Translated from *Uspekhi Khimii*, 51 40-56 (1982) U.D.C. 546.4/9:547.491.5

Metal Selenocyanates

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The literature data on the complex formation reactions involving the SeCN groups in aqueous and non-aqueous solutions are surveyed. The syntheses and properties of metal selenocyanate coordination compounds are described. The bibliography includes 156 references.

CONTENTS

I. Introduction 21
II. Selenocyanate complexes in solutions 21
III. Selenocyanato-compounds containing ligands with electron-donating nitrogen 21
IV. Heteroligand compounds incorporating ligands with electron-donating oxygen 24
V. Coordination selenocyanato-compounds of the acido-type 25
VI. Compounds containing metal-phosphorus and metal-carbon bonds as well as certain other compounds 27

I. INTRODUCTION

Until comparatively recently, selenocyanates were virtually uninvestigated. Compounds of this class have been studied most vigorously in recent years. In view of the increased interest in complex formation reactions involving SeCN groups, we attempted to survey the available literature data on selenocyanates during the period 1970–1979. Other reviews deal with earlier studies[1-5].

II. SELENOCYANATE COMPLEXES IN SOLUTIONS

Since the SeCN groups decompose in aqueous solutions in the presence of the majority of metal ions[1], selenocyanate complexes have been studied mainly in non-aqueous media (Table 1). Naturally the nature of the solvent has a significant influence on the stability and composition of the complexes. The most stable selenocyanate complexes are formed as a rule in acetone. For example, the formation of fairly stable molybdenum complexes $MoOX_{5-n}(NCSe)_n$ and $MoO.(NCSe)_5^{2-}$ (X = Cl [17] or Br, [22] $n = 1-4$) and tungsten complexes $[WCl_{5-n}(NCSe)_n]$ ($n = 1-5$) has been demonstrated in acetone solution[23]. In other non-aqueous solvents the SeCN groups decompose fairly rapidly in the presence of molybdenum and tungsten halides.

Table 1 shows that stable complexes, among those investigated in aqueous solutions, are formed by mercury. It is therefore not surprising that mercury(II) oxide readily dissolves in solutions of potassium selenocyanate[24]. At 25 °C the heat of solution of red HgO in 1 M KNCSe solution is −103 kJ mol^{-1}.[24]

III. SELENOCYANATO-COMPOUNDS CONTAINING LIGANDS WITH ELECTRON-DONATING NITROGEN

In the presence of amines the stability of the SeCN groups increases sharply, which explains the finding that, among the selenocyanato-compounds investigated, the selenocyanato-amine compounds are the most numerous.

When pyridine was saturated with lead selenocyanate (at 80–90 °C) with subsequent cooling of the mixture, pale yellow crystals of $PbPy_2(NCSe)_2$, containing bridging SeCN groups, were precipitated[25]. The properties of the octahedral compounds $MPy_4(NCSe)_2$ (M = Mn, Co, or Ni)[26] and $MPy_2(NCSe)_2$ (M = Mn, Co, or Ni), described previously[1], were investigated[27]. The octahedral configuration of $MPy_2.(NCSe)_2$ is achieved as a result of the bridging function of the SeCN groups.

$[Co(NCSe)(NCS)Py_2]$ has been obtained by the reaction of $Co(NCS)_2$ with KNCSe in an acetone–dioxan mixture, the mixture being subsequently kept in a vacuum desiccator over calcium chloride impregnated with pyridine[28]. Treatment of $[HIr(pip)_4Cl]Cl$ (pip = piperidine) with a saturated aqueous solution of KNCSe led to the isolation of *trans*-$[HIr(pip)_4.NCSE]NCSe$.[29] The compound is diamagnetic; although the formation of the Ir–SeCN bond is characteristic of iridium, ionic NCSe groups and NCSe groups coordinated via the nitrogen atom are present in the compound.

The compound $K[CuR_2SeCN]$, where R is a pyridine-2-carboxylic acid residue, in which the copper atoms have an octahedral environment and the SeCN groups are linked to copper by weak bonds via selenium, has been synthesised[30].

Fairly numerous compounds containing 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been isolated in recent years, mainly from non-aqueous solutions, and investigated (Table 2).[31-46] The compound $[Fe_3(bipy)_7(NCSe)_6]$ has been obtained[47]. Its magnetic moment at 294 K is 3.24 μ_B. Its crystals have an orthorhombic lattice with the parameters $a = 21.77 \pm 0.05$ Å, $b = 25.33 \pm 0.05$ Å, $c = 13.88 \pm 0.04$ Å, and $D_m = 1.66 \pm 0.03$ g cm^{-3}; the probable space group is $Pmnb$.[47]

The complexes $Cu(bipy)(NCSe)_2$, $Cu(phen)(NCse)_2$, and $Cu(bipy)_2(NCSe)_2$ have been isolated from aqueous acetone solutions[35]. In the first two compounds the octahedral configuration of copper is achieved via bridging SeCN groups. Judging from EPR data[35], the copper in the compound $Cu(bipy)_2(NCSe)_2$ has a coordination number of 5. The complex $Mn(phen)_2(NCSe)_2$, isostructural with the corresponding thiocyanate, has also been obtained. The compound contains isoselenocyanato-groups. Its magnetic moment is 5.98 μ_B at 24 °C.[42]

The isoselenocyanato-compounds $Nb(bipy)_2(NCSe_4)$ and $Nb(DMbipy)_2(NCSe)_4$, where DMbipy = 4,4′-dimethyl-2,2′-bipyridyl, have been isolated from acetonitrile solutions, and $Ta(bipy)(NCSe)_5$ has been obtained from dichloromethane[43]. The compound $[Co(bipy)_3][Zn(NCSe)_4(bipy)]$, whose magnetic moment is 5.31 μ_B, has been obtained by the reaction of solutions containing $Co(NCSe)_2$, $Zn(NCSe)_2$, and 2,2′-bipyridyl[48]. A number of lanthanide compounds containing urotropine have been isolated from non-aqueous solutions (Table 2).

The compounds $[Ru(NH_3)_5SeCN]X_2$, where $X = ClO_4^-$, I^-, or PF_6^-, have also been described[49]. The zinc and cadmium compounds incorporating benzimidazole and its derivatives proved to be fairly stable in air[33].

Table 1. The stability constants of selenocyanate complexes in solution*.

