CATIONIC-TYPE SILVER SELENOCYANATE COMPLEXES

![Fig. 1](image)

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

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CATIONIC-TYPE SILVER SELENOCYANATE COMPLEXES

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Silver halides and pseudohalides have increased solubility in the presence of an excess not only of the corresponding anions, but also of silver cations. The possibility of formation of cationic complexes of the type Me_2X^+, where X is an anion, was indicated by V. A. Kistyakovskii (^{1}), who found the complexes Ag_3J^{2+} in solution (^{2}). K. Hellwig came to the same conclusion, observing the migration of iodine to the cathode during electrolysis of the liquid phase of the system $AgNO_3$–AgJ–H_2O (^{3}).

Fig. 1. Dependence of ψ_i on the concentration of $AgNO_3$.
1–ψ_2; 2–ψ_3; 3–ψ_4

Fig. 2. Dependence of ψ_i on the concentration of $AgClO_4$.
1–ψ_2; 2–ψ_3; 3–ψ_4

K. Hellwig studied the solubility of certain silver salts in a solution of $AgNO_3$ and isolated, in crystalline form, compounds of the composition: $2AgNO_3 \cdot AgX$ and $AgNO_3 \cdot AgJ$, where $X = J', CNS', Y = Cl', Br', J'$.

Regarding such compounds as double salts, S. V. Gorbachev (^{4}) calculated their dissociation constants in accordance with the scheme:

$$AgNO_3 \cdot AgX \rightleftharpoons AgNO_3 + AgX.$$

I. A. Kablukov (^{5}), by thermal analysis of the AgBr–$AgNO_3$ system, established the existence of the compound $AgNO_3 \cdot AgBr$. In the melt (^{6}), the compounds $2AgNO_3 \cdot AgJ$, $AgNO_3 \cdot AgJ$, and $AgNO_3 \cdot AgCl$ were also demonstrated.

K. Liser (7), measuring the depression of the freezing point and the electrical conductivity of aqueous solutions of $AgNO_3$ in which AgJ had been dissolved, confirmed the existence of cationic complexes. B. V. Nekrasov also cal-

considers compounds of the type $Ag_nHal(NO_3)_{n-1}$ as complexes with a halide ion as the central ion (8). Using Hellwig' s data on the solubility of silver halides, K. B. Yatsimirsky (9) calculated the overall dissociation constants of the cationic complexes Ag_3J^{2+} $(8.0 \cdot 10^{-15})$, Ag_2Br^+ $(2 \cdot 10^{-10})$ and Ag_2Cl^+ $(2 \cdot 10^{-7})$.

Since the $CNSe^-$ ion has a marked similarity to the J^- ion, it could be assumed that cationic complexes also exist on the basis of silver selenocyanate. It was of interest to compare the stabilities of the selenocyanate complexes with those of the halide complexes, and also to clarify whether the outer-sphere ion affects the course of the complex-formation reaction. For this purpose we studied the solubility of AgCNSe in aqueous solutions of $AgNO_3$ and $AgClO_4$.

Results of the investigation and their discussion

Silver selenocyanate was obtained by an exchange reaction between reagent-grade $AgNO_3$ and KCNSe (99%). Silver perchlorate was obtained from silver nitrate. The latter was converted into the oxide, which was then dissolved in reagent-grade $HClO_4$. The resulting $AgClO_4$ was recrystallized before use.

A series of solutions of $AgNO_3$ and $AgClO_4$ was prepared; these were saturated with freshly prepared AgCNSe. The mixtures were thermostated at 20° until equilibrium was attained, after which the solid phase, consisting of AgCNSe, was filtered off. Silver and selenium were determined in the filtrate. For this purpose an aliquot of the solution was treated with nitric acid, total silver was determined as AgCl (gravimetrically), and selenium was determined argentometrically (10). Experiments on the solubility of AgCNSe in solutions of $AgNO_3$ and $AgClO_4$ were repeated 2-3 times. Construction of the logarithmic dependence of the solubility of AgCNSe on the concentration of the silver salt showed that, in the concentration interval 0.7-3.1 mole/liter, the complexes Ag_2CNSe^+, Ag_3CNSe^{2+} and even Ag_4CNSe^{3+} are formed. The existence of the last com-

