Structure and classification of thiocyanates and the mutual influence of their ligands

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I. Introduction

The linear thiocyanate group can be present in compounds as an anion or as a ligand — a monodentate ligand coordinated to sulfur or nitrogen, or a bridging ligand.

The great coordination ability of the thiocyanate group and a great variety of its bonding modes are responsible for the existence of a relatively great number of coordination compounds in liquid and solid state in which this group occurs.

Several authors gathered together information available on these compounds and discussed them in several review articles. Often these form a part of a broader treatise on pseudohalide anions [180, 210, 20, 32, 33, 169, 74, 112, 145, 199, 137, 12, 170, 187, 138].

In the present paper review and evaluation of past findings on thiocyanates, especially on their structure is attempted. The attention is devoted to the classification of these compounds and to the mutual influence of their ligands (MIL). Special attention is paid to the Cu(II) complexes.

II. Structure of thiocyanates and bonding modes of thiocyanate ligand

Analysis of bonding modes of thiocyanate ligand is based primarily on data gained from the single crystal X-ray diffraction analysis of various thiocyanates.

Coordination of thiocyanate ligand *via* sulfur or nitrogen atom takes place at various bonding angles. While the bonding angle M—S—C varies round the tetrahedral value (*e.g.* in $K_2[Pd(—SCN)_4]$ [156] it is $\approx 109°$ and can drop to the value of $\approx 80°$, *e.g.* in $[Cu(en)_2(—SCN)_2]$ [29]), the bonding angle M—N—C lies near the linear value (*e.g.* for $(Et_4N)_4[U(—NCS)_8]$ [55] it makes 180° but can drop even to $\approx 120°$ *e.g.* for $[Pb(—NCS—)_2]$ [161]). Differences between bonding angles of M—N—C and M—S—C were observed in both terminal and bridging thiocyanate groups.

The interatomic distance C—N varies round the value ≈ 0.115 nm (*e.g.* in $[Mn(top)(—NCS)_2]$ [64] it makes 0.115 nm). The smallest value of this distance, 0.110 nm was found for $(n\text{-}Bu_4N)_3[Er(—NCS)_6]$ [154] and the greatest value, 0.132 nm for $[Cu(en)(—NCS)(—NCS—)]$ [78]. The interatomic distance C—S varies round the value ≈ 0.165 nm (*e.g.* in $K_2[Co(—NCS)_4] \cdot 3H_2O$ [62] it makes 0.166 nm). The minimal value of this distance, 0.151 nm was found for $(Ph_4As)_2[NbO(—NCS)_5]$ [126] and the maximal value, 0.176 nm for $[Co(—NCS—)_6Hg_2] \cdot C_6H_6$ [105].

In most crystal structures the thiocyanate ligand is linear and the bond angle N—C—S diverges only slightly from 180° (*e.g.* in $[Co(py)_2(—NCS—)_4Hg]$ [19] two symmetrically independent thiocyanate ligands have bonding angles 179.0° and 178.8°). We know cases in which a decrease of the value of the bonding angle N—C—S was observed (the deviation from the linearity of NCS group). Thus, *e.g.* in $[Ni(triam)(—NCS)_2]$ [100] and $Rb[Bi(—SCN)_4]$ [75] the values of this bonding angle lie round $\approx 170°$ and in the compounds $[Cu(en)(—NCS)(—NCS—)]$ [78] and $[Cu(NH_3)_2(—NCS)(—NCS—)]$ [114] round $\approx 160°$.

In spite of the fact that the most reliable data on bonding modes of thiocyanate ligand can be obtained from single crystal X-ray diffraction analysis, infrared

spectroscopy is often used for approximative estimation of bonding modes. Next we report such data and we wish to point out the ambiguity and limitations involved in this approach with regard to an exact solution of these problems.

Application of infrared spectroscopy for these purposes is based on the fact that the S- or N-coordinated thiocyanate ligand gives significantly different shifts of absorption bands not only in relation to each other, but in comparison with noncoordinated thiocyanate anion as well. Infrared spectroscopy correlates the mode of coordination of thiocyanate ligand with changes of wavenumbers of three vibrations which occur in the infrared spectra. These are: the pseudosymmetric stretching vibration $v(CN)$, the doubly degenerated deformation frequency $\delta(NCS)$, and the pseudosymmetric stretching vibration $v(CS)$. In the paper [12] is shown that there is a relationship between the values of wavenumbers of all three types of vibrations and the coordination mode. There are, however, certain structural and electronic factors which impair general validity of these criteria [160, 213, 214]. Thus, e.g., positions of the frequencies can be influenced by changes of mass, charge, and size of the central atom. Kharitonov et al. [50] calculated changes in vibrational frequencies for M—NCS, M—SCN, and M—NCS—M in dependence on changes of the bonding angle M—N—C, M—S—C and the relative atomic weight of the element.

In Table 1 wavenumber ranges of infrared spectra for thiocyanate group with various bonding modes are listed, as these were reported in [170]. The actual wavenumber ranges indicate how difficult an unambiguous identification of the

Table 1

Wavenumbers of vibrations of thiocyanate groups in different modes of coordination in infrared spectra (cm^{-1}) [170]

Mode of coordination	$v(CN)$	$v(CS)$	$\delta(NCS)$
$(NCS)^-$	2053	746	486, 471
M—NCS	2100—2050 s, b	870—820 w	485—475
M—SCN	2130—2085 s, sp	760—700 b	470—430
M—NCS—M	2165—2065	800—750	470—440

s — strong, b — broad, w — weak, sp — split.

bonding mode is. From among the reported values the wavenumber of the stretching frequency $v(CS)$ seems to be the most suitable. The identification of this vibration in the spectrum is not quite easy since, first, it is partly overlapped by vibrations from ligands, and, second, its intensity is rather low.

The situation for the bridging coordination mode is also complicated. There are rather broad frequency ranges and these depend on the number and types of

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Table 2

Wavenumbers of stretching vibrations of the thiocyanate ligand in some thiocyanates of Cu(I) and Cu(II) [113]

Compound	v (CN) cm^{-1}	v (CS) cm^{-1}	Interatomic distance, nm		Bridging mode	Ref.
			Cu—N	Cu—S		
[Cu(py)$_2$(—NCS—)$_2$]	2072	824	≈0.2	≈0.30	—NCS—	[181, 168]
[Cu(NH$_3$)$_2$(—NCS)(—NCS—)]	(2096), 2116	807, 796	0.196	0.302^a	—NCS—	[114]
[Cu(—NCS—)]	2173	748, 723	0.189	0.237^a	—NCS—	[113]

a) In the respective compounds there are a few differing Cu—S distances, their mean values are listed in the table.

coordination bonds of the thiocyanate ligand [113]. This can be exemplified by three thiocyanate copper compounds in which the thiocyanate ligand occurs in various bridging modes (Table 2) and in which with the increase of the number of coordination bonds of the thiocyanate group the wavenumber of v(CN) increases significantly and that of v(CS) decreases. This cannot be explained only in terms of σ bonds on the sulfur atom. The effect of Cu—N and Cu—S dative π bonds on reorganization of electron density within the thiocyanate group must be considered, too.

In the case of [Cu(—NCS—)]
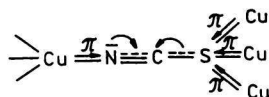
strong π-bonding interactions Cu $\rightarrow$ S can be expected, which are made possible by overlapping of the filled $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals of Cu(I) with vacant orbitals on S atom from the thiocyanate ligand. Evidently, these π-bonding interactions prevail over the π-bonding interactions Cu $\rightarrow$ N and in consequence of this there is a shift of electron density from the space of C—S into the space of C—N.