Complex	t, °C	I	Method**	$\lg\beta_i$	References
		Solvent–H_2O			
$Hg(SeCN)_2$	25	0.3	PG	21.40	[6]
$Hg(SeCN)_3^-$	25	0.3	PG	25.60	[6]
$Hg(SeCN)Thio^+$	25	1.0	SP	27.61	[7]
$Hg(SeCN)_2(Thio)_2$	25	1.0	SP	28.51	[7]
$Hg(SeCN)_3Thio^-$	25	1.0	SP	29.15	[7]
$Cd(SeCN)^+$	25	1.0	PM	1.47	[8]
$Cd(SeCN)^+$	25	1.0	PM	1.98	[9]
$Cd(SeCN)_3^-$	25	1.0	PM	2.84	[8]
$Cd(SeCN)_4^{2-}$	25	1.0	PM	4.04	[8]
$Zn(NCSe)^+$	25	1.0	PM	0.44	[8]
$Zn(NCSe)_2$	25	1.0	PM	0.64	[8]
$Ni(NCSe)^+$	25	variable	PM	1.66	[9]
$Ni(NCSe)^+$	25	1.0	SP	0.99	[10]
$Co(NCSe)^+$	25	1.0	PM	1.49	[9]
$Tl(NCSe)_2^-$	20	1.0	PM	1.7	[11]
$Tl(NCSe)_2^-$	27	2.0	PG	0.88	[12]
$Tl(NCSe)_3^{2-}$	20	1.0	PM	1.55	[11]
$Tl(NCSe)_3^{2-}$	27	2.0	PG	1.24	[12]
$Tl(NCSe)_3^{2-}$ ***	20	2.0	PM	2.08	[11]
		Solvent–DMF			
$Zn(NCSe)^+$	20	1.0	PM	2.60	[13]
$Zn(NCSe)_2$	20	1.0	PM	4.30	[13]
$Zn(NCSe)_3^-$	20	1.0	PM	4.90	[13]
$Cd(SeCN)^+$	25	1.0	PM	2.50	[13]
$Cd(SeCN)_2$	25	1.0	PM	4.04	[13]
$Cd(SeCN)_3^-$	25	1.0	PM	5.28	[13]
$Cd(SeCN)_4^{2-}$	25	1.0	PM	6.00	[13]
$In(NCSe)^{2+}$	25	1.0	PM	7.00	[14]
$In(NCSe)_2^+$	25	1.0	PM	8.75	[14]
$In(NCSe)_3$	25	1.0	PM	10.49	[14]
$Tl(NCSe)_2^-$	20	1.7	PM	1.25	[14]
$UO_2(NCSe)^+$	room	variable	SP	2.11	[15]
$V(NCSe)^{2+}$	room	variable	SP	1.15	[16]
$MoOCl_3(NCSe)^-$	room	variable	SP	2.70	[17]
$Hf(HCSe)_6^{2-}$	room	variable	SP	7.89	[18]
$Zr(NCSe)_6^{2-}$	room	variable	SP	8.11	[18]
		Solvent–DMSO			
$In(NCSe)^{2+}$	25	1.0	PM	5.32	[14]
$In(NCSe)_2^+$	25	1.0	PM	5.87	[14]
$Bi(NCSe)^{2+}$	room	variable	SP	1.45	[19]
$Bi(NCSe)_2^+$	room	variable	SP	2.28	[19]
$Co(NCSe)^+$	room	variable	SP	1.74	[20]
$Ni(NCSe)^+$	room	variable	SP	2.41	[20]
$UO_2(NCSe)^+$	room	variable	SP	2.04	[15]
		Solvent–Acetone			
$Zn(NCSe)_4^{2-}$	room	variable	SP	11.85	[13]
$In(NCSe)_6^{3-}$	room	variable	SP	25.46	[14]
$Bi(NCSe)_6^{3-}$	room	variable	SP	14.00	[19]
$Cd(NCSe)^+$	25	1.0	PM	10.40	[13]
$Cd(NCSe)_2$	25	1.0	PM	12.28	[13]
$Cd(NCSe)_3^-$	25	1.0	PM	14.60	[13]
$Cd(NCSe)_4^{2-}$	25	1.0	PM	15.76	[13]
$In(NCSe)_6^{3-}$	25	1.0	PM	24.49	[14]
$Mn(NCSe)^+$	room	variable	SP	2.61	[21]
$Mn(NCSe)_2$	room	variable	SP	5.00	[21]
$Mn(NCSe)_3^-$	room	variable	SP	6.65	[21]
$Mn(NCSe)_4^{2-}$	room	variable	SP	7.86	[21]
$Ni(NCSe)^+$	room	variable	SP	3.84	[21]
$Ni(NCSe)_2$	room	variable	SP	7.23	[21]
$Ni(NCSe)_3^-$	room	variable	SP	10.32	[21]
$Ni(NCSe)_4^{2-}$	room	variable	SP	13.25	[21]
$Zn(NCSe)^+$	20	1.0	PM	7.30	[13]
$Zn(NCSe)_2$	20	1.0	PM	9.40	[13]
$Zn(NCSe)_3^-$	20	1.0	PM	10.78	[13]
$Zn(NCSe)_4^{2-}$	20	1.0	PM	12.25	[13]
$UO_2(NCSe)^+$	room	variable	SP	3.79	[15]
$V(NCSe)^{2+}$	room	variable	SP	2.74	[16]
$V(NCSe)_2^+$	room	variable	SP	5.92	[16]
		Solvent–CH_3CN			
$Bi(SeCN)_6^{3-}$	room	variable	SP	12.09	[19]
$Cd(NCSe)^+$	25	1.0	PM	10.41	[13]
$Cd(NCSe)_2$	25	1.0	PM	12.29	[13]
$Cd(NCSe)_3^-$	25	1.0	PM	14.62	[13]
$Cd(NCSe)_4^{2-}$	25	1.0	PM	15.78	[13]
$In(NCSe)_6^{3-}$	25	1.0	SP	24.52	[14]
$Mn(NCSe)^+$	room	variable	SP	2.62	[21]
$Mn(NCSe)_2$	room	variable	SP	5.00	[21]
$Mn(NCSe)_3^-$	room	variable	SP	6.66	[21]
$Mn(NCSe)_4^{2-}$	room	variable	SP	7.87	[21]
$Ni(NCSe)^+$	room	variable	SP	3.85	[21]
$Ni(NCSe)_2$	room	variable	PM	7.24	[21]
$Ni(NCSe)_3^-$	room	variable	PM	10.33	[21]
$Ni(NCSe)_4^{2-}$	room	variable	PM	13.27	[21]
$Zn(NCSe)^+$	20	1.0	PM	7.31	[13]
$Zn(NCSe)_2$	20	1.0	SP	9.41	[13]
$Zn(NCSe)_3^-$	20	1.0	SP	10.79	[13]
$Zn(NCSe)_4^{2-}$	20	1.0	SP	12.26	[13]
$UO_2(NCSe)^+$	room	variable	SP	3.80	[15]
$V(NCSe)^{2+}$	room	variable	SP	2.75	[16]
$V(NCSe)_2^+$	room	variable	PM	5.93	[16]

*The following abbreviations have been adopted in Table 1 and in the other tables: Thio = thiourea; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulphoxide; I = ionic strength.

**Notation: PG = polarography; SP = spectrophotometry; PM = potentiometry.

***With addition of 50 vol % of acetone.

The interaction of alcoholic solutions of $M(NCSE)_2$ (M = Co, Ni, or Cu) with 1,1,7,7-tetraethyldiethylenetriamine [$(C_2H_5)_4$..dien] and diethylenetriamine (R) led to the solution of $[M(C_2H_5)_4dien](NCSe)_2$ (M = Co or Ni) and $[CuR_2](NCSe)_2$. In all the compounds the bond between the NCSe groups and the central atom is formed via nitrogen[45].

The kinetics of the substitution of SeCN ligands in $\{Pd..(C_2H_5)_4dien]SeCn\}^+$ by methanol and the influence of Hg^{2+} ions on the rate of the process have been investigated in methanol at 25 °C. It was established that if the SeCN group is linked to palladium via selenium, then the rate of substitution is proportional to the mercury(II) concentration; otherwise the rate is independent of [Hg(II)].[50]

The synthesis of tetragonal bipyramidal compounds $[(Cu..(Pn)_2(SeCN)]NO_3$ and $[Cu(dien)_2(SeCN)]NO_3$, where Pn = propylenediamine and dien = diethylenediamine[51], as well as $[Cu(DBen)_2(NCSE)X]$, where $X = ClO_4^-$ or NO_3^- and DBen = *N*, *N'*-dibenzylethylenediamine[52], has been described. The copper atom in $\{Cu[(C_2H_5)_4dien]NCSe\}(BPh_4)$ has a square planar environment[45].

The octahedral nickel isoselenocyanate complexes $Ni(R-NH_2)_4(NCSe)_2$ and [NiL(NCSe)]NCSe, where $R = CH_3$, $n-C_3H_7$, or $n-C_4H_9$ and L = tetraethylenepentamine, have been isolated from ethanol solutions[44]. It is of interest to note that, in the presence of piperidine, nickel(II) can form not only the octahedral compounds $[Ni(pip)_4(NCSe)_2]$ but also the pentacoordinate compound $[Ni(pip)_3(NCSe)_2]$.[26]

A series of nickel(II) and cobalt(II) compounds with *p*- and *m*-phenylenediamines (phn) have been obtained[53]. The compounds $Co(m\text{-phn})_2(NCSe)_2$, $Ni(m\text{-phn})_2(NCSe)_2$, $Ni(m\text{-phn})(NCSe)_2$, $Ni(p\text{-phn})(NCSe)_2$, and $Co(p\text{-phn})(NCSe)_2$ contain bridging SeCN groups. An octahedral structure was attributed to all the nickel(II) complexes on the basis of their effective magnetic moments[53].

The magnetic properties and EPR, infrared, and electronic spectra of the complexes $[ML_2(NCSe)_2][BPh_4]_2$, where M = Ni or Cu and L = 2,2',2''-triaminotriethylamine, have been investigated. It was established that the nickel complexes have a dimeric structure with octahedral coordination established via bridging SeCN groups, while the copper complexes have a trigonal bipyramidal structure[54].

Table 2. Fundamental vibrational frequencies of the SeCN groups (cm^{-1})*.