Table 1

Solubility of AgCNSe in $AgNO_3$ solutions

Initial concentration of $AgNO_3$, mole/liter	Solubility of AgCNSe, mole/liter	Equilibrium concentration of $AgNO_3$	Φ	$\psi_2 = \frac{\Phi}{[Ag^+]^2}$	$\psi_3 = \frac{\Phi}{[Ag^+]^3}$	$\psi_4 = \frac{\Phi}{[Ag^+]^4}$
0.736	$0.375 \cdot 10^{-3}$	0.736	$0.069 \cdot 10^{13}$	$1.27 \cdot 10^{12}$	$1.73 \cdot 10^{12}$	$2.35 \cdot 10^{12}$
1.192	$1.00 \cdot 10^{-3}$	1.191	$0.298 \cdot 10^{13}$	$2.10 \cdot 10^{12}$	$1.77 \cdot 10^{12}$	$1.48 \cdot 10^{12}$
1.521	$1.49 \cdot 10^{-3}$	1.520	$0.566 \cdot 10^{13}$	$2.45 \cdot 10^{12}$	$1.68 \cdot 10^{12}$	$1.12 \cdot 10^{12}$
1.728	$2.12 \cdot 10^{-3}$	1.726	$0.914 \cdot 10^{13}$	$3.08 \cdot 10^{12}$	$1.78 \cdot 10^{12}$	$1.03 \cdot 10^{12}$
1.860	$2.50 \cdot 10^{-3}$	1.858	$1.16 \cdot 10^{13}$	$3.36 \cdot 10^{12}$	$1.80 \cdot 10^{12}$	$0.98 \cdot 10^{12}$
2.097	$3.45 \cdot 10^{-3}$	2.094	$1.81 \cdot 10^{13}$	$4.11 \cdot 10^{12}$	$1.96 \cdot 10^{12}$	$0.95 \cdot 10^{12}$
2.687	$6.36 \cdot 10^{-3}$	2.681	$4.26 \cdot 10^{13}$	$5.93 \cdot 10^{12}$	$2.20 \cdot 10^{12}$	$0.83 \cdot 10^{12}$
3.022	$8.48 \cdot 10^{-3}$	3.014	$6.39 \cdot 10^{13}$	$7.03 \cdot 10^{12}$	$2.33 \cdot 10^{12}$	$0.78 \cdot 10^{12}$

Table 2

Solubility of AgCNSe **in** $AgClO_4$ **solutions**

Initial concentration of $AgClO_4$, mole/liter	Solubility of AgCNSe, mole/liter	Equilibrium concentration of $AgClO_4$	Φ	ψ_2	ψ_3	ψ_4
1.045	$1.10 \cdot 10^{-3}$	1.044	$0.287 \cdot 10^{13}$	$2.63 \cdot 10^{12}$	$2.52 \cdot 10^{12}$	$2.42 \cdot 10^{12}$
1.305	$1.98 \cdot 10^{-3}$	1.303	$0.645 \cdot 10^{13}$	$3.80 \cdot 10^{12}$	$2.92 \cdot 10^{12}$	$2.24 \cdot 10^{12}$
1.381	$2.12 \cdot 10^{-3}$	1.379	$0.731 \cdot 10^{13}$	$3.85 \cdot 10^{12}$	$2.79 \cdot 10^{12}$	$2.02 \cdot 10^{12}$
1.796	$4.35 \cdot 10^{-3}$	1.792	$1.949 \cdot 10^{13}$	$6.07 \cdot 10^{12}$	$3.39 \cdot 10^{12}$	$1.89 \cdot 10^{12}$
1.943	$6.61 \cdot 10^{-3}$	1.937	$3.20 \cdot 10^{13}$	$8.53 \cdot 10^{12}$	$4.40 \cdot 10^{12}$	$2.27 \cdot 10^{12}$

Initial concentration of $AgClO_4$, mole/liter	Solubility of AgCNSe, mole/liter	Equilibrium concentration of $AgClO_4$	Φ	ψ_2	ψ_3	ψ_4
2.093	$7.01 \cdot 10^{-3}$	2.086	$3.66 \cdot 10^{13}$	$8.40 \cdot 10^{12}$	$4.03 \cdot 10^{12}$	$1.93 \cdot 10^{12}$
3.008	$2.24 \cdot 10^{-2}$	2.986	$1.67 \cdot 10^{14}$	$1.88 \cdot 10^{13}$	$6.37 \cdot 10^{12}$	$2.10 \cdot 10^{12}$

Previously, only tentative suggestions had been made regarding the existence of a complex of this composition (3). Data on the composition of these complexes were confirmed in calculating their dissociation constants by Leden' s method (11). The results of the investigation are presented in Tables 1–2 and in Figs. 1–2.

The function Φ was calculated approximately as $\frac{S[Ag^+]}{Pr}$ (12), where $[Ag^+]$ is the equilibrium concentration of silver ions, S is the solubility of AgCNSe. The value of the solubility product (Pr) of AgCNSe was taken as $4 \cdot 10^{-16}$ (13).

