nickel and cobalt, and also their molecular compounds containing $SeCN^-$ ions in the inner sphere. The starting materials in our investigations were NaSeCN, KSeCN (synthesized as described in ([4])), and the perchlorates of cobalt and nickel (obtained by the action of perchloric acid on the corresponding carbonates ([5])). Water, methanol, and acetone were used as solvents. The latter were carefully purified and rendered absolute. The initial concentrations of sodium and potassium selenocyanates were determined from selenium; cobalt, by a gravimetric method (the weighing form $CoSO_4$); and nickel, with the aid of dimethylglyoxime. Since nickel and cobalt salts were used in the form of crystalline hydrates, in the study of nonaqueous solutions a constant water concentration (less than 0.5% by volume) was maintained throughout the series of experiments.

Aqueous solutions of cobalt selenocyanates, and especially of nickel selenocyanates, are characterized by low stability. The solutions are more stable if they contain an excess of nickel or cobalt salt with respect to the selenocyanate ion. This indicates the greater stability of the simplest complexes $CoSeCN^+$ and $NiSeCN^+$. Their composition was established spectrophotometrically at 510 mμ (in the case of cobalt) and 330 mμ (for nickel). In composition, $CoSeCN^+$ and $NiSeCN^+$ resemble the corresponding rhodanides ([6,7]). In aqueous solutions, for $CoSeCN^+$ it was possible to determine the dissociation constant by the potentiometric method. To measure the equilibrium concentrations of $SeCN^-$ ions, an indicator electrode of the second kind, Ag | AgSeCN, was used. The dissociation constant of $CoSeCN^+$ ($K = 6.8 \cdot 10^{-2}$) is of the same order as that for $CoCNS^+$. It was not possible to determine the dissociation constant of $NiSeCN^+$, because of the rapidly occurring decomposition of the solutions.

The interaction between $SeCN^-$ and the ions of the corresponding metals in methanol was studied by the methods of electrical conductivity and spectropho-

Figure 1. Formation curves in the system Me^{2+}—$SeCN^{-}$—CH_3OH. 1 –cobalt salt, 2 –nickel salt (the numerical values on the abscissa axis in parentheses refer to 1).

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tometry. In the study of isomolar series of solutions $Co(ClO_4)_2$–NaSeCN, as well as $Ni(ClO_4)_2$–NaSeCN, by the conductivity method, a diffuse minimum is found on the composition-property diagram (the electrical conductivity of pure salts in methanol changes linearly), indicating the formation of the complexes $Me(SeCN)_3^-$, $Me(SeCN)_4^{2-}$.

A more complete picture of complex formation can be established spectrophotometrically. Methanolic solutions of $Co(ClO_4)_2$ containing a small excess of $SeCN^-$ ions are characterized by the presence of two maxima at 520 and 630 mµ. As the concentration of $SeCN^-$ increases, the first maximum decreases and the second increases. Measurement of the optical density of iso-

equimolar series of solutions showed that, for cobalt, regardless of the initial concentrations of the components, which were varied from 0.05 to 0.5 mole/liter, at $\lambda = 520$ mμ only the complex $CoSeCN^+$ can be detected. A methanolic solution of $Ni(ClO_4)_2$ has an absorption maximum in the region of 400 mμ. The optical density of $Ni(ClO_4)_2$ solutions increases sharply upon addition of NaSeCN (especially in the 320-330 mμ region). The light-absorption curve of these solutions also retains the band at 400 mμ, but its intensity is appreciably higher than for pure $Ni(ClO_4)_2$. Taking this into account, we measured the optical densities of equimolar series of solutions at 320 and 400 mμ. It turned out that, by varying the initial concentrations of the components, it is possible thereby to reveal the complexes $NiSeCN^+$, $Ni(SeCN)_2$, $Ni(SeCN)_3^-$.

Fig. 1. Formation curves in the system Me^{2+}—$SeCN^{-}$—CH_3OH. 1 –cobalt salt, 2 –nickel salt (the numerical values on the abscissa axis in parentheses refer to 1)

Naturally, it was assumed that more complex species could be detected with a large excess of addend. Therefore we measured the optical density of solutions with a constant concentration of the central ions and an increasing concentration of $SeCN^-$ ions. The data obtained were treated according to Bjerrum ([8]). The optical density was measured at 630 mμ (for cobalt) and 320 mμ (for nickel). On the basis of the data obtained, a "formation curve" was constructed. As can be seen from Fig. 1, for nickel the maximum value $\bar{n} = 4$, and for cobalt $\bar{n} = 6$. Our data agree with those of West ([9]), who showed the formation of $Co(CNS)_6^{4-}$ in aqueous-alcoholic solution.