Compound	ν (C N	ν(CSe)	δ(SeCN)	Type of coordination of SeCN groups	Refs.
Ba (bipy)$_2$(NCSe)$_2$	2085	575	420	Ba—NCSe	[31]
Ba(phen)$_2$(NCSe)$_2$	2090	575	412	Ba—NCSe	[31]
Ba(phen)$_3$(NCSe)$_2$	2065	552	—	SeCN⁻	[31]
Ca (bipy)$_2$(NCSe)$_2$	2080,2090	588	433	Ca—NCSe	[31]
Ca(phen)$_2$(NCSe)$_2$	2075	587		Ca—NCSe	[31]
Cd$(CH_3NH_2)_2$(NCSe)$_2$	2090	580	410	Cd—NCSe	[32]
Cd$(C_2H_5NH_2)_2$(NCSe)$_2$	2105	585	405	Cd—NCSe	[32]
Cd$(C_3H_7NH_2)_2$(NCSe)$_2$	2090	577	407	Cd—NCSe	[32]
Cd$(C_4H_9NH_2)_2$(NCSe)$_2$	2085	—	407	Cd—NCSe	[32]
Cd(MBia)$_2$(NCSe)$_2$	2102	—	—	Cd—NCSe	[33]
Cd(MBia)$_2$(NCSe)$_2$	2112,2125	—	—	Cd—NCSe—Cd	[33]
Cd(DMBia)$_2$(NCSe)$_2$	2096, 2112,2130	—	—	Cd—NCSe—Cd	[33]
CdQ$_2$(NCSe)$_2$	2107,2120	565	407	Cd—NCSe—Cd	[34]
CdQ(NCSe)$_2$	2114,	630,	—	Cd—NCSe—Cd	[34]
CdZ$_2$(NCSe)$_2$	2125,2135	565			
	2102, 2125,2135	588	425	Cd—NCSe—Cd	[34]
Cuphen(NCSe)$_2$					
Cudipy(NCSe)$_2$	2110	—	415	Cu—NCSe—Cu	[35]
Cu(dipy)$_2$(NCSe)$_2$	2096,2117	—	432	Cu—NCSe—Cu	[35]
	2062,	—	443	Cu—NCSe; SeCN⁻	[35]
Cu$(CH_3NH_2)_2$(NCSe)$_2$	2073,2113				
Ga(phen)$_3$(NCSe)$_3$	2115	—	—	Cu—NCSe—Cu	[35]
Ga (bipy)$_3$(NCSe)$_3$	2060	—	—	SeCN⁻	[36]
Ga(Urt)$_3$(NCSe)$_3$	2060	—	—	SeCN⁻	[36]
Hf (bipy)$_2$(NCSe)$_4$	2082,2070	643	—	Ga—NCSe	[37]
Hf(phen)$_3$(NCSe)$_4$	2015	—	—	Hf—NCSe	[38]
In(phen)$_3$(NCSe)$_3$	2015,2060	—	—	Hf—NCSe	[38]
[HIr(pip)$_4$NCSe]NCSe	2050	—	—	SeCN⁻	[36]
	2080,2050	643, 641	483	Ir—NCSe, SeCN⁻	[29]
Ln(Urt)$_2$(NCSe)$_3$·nCH$_3$OH (Ln=Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu)	2068— —2092	—	—	Ln—NCSe	[39]
Ln (bipy)$_3$(NCSe)$_3$ (Ln=Sc, Y, La, Ce, Pr, Nd, Sm, Eu,Ga)	2035— —2085	—	—	Ln—NCSe	[39—41]
Ln (bipy)$_2$(NCSe)$_3$·2CH$_3$OH (Ln=Sc, Y, La, Ce, Pr, Nd. Sm, Eu, Gd, Lu)	2033— —2093	—	—	Ln—NCSe	[39—41]
Ln(phen)$_3$(NCSe)$_3$(Ln=Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Lu)	2040— —2060	—	—	Ln—NCSe	[39—41]
Mg (bipy)$_2$(NCSe)$_2$	2075	630	—	Mg—NCSe	[31]
Mg(phen)$_2$(NCSe)$_2$	2076	625	—	Mg—NCSe	[31]
Mn(phen)$_2$(NCSe)$_2$	2062,2065	620	433	Mn—NCSe	[42]
Nb (bipy)$_2$(NCSe)$_4$	2050,2025	698	468	Nb—NCSe	[43]
Nb(DMbipy)$_2$(NCSe)$_4$	2040, 2055,2085	695	450	Nb—NCSe	[43]
Ni$(C_4H_9NH_2)_4$(NCSe)$_2$	2085,2110	>580	425	Ni—NCSe	[44]
[Ni{$(C_2H_5)_4$dien}NCSe]Ph$_4$B	2094	—	420	Ni—NCSe	[45]
Ni$(CH_3NH_2)_4$(NCSe)$_2$	2100	>580	423	Ni—NCSe	[44]
Ni$(C_3H_7NH_2)_4$(NCSe)$_2$	2095	>580	426	Ni—NCSe	[44]
Sr (bipy)$_2$(NCSe)$_2$	2075,2125	568, 580	—	Sr—NCSe	[31]
Sr(phen)$_3$(NCSe)$_2$	2060	552	—	SeCN⁻	[31]
Ta (bipy)(NCSe)$_5$	1930	697	465	Ta—NCSe	[43]
UO$_2$(bipy)$_2$(NCSe)$_2$	2048	—	—	U—NCSe, SeCN⁻	[46]
UO$_2$(phen)$_2$(NCSe)$_2$	2051	—	—	U—NCSe, SeCN⁻	[46]
ZnQ$_2$(NCSe)$_2$	2095	680	—	Zn—NCSe	[34]
ZnZ$_2$(NCSe)$_2$	2095,2108	675	—	Zn—NCSe	[34]
Zr (bipy)$_2$(NCSe)$_4$	2010	—	—	Zr—NCSe	[38]
Zr(phen)$_3$(NCSe)$_4$	2060,2090	—	—	Zr—NCSe, SeCN⁻	[38]

* The following abbreviations have been adopted in Table 2: Q = benzoxazole; Z = 2-methylbenzoxazole; Bia = benzimidazole; MBiA = methylbenzimidazole; DMBia = dimethylbenzimidazole; Urt = urotropine; dien = diethylenediamine; Dmbipy = 4,4'-dimethyl-2,2'-bipyridyl.

Copper(II) selenocyanate complexes with diguanide (L) derivatives having the composition $[CuL_2](NCSe)_2$, in which the NCSe groups are ionic judging from infrared absorption spectra, have been studied; on the other hand, the Cu–SeCN bond is present in the compound $CuL(SeCN)_2$.[55]

The compounds $Cu(Ben)_2(SeCN)(NO_3)$ and $Ni(Ben)_2.(SeCN)(NO_3)$ have been isolated after the interaction of nickel and copper nitrates with benzylethylenediamine (Ben) in ethanol and subsequent treatment of the product with potassium selenocyanate, while the interaction with *N,N'*-dibenzylethylenediamine (DBen) led to $Ni(DBen)_2(NCSe)_2$ and $Co(DBen)_2(NCSe)_2$. It was shown that the last two complexes are octahedral, while $Cu(Ben)_2(SeCN)(NO_3)$ and $Ni(Ben)_2(SeCN)(NO_3)$ are tetrahedral[56]. Bridging SeCN groups have been detected in the compound $Cu(Ben)_2(SeCN).(NO_3)$, while the remaining complexes contain isoselenocyanato-groups[56].

The nickel and cobalt complexes of certain diamines can also be classified as isoselenocyanates: $ML_2(NCSe)_2$, where $L = NH_2NH_2$, *o*-$(NH)_2C_6H_4$, or ethylenediamine (En).[57] The interaction of hot solutions of $M(ClO_4)_2.6H_2O$ (M = Mn, Fe, Co, Ni, or Cu) in ethanol with LiNCSe in the presence of 2,3,5,6-tetrakis (6-methyl-2-pyridyl)pyrazine (L) led to the formation of the isoselenocyanato-compounds $ML(NCSe)_2$.[58] A series of complexes with dihydrazinophthalazine (Dhph) have been isolated from aqueous solutions: $[Cu_2(Dhph)(SeCN)_2].4H_2O$, $[M(Dhph)(SeCN)_2].2H_2O$ (M = Zn, Co, or Ni), and $[M(Dhph)(SeCN)_2]$ (M = Cd or Mn).[59] The copper complex is diamagnetic and its organic ligand has a bridging function and is bidentate, i.e. the coordination number of copper is 4. In the remaining compounds dihydrazinophthalazine is tetradentate and the coordination of the metal is 6.[59]

The compound [CoL(NCSe)]NCSe, where L is the corresponding Schiff base, has been obtained by the reaction of cobalt(II) acetate with pyridine-2-carboxaldehyde and bis-(3,3'-aminopropyl)amine in the presence of triethyl orthoformate in an atmosphere of nitrogen with subsequent addition of KNCSe.[60] A series of cobalt compounds $Co(NCSe)_2.nA$, where A = diaminobiphenyl and its derivatives, have been described. They are all high-spin compounds in which the cobalt atom has a hexacoordinate environment[61]. Isoselenocyanato-groups are present in the compounds $NiL_2.(NCSe)_2$, where L = 3,3'-bis(aminopropyl) ether, while the nickel ion has a pseudo-octahedral environment[62].