In the case of [Cu(NH$_3$)$_2$(—NCS)(—NCS—)]
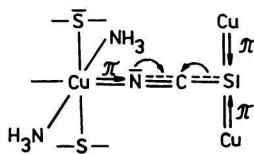
the π-backbonding to the sulfur atom is possible also due to overlapping of $3d_{xz}$ and $3d_{yz}$ orbitals on Cu(II) and S atoms. This backbonding is weaker than that in the previous case not only as a consequence of decrease of the number of coordination σ bonds of sulfur but also because of a weaker overlapping caused by a greater interatomic distance Cu—S (Table 2).

In the case of $[Cu(py)_2(—NCS—)_2]$
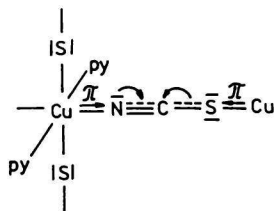
the considered π-bonding transfer is even smaller. We can expect that the effect of Cu—S π bonds on shift of the electron density in thiocyanate ligands will be the smallest (smaller than the influence of Cu—N π bonds). Thus the observed shifts of the wavenumber can be explained [113].

Apart from infrared spectroscopy other physicochemical methods are used for determination of the mode of coordination of thiocyanate ligand [12, 170, 171, 107, 155, 201]. Since these methods cannot give an unambiguous answer on the mode of bonding either in the coordination polyhedron (differentiation between axial and equatorial interactions), or in the crystal structure (discrimination of the nature of bridging mode), the single crystal X-ray diffraction analysis remains the most reliable method for these purposes.

a) *Classification of thiocyanates*

On the basis of X-ray single crystal diffraction analysis we found 38 different cases which we designate further as "coordination types" (CT). In Table 3 the basis on which the classification has been performed is shown.

i) *Complexes with monodentate thiocyanate ligands*

We classified the crystal structures of thiocyanate complexes with monodentate thiocyanate ligands as follows:
— homogeneous thiocyanates (Table 4),
— heterogeneous thiocyanates with monodentate ligands (Table 5),
— heterogeneous thiocyanates with chelate ligands (Table 6),
— heterogeneous thiocyanates with monodentate and chelate ligands (Table 7).
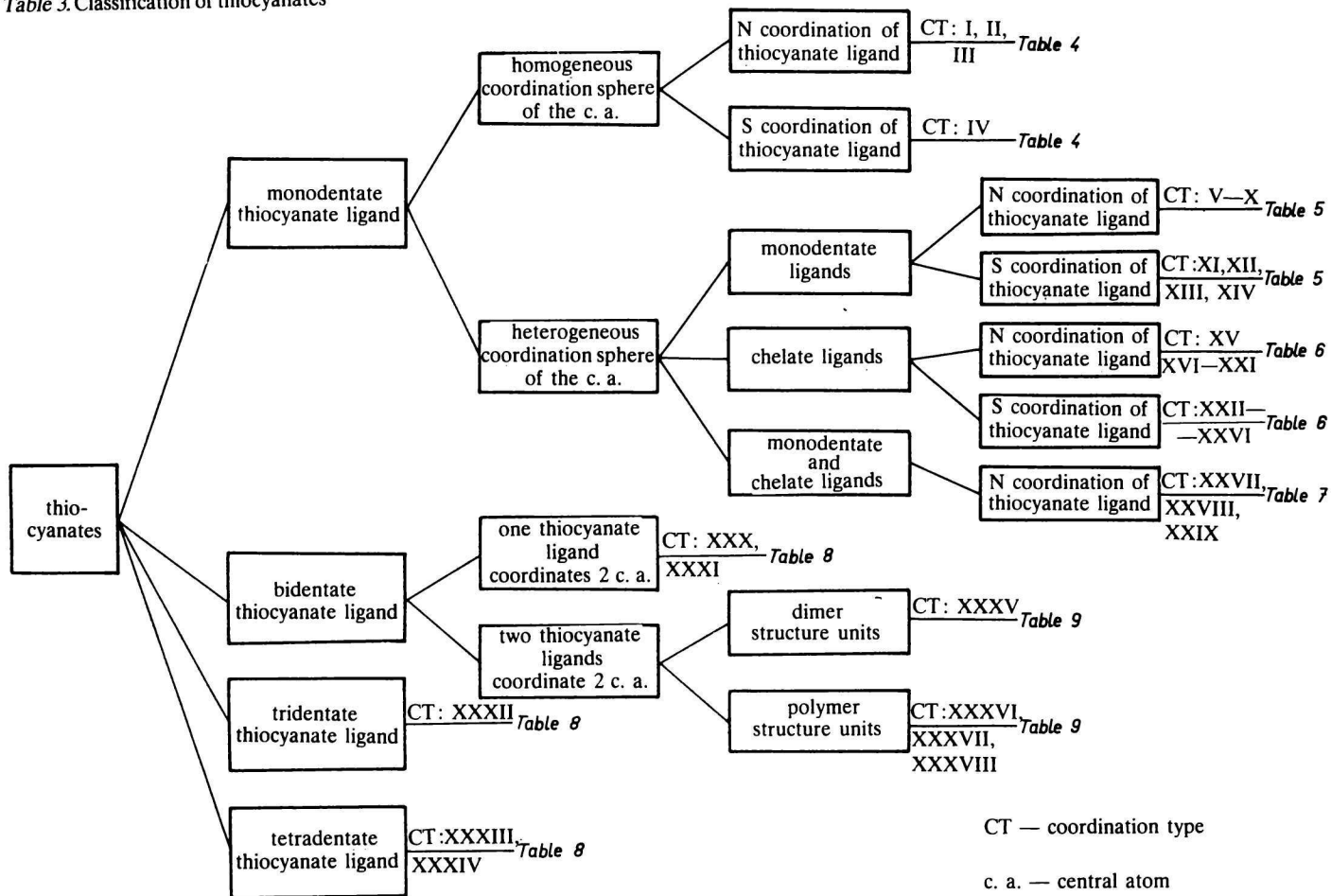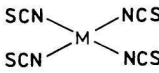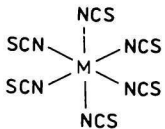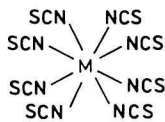
Table 3. Classification of thiocyanates

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thio-cyanates
├── monodentate thiocyanate ligand
│   ├── homogeneous coordination sphere of the c. a.
│   │   ├── N coordination of thiocyanate ligand — CT: I, II, III — Table 4
│   │   └── S coordination of thiocyanate ligand — CT: IV — Table 4
│   └── heterogeneous coordination sphere of the c. a.
│       ├── monodentate ligands
│       │   ├── N coordination of thiocyanate ligand — CT: V—X — Table 5
│       │   └── S coordination of thiocyanate ligand — CT: XI, XII, XIII, XIV — Table 5
│       ├── chelate ligands
│       │   ├── N coordination of thiocyanate ligand — CT: XV XVI—XXI — Table 6
│       │   └── S coordination of thiocyanate ligand — CT: XXII——XXVI — Table 6
│       └── monodentate and chelate ligands
│           └── N coordination of thiocyanate ligand — CT: XXVII, XXVIII, XXIX — Table 7
├── bidentate thiocyanate ligand
│   ├── one thiocyanate ligand coordinates 2 c. a. — CT: XXX, XXXI — Table 8
│   └── two thiocyanate ligands coordinate 2 c. a.
│       ├── dimer structure units — CT: XXXV — Table 9
│       └── polymer structure units — CT: XXXVI, XXXVII, XXXVIII — Table 9
├── tridentate thiocyanate ligand — CT: XXXII — Table 8
└── tetradentate thiocyanate ligand — CT: XXXIII, XXXIV — Table 8
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CT — coordination type

c. a. — central atom

Table 4

Survey of homogeneous thiocyanates

Coordination type (CT)	Compound	Ref.
I SCN—M—NCS (tetrahedral)	$K_2[Co(-NCS)_4] \cdot 4H_2O$ $K_2[Co(-NCS)_4] \cdot 3H_2O$ $(nitr)_2[Co(-NCS)_4]$	[223] [64] [48]
II NCS—M—NCS (octahedral)	$(AsPh_4)_3[In(-NCS)_6]$ $Ho[Cr(-NCS)_6]$ $K_3[Mo(-NCS)_6] \cdot H_2O \cdot CH_3COOH$ $(n\text{-}Bu_4N)_3[Er(-NCS)_6]$	[68] [127] [130] [154]
III SCN—M—NCS (8-coordinate)	$(Et_4N)_4[U(-NCS)_8]$	[55]
IV NCS—M—SCN (tetrahedral)	$K_2[Cd(-SCN)_4] \cdot 2H_2O$ $K_2[Pd(-SCN)_4]$ $(PPh_4)_2[Hg(-SCN)_4]$ $Rb[Bi(-SCN)_4]$	[221] [156] [191] [75]

