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METAL SELENOCYANATES AND THEIR PROPERTIES

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CONTENTS

I. Introduction 901
II. Selenocyanogen and its properties 902
III. Analytical chemistry of the $SeCN^-$ ion 902
IV. Simple selenocyanates and their properties 902
V. Selenocyanates of heavy metals 903
VI. Complexes based on metal selenocyanates 904
VII. Complex formation involving the selenocyanate ion as ligand and as central ion 904
VIII. Selenocyanato-complexes in non-aqueous solutions 905
IX. Complex-forming characteristics of the $SeCN^-$ ion 906
X. The structure of selenocyanates 906

I. INTRODUCTION

Selenocyanates find practical use as sensitisers in photographic emulsions and for the preparation of organic derivatives of selenium. The use of selenocyanates is very promising for the production of metal selenides, which are of great value in electronics. It may also be assumed that the selenocyanates will find use in analytical chemistry, especially in various titrations in non-aqueous solutions and also in the separation of selenium and tellurium with the object of obtaining these elements in a high state of purity.

Investigation of the selenocyanates is also of great theoretical significance in connection with the more profound elucidation of the chemical individuality of selenium. Nevertheless, there are no reviews on the selenocyanates. Only the dissociation constants of silver, mercury, and cadmium selenocyanates are given in a handbook[1]. Even the book by Williams[2] on cyanogen and its compounds with various elements gives only general information about a few metal selenocyanates.

The present paper is the first attempt to systematise published information on the selenocyanates.

II. SELENOCYANOGEN AND ITS PROPERTIES

Selenocyanogen has been prepared by a method similar to that used for the preparation of thiocyanogen[3], an ethereal solution of iodine being allowed to act on silver selenocyanate[4]:

$$2AgSeCN + I_2 = 2AgI + (SeCN)_2.$$

Selenocyanogen is a yellow powder soluble in light petroleum, chloroform, and carbon tetrachloride. It decomposes when dissolved in water. In the solid state it keeps well under a vacuum. Its structure may be represented as two isomers N≡C–Se–Se–C≡N and Se=C=N–N=C=Se.

By analogy with thiocyanogen, selenocyanogen can combine with metals and also form compounds with some non-metals. For example, a compound with selenium is known; this consists of an unbranched chain with three atoms of bivalent selenium in the middle and CN groups at the ends. The distances between the atoms in $Se(SeCN)_2$ have been found[15] to be Se–Se (2.33 Å), Se–C (1.83 Å), and C–N (1.05 Å). The Se–Se–Se valence angle is 101°.

Caesium trisselenocyanate $Cs(SeCN)_3$, which may be regarded as a polyhalide type of compound, has been obtained by the action of an ethereal solution of selenocyanogen on an alcoholic solution of caesium selenocyanate. Caesium trisselenocyanate consists of reddish brown monoclinic prisms stable in air; it is soluble in alcohol but is decomposed by water[6]. It has been shown that the compounds $KNCSeI_2$, $K(NCSe)_2I$, and $K(NCSe)_3$ are formed in the potentiometric titration of KNCSe with iodine solution.

Selenocyanic acid HNCSe was obtained by Crookes by the action of hydrogen sulphide on $Pb(SeCN)_2$ suspended in water[7]:

$$Pb(SeCN)_2 + H_2S = PbS + 2HNCSe.$$

HNCSe is known only in solution. It dissolves iron and zinc with liberation of hydrogen and displaces carbon dioxide from carbonates.

III. ANALYTICAL CHEMISTRY OF THE $SeCN^-$ ION

The quantitative analysis of selenocyanate solutions may be carried out by the usual argentometric titration with diphenylcarbazone[8], and also by potentiometric titration of the appropriate solutions with silver nitrate[19] or mercury perchlorate[10].

In the analysis of small quantities of selenocyanates, good results may be obtained by argentometric determination of the selenium[11]. The selenocyanate ion is converted to selenite by the action of nitric acid; an excess of silver nitrate and crystalline hydrazinium sulphate are added to the acid solution. Part of the silver is converted into silver selenide. The excess of silver nitrate is titrated against ammonium thiocyanate.

The concentration of selenocyanates soluble, or even slightly soluble in water, may be conveniently determined as selenium. The selenocyanates are decomposed with hydrochloric acid:

$$KNCSe + HCl = KCl + HCN + Se.$$

The selenium that separates is filtered off, dried at 100–110°, and weighed. This method gives good results in the analysis of salts in which the selenocyanate ion is not strongly bound. Apart from selenocyanates of the alkali and alkaline-earth metals, the salts of cadmium, cobalt, nickel, and even lead may be analysed by the method. The selenocyanates of silver, mercury, copper, and platinum are not completely decomposed by hydrochloric acid, part of the selenium appearing to be precipitated as selenide.

In recent years highly sensitive methods for the determination of selenium with the use of organic reagents have been developed[12–14]. These methods have been reviewed by Ryabchikov and Nazarenko[15]. The reagents may also be used in the analysis of selenocyanates.