Manganese(II), cobalt(II), zinc, and cadmium compounds containing *N,N*-diethylnicotinamide (DENA) have been isolated from acetone solution: $[Ni(DENA)_2(NCSE)_2].2H_2O$,[63] $[Cd(DENA)_2(NCSe)_2$,[64] $[Zn(DENA)_2(NCSe)_2(H_2O)_2]$,[65] $Mn(DENA)_2(NCSE)_2$, $[Co(DENA)_2(NCSe)_2(H_2O)_2]$, and $[Co(DENA)_4(NCSe)_2]$.[66] The state of bivalent manganese, cobalt, nickel, zinc, and copper complexes with *N,N'* diethylnicotinamide, nicotinamide, acetamide, and propionamide in aqueous solutions and in solutions in organic solvents has been studied[67]. The cadmium complex of nicotinamide $Cd(NA)(NCSe)_2$ has also been obtained. The coordination of nicotinamide in this compound is via the nitrogen heteroatom, while the NCSe groups are also coordinated via nitrogen[68].

A series of analogues of vitamin B_{12} of the type $Co(NCSe).(OH)_2R$, where R = purine or pyrimidine derivative, have been described[69].

Manganese selenocyanate complexes with *o,o'*-, *m,m'*-, and *p,p'*-diaminobiphenyls (Q) and with *p,p'*-diaminodiphenylmethane (L) have been synthesised by adding concentrated solutions of Q or L to an alcoholic solution of $Mn(NCSe)_2$; $Mn(o,o'\text{-}Q)_2(NCSe)_2$, $Mn(m,m'\text{-}Q)_2(NCSe)_2$, $Mn(p,p'\text{-}Q)_3(NCSe)_2$, and $Mn(p,p'\text{-}L)_3(NCSe)_2$.[70] Infrared

absorption spectra and magnetic properties led to the conclusion that the manganese atom in the complexes has coordination number 6.[70]

The complexes $MnL_4.(NCSe)_2$ have been synthesised by refluxing an ethanol solution of $Mn(NCSe)_2$ with pyridine, β- and γ-picolines, 3,5-lutidine, 4-ethylpyridine, and isoquinoline. The compounds contain isoselenocyanato-groups and the manganese atom has an octahedral environment[71].

The complexes $M(BH)_2(NCSe)_2$ have been synthesised by the reaction of manganese, cobalt, nickel, and zince selenocyanates with benzoylhydrazine (BH) in ethanol or acetone. It was established that the nickel and cobalt complexes are isostructural[72]. The compounds $CdL_2(NCSe)_2$, where L = benzoxazole and its derivatives, have been isolated from non-aqueous media[34]. The compounds $Zn(Ampy)_2(NCX)_2$ (X = O or Se and Ampy = 2-aminopyridine) have been shown to be isostructural. In these compounds zinc has a tetrahedral environment and some of the aminopyridine molecules are coordinated to zinc via the nitrogen of the amino-group, while others are coordinated via the nitrogen of the heterocycle. The NCSe groups are monodentate and are linked to zinc via *nitrogen*[73].

New cobalt(III) chelates of the type $[CoLA_2]SeCN$, incorporating ethylenediaminobisacetylacetone (L), ethyl- or n-propyl-amine (A), and SeCN groups, have been synthesised[91].

Copper(II) compounds containing ethylenediamine (En) have been isolated from aqueous ethanol solutions: $CuEn_2.(SeCN)X$, where $X = Cl^-$, Br^-, SCN^-, or NO_3^-. The coordination polyhedron of the central atom consists of a distorted pseudosquare pyramid or a square bipyramid[75]. The interaction of $Cu(CH_3COO)_2$ with L and KNCSe, where L = β-(2-pyridyl)ethylamine or 2-pyridylmethylamine, in absolute methanol in an atmosphere of nitrogen led to the formation of the compound $CuL(NCSe)_2$, where L behaves as a tridentate ligand[76].

The interaction of $CuLCl_2$, where L = 1,4-diphenyl-2-thioammeline, with KNCSe in dry *N,N*-dimethylformamide yielded the compound $CuL(SeCN)_2$, in which the SeCN groups are coordinated via the selenium atom, while the organic ligand is coordinated via the nitrogen and sulphur atoms[77]. Tetrahedral isoselenocyanate complexes with benzimidazole (Bia) and its derivatives have been obtained from ethanol solutions: $Co(MBia)_2(NCSe)_2$, $Co(DMBia)(NCSe)_2$, and $Co(Bia)(NCSe)_2$; here the organic ligand is bound to the metal via the nitrogen atom in the 3-position in the imidazole ring[78].

Much attention has been devoted recently to the study of the cobalt(III) complexes of *trans*-dioximes having the general composition $[Co(HD)_2L(SeCN)].nH_2O$, where HD is a dimethylglyoxime residue and L = 3-cyanopyridine[79], 4-cyanopyridine, pyridine, 4-aminopyridine[80], 2-aminopyridine[81], PPh_3, $PPh_2(n\text{-}Bu)$, PPh_2Me, P(n-Bu), $P(OPh)_3$, $P(O\text{-}n\text{-}Bu)_3$, $P(OMe)_3$, $P(O\text{-}iso\text{-}Pr)_3$, 4-acetylpyridine[82], piperidine, 3-chloropyridine, NH_3, or $PrNH_2$.[83] In all these compounds the bond between the SeCN groups and the central atom is formed via selenium. They have been shown to exhibit an antibacterial activity and the spectrum of the antimicrobial activity of dioxime complexes of this type (in which L are various sulphanilamides[84,85] and sulphanilylpyridines[86-88]) has been expanded relative to the initial complexes and sulphanilylpyridines.

The complexes *trans*-$[Co(HDph)_2LNCSe].H_2O$, where HD is diphenylglyoxime, and L = *p*-aminobenzenesulphonylguanidine[89], 2-(*p*-aminobenzenesulphonyl)pyridine[88], or 4-sulphanilylpyridine[86], have been obtained. The thermal stability of the complexes with the last ligand depends on the nature of the acido-ligand X (Cl, Br, I, NCO, NCS, or NCSe), reaching a maximum in the selenocyanate complex[86].

Dinuclear complexes of the type *trans*-$[ACo(HD)_2\text{–}SeCN\text{–}Co(HD)_2SeCN]$, where HD is a dimethylglyoxyme residue and A = PPh_3, $PPh_2(n\text{-}Bu)$, $P(OPh)_3$, or $P(OCH_3)_3$, are formed in solvents with a low dielectric constant, for example in dichloromethane; in these complexes the terminal SeCN groups are coordinated to cobalt via the selenium atom regardless of the nature of A.[82] The bridged complexes $\{RCo(HL)_2\}\text{–}NCSe\text{–}\{Co(HL)_2Q\}$, where R = CH_3 or CF_3 and Q = piperidine, have been isolated from chloroform[83].

The compounds $[Co(HL)_2(NO_2)(NCSe)]$, where HL is a methylisopropylglyoxime residue[90] and the new cobalt(III) chelates $[CoZQ_2]SeCN$ (H_2Z is a tetradentate ligand consisting of the Schiff base obtained from acetylacetone and ethylenediamine, namely ethylenedi-iminobisacetylacetone, and Q are amines ($C_2H_5NH_2$, $n\text{-}C_3H_7NH_2$, or $CH_2=CH\text{–}CHNH_2$),[91] have also been obtained. The complex acid $H[Co(DH)_2.(NCSe)_2].H_2O$, which is sparingly soluble in water and is resistant to the action of inorganic acids, as well as a whole series of its salts (DH = cyclohexane-1,2-dione dioxime residue)[92] and $H[Co(HL)_2(NCSe)_2]$, where HL = diaminoglyoxime residue[93], have been isolated.