Within the above groups the crystal structures are arranged into subgroups which form a certain "coordination type". For this classification we used the following criteria:

— mode of coordination of thiocyanate ligand to the central atom,
— number of thiocyanate ligands coordinated to one central atom,
— mutual positions of thiocyanate ligands in the coordination sphere of the central atom,
— denticity of other ligands present in the coordination sphere.

In the group of homogeneous thiocyanates (Table 4), four, six or eight thiocyanate ligands are attached to the central atom in its coordination sphere. When there are four thiocyanate ligands, these can be N- or S-bonded, which depends on the properties of the central atom. For a higher coordination number (6 or 8) coordination through nitrogen atom seems to be favoured. The crystal structure with six thiocyanate ligands coordinated by sulfur atom has not been solved up till now. Thus, e.g., in complex ions $[Rh(-SCN)_6]^{3-}$, $[Ir(-SCN)_6]^{3-}$, and $[Pt(-SCN)_6]^{2-}$ the coordination of six thiocyanate ligands by sulfur atom was

Table 5

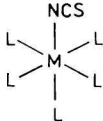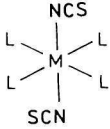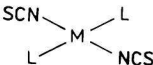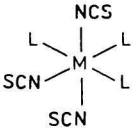Survey of heterogeneous thiocyanates with monodentate ligands
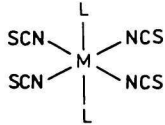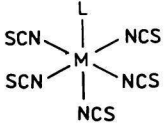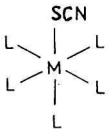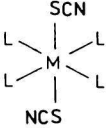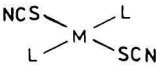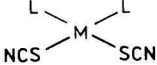
Coordination type (CT)	Compound	Ref.
V	$[Co(NH_3)_5(-NCS)]Cl_2$	[202]
VI	$[Mn(tu)(-NCS)_2]$ $[Ni(quin)_2(H_2O)_2(-NCS)_2] \cdot 2\,(quin)$ $[Fe(py)_4(-NCS)_2]$ $[Ni(py)_4(-NCS)_2]$ $[Ni(4\text{-pic})_4(-NCS)_2]$ $[Ni(NH_3)_4(-NCS)_2]$ $[Ni(tu)_2(-NCS)_2]$ $[Zn(dena)_2(H_2O)_2(-NCS)_2]$	[163] [67] [203] [3] [5] [182] [162] [25]
VII	$[Zn(an)_2(-NCS)_2]$ $[Cu(NH_3)_2(-NCS)(-NCS-)]$	[198] [114]
VIII	$NH_4[Ni(NH_3)_3(-NCS)_3]$	[182]
IX	$(NH_4)_2[Ni(NH_3)_2(-NCS)_4] \cdot H_2O$	[182]
X	$(AsPh_4)_2[NbO(-NCS)_5]$	[126]
XI	$[Co(NH_3)_5(-SCN)]Cl_2 \cdot H_2O$	[202]

Table 5 (Continued)

Coordination type (CT)	Compound	Ref.
XII (structure diagram)	$[Cu(NH_3)_4(-SCN)_2]$	[183]
XIII (structure diagram)	$[Pd(Ph_2Bu)_2(-SCN)_2]$ $[Pt(py)_2(-SCN)_2]$	[21] [38]
XIV (structure diagram)	$[Hg(PPh_3)_2(-SCN)_2]$	[150]

inferred from infrared and electronic spectral data [193, 194, 188]. There are, however, also such cases (*e.g.* $[Re(NCS)_6]^{2-}$ and $[Re(NCS)_6]^-$), in which the authors [20, 170, 169] have different opinions on the coordination mode of thiocyanate ligands.

Among the heterogeneous thiocyanate complexes with monodentate ligands the N-bonded monodentate thiocyanates prevail (Table 5). In heterogeneous thiocyanate complexes, the crystal structure of which is known, maximum two S-bonded thiocyanate ligands can be present, while for N-bonded ligands the maximum number is five.

Heterogeneous thiocyanates with chelate ligands (Table 6) show a great coordination ability of thiocyanate ligand. Thiocyanate ligands can occur in *cis* and *trans* positions in the coordination polyhedron and they can occupy equatorial and axial positions as well. It is remarkable that in the presence of chelate ligands (in distinction to monodentate ligands), in the coordination sphere utmost two thiocyanate ligands are bonded as monodentate ligands.

In the group of heterogeneous thiocyanates with monodentate and chelate ligands (Table 7) only crystal structures with N-coordinated thiocyanate ligand have been known up till now. In agreement with the above said, also in this type of compounds, utmost two monodentate thiocyanate ligands are present.

ii) *Compounds with bridging thiocyanate groups*

Crystal structures of thiocyanates with bridging thiocyanate ligands were divided into two groups:

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Table 6

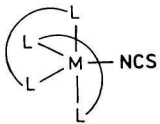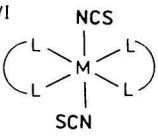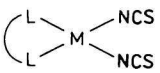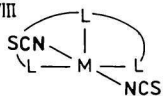Survey of heterogeneous thiocyanates with chelate ligands
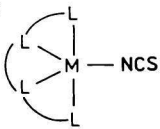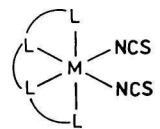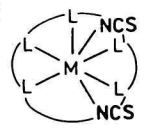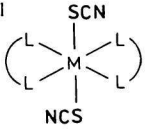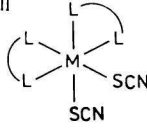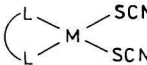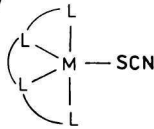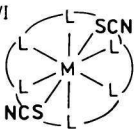
Coordination type (CT)	Compound	Ref.
XV — M with L, L, L, L and NCS	[Cu(tn)₂(—NCS)](ClO₄)	[39]
XVI — NCS/SCN trans, L L L L	[Ni(en)₂(—NCS)₂]	[28]
	[Zn(N₂H₄)₂(—NCS)₂]	[70]
	[Ni(N₂H₄)₂(—NCS)₂]	[71]
	[Ni(thiosem)₂(—NCS)₂]	[76]
	[Cu(aep)₂(—NCS)₂]	[134]
XVII — M with L L and NCS, NCS	[Cu(en)(—NCS)(—NCS—)]	[78]
XVIII — SCN, L, M, L, NCS	[Ni(N₃As)(—NCS)₂]	[60]
	[Cu(den)(—NCS)₂]	[40]
	[Cu(dpt)(—NCS)₂]	[11]
XIX — M with L L L L and NCS	[Cu(triam)(—NCS)](NCS)	[109]
	[Zn(triam)(—NCS)](NCS)	[8]
	[Cu(bispictn)(—NCS)](NCS)	[41]
XX — M with L L L L and NCS, NCS	[Ni(triam)(—NCS)₂]	[100]
	[Co(triam)(—NCS)₂]·(NCS)·H₂O	[136]
XXI — M with L L L L L and NCS, NCS	[Fe(pop)(—NCS)₂](ClO₄)	[72]
	[Mn(pep)(—NCS)₂]	[63]
	[Mn(top)(—NCS)₂]	[64]
XXII — SCN/NCS trans, L L L L	[Cu(en)₂(—SCN)₂]	[29]
	[Cu(tn)₂(—SCN)₂]	[6]

Table 6 (Continued)

Coordination type (CT)	Compound	Ref.
XXIII	[Hg(phen)$_2$(—SCN)$_2$]	[18]
XXIV	[Hg(en)(—SCN)$_2$]	[66]
XXV	[Cu(trien)(—SCN)](NCS)	[153]
XXVI	[Pb(tetraxa)(—SCN)$_2$]	[159]
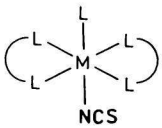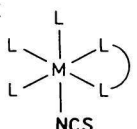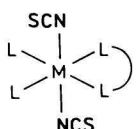
— two central atoms are coordinated by one bridging thiocyanate ligand (Table 8),
— two central atoms are coordinated by two bridging thiocyanate groups (Table 9).