From the "formation curve" approximate values were found, first stepwise and

Fig. 2. Formation curve in the system Ni^{2+}—$SeCN^{-}$—CH_3COCH_3 at $\lambda = 370$ mµ

Figure 2: Fig. 2. Formation curve in the system Ni^{2+}—$SeCN^{-}$—CH_3COCH_3 at $\lambda = 370$ mµ

then the overall dissociation constants of the corresponding complexes were calculated (see Table 1). The dissociation constant of $CoSeCN^{+}$ was found by the method of N. P. Komar' (^{6}).

Table 1

Dissociation constants	$Ni(SeCN)_m^{2-m}$	$Co(SeCN)_m^{2-m}$	Dissociation constants	$Ni(SeCN)_m^{2-m}$	$Co(SeCN)_m^{2-m}$
K_1	$2.0 \cdot 10^{-3}$	$2.1 \cdot 10^{-4}$	K_4	$1.8 \cdot 10^{-7}$	$8.5 \cdot 10^{-6}$
K_2	$3.6 \cdot 10^{-5}$	$4.2 \cdot 10^{-5}$	K_5	–	$4.6 \cdot 10^{-6}$
K_3	$2.0 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$	K_6	–	$2.8 \cdot 10^{-6}$

In acetone solutions, compared with methanolic solutions, the complex-formation reaction proceeds more readily. This can be shown already by measuring the electrical conductivity of equimolar series $Co(ClO_4)_2$—NaSeCN, $Ni(ClO_4)_2$—NaSeCN, and also $Co(SeCN)_2$—KSeCN. In this case, on the χ—composition diagram there is a minimum indicating the formation of $Me(SeCN)_3^{-}$ complexes. Spectrophotometry of equimolar series in acetone makes it possible to detect the complexes $CoSeCN^{+}$ (at $\lambda = 530$ mμ) and $Co(SeCN)_4^{2-}$ (at $\lambda = 630$ mμ), similarly to what was established for rhodanides (^{10}). For nickel, by the Ostromyslensky-Job method, the complexes $Ni(SeCN)_2$, $Ni(SeCN)_3^{-}$, $Ni(SeCN)_4^{2-}$ can be established at ($\lambda =$

–325 mµ) and $Ni(SeCN)_6^{4-}$ (at $\lambda = 380$ mµ). The latter complex was demonstrated by constructing the "formation curve" shown in Fig. 2.

Thus, in acetone the highest complex for cobalt is $Co(SeCN)_4^{2-}$, and for nickel –$Ni(SeCN)_6^{4-}$. This can be explained by the greater affinity of acetone for the cobalt ion than for the nickel ion, and by its entry, together with $SeCN^{-}$ addends, into the inner sphere. For $CoSeCN^{+}$ the dissociation constant was calculated and found to be $1 \cdot 10^{-8}$. The dissociation constant of $Co(SeCN)_4^{2-}$, found by Komar' (^{6}), is $7 \cdot 10^{-14}$. Nickel selenocyanates in acetone are less stable ($K_1 = 4 \cdot 10^{-4}$, $K_4 = 4.1 \cdot 10^{-11}$). The latter constants were determined from the "formation curve" (Fig. 2). Study of complex formation in solution showed that replacement of water by a nonaqueous solvent leads to a complication of the composition of the complexes and also causes a sharp strengthening of them.