IV. HETEROLIGAND COMPOUNDS INCORPORATING LIGANDS WITH ELECTRON-DONATING OXYGEN

The majority of the compounds considered here are presented in Table 3. In all the compounds with dimethyl sulphoxide (DMSO) the latter is bound to the central atom via oxygen. On the other hand, the mode of coordination of the SeCN groups depends both on the nature of the central atom and on the composition of the complex (Table 3). In the isostructural complexes $M(DMSO)_4(NCSe)_2$ (M = Fe, Co, Mn, or Ni) the central atom has the octahedral configuration Mo_4N_2, probably with the *trans*-location of the isoselenocyanato-groups[96]. In the compound $Cd(DMSO)_2(NCSe)_2$ the cadmium atoms are linked together to infinite chains via bridging SeCN groups. The DMSO molecules complete the polyhedron to form an octahedron. The interatomic distances are Cd–Se = 2.773 Å, Cd–N = 2.26 Å, and Cd–O = 2.30 Å; the SeCN and CdNC angles are 171.5° and 172.6° respectively[100]. The compound $Pb(DMSO)_2(NCSe)_2$ apparently has an analogous structure[25]. The bonds between the SeCN groups and the central atom in the compounds $M(MFA)_4(NCSe)_2$ and $M(DMA)_4(NCSe)_2$ (M = Mn, Co, Ni, or Zn, MFA = *N*-methylformamide, and DMA = *N,N*-dimethylacetamide) are formed via nitrogen, while the organic ligand is linked via oxygen[73,101,102].

Structural study of $Ni(DMA)_4(NCSe)_2$ crystals showed that they are monoclinic and have the lattice parameters $a = 7.67$ Å, $b = 10.40$ Å, $c = 9.74$ Å, and $\gamma = 114°$. The crystals of this compound are isostructural with those of *trans*-$Ni(DMA)_4(NCSe)_2$, in which the SeCN groups are linked to nickel via nitrogen and DMA molecules are linked via oxygen[74].

The compound $Cd(DMF)_2(NCSe)_2$ has been isolated from alcoholic solutions containing $Cd(SeCN)_2$ and *N,N*-dimethylformamide (DMF). It contains bridging SeCN groups, while the bond between DMF and cadmium is formed via oxygen[103], as in the other compounds presented in Table 3. Many selenocyanato-compounds containing antipyrine (A) and diantipyrylmethane (D) are known (Table 3). In all these compounds the organic ligand is linked to the central atom via oxygen, occupying one (antipyrine) or two (diantipyrylmethane) coordination sites. Gallium and indium selenocyanate complexes containing alkyl- or aryl-phosphine oxides have also been studied[37]. Table 3 shows that in all cases

an M–NCSe bond is formed and the central atom acquires an octahedral configuration.

The extraction of uranyl selenocyanates with chloroform solutions of certain oxygen-containing organic reagents has been studied[104]. The composition of the extracted compounds has been established by the equilibrium shift method: $UO_2L_3(NCSe)_2$ (L = antipyrine, triphenylphosphine oxide, or hexamethylphosphoramide) and $UO_2L_2(NCSe)_2$ (L = diantipyrylmethane and phenyldiantipyrylmethane)[104].

Table 3. Fundamental vibrational frequencies of the SeCN groups (cm^{-1})*.

Compound	ν (CN)	ν (CSe)	δ (SeCN)	Type of coordination of SeCN groups	Refs.
$Bi(DMSO)_6(SeCN)_3$	2050, 2110	553	—	Bi—SeCN	[94]
$Bi(DMF)_3(SeCN)_3 \cdot 2DMFA$	2110, 2123	545	—	Bi—SeCN	[94]
$Bi(HMP)_3(NCSe)_3$	2100	640	—	Bi—NCSe	[95]
$Cd(DMSO)_{12}(SeCN)_2$	2115, 2131	580	—	Cd—SeCN	[96]
$Cd(HMP)_2(NCSe)_2$	2195, 2080	575	—	Cd—NCSe, Cd—SeCN—Cd	[97]
$Co(DMSO)_4(NCSe)_2$	2095	610	—	Co—NCSe	[96]
$Co(HMP)_2(NCSe)_2$	2082	650	425	Co—NCSe	[97]
$Cr(HMP)_3(NCSe)_3$	2080, 2095, 2110	620	405, 442	Cr—NCSe	[95]
$Fe(DMSO)_4(NCSe)_2$	2081, 2030	610	—	Fe—NCSe	[96]
$GaA_3(NCSe)_3$	2070	625	—	Ga—NCSe	[36]
$GaD(NCSe)_3$	2062, 2082, 2100	620	—	Ga—NCSe	[36]
$Ga\{OP(C_3H_7)_3\}_3(NCSe)_3$	2070, 2170	650 617	432	Ga—NCSe	[37]
$Ga\{OPPh_3\}_3(NCSe)_3$	2070, 2055	618	—	Ga—NCSe	[37]
$In(DMF)_3(NCSe)_3$	2070	618	—	In—NCSe	[36]
$In(DMSO)_3(NCSe)_3$	2065, 2080	615	—	In—NCSe	[36]
$In(HMP)_3(NCSe)_3$	2075, 2095	650	432	In—NCSe	[95]
$La(HMP)_3(NCSe)_3$	2070	605	426	La—NCSe	[95]
$LnD_2(NCSe)_3$ (Ln=Ce, La, Lu, Nd)	2050—2060	—	—	Ln—NCSe	[39]
$LnD_3(NCSe)_3$ (Ln=Ce, Pr, Eu, La, Lu, Gd, Nd, Sm)	2060—2080	—	—	Ln—NCSe	[39]
$LnD_4(NCSe)_3$ (Ln=La, Ce, Pr, Nd, Lu)	2060—2065	—	—	$SeCN^-$	[39]
$Ln(HMP)_5(NCSe)_3$(Ln=Ce, Pr, Nd)	2070—2080	605—610	~430	Ln—NCSe	[98]
$Ln(HMP)_4(NCSe)_3$(Ln=La, Sm—Lu)	2050—2090	~615	~440	Ln—NCSe	[93, 95]
$Mn(DMSO)_4(NCSe)_2$	2075	610	—	Mn—NCSe	[96]
$Mn(HMP)_2(NCSe)_2$	2065	645, 655	426, 420	Mn—NCSe	[97]
$Ni(DMSO)_4(NCSe)_2$	2098	618	—	Ni—NCSe	[96]
$Ni(HMP)_2(NCSe)_2$	2138, 2110	620	—	Ni—NCSe—Ni; Ni—NCSe	[94]
$Pb(DMSO)_2(NCSe)_2$	2096, 2141	543	403	Pb—NCSe—Pb	[25]
$Sc(HMP)_3(NCSe)_3$	2060, 2085	650	440	Sc—NCSe	[95]
$ScD_3(NCSe)_3$	2060	—	—	Sc—NCSe	[39]
$ScD_4(NCSe)_3$	2052, 2062	—	—	$SeCN^-$	[39]
$UO_2(DMSO)_3(NCSe)_2$	2046, 2069	630	—	U—NCSe	[46]
$UO_2(Diox)_3(NCSe)_2$	2050	635	—	U—NCSe	[15]
$UO_2D_2(NCSe)_2$	2060, 2070	—	—	U—NCSe	[46]
$UO_2A_3(NCSe)_2$	2055	592	—	U—NCSe	[46]
$VO(HMP)_3(NCSe)_2$	2100, 2110	—	—	V—NCSe	[99]
$YD_2(NCSe)_3$	2065	—	—	Y—NCSe	[39]
$YD_3(NCSe)_3$	2070, 2085	—	—	Y—NCSe	[39]
$YD_4(NCSe)_3$	2065	—	—	$SeCN^-$	[39]
$Y(HMP)_3(NCSe)_3$	2050, 2060, 2070	635	436	Y—NCSe	[95]
$Zn(HMP)_2(NCSe)_2$	2090	650	425	Zn—NCSe	[97]

* The following abbreviations have been adopted in Table 3: A = antipyrine; D = diantipyrylmethane; HMP = hexamethylphosphoramide; Diox = 1,4-dioxan.

Selenocyanato-compounds containing hexamethylphosphoramide (HMP) are formed readily when acetone or alcoholic solutions of the corresponding metal selenocyanates are treated with HMP [95–99] (Table 3). In all the compounds HMP is linked to the central atom via oxygen. Compounds having the composition $M(HMP)_2(NCSe)_2$ (M = Mn, Co or Zn) are isostructural. The study of the magnetic properties and the electronic absorption spectra indicated an octahedral structure of the cobalt compound. However, the nickel compound is not isostructural with the analogous cobalt, zinc, and manganese compounds. On the other hand, the magnetic moment, which amounts to 3.6 μ_B, rules out a planar structure of $Ni(HMP)_2(NCSe)_2$. Nickel in the above compound probably has a coordination number of 5 owing to the bridging SeCN groups. In air the compound readily combines with water and is converted into the dihydrate. Judging from the electronic absorption spectra and the magnetic moment (3.02 μ_B), the nickel in the compound is octahedral and the SeCN groups are *N*-linked to nickel[97]. Bridging isoselenocyanato-groups are present in $Cd(HMP)(NCSe)_2$ and the cadmium atom has a tetrahedral environment[97].