In establishing the "coordination types" within the first group, the bridging modes of thiocyanate ligands were examined with regard to the number of bonds to sulfur and nitrogen atom. Following modes were found:

— two central atoms coordinated by nitrogen atom,
— one central atom coordinated by nitrogen atom and the second by sulfur atom,
— one central atom coordinated by nitrogen atom and two central atoms coordinated by sulfur atom,
— two central atoms coordinated by nitrogen atom and two central atoms coordinated by sulfur atom,
— one central atom coordinated by nitrogen atom and three central atoms coordinated by sulfur atom.

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Table 7

Survey of heterogeneous thiocyanates with monodentate and chelate ligands

Coordination type (CT)	Compound	Ref.
XXVII	[Ni(en)$_2$Cl(—NCS)]	[206]
	[Ni(en)$_2$Br(—NCS)]	[6]
	[Ni(en)$_2$(NO$_2$)(—NCS)]	[207]
	[Co(en)$_2$(SO$_3$)(—NCS)]·2H$_2$O	[10]
	[Co(en)$_2$(NO$_2$)(—NCS)](NCS)	[26]
XXVIII	[Mo(bipy)(π-C$_3$H$_5$)(CO)$_2$(—NCS)]	[101]
	[Mo(phen)(π-C$_4$H$_7$)(CO)$_2$(—NCS)]	[102]
XXIX	[Nb(dion)(OC$_2$H$_5$)$_2$(—NCS)$_2$]	[59]

In the second group of complexes the bridging thiocyanates have only two points of attachment: one central atom is coordinated by nitrogen, the other one by sulfur atom. The "coordination types" in this group were classified on the basis of structural formations in their crystal structure (dimers or chain structure) and with regard to the mutual orientation of thiocyanate ligands to each other in the coordination sphere.

From the above said it follows that the thiocyanate ligand can coordinate one or two central atoms *via* nitrogen atom, and one, two or three central atoms *via* sulfur atom. By combination of these five alternatives eleven possible coordination modes for thiocyanate ligand are obtained. Compounds in which thiocyanate group is present as anion can be considered the twelfth possible coordination mode of this group.

	NCS— 15	(NCS =)	(NCS ≡)
—NCS 45	—NCS— 30	—NCS = 6	—NCS ≡ 1
= NCS 2	(= NCS—)	= NCS = 1	(= NCS ≡)

Table 8
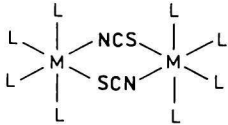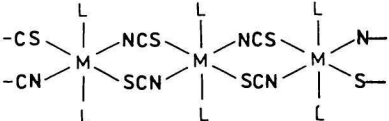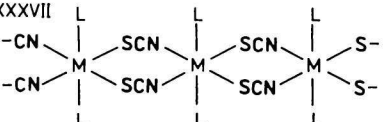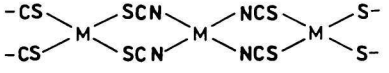
Thiocyanate complexes with ligands in various bridging modes

Coordination type (CT)	Compound	Ref.
XXX $M—N—M$ $\overset{\underset{\text{C}}{\text{C}}}{\text{S}}$	$[Cu(en)_2(—NCS—)](ClO_4)$	[42]
	$[Cu(aebg)(—NCS—)j(NCS)$	[7]
XXXI $M—NCS^{—M}$	$[Cu(en)_2(—NCS—)_2Hg(—SCN)_2]$	[196]
	$[Hg(AsPh_3)(—NCS—)_2]$	[106]
	$[Co(—NCS—)_4Hg]$	[110]
	$[HgCl(—NCS—)]$	[222]
	$[Cu(—NCS—)_4Hg]$	[133]
	$[Cd(den)(—NCS)(—NCS—)]$	[44]
	$[Co(py)_2(—NCS—)_4Hg]$	[19]
	$[Cu(sal)(—NCS—)]$	[61]
	$[Hg(tricyclo)(—SCN)(—NCS—)]$	[2]
	$(PPh_4)[Hg(—SCN)_2(—NCS—)]$	[190]
	$[Cu_2(NH_3)_3(—NCS—)_3]$	[77]
	$[Co(—NCS—)_6Hg_2]\cdot(C_6H_6)$	[105]
XXXII $M—NCS\overset{—M}{\underset{—M}{}}$	$[Ag(—NCS—)]$	[142]
	$NH_4[Ag(—NCS—)](NCS)$	[143]
	$[Cu(—NCS—)_4Hg]$	[133]
	$[Ag(PPr_3)(—NCS—)]$	[173]
	$[Cu(NH_3)_2(—NCS)(—NCS—)]$	[114]
	$[Cu(en)(—NCS)(—NCS—)]$	[78]
	$[Cu_2(NH_3)_3(—NCS—)_3]$	[77]
	$[Co(—NCS—)_6Hg_2]\cdot(C_6H_6)$	[105]
XXXIII $\overset{M}{\underset{M}{}}NCS\overset{M}{\underset{M}{}}$	$[Pb(—NCS—)_2]$	[161]
XXXIV $M—NCS\overset{M}{\underset{M}{\overset{M}{}}}$	$[Cu(—NCS—)]$	[115]

From among the assumed coordination modes four, designated by parentheses in the above table, were not yet observed. The numbers in the table designate the percentage of the occurrence of the coordination mode in crystals under investigation.

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Table 9

Dimer and chain thiocyanate complexes with bridging thiocyanate ligand

Coordination type (CT)	Compound	Ref.
XXXV	$[Ni_2(en)_4(—NCS—)_2](ClO_4)_2$	[208]
	$[Ni_2(en)_4(—NCS—)_2]I_2$	[209]
	$[Pt_2(PPr_3)_2Cl_2(—NCS—)_2]$	[103]
	$[Ni_2(4\text{-}pic)_6(—NCS)_2(—NCS—)_2]$	[144]
	$[Cu_2(PPh_2Me)_4(—NCS—)_2]$	[83]
	$[Hg_2Br_2(—NCS—)_2]$	[222]
	$[Cu_2(den)_2(ClO_4)_2(—NCS—)_2]$	[43]
	$[Ni_2(NH_3)_6(—NCS)_2(—NCS—)_2]$	[184]
XXXVI	$[Cu(4\text{-}pic)_2(—NCS—)_2]$	[192]
	$[Co(py)_2(—NCS—)_2]$	[181]
	$[Cu(py)_2(—NCS—)_2]$	[181]
	$[Ni(etu)_2(—NCS—)_2]$	[164]
	$[Ni(tam)_2(—NCS—)_2]$	[46]
	$[Co(H_2O)_2(—NCS—)_2]\cdot H_2O$	[45]
	$[Cd(etu)_2(—NCS—)_2]$	[47]
	$[Ni(NH_3)_2(—NCS—)_2]$	[185]
	$[Cd(dena)(—NCS—)_2]$	[24]
XXXVII	$[Sn(CH_3)_2(—NCS—)_2]$	[52]
XXXVIII	$[Zn(—NCS—)_2]$	[9]

b) *Various coordination modes of thiocyanate groups in one compound*

Reviews on coordination modes of thiocyanate ligands in Chapter II/a are not exhaustive. Some thiocyanate ligands occurring in one compound can be coordinated in one of the discussed modes or the coordination modes can be combined. In compounds with known crystal structure the following coordination modes were observed:

Unidentate —NCS ligand and anion (NCS)⁻ (Fig. 1).
Unidentate —SCN ligand and anion (NCS)⁻ (Fig. 2).
Bridging >NCS ligand and anion (NCS)⁻ (Fig. 3).
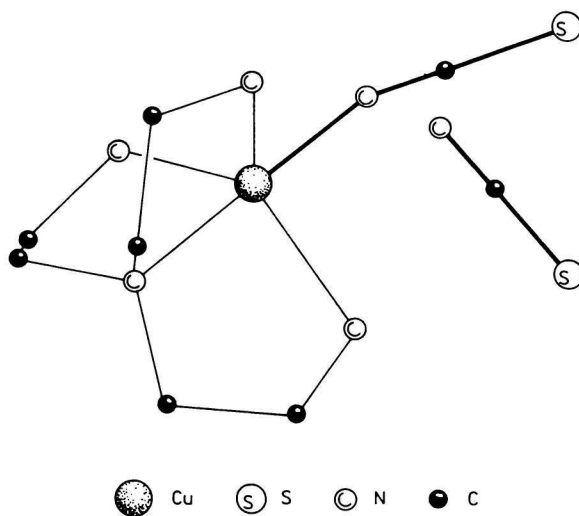
Fig. 1. Schematic representation of coordination of thiocyanate ligands ·
in [Cu(triam)(—NCS)](NCS) [109].
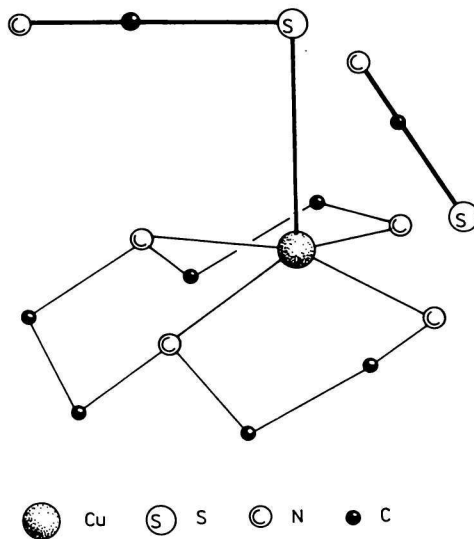
Fig. 2. Schematic representation of coordination of thiocyanate ligands
in [Cu(trien)(—SCN)](NCS) [153].
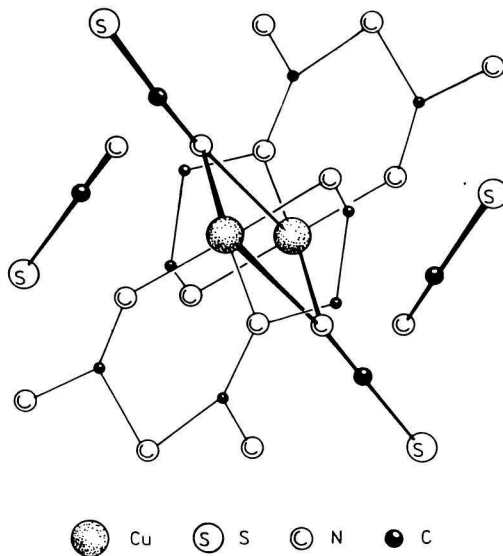
Fig. 3. Schematic representation of coordination of thiocyanate ligands
in [Cu(aebg)(—NCS—)](NCS) [7].
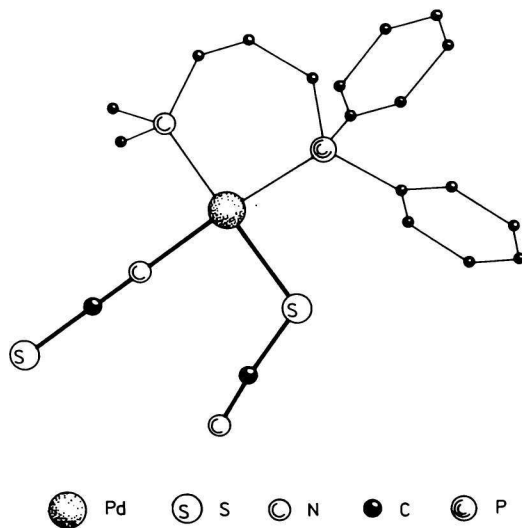
Fig. 4. Schematic representation of coordination of thiocyanate ligands
in [Pd(PPHN)(—NCS)(—SCN)] [22].

Unidentate —NCS and —SCN ligands (Fig. 4).
Unidentate —NCS and bridging —NCS— ligands (Fig. 5).
Unidentate —NCS and bridging —NCS < ligands (Fig. 6).
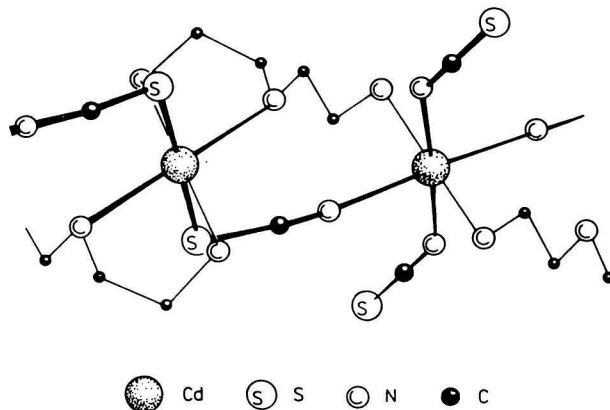
Fig. 5. Schematic representation of coordination of thiocyanate ligands
in [Cd(den)(—NCS)(—NCS—)] [44].
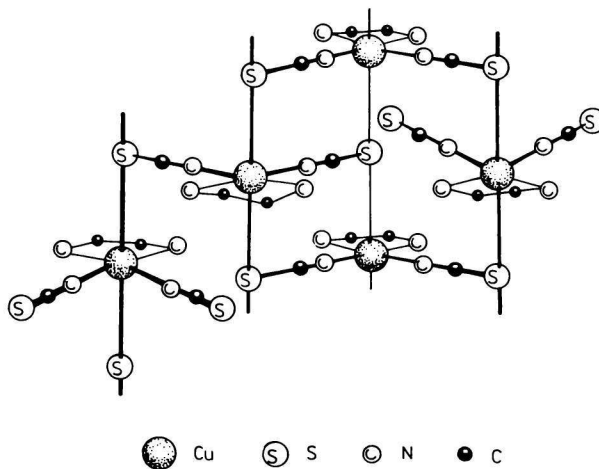
Fig. 6. Schematic representation of coordination of thiocyanate ligands
in [Cu(en)(—NCS)(—NCS—)] [78].

Unidentate —NCS and bridging $M{<}^{NCS}_{SCN}{>}M$ ligands (Fig. 7).

Unidentate —SCN and bridging —NCS— ligands (Fig. 8).
Bridging —NCS— and —NCS   ligands (Fig. 9).