IV. SIMPLE SELENOCYANATES AND THEIR PROPERTIES

The most studied compound of this series is potassium selenocyanate, first obtained by the fusion of selenium with potassium hexacyanoferrate(II).[16] It may be assumed that this reaction proceeds in the same way as the reaction of sulphur with potassium hexacyanoferrate(II):

$$6Se + 2K_4Fe(CN)_6 = 6KNCSe + FeK_2Fe(CN)_6.$$

White crystals of KNCSe are obtained when the melt is extracted. Since the selenocyanate ion is easily decomposed in the presence of water, absolute alcohol has replaced water in the extraction[7].

Later, methods for the preparation of KNCSe were proposed in which selenium was dissolved in a concentrated aqueous solution of KCN[4,17] or fused with potassium cyanide[18], the melt being subsequently extracted with water[19].

A very pure product was also obtained by boiling a suspension of selenium and potassium cyanide in absolute alcohol[20]. However, because of the interaction of the selenocyanate ion with alcohols and the formation of volatile evil-smelling alkyl selenides, this method is also inconvenient. A very unpleasant odour is also noticed in the extraction with alcohol of the product obtained by sintering selenium with potassium cyanide or potassium hexacyanoferrate(II). It is therefore more convenient to use acetone in the extraction[21]. A perfectly pure preparation of KNCSe was obtained by the reaction of selenium with potassium cyanide in liquid ammonia[22].

There are reports in the literature on the preparation of sodium selenocyanate by boiling red selenium with sodium cyanide in absolute alcohol[20]. Sodium selenocyanate may be obtained in good yield also by fusing selenium with sodium cyanide[21]. The density of sodium selenocyanate is 2.490 and that of potassium selenocyanate 2.347 g cm^{-3}.[20]

Caesium selenocyanate is also mentioned in the literature[6], but nothing is said about the properties of this salt. Ammonium selenocyanate was first obtained by Crookes by neutralising HNCSe with ammonia[7]. Later this salt was prepared by double decomposition between $(NH_4)_2SO_4$ and KNCSe in absolute alcohol[23], and its very poor stability noted.

Recently a communication was published on hydrazinium selenocyanate[24]. The tendency of this salt to isomerise was noted:

$$N_2H_5NCSe \rightleftharpoons H_2N–CSe–NH–NH_2.$$

Equilibrium in this reaction is rapidly reached in the presence of acetone and corresponds to 35% conversion of hydrazinium selenocyanate into the semicarbazide.

The selenocyanates of the alkaline-earth metals were first described by Crookes[7]. Since the salts he obtained were only analysed qualitatively, some caution must be used in dealing with his results. This refers particularly to the simple formulae for the salts put forward by Crookes. All the salts of the alkaline-earth metals and magnesium were obtained by the action of selenocyanic acid on the corresponding carbonates, with subsequent evaporation of the solutions over sulphuric acid in a vacuum desiccator.

As far as the properties of this group of compounds are concerned, there is more or less complete information in the literature on potassium selenocyanate. This is a colourless compound crystallising in the form of white acicular crystals, which deliquesce in air and are readily decomposed by acid vapours. When heated in a sealed vessel, potassium selenocyanate melts without decomposition; when heated in air, it decomposes at 100°. It dissolves readily in water, producing an appreciable reduction in temperature. The aqueous solution is alkaline; when the pH of the solution is reduced to 5, the salt begins to decompose.

Potassium selenocyanate behaves differently in the presence of foreign ions. As Lodzinska has pointed out, introduction of the ions Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+} has no effect on decomposition pH of the salt[25]: in the presence of these cations, potassium selenocyanate begins to decompose, when hydrochloric acid is added, at pH 5.5–4.9. In the presence of the cations Cd^{2+}, Hg^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, and Cr^{3+}, however, decomposition begins somewhat earlier, at pH > 6. The cations Ni^+, Co^{2+}, and Cu^{2+} decompose the selenocyanate ion still earlier, at pH > 7. According to Lodzinska, even at concentrations of cobalt, nickel, or copper cations of 10^{-4} g-ion litre^{-1} decomposition of $SeCN^-$ begins at a hydrogen-ion concentration of 10^{-8} g-ion litre^{-1}.

The electrical conductivity of aqueous solutions of potassium selenocyanate has also been studied; according to Birckenbach, the equivalent conductivity at infinite dilution is 119.5 at 18° and 138.2 at 25°.[26] The decomposition voltage of KNCSe was found to be 1.10 V.[6,27].

From a study of decomposition voltages and also calculation of the electron affinity of atoms and groups of atoms, Birckenbach concluded that the selenocyanate ion has properties closely similar to those of the halide ions. According to this worker, the selenocyanate ion should be placed before the iodide ion in the sequence of halide and pseudohalide ions:

$SeCN^-$, I^-, SCN^-, CN^-, Br^-, N_3^-, Cl^-, OCN^-, CNO^-, F^-.