All the compounds $M(HMP)_3(NCSe)_3$ in Table 3 contain isoselenocyanato-groups. This is somewhat unexpected for bismuth, because the formation of Bi–SeCN bonds is more characteristic of this element[95,99]. Evidently the "inversion" of the bond linking the SeCN groups in this instance is due to the steric hindrance caused by hexamethylphosphoramide.

Blue crystals of $VO(HMP)_3(NCSe)_2$ have been obtained by adding an excess of KNCSe and HMP to an acetone solution of $VOCl_2$. The compound is isostructural with the analogous thiocyanate. The values of ν(VO) for the thiocyanato- and selenocyanato-compounds are the same (965 cm^{-1}), which may be regarded as proof of the *trans*-position of the HMP molecules relative to vanadyl oxygen and not of XCN groups[99]

Lanthanide selenocyanate complexes with nonamethylimidophosphoramide (NIPA) have been isolated from acetone: $Ln(NIPA)_3(NCSE)_3$ (Ln = Pr, Nd, or Sm) and $Ln_2(NIPA)_5 \cdot (NCSe)_3$ (Ln = Gd, Tb, Er, Tm, or Lu), which are isostructural with the analogous thiocyanates. As for thiocyanates, the coordination number in the selenocyanates decreases from nine (Pr, Nd, and Sm) to eight (Gd–Lu).[105]

V. COORDINATION SELENOCYANATO-COMPOUNDS OF THE ACIDO-TYPE

Coordination compounds of the acido-type containing only SeCN groups in the anion can be obtained (with the exception of the mercury compounds) solely from non-aqueous solutions. Table 4 shows that in all the compounds considered the mode of coordination of the SeCN groups most characteristic of the complex-forming metal is retained[1,109]. It is of interest that the octahedral environment of the central atom in the compounds $(UrtH)_2[M(NCSe)_4]$ (M = Co or Ni and Urt = urotropine) is achieved not only via the SeCN groups but also with the aid of the cation[106].

The compounds $[(CH_3)_4N]_4[Fe(NCSe)_6]$, $[(C_2H_5)_4N]_3 \cdot [Fe(NCSe)_5(H_2O)]$, $[C_4H_9)_4N]_2[Fe(NCSe)_4]$, and $[(C_4H_9)_4N]_3 \cdot [Fe(NCSe)_6]$, which are high-spin complexes and contain isoselenocyanato-groups, have been obtained by the method already described[110], isolated, and investigated[111]. A similar type of coordination has also been observed in the octahedral compounds $R_4[Co(NCSe)_6]$, $R_3[Fe(NCSe)_5(H_2O)]$, $R_3[V(NCSe)_6]$, $R_3[Mo(NCSe)_6]$, and $R_3[MoO(NCSe)_5]$, where $R = (C_2H_5)_4N^+$,[112] and also in $R'_3[Cr(NCSe)_6]$, where $R' = K^+$ or $(C_4H_9)_4N^+$.[113]

When $[(C_4H_9)_4N]_2Re_2Cl_8$ was allowed to react with KNCSe in ethanol or acetonitrile, it was possible to isolate the rhenium compound $[(C_4H_9)_4N]_2[Re_2(NCSe)_8]$. Judging from the wavenumber ν(CN) = 2050 cm^{-1}, the SeCN groups are linked to the rhenium atom via nitrogen[114]. In the presence of $SeCN^-$ ions, rhenium pentachloride forms polymeric complexes in acetone via bridging SeCN groups[115].

The compounds of Group V elements $K[M(NCSe)_6]$ (where M = Nb or Ta), $K_2[Nb(NCSe)_6]$, and $[Ph_4As][Ta(NCSe)_6]$ have been obtained from acetonitrile solutions[116]. It also proved possible to isolate from acetonitrile the compounds $K_2[Zr.(NCSe)_6]$, $K_2[Hf(NCSe)_6]$,[117] $[(C_2H_5)_4N]_4[Pa(NCSe)_8]$, and $[(C_2H_5)_4N]_4[U(NCSe)_8]$.[118] X-Ray diffraction study showed that the last two compounds are isostructural and belong to the tetragonal system (the lattice parameters are $a = 11.82$ Å and $c = 23.49$ Å for the first compound and $a = 11.80$ Å and $c = 23.36$ Å for the second)[118].

Table 4. Fundamental vibrational frequencies of the SeCN groups in selenocyanates of the acido-type (cm^{-1})*.

Compound	ν (CN)	ν (CSe)	δ (SeCN)	Type of coordination of SeCN groups	Refs.
$(UrtH)_2Co(NCSe)_4$	2083, 2095	—	—	Co—NCSe	[106]
$[(C_4H_9)_4N]_3[Ga(NCSe)_6]$	2075	615, 635	—	Ga—NCSe	[36]
$[Ph_4As]_3[Ga(NCSe)_6]$	2060	612	—	Ga—NCSe	[37]
$Ba[Ga(NCSe)_4]\cdot 6THF$	2075	612	440	Ga—NCSe	[37]
$[(C_4H_9)_4N]_3[Zn(NCSe)_6]$					
Ln : Dy	2047	644	434	Dy—NCSe	[107]
Er	2050	646	435	Er—NCSe	[107]
Nd	2058	615	428	Nd—NCSe	[107]
Pr	2058	613	425	Pr—NCSe	[107]
Ho	2048	642	433	Ho—NCSe	[107]
$[(C_2H_5)_4N]_2[MoO(NCSe)_5]$	2060	650	470	Mo—NCSe	[17]
$K_2Nb(NCSe)_6$	1985, 2070	710, 740	490, 459	Nb—NCSe	[92]
$KNb(NCSe)_6$	1918, 1961	740, 972	449, 459	Nb—NCSe	[92]
$(UrtH)_2Ni(NCSe)_4$	2098, 2105	606	438, 426, 431	Ni—NCSe	[106]
$KTa(NCSe)_6$	1925, 1972 2001, 2075	763, 779	449, 455	Ta—NCSe	[92]
$Li_3[Bi(SeCN)_6]\cdot 3Act$	2110	545	405	Bi—SeCN	[108]
$[Ph_4As][Ta(NCSe)_6]$	1925, 1981, 2035	749	468	Ta—NCSe	[92]
$Na_3[Bi(SeCN)_6]$	2073, 2085, 2110	535, 548	405	Bi—SeCN	[108]
$Ca_3[Bi(SeCN)_6]_2\cdot 10Diox$	2112	—	400	Bi—SeCN	[108]
$Sr_3[Bi(SeCN)_6]_2\cdot 2Diox$	2100	532	400	Bi—SeCN	[108]
$Mn_3[Bi(SeCN)_6]_2\cdot 10Diox$	2120	530	400	Bi—SeCN	[108]
$KBa[Bi(SeCN)_6]\cdot 2Act$	2093	545, 557	500	Bi—SeCN	[108]
$Li_2Bi(SeCN)_5\cdot 3Diox$	2085, 2130	545, 573	403, 455	Bi—SeCN—Bi	[108]
$Mg_3[Bi(SeCN)_6]_2\cdot 9Diox$	2131	—	406	Bi—SeCN—Bi	[108]
$Pb[Hg(SeCN)_3]_2$	2124, 2140, 2158	535, 545	405	Hg—SeCN—Hg	[93]
$KCd(SeCN)_3$	2096, 2113, 2122, 2132	540, 547	405, 420	Cd—SeCN—Cd	[93]
$KHg(SeCN)_3$	2122, 2142	535, 543	—	Hg—SeCN—Hg	[93]
$KPb(SeCN)_3$	2080, 2118, 2140	532, 579	420	Pb—SeCN—Pb	[25]
$[(C_4H_9)_4N]_3[UO_2(NCSe)_5]$	2050, 2070	610	—	U—NCSe	[15]
$[(C_2H_5)_4N]_3[UO_2(NCSe)_5]$	2040, 2060	625	—	U—NCSe	[15]

* The following abbreviations have been adopted in Table 4: Urt = urotropine; Diox = 1,4-dioxan; Act = acetone.

The uranyl selenocyanates $[(C_4H_9)_4N]_3[UO_2(NCSe)_5]$ and $[(C_2H_5)_4N]_3[UO_2(NCSe)_5]$ were isolated from methanol[15]. All the compounds mentioned above contain isoselenocyanato-groups. The formation of the Bi–SeCN bond is more characteristic of bismuth selenocyanates; bridging selenocyanato-groups are present in the mercury, lead, and cadmium compounds (Table 4).