Bridging —NCS—, —NCS <, and $M{<}^{NCS}_{SCN}{>}M$ ligands (Fig. 10).
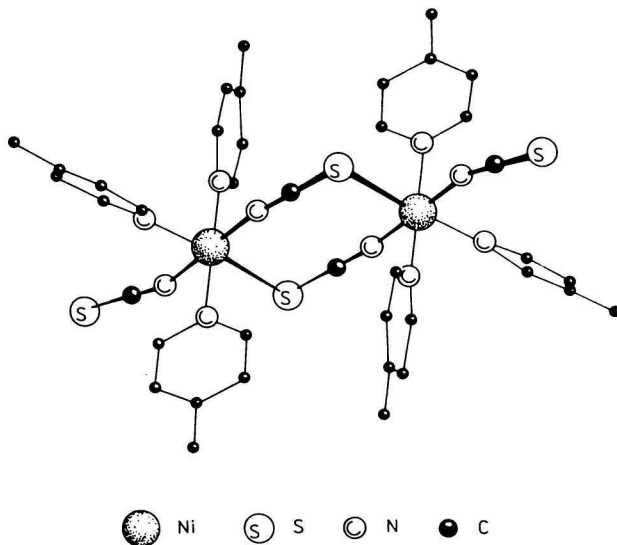
Fig. 7. Schematic representation of coordination of thiocyanate ligands in [Ni₂(4-pic)₆(—NCS)₂(—NCS—)₂] [144].
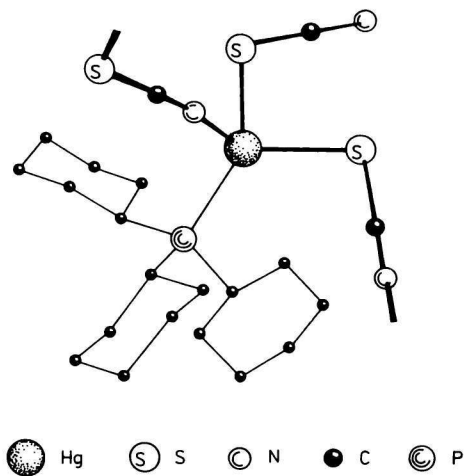
Fig. 8. Schematic representation of coordination of thiocyanate ligands in [Hg(tricyclo)(—SCN)(—NCS—)] [2].
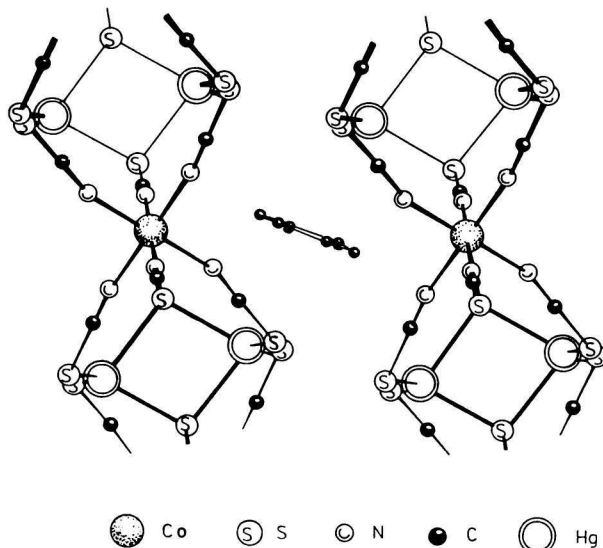
Fig. 9. Schematic representation of coordination of thiocyanate ligands
in [Co(—NCS—)₆Hg₂]·(C₆H₆) [105].
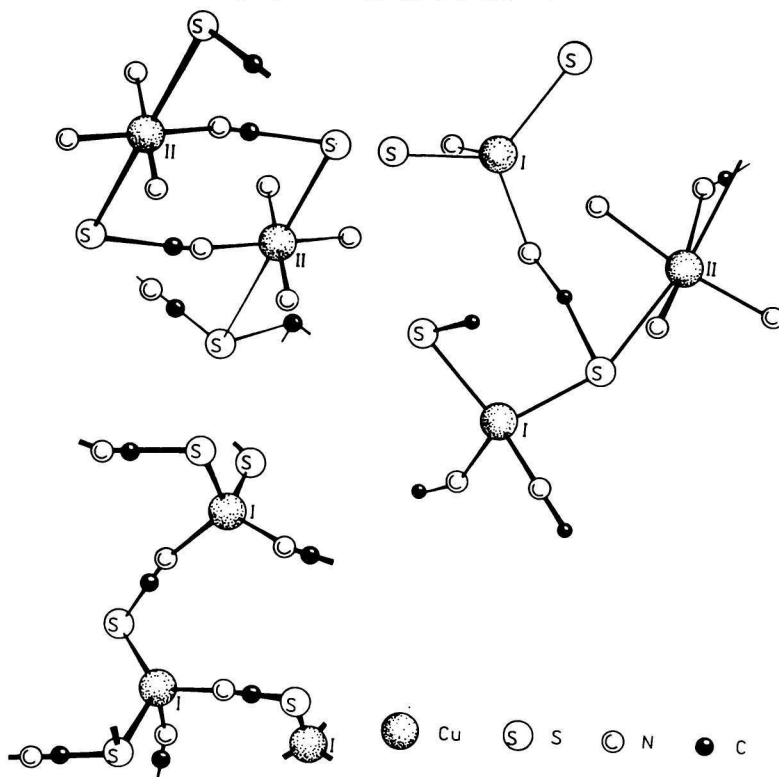
Fig. 10. Schematic representation of coordination of thiocyanate ligands
in [Cu₂(NH₃)₃(—NCS—)₃] [77].

III. Mutual influence of ligands (MIL) in solid thiocyanates

The bonding properties of thiocyanate ligand can be evaluated from crystallochemical and chemical standpoint. In terms of Pearson's classification of "soft" and "hard" acids and bases, with regard to different polarizability of atoms, the thiocyanate ligand coordinated by sulfur atom is a "soft", and that coordinated by nitrogen atom a "hard" base [41, 141, 176, 178]. Owing to its relatively low ionization energy, high polarizability, and available dative π bonds, sulfur as donor atom has, in comparison with nitrogen atom, greater potential possibilities to affect the oxidation-reduction properties of the central atom [218]. For the bonding properties of this ligand the whole system of three atoms is responsible (in the cases of other ligands containing S- and N-donor atoms analogous properties were not observed [169]).

The coordination mode of thiocyanate ligand in compounds depends on properties of the central atom and on properties of other ligands in the coordination sphere.

In a simplified manner the effect of the nature of central atom on the coordination mode of the thiocyanate ligand can be shown on the homogeneous thiocyanates. The unidentate thiocyanate ligand is coordinated with Rh(III), Ir(III), Pd(II), Pt(IV), Pt(II), Ag(I), Au(III), and Hg(II) through sulfur atom, and with the remaining transition metals through nitrogen atom [170].

Transition metals with N- or S-bonded thiocyanate ligand are divided into classes a and b [1]. Transition metals with positive values of standard electrode potentials form the class b [139]. With heterogeneous ligands the situation is more complicated and the original subdivision into classes a and b is modified by the nature of the other ligands present in the coordination sphere.