V. SELENOCYANATES OF HEAVY METALS†

Selenocyanates of heavy metals that were sparingly soluble in water were obtained before other selenocyanates. They were prepared by the action of a solution of potassium selenocyanate on the corresponding salt of the metal. Thus, Crookes obtained silver selenocyanate as a slightly soluble white compound[7]. Later silver selenocyanate was isolated by other workers[4,20], who found its density to be 4.602[20] and its solubility product to be 4.0×10^{-16} at 18–20°.[27] Crookes noted that when potassium selenocyanate was added to salts of bivalent copper a brown precipitate was formed. He assumed that this was copper selenocyanate. However, the compound was not obtained in the pure state. Attempts to obtain the selenocyanate of univalent copper was also unsuccessful for a long time[28].

We have prepared the salt CuSeCN from acetone solution[29]: a solution of KNCSe is saturated with copper(I) chloride, and CuSeCN is precipitated by the introduction of a small quantity of water. The salt obtained in this way is a white powder, sparingly soluble in water, alcohol, and acetone. The solubility product of CuSeCN, measured potentiometrically at 20°, is 1.82×10^{-10}.

Crookes mentions the preparation of $Zn(SeCN)_2$ by dissolving zinc or its oxide in selenocyanic acid, but he gives no analytical results on the salt and says nothing about its properties[7].

Cadmium selenocyanate is obtained much more easily than the zinc salt from aqueous solution because of its lower solubility[30]. $Cd(SeCN)_2$ is obtained by mixing solutions of cadmium nitrate and potassium selenocyanate, rapidly filtering the solution, and drying the product[30]. This salt is also obtained from non-aqueous solutions. The solubility product of $Cd(SeCN)_2$ at 20° is 1.93×10^{-5}.[30] The salt is sparingly soluble not only in water but also in alcohol and acetone; it dissolves readily in the presence of an excess of selenocyanate or iodide ions.

Mercury selenocyanate, which was prepared by Cameron and Davy by the action of KNCSe on mercury(II) acetate solution, is very similar to the cadmium salt[23]. It was also obtained by Rosenheim and Pritze, using $HgCl_2$ and KNCSe as starting materials[31]. $Hg(SeCN)_2$ separates from water as a white mass; it is sparingly soluble in water, and readily soluble in the presence of selenocyanates, iodides, and cyanides of the alkali metals.

With its poor solubility in water, mercury(II) selenocyanate is very similar to the iodide and the thiocyanate. Cadmium selenocyanate, however, differs markedly from the iodide and the thiocyanate. Being sparingly soluble in water, in contrast to the latter, cadmium selenocyanate closely resembles the mercury salts. In solubility and thermal stability, $Hg(SeCN)_2$ is more reminiscent of the iodide than of the other halides. There is a still greater similarity in this respect between the salts of univalent mercury. Cameron and Davy also obtained mercury(I) selenocyanate by the action of potassium selenocyanate on mercury(I) nitrate[23]. The salt $Hg_2(SeCN)_2$, like HgI_2, has an olive green colour.

Of the elements of Group III of the Periodic System, only thallium selenocyanate is known; this was obtained by the action of potassium selenocyanate on an aqueous–alcoholic solution of thallium acetate[20], a yellow precipitate of TlSeCN, sparingly soluble in water, being formed. The specific gravity of TlSeCN is 5.462.[20]

Lead selenocyanate was obtained in the same way as the thallium salt[7,20,32]. Spacu prepared the salt Pb(OH)SeCN.[33] The compound $Pb(SeCN)_2$ is a finely crystalline pale yellow powder with a density of 4.694.[20,32] It turns red on exposure to sunlight. When heated, lead selenocyanate decomposes at a temperature somewhat above 100°, without reaching the melting point. At 20° a saturated aqueous solution of lead selenocyanate has a concentration of 0.00239 M.[32] It is practically insoluble in acetone and

† The term "heavy metal" is used by the Reviewers to include such transition metals as copper and zinc (Ed. of Translation).

alcohol. The solubility product of $Pb(SeCN)_2$ at 20° is 3.34×10^{-7} (ionic strength of solution ~ 4.[32]

The problem of preparing selenocyanates of the transition metals — iron, cobalt, nickel, etc. — is considerably more complicated. Spacu showed that $Co(NCSe)_2$ exists in solution, but he dod not succeed in obtaining the compound in the solid state[34].

Crookes tried to prepare iron(II) selenocyanate by the action of HNCSe on FeO, but only free selenium was obtained[7]. Attempts to prepare iron selenocyanate by the action of aqueous solutions of potassium selenocyanate on an iron(II) salt solution were also unsuccessful.

VI. COMPLEXES BASED ON METAL SELENOCYANATES

Because of the poor stability of the $SeCN^-$ ion, and because many cations become more stable when converted from hydrates to ammines, most work on the preparation of selenocyanato-complexes has been devoted to compounds containing ammonia or various organic amines in their structure.