Among heteroligand complexes of the acido-type, the mercury and cadmium compounds have been studied most thoroughly (Table 5). The compounds $K_2[Cd(SeCN_2)SCN)_2]$, $K_4[Cd(SeCN)_4(SCN)_2].0.5$ Act, $K_2[Cd(SeCN)_2(Hal)_2]$ (where Hal = Cl or Br), $K_4[Cd(SeCN)_4I_2].0.5$ Act, and $K_2[Cd(SeCN)_3I]$. Act were synthesised by crystallisation from acetone solutions containing CdX_2 ($X = SCN^-$, Cl^-, Br^-, or I^-) and KNCSe in proportions of 1 : 2 or 1 : 4 [120,124] [Act = acetone (Ed. of Translation)]. It follows from infrared spectroscopic data that $K_2[Cd(SeCN)_2(SCN)_2]$ contains both terminal Cd–SeCN bonds and bridging Cd–SeCN–Cd linkages[120]. Bridging SeCN groups are also present in $K_2[Cd(SeCN)_2(Hal)_2]$, while in the compound $K_4[Cd(SeCN)_4I_2]$ the SeCN groups are linked to the central atom via selenium[120,124]. Cadmium compounds incorporating together with SeCN groups the non-linear $N(CN)_2$ and $C(CN)_3$ groups have also been obtained (Table 5). All these compounds except $K_2\{Cd[C(CN)_3]_2.(NCSe)_2\}$ contain isoselenocyanato-groups. The last compound contains bridging SeCN groups.

The mercury compounds $K_2[Hg(SeCN)_2A_2]$, where $A = Br^-$, I^-, or SCN^-, have been isolated from acetone[124]. SeCN groups linked to mercury via selenium are present in these complexes and also in $Ba[Hg(SeCN)_2(SCN)_2].2Act$, but the presence of SeCN bridges may be suggested in $K_2[Hg(SeCN)_2.Br_2]$, in view of the band at 2138 cm^{-1}.[122] Bridging SeCN groups are also present in the compound $Ba[Hg(SeCN)_2.Br_2].Act$.

When $Hg(SeCN)_2$ is dissolved in acetone solutions of $M(NCSe)_2$ (M = Mn or Co), the compounds $M[Hg(SeCn)_2(SCN)_2]$ are formed[124]. The compounds $M[Hg(XCN)A_2]$, where M = Mn, Co, Ni, Zn, or Cu and X = S or Se, have been obtained similarly[123]. Table 5 shows that the spectra of all the compounds of the type $M[Hg(SeCN)_2(SCN)_2]$, where M = Mn, Co, Ni, or Zn, contain high-frequency ν(CN) components in the range 2135–2160 cm^{-1}, which indicates the presence of bridging XCN groups in these compounds. Bridging XCN groups have also been found in $Cu[Hg(SeCN)_2(SCN)_2]$.[123]

When $M(SCN)_2$ (M = Ni, Zn, or Ba) was allowed to react with $Hg(SeCN)_2$ in ethanol or acetone, the compounds $NiHG(SCN)_2(SeCN)_2.Act$, $ZnHg(SCN)_2(SeCN)_2$, and BaHg.

Table 5. Fundamental vibrational frequencies in heteroligand complexes (cm^{-1}).

Compound	SeCN groups			Other acido-groups			Refs.
	ν (CN)	ν (CSe)	δ (SeCN)	ν (CN)	ν (CS)	δ (SCN)	
$[(CH_3)_4N][Au(CN)_2(SeCN)_2]$	2139	533	—	2176	—	—	[119]
$K_2Cd(SeCN)_2(SCN)_2$	2113, 2123, 2135	543, 552	413, 442	2090, 2094	722, 729	438, 444, 458, 473	[120]
$K_2Cd(SeCN)_2Cl_2$	2095, 2110, 2119, 2122	543, 550, 80	403, 402	—	—	—	[120]
$K_2Cd(SeCN)_2Br_2$	2109, 2151	545, 582	404	—	—	—	[120]
$K_4Cd(SeCN)_4(SCN)_2\cdot 0.5Act$	2113, 2122, 2132	540, 551	415, 425	2050, 2091	722, 730, 750	438, 446, 460	[120]
$K_2Cd(SeCN)_3I\cdot Act$	2096, 2112, 2132	534, 632	403	—	—	—	[120]
$K_4Cd(SeCN)_4I_2\cdot 0.5Act$	2074, 2111	540	418	—	—	—	[120]
$[Ph_4P]_2[Cd\{N(CN)_2\}_2(NCSe)_2]$	2080	590	410	2225, 2165	—	—	[121]
$K_4[Cd\{N(CN)_2\}_4(NCSe)_2]$	2105, 2120	—	405	2160	—	—	[121]
$K_2[Cd\{C(CN)_3\}_2(NCSe)_2]$	2125, 2150	590	400	2170, 2220	—	—	[121]
$K_4[Cd\{C(CN)_3\}_2(NCSe)_2]$	2080, 2110	594	415	2180, 2205, 2240	—	—	[121]
$K_2[Hg(SeCN)_2Br_2]$	2125, 2138	531, 539	425	—	—	—	[122]
$K_2[Hg(SeCN)_2I_2]$	2118	546, 621	413	—	—	—	[122]
$K_2[Hg(SeCN)_2(SCN)_2]$	2110	548	424	2110	728	—	[122]
$Ba[Hg(SeCN)_2Br_2]\cdot Act$	2107, 2119, 2138, 2143, 2154	545, 557	410	—	—	—	[122]
$Ba[Hg(SeCN)_2(SCN)_2]$	2120	553, 570	403, 457, 470	2080	747	—	[122]
$Mn[Hg(SeCN)_2(SCN)_2]$	2120, 2135	622	402, 420	2120, 2135	790, 805	—	[123]
$Co[Hg(SeCN)_2(SCN)_2]$	2139, 2146	639	426, 436	2139, 2146	801	—	[123]
$Ni[Hg(SeCN)_2(SCN)_2]$	2160	609	413, 425	2160	768	—	[123]
$Zn[Hg(SeCN)_2(SCN)_2]$	2158	630	404, 420	2158	798, 730	—	[123]
$Cu[Hg(SeCN)_2(SCN)_2]$	2160, 2180	623	405, 427	2160, 2180	760, 830	—	[123]

.$(SCN)_2(SeCN)_2$.Act were obtained[26]. The interaction of $BaBr_2$ with $Hg(SeCN)_2$ in an acetone–water mixture yielded the complex $BaHg(SeCN)_2Br_2$.Act.[28] The compound *trans*-$[(CH_3)_4N][Au(CN)_2(SeCN)_2]$ was isolated from acetone after the double decomposition reaction between KNCSe and *trans*-$[(CH_3)_4N][Au(CN)Cl_2]$.[119] The mixed bismuth complexes $K_3[Bi(SeCN)_3(SCN)_3]$, $K_2[Bi(SeCN)_2(SCN)_3]$, and KBi(SeCN). .$(SCN)_3$ have also been synthesised[125].

When an aqueous solution of $Rh(CH_3COO)_4.2H_2O$ was allowed to interact with potassium selenocyanate, the complex $Rh_2(CH_3COO)_4$.KNCSe.$2H_2O$ was obtained, in which the SeCN groups are of the bridging type[126,127]. A comparative study of the compounds $Rh(RCOO)_2$.KNCSe.$2H_2O$ (R = H, CH_3, CH_2Cl, or C_2H_5) has been made. In these compounds the SeCN groups are of the bridging type and the formula $K[Rh(RCOO)_4NCSe].2H_2O$ can be attributed to the compounds [126]. The beryllium compounds $[Be(DMF)_3Cl]SeCN.3.5DMF$ and $K[Be(DMF)(NCSe)_3].4DMF$ [128] as well as a series of cobalt, manganese, and zinc compounds, namely $K_2[M(NCS)_2(NCSe)_2]$. .*n*Diox (M = Mn, Co, or Zn) and $Na_2[Co(NCSe)_2(NCS)_2]$. .5.5 Diox, in which the SeCN groups are linked to the central atom via nitrogen, have been obtained from non-aqueous solusolutions[129]. Only one absorption band near 16000 cm^{-1}, indicating a tetrahedral environment of the cobalt atom, has been observed in the electronic spectra of the cobalt compounds. The influence of the size of the outer cation on the coordination of the SeCN group was traced in relation to the cobalt selenocyanates $[(C_4H_9)_4N]_3[Co(CN)_5(NCSe)]$, $Cs_3[Co.(CN)_5SeCN]$, $[(CH_3)_4N]_3[Co(CN)_5SeCN]$, $[(CH_3)_4N]_3.[Co(CN)_5.NCSe]$, and $[Co(NH_3)_6][Co(CN)_5SeCn]$. The products are $[Co(CN)_5SeCn]^{3-}$ for M = K or Cs, a mixture of $[Co(CN)_5.SeCn]^{3-}$ and $[Co(CN)_5NCSe]^{3-}$ for $M = (CH_3)_4N$, and $[Co(CN)_5NCSe]^{3-}$ for $M = (C_4H_9)_4N$.