The following forms are known:

a) Compounds, both in class a and b, in which thiocyanate ligands are attached to the central atom in both possible modes, $e.g.$

$[Pd(phen)(-SCN)_2]$ [23, 35, 189]
$[Pd(5-NO_2phen)(-NCS)_2]$ [23, 189]
$[Pt(SbPh_3)_2(-SCN)_2]$ [35]
$[Pt(AsPh_3)_2(-NCS)_2]$ [35]
cis-$[Mn(CO)_4(-NCS)_2]$ [215]
cis-$[Mn(CO)_4(PPh_3)(-SCN)]$ [69]
$[Cu(bipy)_2(-NCS)_2]$ [211]
$[Cu(en)_2(-SCN)_2]$ [54, 29]
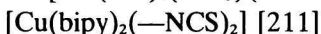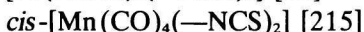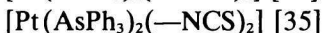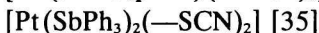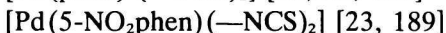
b) Compounds, both in class a and b, of identical composition which occur in two forms distinguished by the coordination mode of their thiocyanate ligand to the central atom (linkage isomers) [91], such as

[Co(NH₃)₅(N̄CS̄)]Cl₂ [30, 202]
[Co(bipy)₂(N̄CS̄)]⁺ [13, 151]
[Pd(bipy)(N̄CS̄)₂] [35]
[Cu(tripyam)(N̄CS̄)₂] [135]
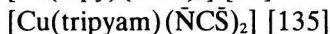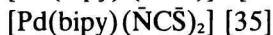
c) Compounds in which the thiocyanate ligand is bonded in both possible ways in one coordination sphere, *e.g.*

[Pd(PPh₂Et)(—NCS)(—SCN)] [157]
[Cu(tripyam)(—NCS)(—SCN)] [135]

We regard the effect of properties of ligands L on the coordination modes of thiocyanate ligand as a special manifestation of MIL in the thiocyanate complexes. Under the term MIL we understand the interactions of ligands in complexes with various symmetry which take place between ligands through the central atom and which affect various properties of individual ligands and of the whole complex, as it is observed *e.g.* in substitution reactions [58], in internal oxidation-reduction reactions [85], in changes of geometry of the complex [84], in reactivity of ligands [84], *etc.* but also in other static effects [165].

Various approaches to the explanation of the mode of coordination of the thiocyanate ligand were attempted [170, 16, 69, 111, 177, 36, 14, 57, 27, 34, 17, 35, 189, 217]. On the basis of certain analogies in effects of the ligands and solvents on the coordination of the unidentate thiocyanate ligand *Norbury* [170] suggested the following generalization in the field of π-bonding hypothesis

Transition metal	σ-Donor ligand	Solvent		π-Acceptor ligand
		high ε	low ε	
Class *a*	—NCS	—NCS	—SCN	—SCN
Class *b*	—SCN	—SCN	—NCS	—NCS

It is possible to show that the statement in the paper [170] cannot be applied generally. The cooperative effects of ligands in thiocyanates with reference to compounds [Pd(NH₃)₂(—SCN)₂] and [Pd(PEt₃)₂(—NCS)₂] were first pointed out by *Turco* and *Pecile* [217]. They showed that by substitution of a σ-donor ligand by another with σ- and π-bonding properties a change in the mode of coordination of the thiocyanate ligand takes place. A relatively great number of palladium(II) complexes were prepared, both with S-coordinated thiocyanate ligand in combination with N-donor atom of the ligand L and with N-coordinated thiocyanate ligand in combination with P-donor atom of the ligand L. Experimental data obtained for these complexes confirmed the above findings.
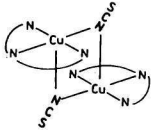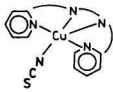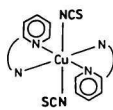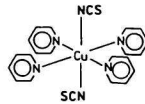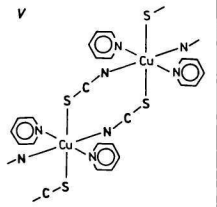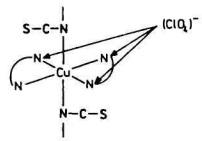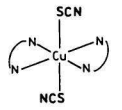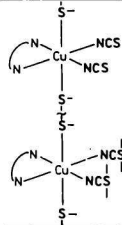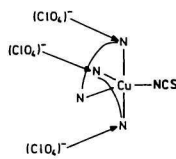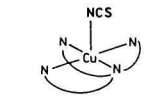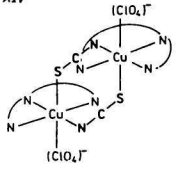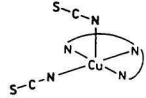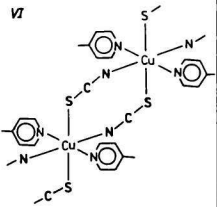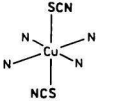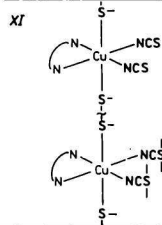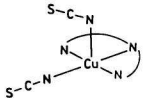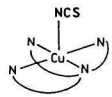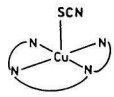
We want to stress that any arbitrary substitution of σ-bonding ligand by another with σ- or π-bonding properties will not necessarily bring about a change in the coordination mode of the thiocyanate ligand. Thus, *e.g.*, in compounds $[PdL_2(-SCN)_2]$ where L = NH$_3$ [217, 216], py [23, 189], 4-pic [35], 4-NO$_2$py [23], 4-CNpy [23], 4-Clpy [56], 4-NH$_2$py [56] by substituting the σ-bonding ligand by ligands with various σ- or π-bonding properties and with N-donor atom, no change in the coordination mode will take place. For compounds $[Pt(NH_3)_2(-SCN)_2]$ [104, 217] and *cis*- and *trans*-$[Pt(py)_2(-SCN)_2]$ [104, 189] analogous conclusions as for compounds of Pd(II) can be drawn. Here the mode of coordination of the thiocyanate ligand did not change even when the positions of ligands in the coordination sphere were different.

Either in compounds $[Ni(NH_3)_4(-NCS)_2]$ [220] and $[Ni(py)_4 (-NCS)_2]$ [195, 166, 167, 54, 3, 204] an analogous interchange of ligands did not cause changes in coordination mode of the thiocyanate ligand. The thiocyanate ligand is coordinated to the "hard" central atom, in distinction to Pd(II) and Pt(II), through nitrogen atom.

The other class *a* transition metal, cobalt, shows different bonding properties of the thiocyanate ligand in complexes of Co(II) and Co(III). In complexes of Co(II), *e.g.* in $[Co(py)_4(-NCS)_2]$ [73, 49, 128, 129], with pseudooctahedral symmetry, and in complexes $[Co(py)_2(-NCS)_2]$ [128, 129, 140] with tetrahedral symmetry, the thiocyanate ligand is coordinated through nitrogen atom. While in complexes of Co(II) the N coordination prevails, in Co(III) complexes both N and S coordination are equally favoured. This is proved by the existence of linkage isomers $[Co(NH_5)_5(\bar{N}C\bar{S})]Cl_2$ [174, 202], $K_3[Co(CN)_5(\bar{N}C\bar{S})]$ [205, 31], while Co(II) has not been known to form such linkage isomers.

Comparison of complexes of the next transition metal from the class *a*, copper, $[Cu(NH_3)_4(-SCN)_2]$ [184, 183, 186] with $[Cu(py)_4(-NCS)_2]$ [54] shows that, in distinction to the above cases, changes in bonding behaviour of N-donor ligands will cause changes in coordination mode of the thiocyanate ligands. The modes of coordination of unidentate thiocyanate ligands in the coordination sphere of Cu(II) are opposite to those assumed by *Norbury* in his generalization [170] for class *a* transition metals. This seeming inconsistency can be explained by the fact that the central atom Cu(II) occupies a boundary position in the above-mentioned classification [219]. Consequently it is not surprising that even small changes in bonding properties of the ligand L (for L = NH$_3$ or py) will cause the change in the coordination mode of the monodentate thiocyanate ligand.

Owing to the ability of the central atom Cu(II) to reflect slight changes of properties of ligands in its plastic coordination polyhedron [93, 94] and owing to the ability of the thiocyanate ligands to respond to such changes by changes of their bonding properties, the thiocyanate copper(II) compounds are excellent objects for study of the MIL.