Spacu and his coworkers studied compounds of this type. They succeeded in obtaining the following compounds with pyridine (Py)[34]: $MPy_4(NCSe)_2$ (with Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Fe^{2+}), $MPy_2(NCSe)_2$ (with Cd^{2+} and Zn^{2+}), and $NiPy_6(NCSe)_2$. The salt $CoPy_4(NCSe)_2$ was converted into $CoPy_2(NCSe)_2$ when kept in a vacuum at 70°.

Besides pyridine, Spacu introduced hexamethylenetetramine (Hex) as a ligand and obtained the salt $MHex_2(H_2O)_4 \cdot (NCSe)_2$, where M = Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}, or Fe^{2+}.[34] A large number of compounds were obtained with ethylenediamine[36-38]. The selenocyanates of nickel, cobalt, copper, cadmium, and manganese also form complexes with toluidine, benzidine, ammonia[33], and phenylhydrazine[39]. Quite recently the salt $Cu(NH_3)_4(NCSe)_2$ has been obtained from aqueous solution[40].

Other compounds containing amines are the complex salts $[(CH_3)_4N]_2[Co(NCSe)_4]$ and $[Et_4N]_2[Co(NCSe)_4]$, where Et_4N is tetraethylammonium[41].

Spacu compared selenocyanates with the corresponding thiocyanates, and found little difference in their properties; salts containing amines with the SeCN group are somewhat less soluble than analogous salts with the SCN group.

Some molecular selenocyanates separate from liquid ammonia when selenium acts on metal cyanides[22]: magnesium, aluminium, and zinc selenocyanates have been obtained in this way. Zinc selenocyanate $Zn(SeCN)_2 \cdot 4NH_3$ melts with slight decomposition when heated in a vacuum to 100°. Magnesium selenocyanate $Mg(NCSe)_2 \cdot 4NH_3$ decomposes when heated to 135°. When heated in a vacuum to 70° $Al(NCSe)_3 \cdot 5NH_3$ loses 2–2.5 molecules of ammonia, but at 75° it decomposes completely.

By analogy with ammine complexes, it would appear that many selenocyanates, unobtainable under ordinary conditions, might be obtained from ketone and ether solutions. This applies in particular to salts of the transition elements. This hypothesis has been partially confirmed in the case of cobalt and nickel selenocyanates with dioxan, which will be discussed below.

VII. COMPLEX FORMATION INVOLVING THE SELENOCYANATE ION AS LIGAND AND AS CENTRAL ION

Potentiometric study of the Ag^+–$SeCN^-$–H_2O system has demonstrated the existence of $Ag(SeCN)_3^{2-}$ complexes with a dissociation constant of 1.3×10^{-14}.[28,42] With a higher concentration of KNCSe in aqueous solution, $Ag(SeCN)_4^{3-}$ is formed. Under conditions such that the solubility method in aqueous solution is applicable, it can be shown that AgSeCN is formed[42].

The salt $KAg_2(SeCN)_3$ has been obtained when aqueous solutions of potassium selenocyanate are saturated with silver selenocyanate[43]. This salt is stable in air and sparingly soluble in water. Colourless crystals of $KAg(SeCN)_2$ separate from aqueous solution as regular cubes, in addition to crystals of $K_3Ag(SeCN)_4$ and finely acicular colourless crystals of $K_2Ag(SeCN)_3$. The last salt is better prepared from alcoholic and acetone solutions[43]. It has also been shown by the solubility method in aqueous solution that the mixed complexes $Ag(SeCN)_2 \cdot SCN^{2-}$[44] and $AgI(SeCN)_2^{2-}$[45] are formed. The salts $K_2Ag(SeCN)(SCN)_2$, $KAg_2(SeCN)_2(SCN)$,[44] and $KAg_2(CNSe) \cdot I_2$[45] have been obtained crystalline; the complexes $AgI_3(SeCN)^{3-}$ and $Ag(SeCN)_3(SCN)^{3-}$ have been detected potentiometrically[45].

Both in the character of complex formation and in stability the selenocyanato-complexes are reminiscent of iodo- and thiocyanato-complexes[46,47]. They are, however, more stable than the thiocyanato-complexes. It is for this reason that silver forms comparatively readily mixed selenocyanatothiocyanato- and halogenoselenocyanato- - complexes[45].

It has also been found that selenocyanates, like halides and thiocyanates[48-51], form silver complexes of cationic type[52]. A study of the solubility of AgSeCN in aqueous solutions of $AgNO_3$ and $AgClO_4$ has shown that the complexes Ag_2SeCN^+, Ag_3SeCN^{2+}, and Ag_4SeCN^{3+} are formed[52]. It is interesting to note that the solubility of AgSeCN at corresponding concentrations of $AgNO_3$ is very close to the solubility of silver iodide[51]. However, in contrast to the selenocyanate system, the iodide system has no complex with coordination number 4.[49-51]. Crystalline $[Ag_3SeCN] \cdot (NO_3)_2$ and $[Ag_2SeCN]ClO_4$ are obtained from aqueous solution. These salts are stable in air but are decomposed to AgSeCN by water[52].