The iron(III) complex $[(C_4H_9)_4N]_3[Fe(CN)_5(NCSe)]$ has been isolated from acetone[131]. A series of mixed chromium(III) compounds have been obtained: $[(C_4H_9)_4N]_3[Cr(CN)(NCSe)_5]$, $[(C_4H_9)_4N]_3[Cr(CN)_2.(NCSE)_4]$, $[(C_4H_9)_4N]_3[Cr(CN)_3(NCSe)_3]$, and $[(C_4H_9)_4N]_3[Cr(CN)_4(NCSe)_2]$.[132] The study of the electronic absorption spectra showed that the 18000 cm^{-1} band, due to the *d*–*d* transition, undergoes a hypsochromic shift with decrease of the number of selenocyanato-groups from six to two. The intensity of the charge-transfer bands in the range 28500–30500 cm^{-1} decreases in the same sequence[132].

Polymeric cobalt, nickel, and mercury compounds containing the SCN and SeCN groups have been synthesised[133,134]. The structure of $MHg(SeCN)_4$, where M = Mn or Fe, has been studied[135]. The Co–NCSe–Ag bridging linkages have been detected in $Co[Ag(SeCN)_2]_2$ [136] and the M–NCSe–Hg linkages have been found in $(SeCN)_2L_2M(NCSe)_2Hg(PPh_3)_2$, where M = Co, Ni, Cu, or Zn and L = nicotinamide[137].

VI. COMPOUNDS CONTAINING METAL–PHOSPHORUS AND METAL–CARBON BONDS AS WELL AS CERTAIN OTHER COMPOUNDS

A series of metal complexes of triphenylphosphine (Ph_3P) and triphenylarsine (Ph_3As) have been obtained from non-aqueous solutions. Thus the SeCN groups in *trans*-$Rh(Ph_3P)(CO)NCSe$, $Ir(Ph_3P)_2CO(Act)NCSe$, $Au(Ph_3P)SeCN$, and $Au(Ph_3As)SeCN$ are linked to the rhodium and iridium atoms via nitrogen and to the gold atom via selenium[138]. According to the authors[139], the compound $Pd(Ph_3P)_2(SeCN)_2$ contains Pd–SeCN bonds in the solid state.

The orange crystals of $Ru(CO)(Ph_3P)_2(NCSe)_2$ have been obtained by the reaction of $Ru(CO)_3(Ph_3P)$ with an excess of $(NCSe)_2$ in benzene. A whole series of iridium compounds have been synthesised: $[IrL_2(SeCN)_2]BPh_4$ (where $L = Ph_2.PC_2H_4PPh_2$), $Ir(Ph_3P)_2(SeCN)_2Cl$, and $Ir(CO)(Ph_3P)_2.Cl(SeCN)_2$.[140] The compounds *trans*-$M(Ph_3P)_2(SeCN)_2$ (M = Pt or Pd) have been obtained by the reaction of equivalent amounts of $(NCSe)_2$ and the corresponding ML_4 in benzene[140]. The NCSe groups in *trans*-$[(Ph_3P)_2PtHSeCN]$ and $\{[(C_4H_9)_4P]_2PtHSeCN\}$ are linked to platinum via the nitrogen atom[141].

The dimer $[(CH_3)_2Au(NCSe)_2]$ with a bridging SeCN group has been obtained; its interaction with triphenylphosphine in absolute ether gives rise to the complex $(CH_3)_2Au(SeCN).(PH_3P)$, which, however, has not been isolated in a pure state[142]. The compound [MoOClL]Cl, where L = 1,2-bisdiphenylphosphinoethane, has been isolated from a methanol solution[143]. The pentacoordinate complexes CoLNCSe and CoL′(NCSe), which have a trigonal bipyramidal structure, have been obtained by the reaction of COLBr [HL = $P(CH_2.COCH_2R)O(OEt)_2$, R = NEt_2] and [HL′ = $P(CH_2COCH_2R)O.(OEt)_2$, R = $\overline{NCH_2CH_2CH_2CH_2CH_2}$] with KNCSe in dry acetone[144]. The organic ligand is tridentate in both cases; it is coordinated to the cobalt atom via the oxygen of the C=O and P=O groups and via the nitrogen atom, one of the oxygen atoms behaving as a bridging group[144].

The complexes $M(CO)_5(RSeCN)$, where M = chromium or tungsten and R = alkyl or aryl, have also been obtained. The solid compounds are resistant to heat and light. The SeCN group is coordinated to the central atom via the nitrogen atom[145]. The compounds $R_2TlSeCN$ (R = phenyl or *o*-, *m*-, and *p*-tolyl) in which, judging from infrared spectroscopic data, the SeCN groups are linked to thallium via selenium, have been obtained from non-aqueous solutions[146]. The complex $(CH_3)_2N_4BSeCN$ has been synthesised by refluxing $(CH_3)_2NBCl$ with a small excess of AgSeCN in benzene in an atmosphere of nitrogen[147]. The compound [CuLNCSe[.CH_3OH, where L is the macrocyclic ligand 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetra-aza-2,14-dioxacyclotetradeca-3,5,10,12-tetraene has been isolated[148].

The sparingly soluble complexes $Cp_2Ti(NCSe)_2$, $Cp_2Ti.(CN)(NCSe)$, $Cp_2V(NCSe)_2$, $Cp_2Cr(NCSe)(SCN)$, and $Cp_2.M(CN)(NCSe)$, where M = V or Cr, have been synthesised by the reaction of $Cp_2Ti(CO)_2$, Cp_2V, and Cp_2Cr (Cp = cyclopentadienyl) with $(SeCN)_2$ and $Se(CN)_2$ in ether in an atmosphere of nitrogen[149].

The synthesis of the compounds $(\eta^5\text{-}C_6H_5)RhL(SeCN)_2$ (R = H or CH_3) has been mentioned[150]. The complexes are obtained by the interaction of $(\eta^5\text{-}C_5R_5)RhLCl_2$ with $NCSe^-$, where L = CNR′ and R′ = C_6H_{11}; the SeCN groups are coordinated to rhodium via selenium.

The synthesis of the compound $CF_3HgSeCN$ has been described[151]. After the reaction of $Cu(SeCN)_2$ with a two-fold excess of $CpFeC_5H_4HgCl$, where Cp = $\pi\text{-}C_5H_5$, the complex $CpFeC_5H_4SeCN$ was isolated[152].

An X-ray diffraction study has been made of the compound $KSe(SeCN)_3.0.5H_2O$.[153] The selenotriselenocyanate ions are dimerised to form almost planar groups. All six cyano-groups of the dimeric anion are located on one side of its middle plane. The C≡N (1.21–1.45 Å) and Se–C (1.808 to 1.876 Å) bond lengths have been determined.

The selenotriselenocyanate ions in the rubidium compound $RbSe(SeCN)_3.0.5H_2O$ with an analogous composition are combined into dimers with a similar geometry, which can be regarded as two selenodiselenocyanate molecules linked together via the bridging selenium atoms of two selenocyanate ions. The eight selenium atoms of the dimer are located in approximately the same plane, on one side of which there are six cyano-groups. The coordination of the central selenium atoms is square planar and the four Se–Se

bonds (2.391–2.409 Å) are in the *trans*-positions relative to the four long bonds (3.127–3.331 Å).[154]

The structure of the compound $[(CH_3)_4N][C_6H_5Te(SeCN)_2]$ has also been investigated. It was shown to be isomorphous with the corresponding thiocyanate[155]. The parameters of the monoclinic lattice of the selenocyanate are as follows: $a = 15.840$ Å; $b = 9.341$ Å; $c = 23.384$ Å; $\beta = 100.67°$; $Z = 8$; space group $C2/c$. The coordination of the Te atoms in the anions is of the planar trigonal type due to the phenyl carbon atom. The Se–Te–Se groups are almost linear and the selenocyanate group is linear.

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Thus, since the $SeCN^-$ ions are fairly stable in non-aqueous media, there are considerable prospects for the use of the latter in the synthesis of new compounds incorporating SeCN groups. Further study of compounds of this class will lead to the discovery of their practical applications, for example, in analytical chemistry and in the synthesis of heavy metal selenides and physiologically active preparations[156].

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