As is seen from Figs. 1, 2, by extrapolating the values of ψ_i to zero concentration of silver ions, β_i was found (intercepts on the ordinate), and the dissociation constants of the corresponding complexes were then calculated as $\frac{1}{\beta_i}$.

The values thus obtained are given in Table 3.

From the data given above it is evident that, in aqueous solutions in the presence of silver nitrate and perchlorate, complexes of the same composition exist. It should be noted that formation of Ag_4CNSe^{3+} in the presence of silver nitrate, as compared with $AgClO_4$ solutions, is more difficult (see Fig. 1). In both solutions there is good agreement between the dissociation constants of the simplest complexes. For the Ag_4CNSe^{3+} complex, the dissociation constants differ somewhat (see Table 3). The solubility of silver selenocyanate in the presence of $AgClO_4$ and $AgNO_3$ also differs.

Table 3

Values of the dissociation constants of the complexes

	Nitrate solutions	Perchlorate solutions
$K_2 = \frac{[Ag^+]^2[CNSe^-]}{[Ag_2CNSe^+]}$	$2 \cdot 10^{-12}$	$2 \cdot 10^{-12}$

	Nitrate solutions	Perchlorate solutions
$K_3 = \frac{[Ag^+]^3[CNSe^-]}{[Ag_3CNSe^{2+}]}$	$5.6 \cdot 10^{-13}$	$5.9 \cdot 10^{-13}$
$K_4 = \frac{[Ag^+]^4[CNSe^-]}{[Ag_4CNSe^{3+}]}$	$9.1 \cdot 10^{-13}$	$4.8 \cdot 10^{-13}$

In strength, the cationic complexes of silver based on the selenocyanate ion are very close to the corresponding iodide complexes. Thus, the dissociation constant of Ag_3J^{2+} is $8.0 \cdot 10^{-15}$ (9), while the dissociation constant of Ag_3CNSe^{2+} is $5.6 \cdot 10^{-13}$ (in the presence of $AgNO_3$).

To trace the difference in the formation of cationic complexes based on halides and pseudohalides, let us compare the solubilities of the corresponding salts in silver nitrate solutions with a concentration of 3 mol/l. The following values are obtained: AgCNSe $8.4 \cdot 10^{-3}$; AgJ $9.4 \cdot 10^{-3}$ (3); AgCNS $2.6 \cdot 10^{-3}$ (3) mol/l. The solubility of AgJ and AgCNS was determined at 25° (3). Thus, in its ability to form complexes with silver, the CNSe ion is closer to the J^- ion than to CNS^-, Cl^-, Br^-. By the solubility of AgX salts in 3M $AgNO_3$ solution, the halide and pseudohalide ions may be arranged in the series

$$J^- > CNSe^- > Cl^- > CNS^- > Br^-.$$

We also attempted to isolate salts containing cationic complexes in their composition. For this purpose, aqueous solutions of $AgNO_3$ and $AgClO_4$ (approximately 3 mol/l) were prepared. The solution was heated to 60–70°, then freshly prepared AgCNSe was added to saturation. The excess AgCNSe was rapidly separated, and the filtrate was left for crystallization. From the nitrate solution, white, slightly brownish, very small crystals stable in air were obtained. They are decomposed by water with liberation of AgCNSe; they dissolve without decomposition in $AgNO_3$ solutions; on heating to 118–120° they decompose.

To determine the composition of the salt obtained, a sample was treated with hot water; the AgCNSe that separated was filtered off, washed with water and alcohol, and dried at 100°. Silver was determined in the filtrate by titration with 0.01 N NaCl.

Found, %: $AgNO_3$ 61.2; 61.3; 61.0; AgCNSe 37.6; 38.7; 39.1
$(Ag_3CNSe)(NO_3)_2$. Calculated, %: $AgNO_3$ 61.5; AgCNSe 38.5

From a solution of $AgClO_4$, upon saturation with AgCNSe, white needle-like crystals were isolated; they are stable in air and do not decompose when heated to 150°. At a higher temperature the salt obtained from solutions of $AgClO_4$

decomposes with an explosion. It also decomposes upon dissolution in water. The composition of the salt corresponds to the formula $(Ag_2CNSe)\,ClO_4$.

Found, %:	$AgClO_4$ 49.20; 49.23;	AgCNSe 49.90; 49.70
$(Ag_2CNSe)\,ClO_4$. Calculated, %:	$AgClO_4$ 49.23;	AgCNSe 50.77

Thus, the synthesis of molecular compounds, like the solubility data, makes it possible to draw a conclusion about the influence of nonspherical ions on the interaction between $CNSe^-$ and Ag^+ ions.

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Note: Figure translations are in progress. See original paper for figures.