It is also possible that some other metals form selenocyanato-complexes with a central anion. Thus, it may be assumed that similar complexes with mercury (Hg_2SeCN^{3+}) and even cadmium (Cd_2SeCN^{3+}) exist.

The formation of a cadmium complex $Cd(SeCN)_4^{2-}$ with a dissociation constant of 2.5×10^{-4} has been demonstrated polarographically[28]. A potentiometric study of aqueous and aqueous–acetone solutions has revealed the existence not only of $Cd(SeCN)_4^{2-}$ but also of other complexes — $Cd(SeCN)_6^{4-}$, $Cd(SeCN)_5^{3-}$, $Cd(SeCN)_3^-$, $Cd(SeCN)_2$, and $Cd(SeCN)^+$ — the dissociation constants of which have been calculated[30].

As with the halides, mercury forms more stable selenocyanates than cadmium. Thus, the dissociation constant of $Hg(SeCN)_4^{2-}$ is 2.8×10^{-30}, and that of $Hg(SeCN)_3^-$ is 3.8×10^{-27}.[28]

The complexes $Hg(SeCN)Cl$, $Hg(SeCN)_2$, $Hg(SeCN)_3^-$, and $Hg(SeCN)_4^{2-}$ have been detected by the conductometric titration of an aqueous solution of $HgCl_2$ with KNCSe solution[53].

Some mercury selenocyanates have been obtained in the solid state[31]. The salt Hg(SeCN)Cl and also the salt $KHg(SeCN)_3$, which is sparingly soluble in cold water and alcohol, have been obtained from aqueous solution. The latter salt was previously obtained by Cameron and Davy[23]. Potassium tetrakisselenocyanatomercurate, readily soluble in water and alcohol, was obtained in the form of large amber-yellow plates. With the use of an aqueous solution of this salt the sparingly soluble compounds $MHg(SeCN)_4$, where M = Zn, Co, Pb, or Cu, have been isolated[31,53]. According to Swinarski and Lodzinska, the solubility of the $MHg(SeCN)_4$ salts in water, acetone, and aqueous alcohol decrease in the order Cd > Co > Zn.[54] The solubility product of $CuHg(SeCN)_4$ in aqueous solution is $1.59 \times \times 10^{-10}$.[55] The lattice parameters and the coefficient of thermal expansion of $CoHg(SeCN)_4$ crystals have been determined[56].

Formation of the sparingly soluble $M[Hg(SeCN)_3]_2$, where M = Zn, Pb, or Cu, has been demonstrated, and the double salt $4Co[Hg(SeCN)_3]_2.Co(CH_3COO)_2$ has also been prepared[53].

Complex mercury salts of mixed type $KHg(SeCN)(CN)_2$ and $KHg(SeCN)Hal_2$ were obtained by Cameron and Davy[23]; they were prepared by the action of mercury halides on an alcoholic solution of KNCSe.

The selenocyanate complexes of lead have been studied only recently. A potentiometric study of aqueous solutions has shown that $Pb(SeCN)_6^{4-}$ ($K_6 = 1.41 \times 10^{-4}$ at 20°) is formed[57]. This complex was also detected in a study of the heterogeneous $Pb(SeCN)_2$–KNCSe–H_2O system by the solubility method[32]. The salt $K_4Pb(SeCN)_6$, which is sparingly soluble in water and acetone, was obtained from an aqueous–acetone (7 M with respect to acetone) solution of KNCSe by saturating it with lead selenocyanate[32].

The selenocyanates of the transition metals have been little studied. We have been able to demonstrate the existence of $CoNCSe^+$ and to calculate its dissociation constant ($K = 0.063$) by spectrophotometry[58]. The existence of the nickel complex $NiNCSe^+$ has been demonstrated in the same way[59,60].

Ablov and Samus' obtained dimethylglyoximatocobalt(III) complexes containing the selenocyanato-group[61]. Fine plates of the potassium salt and rhombic prisms of the ammonium salt $M[Co(DH)_2(NCSe)_2]$, where M = K or NH_4 [and DH = HON : C(CH$_3$).C(CH$_3$) : NO– (Ed. of Translation)], were obtained from an aqueous–alcoholic solution. A solution of the latter salt gives characteristic precipitates with Cd^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Mg^{2+} cations. When hydrochloric acid is added to solutions of $K[Co(DH)_2(NCSe)_2]$, the acid $H[Co(DH)_2(NCSe)_2]$, which is sparingly soluble in water, is obtained; the action of alkali gives $[Co(DH)_2.(NCSe)H_2O].H_2O$.

When an alcoholic solution of potassium selenocyanate acts on H_2PtCl_6, a red-brown precipitate is formed, and when this is recrystallised from alcohol, it gives very fine hexahedral plates of $K_2Pt(SeCN)_6$[62,63]. If the preparation is carried out in aqueous solution, potassium hexakisselenocyanatoplatinae is obtained as a crystalline dihydrate[64]. Recrystallisation of this product from alcohol yields the anhydrous salt. Ammonium hexakisselenocyanatoplatinate $(NH_4)_2Pt(SeCN)_6$ is obtained as black rhombic crystals[65].