Fig. 2. Formation curve in the system Ni^{2+}—$SeCN^{-}$—CH_3COCH_3 at $\lambda = 370$ mµ

Complex formation proceeds most readily in acetone. Taking this into account, in acetone solution we carried out an exchange reaction between KSeCN and the corresponding nitrates, taken in a ratio of 2 : 1. After separation of the KNO_3 precipitate, dioxane was added to the solution. In the case of nickel, bluish-green crystals of $Ni(SeCN)_2 \cdot 6C_4H_8O_2$ were formed, soluble in acetone and water. For cobalt, in an analogous way, a light-brown powder soluble in acetone, of composition $Co(SeCN)_2 \cdot 4C_4H_8O_2$, was obtained. Analysis* of these salts gave the following:

$Ni(SeCN)_2 \cdot 6C_4H_8O_2$. Found, %: Ni 7.30; Se 19.90
Calculated, %: Ni 7.35; Se 19.80

$Co(SeCN)_2 \cdot 4C_4H_8O_2$. Found, %: Co 9.80; Se 25.20
Calculated, %: Co 9.51; Se 25.44

On keeping $Co(SeCN)_2 \cdot 4C_4H_8O_2$ under dioxane, pink crystals of $Co(SeCN)_2 \cdot 6C_4H_8O_2$ were obtained.

$Co(SeCN)_2 \cdot 6C_4H_8O_2$. Found, %: Co 7.48; Se 19.65
Calculated, %: Co 7.40; Se 19.75

The salts $Ni(SeCN)_2 \cdot 6C_4H_8O_2$ and $Co(SeCN)_2 \cdot 6C_4H_8O_2$ rapidly lose dioxane, turning into powders of dark-brown $Ni(SeCN)_2$ or pale-pink $Co(SeCN)_2 \cdot 2C_4H_8O_2$ color, readily soluble in water. It has not yet been possible to obtain $Co(SeCN)_2$.

$Ni(SeCN)_2$. Found, %: Ni 21.30; Se 58.42
Calculated, %: Ni 21.80; Se 58.75

$Co(SeCN)_2 \cdot 2C_4H_8O_2$. Found, %: Co 13.4; Se 35.0
Calculated, %: Co 13.25; Se 35.5

Using anhydrous $CoCl_2$ and KSeCN, taken in a ratio of 1 : 4, as starting salts, we obtained a green powder of composition $K_2Co(SeCN)_4 \cdot 3C_4H_8O_2$.

$K_2Co(SeCN)_4 \cdot 3C_4H_8O_2$. Found, %: K 9.7; Co 7.28; Se 38.47
Calculated, %: K 9.52; Co 7.18; Se 38.47

* The analytical data for all salts synthesized by us are given as averages from several determinations.

If NaSeCN is taken instead of KSeCN, then under the same conditions it is possible to obtain shiny blue plates, soluble in acetone and water. Analysis of the salt obtained indicates the composition $Na_2Co(SeCN)_4 \cdot 7C_4H_8O_2$.

Found, %:	Co 5.15; Se 27.75
$Na_2Co(SeCN)_4 \cdot 7C_4H_8O_2$. Calculated, %:	Co 5.17; Se 27.70

It was not possible to obtain salts of analogous composition for nickel.

If dioxane ($\sim 50\%$ by volume) is introduced into an acetone solution containing Co^{2+} and $SeCN^-$ in a ratio of 1 : 6, very small plates immediately separate, turning into an amorphous blue mass. The powder obtained is soluble in acetone and is decomposed by water. This salt corresponds to the composition $K_3Co(SeCN)_5 \cdot 3C_4H_8O_2$.

Found, %:	K 12.5; Co 6.00; Se 41.20
$K_3Co(SeCN)_5 \cdot 3C_4H_8O_2$. Calculated, %:	K 12.11; Co 6.12; Se 41.0

On recrystallization from an acetone-dioxane mixture, the composition of this salt does not change.

From an acetone solution obtained by mixing solutions of $Ni(NO_3)_2$ and KSeCN in a ratio of 1 : 6, after separation of the KNO_3 precipitate, the salt $K_4Ni(SeCN)_6 \cdot 2CH_3COCH_3$ crystallizes. This salt forms as very small blue crystals, rapidly decomposing in air.

Found, %:	Ni 6.16; Se 49.63
$K_4Ni(SeCN)_6 \cdot 2CH_3COCH_3$. Calculated, %:	Ni 6.14; Se 49.50

The data we have obtained make it possible to conclude that nickel is more prone to the formation of $Ni(SeCN)_6^{4-}$ complexes than cobalt, for which $Co(SeCN)_4^{2-}$ is formed more readily. The data on the composition and stability of the complex selenocyanates, as well as on the synthesis of the corresponding salts, indicate a great similarity between the selenocyanates of cobalt and nickel and their rhodanides ([11,12]).

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