VIII. SELENOCYANATO-COMPLEXES IN NON-AQUEOUS SOLUTIONS

As has been mentioned above, the selenocyanates are very sensitive to acids, and even to water. This appears to be due to the instability of the Se–C bond and also to the hydration of selenocyanate ions.

When it is considered that the introduction of non-aqueous solvents promotes a reduction in the hydration of ions[66], increased stability of the selenocyanates of many metals may be expected even in mixed solvents. The stability of the selenocyanate ion, and of complexes formed from it, is still more noticeably improved in solvents not capable of entering into solvolysis reactions with various salts. For this reason, even selenocyanates of the alkali metals are more stable in acetone and some other solvents than in water or alcohols. This is why the formation of copper(I) selenocyanato-complexes has been established in acetone by a study of the CuCl–KNCSe–CH_3COCH_3 system by the solubility method[29]. The salt KCu(SeCN)Cl is obtained as colourless crystals on crystallisation of the corresponding solution; it is decomposed by water and by alcohol with separation of CuSeCN[29]. Mixed selenocyanatothiocyanato-complexes of copper can also be shown to exist in acetone[44].

Copper(I) selenocyanate is very soluble in an acetone solution of KNCSe. It may be supposed that in this case, as with thiocyanates[67], the complex salts $K_2Cu(SeCN)_3$ and $K_3Cu(SeCN)_4$ are formed. However, the exact structure of the complexes formed on dissolution of CuSeCN has not been established, because the system undergoes rapid decomposition.

Reduction in the hydration of ions by the introduction of non-aqueous solvents, other conditions being similar, leads to the formation of higher complexes[66]. This is illustrated by silver selenocyanates. In aqueous solution the complex $Ag(SeCN)_3^{2-}$ is formed, but in a solution 7 M with respect to acetone, at the same concentrations of $NCSe^-$ ions, the complex $Ag(SeCN)_4^{3-}$ is formed[42]. A similar effect is observed in aqueous–methanolic and aqueous–dioxan solutions[68,69]. The complex $Ag(SeCN)_4^{3-}$ is mainly formed in high concentrations of methanol and in pure methanol[68].

From an alcoholic solution of potassium selenocyanate and gold(I) chloride, Clarke obtained fine, dark red crystals that rapidly decomposed[62]; he considered that these crystals corresponded to the salt $KAu(SeCN)_2$ (Au found 48.31%, compared with 43.94% calculated).

The interaction between potassium and cadmium selenocyanates in methanolic solution has been studied by electrical conductivity measurements, and the complex $Cd(SeCN)_3$ detected[30]. The salts $KCd(SeCN)_3.3CH_3COCH_3$, $K_2Cd(SeCN)_4.2CH_3COCH_3$, $K_2Cd(SeCN)_4$, $K_4Cd(SeCN)_6$, and also a number of cadmium halogenoselenocyanates have been obtained from acetone solution[70].

The dependence of the solubility of lead selenocyanate on the concentration of potassium selenocyanate in acetone solution has been studied, and formation of the complex $Pb(SeCN)_3^-$ demonstrated[32]. When the acetone solution is evaporated, the salt $KPb(SeCN)_3$ is obtained in fine silky yellowish green needles. The salt is readily soluble in acetone, but is decomposed by water[32].

We have studied the selenocyanato-complexes of cobalt and nickel in acetone and methanol solutions[58–60]. The formation of complexes from $MSeCN^+$ to $M(NCSe)_6^{4-}$, where

M = Co or Ni, has been demonstrated in these solutions by spectrophotometric and conductivity methods, and the dissociation constants of these complexes have been calculated.

The formation of nickel selenocyanato-complexes in dimethylformamide has also been studied. It has been shown that in this solvent complexes from $NiNCSe^+$ to $Ni(NCSe)_4^{2-}$ are formed. A comparison of the dissociation constants of nickel selenocyanates in different solvents shows that these complexes are most stable in acetone[71].

Complex selenocyanates of nickel and cobalt have been prepared from acetone solution[58-60]. Information on the composition, stability, and preparation of cobalt and nickel selenocyanates indicates that they are very similar to the thiocyanates[72,73].

Selenocyanates of manganese, cobalt, and nickel of composition $M(DMF)_4(NCSe)_2$ have been separated from dimethylformamide[40].

IX. COMPLEX-FORMING CHARACTERISTICS OF THE $SeCN^-$ ION

The selenocyanate ion behaves as a pseudohalide ligand in complex-forming reactions. To determine the position occupied by this ion in the sequence of its analogues, we shall examine some selenocyanato-complexes and compare then with iodo-and thiocyanato-complexes.

From the dissociation constants of silver complexes of analogous composition with different ligands, it is easy to see that the selenocyanate ion is very close to the iodide ion in its complex-forming power[46,47]. The selenocyanato--complexes of silver are, however, more stable than the thiocyanato-complexes. In comparison with the latter, the selenocyanates separate more easily from solutions in equilibrium with a precipitate of the simple salt. Moreover, silver selenocyanates are easily formed as dinuclear complexes, which are reminiscent of iodo-complexes. Therefore, in their complexing power for silver ions selenocyanate and thiocyanate ions may be arranged in the series $I^- \geqslant NCSe^- > NCS^-$.

An analogous series is established on comparing the dissociation constants of thiocyanato-[74,75], iodo-[66,76], and selenocyanato-[36,57] complexes of lead, mercury, and cadmium.

It would seem that the above sequence of complex-forming power should be observed also in other cases. However, this is not so. Cobalt thiocyanates from $CoNCS^+$ to $Co(NCS)_4^{2-}$ are known in aqueous solution[77], but the selenocyanate ion forms only the simplest complex, and iodo-complexes of cobalt have not been detected in water at all. In this case, therefore, the sequence of complex--forming power I^-, $NCSe^-$, NCS^- is in the reverse order. This applies to a still greater degree to nickel compounds[60,78].

Copper(II) thiocyanates have been described in the literature, but it appears that copper(II) selenocyanates are not formed[79,80].

X. THE STRUCTURE OF SELENOCYANATES

The NCS group can be linked to metals through the nitrogen atom (isothiocyanate group), through the sulphur atom (thiocyanate group), and through the nitrogen and sulphur simultaneously (bridge thiocyanate group). It has been shown, for example, that in nickel and cobalt thiocyanato-complexes the ionic character of the M–NCS bond predominates, while in the thiocyanates of mercury, platinum, and silver the covalent character of the bond through sulphur predominates[81-83]. Since thiocyanates and selenocyanates are similar in properties, it is reasonable to suppose that the group NCSe can also form three types of bonds.

Two lines, at 2074 cm^{-1} (2051) and 575 cm^{-1}, have been found in the Raman spectrum of aqueous solutions of KNCSe; these can be assigned to C–N and C–Se vibrations[84,85]. From this it was concluded that potassium selenocyanate had an ionic structure, and the structure $Se-C\equiv N$ was assigned to the $NCSe^-$ group. The same conclusion has been reached from study of the infrared spectra of KNCSe[41,86].

Examination of the infrared spectra of the compounds $CoA_2(NCSe)_2$ and $B_2Co(NCSe)_4$, where A is an amine and B is tetraalkylammonium or tetraarylarsonium, has shown that the selenocyanate group is attached to Co through N.[41,87,88].

Since $CoPy_2(NCS)_2$ and $CoPy_2(NCSe)_2$ have the same magnetic moment (5.1 β), an octahedral structure has been assigned to the latter compound. In solution in polar organic solvents, however, these compounds appear to have a tetrahedral configuration[35].

The compounds $CoHg(SeCN)_4$ and $CoHg(SCN)_4$ have been shown to be isomorphous[89]. Construction of Patterson projections confirmed the identity of the two structures. Therefore, in $CoHg(SeCN)_4$ the NCSe group forms a bridge between Hg and Co [as does the SCN bond in $CoHg(SCN)_4$[90]]; the selenocyanato-ligand is linked to mercury through the selenium, and to cobalt through the nitrogen[89]. The bidentate character of $NCSe^-$ in the $CoHg(SeCN)_4$ complex is obvious from infrared spectra[41,87]. The bridge structure also appears to occur in the silver selenocyanates[41]. In the $K_2Pt(SeCN)_6$ and $K_2Hg(SeCN)_4$ complexes the link between the selenocyanate group and the central atom is effected through the selenium[88].

A detailed study of the structure of the selenocyanates of the transition metals has begun in the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. Already results have been published of X-ray structure studies on the compounds $MA_4(NCSe)_2$ (where M = Co or Ni and A is dimethylformamide)[91]. These compounds are paramagnetic; the magnetic susceptibility of the cobalt salt is 3.22 β. X-Ray structure analysis has shown that in $MA_4(NCSe)_2$ the selenocyanate groups enter the inner sphere of the complex $[MA_4(NCSe)_2]$, which has an octahedral *trans*-configuration[91]. The NCSe group is linked to the central atom through the nitrogen, and the M–N=C angle is close to 180°.

A comparison of the stability of selenocyanato-complexes and their structure shows that those compounds in which the NCSe group is linked to the central atom through the selenium are more stable than the corresponding thiocyanates. Compounds in which the NCSe group is linked through the nitrogen, however, are less stable than the thiocyanates.

It will be seen from the above review of the literature that, right up to the 1950's, the number of metals that formed known coordination compounds with $NCSe^-$ ions was extremely small. Attempts to prepare selenocyanates of

a number of metals may have failed because aqueous solutions were used. Only selenocyanates of those metals that form stable complexes with $NCSe^-$ could be studied in water.

The range of existence of selenocyanato-complexes has been considerably extended by the use of non-aqueous solvents. With non-aqueous solutions it has become possible to study more fully both the compounds of the metals that form stable selenocyanates and the salts of such metals as cobalt, nickel, and copper, which do not form selenocyanato-complexes in water.

Comparison of results in the literature on selenocyanato-complexes shows that even metals with identical electron shells differ in their power of coordinating selenocyanate ligands. With the exception of the zinc subgroup, it is impossible in other groups of metals to trace a strict sequence in the stability of their complexes with their atomic number. Thus, in the copper subgroup, silver forms selenocyanato-complexes most easily. In Group III indium should form selenocyanato-complexes more readily than other metals in the tervalent state. Because of the high oxidation potential of Tl^{3+}, thallium, like lead, can form selenocyanates only in its lower valency state.

If the metals are compared according to Periods, the following points may be noted. In the Sixth Period the most stable selenocyanates in aqueous solution are formed by quadrivalent platinum and bivalent mercury, in the Fifth Period by silver and cadmium, and in the Fourth Period by cobalt. Therefore, as we go from the Sixth to the Fourth Period, the centre of complex formation is displaced to the left. From this it may be assumed that selenocyanates will be formed by iron, manganese, and other metals in this Period.

It is quite probable that in non-aqueous solvents selenocyanates not only of Fe^{2+}, Fe^{3+}, Cr^{3+}, Mn^{2+}, and Zn^{2+}, but even of gallium, tin, and other metals can be obtained.

Extension of the number of selenocyanates will permit this class of compounds to be characterised more fully and open the way to their practical use‡.

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‡ While this review was being prepared for the press, new papers appeared. The infrared spectra of *trans*-$[MA_4(NCSe)_2]$ (M = Ni, Co, Mn; A = dimethylformamide) and also of the compounds $Cu(NH_3)_4(SeCN)_2.H_2O$ and $KAg(SeCN)_2$ have been discussed[92]. The infrared spectra of some inorganic selenocyanates have been presented and reviewed[93]. A theoretical (semiempirical) analysis of the infrared spectra of selenocyanato-complexes has been made[94,95].

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STUDY OF THE THERMAL STABILITY OF INORGANIC PEROXO-COMPOUNDS BY THE DIFFERENTIAL THERMAL ANALYSIS METHOD

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The inorganic peroxo-compounds are special higher forms of oxygen compounds of the elements and every year they acquire new fields of use. The diverse use of the different types of this broad class of compounds is determined not only by their oxygen content, which can be readily released in active form, but also by the singular nature of the bonding to oxygen in their molecules.

The presence of the peroxo-group, the so-called "oxygen bridge" was thought until recently to be sufficient for defining "inorganic peroxo-compounds". A detailed study of the structure and properties of a series of peroxo-compounds, made in the 'thirties of the present century, with the active participation of Soviet scientists, showed that this concept embraces at least nine groups of compounds, which are distinguished by the nature of the bond between the oxygen atoms in the bridge and by the nature of the bond between the oxygen bridge and the atoms of the element forming the peroxo-compounds. Some authors tend to include all the inorganic peroxo-compounds within the framework of complex compounds dividing them into three groups: polyoxides, peroxo-acids, and peroxohydrates. However, the group of polyoxides includes peroxo-compounds with a crystal lattice consisting of metal ions (predominantly of the Ia and IIa subgroups of the Periodic System) and the molecular anions O_2^{2-}, O_2^-, and O_3^- respectively, which differ both in their structure and in the nature and length of the O–O bond. The bonds of the metal atoms with the oxygen bridge in these compounds are of the ionic type, whereas in other peroxo-compounds the peroxo-group as such or in the form H_2O_2 or HO_2 is joined to the atom of the element forming the peroxo-compound by a coordinate, not an ionic bond. It is therefore desirable to keep the division of inorganic peroxo-compounds into simple and complex.

The simple inorganic peroxo-compounds can be subdivided into four groups: (1) the hydrogen peroxides, which are characterised by the presence of the hydrogen peroxide ion HO [presumably HO_2^- (Ed. of Translation)]; (2) the peroxides, characterised by the presence of the peroxide ion O_2^{2-}; (3) the superoxides, characterised by the presence of the superoxide ion O_2^-; (4) the ozonides, characterised by the presence of the ozonide ion O_3^-.

The complex peroxo-compounds can be subdivided into five groups: (1) peroxo-acids and their salts, in which the peroxo-group forms part of the complex anion, mono- and poly-nuclear representatives of this group being known; (2) peroxo-complexes which are neither peroxo-acids nor their derivatives, represented by compounds which include in the inner sphere a peroxo-group (peroxo-complexes), or hydrogen peroxide (perhydro-complexes [Russian nomenclature (Ed. of Translation)]), or the hydrogen peroxo-group (hydrogen peroxo-complexes); (3) peroxide hydrates — addition compounds of peroxides with water of crystallisation; (4) peroxohydrates — molecular compounds of