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[Cu(aebg)(-NCS-)](NCS) [7]			
I			

Table 10

Schematic representation of the coordination sphere of Cu(II) in some thiocyanates

[Cu(en)₂(-NCS-)](ClO₄) [42]	[Cu(tn)₂(-NCS)](ClO₄) [39]	[Cu₂(den)₂(ClO₄)₂(-NCS-)₂] [43]
IX	*XII*	*XIV*

[Cu(bispictn)(-NCS-)](NCS) [11]	[Cu(py)₄(-NCS)₂] [54]	[Cu(NH₃)₄(-SCN)₂] [183]	[Cu(en)₂(-SCN)₂] [29]	[Cu(tn)₂(-SCN)₂] [6]	[Cu(den)(-NCS)₂] [40]
II	*IV*	*VII*	*X*	*XIII*	*XV*

[Cu(aep)₂(-NCS)₂] [134]	[Cu(py)₂(-NCS-)₂] [181]	[Cu(NH₃)₂(-NCS)(-NCS-)] [114]	[Cu(en)(-NCS)(-NCS-)] [78]		[Cu(dpt)(-NCS)₂] [41]
III	*V*	*VIII*	*XI*		*XVI*

[Cu(4-pic)₂(-NCS-)₂] [192]	[Cu(triam)(-NCS)](NCS) [109]	[Cu(trien)(-SCN)](NCS) [153]
VI	*XVII*	*XVIII*

a) *Mutual influence of ligands in thiocyanate compounds*

At the beginning spontaneous oxidation-reduction processes in the inner sphere of Cu(II) complexes were found to take place as a consequence of MIL [86—90]. Later it has been found that also stereochemical consequences in Cu(II) complexes are due to the MIL [84, 93] and that the MIL through the central atom has a dominant role [148].

In this part of our paper we wish to show that in solid thiocyanate copper(II) compounds the MIL can affect:
— the mode of the coordination of thiocyanate ligand,
— the bonding parameters of the thiocyanate ligand,
— the chemical transformations of the thiocyanate ligand.

i) *Effects of the MIL on the coordination mode of thiocyanate ligand*

Table 10 shows schematic representation of coordination modes of ligands in individual coordination polyhedra of Cu(II) thiocyanate complexes with known structure. Data for $[Cu(py)_4(-NCS)_2]$ were obtained by indirect physicochemical methods. (The individual complexes are designated by Roman numerals and these are used throughout this chapter when referring to these complexes.)

The thiocyanate ligand in the heterogeneous coordination sphere of Cu(II) (tetragonal-pyramidal and tetragonal-bipyramidal symmetry of the coordination polyhedron) can occur as monodentate or bridging ligand occupying the equatorial or axial positions in the coordination polyhedron. In the equatorial plane the monodentate thiocyanate ligand is coordinated through nitrogen only, in the axial direction both N or S bonding may occur. Hence it follows that the change of S or N coordination of a monodentate thiocyanate ligand in thiocyanate copper(II) complexes, understood as a consequence of the MIL, can be observed only in axial positions of the coordination polyhedron. We assume a relationship between the changes in the coordination mode of thiocyanate ligand in the above cases and the concept of equatorial-axial influence (as a special concrete manifestation of the MIL) [225].

For explanation of S coordination of the monodentate thiocyanate ligand in the compounds *VII, X, XIII* and of N coordination in compounds *II—IV*, the π-bonding hypothesis seems to be acceptable. The π-acceptor capacity of ligands $L = NH_3$, en, tn in compounds with S-coordinated thiocyanate ligand differs considerably from that of ligands $L =$ py, aep, bispictn in compounds with N-coordinated thiocyanate ligand. However, some findings indicate that also in Cu(II) complexes the coordination mode of the thiocyanate group can be affected, apart from the type of bonding interactions of the central atom with ligands in the equatorial plane, also by other factors, from among which direct interactions of

ligands influenced by their geometry and conformation properties should not be disregarded [226].

In compounds with bridging coordination of the thiocyanate ligand (*e.g. I, IX, V, VI, VIII, XIV, XI*) the thiocyanate ligand is coordinated by sulfur atom only in axial positions of the coordination polyhedron of Cu(II). Comparison of compounds *VIII, IX* with *V* and *VI* suggests that the differing π-acceptor capacity of the other ligands L affects also the bridging coordination of the thiocyanate ligand. Compounds *VIII* and *XI* (L = NH$_3$ or en) have tridentate sulfur atom in their thiocyanate bridging group; in compounds *V* and *VI* (L = py or 4-pic) the sulfur atom in the bridging thiocyanate ligand is bidentate.

In the infrared spectra of the compound *V* (L = py) in which all the thiocyanate ligands have an equivalent bidentate bridging function a simple band v(CN) was observed. The compound *VIII* (L = NH$_3$) in which there is one terminal and one tridentate bridging thiocyanate group, gives a clearly split band v(CN) (Table 11). Similar differences in splitting of bands v(CN) were observed for compounds [CuL$_2$(NCS)$_2$] where L = picolines or 2,4-lutidine, on the one hand, and the remaining lutidines on the other hand [131]. For compounds in which L are the remaining lutidines, the extent and nature of their splitting allow for the assump-

Table 11

Wavenumbers of vibrations of the thiocyanate ligand in the compounds [CuL$_2$(NCS)$_2$] in solid state (cm^{-1}) [131]

Compound with L	v(CN)	v(CS)		δ(NCS)	
NH$_3$	2096 s, 2116 s	796 m,	807 m		
py	2072 s	824 m		468 w,	475 w
2-pic	2100 s, 2117 sh	837 w		471 m^a	
3-pic	2077 s	816 m^a,	823 sh^a	470 m,	476 m
4-pic	2080 s, 2100 sh	794 w,	805 sh^a 810 sh^a	477 m	
2,3-lut	2072 s, 2122 s	753 w,	807 m	465 w^a,	473 w^a 478 sh^a
2,4-lut	2078 s, 2094 sh	815 sh^a,	818 s 825 sh^a	473 m	
2,5-lut	2070 s, 2100 s	813 sh^a,	824 s	471 m,	476 sh
2,6-lut	2054 s, 2080 s 2094 sh	847 s		458 m,	472 m 477 sh
3,4-lut	2092 s, 2136 s	825 m^a,	832 m^a	468 sh,	474 w
3,5-lut	2092 s, 2110 s	800 w,	821 w	458 sh,	464 w

s — strong, m — medium, w — weak, sh — shoulder.
a) cannot be distinguished from bands assigned to the ligand L.

tion that two kinds of thiocyanate ligands are present which differ in their mode of coordination, similarly as in compound *VIII* [51, 131]. This phenomenon can be accounted for by combined action of electronic effects of the respective ligands, together with π-acceptor capacity. It is known that lutidines are weaker π acceptors than picolines [37] and the presence of methyl groups in position 3 and 5 emphasizes this ability.

Ligands ammonia, ethylenediamine, lutidines, in distinction to pyridine, picolines, and 2,4-lutidine, diminish considerably the positive effective charge on the central atom Cu(II) by which they weaken its "hard" character. In general, for Cu(II) compounds such a change leads to an increased inclination towards S coordination of the thiocyanate ligand [41]. In the bridging thiocyanate ligands a decrease of π-acceptor properties of the ligand L will lead to an increase of number of coordination bonds on sulfur atom. The existence of relationship between the number of coordination bonds on sulfur atom in the bridging thiocyanate ligand and the positive effective charge on the central atom can be demonstrated also by analysis of bonding properties of the thiocyanate ligand in [Cu(—NCS—)] [115, 108, 211]. In this compound the tetradentate sulfur atom corroborates this assumption.

Complexes *IX, X, XII*, and *XIII* can be used to show (Table 10) how the mode of coordination of the thiocyanate ligand can be affected by counterion effects. Substitution of one thiocyanate ligand by a perchlorate anion in complexes *X* and *XIII* gives rise to formation of complexes *IX* and *XII* in which the perchlorate ion is beyond the primary coordination sphere. By relatively weak interactions (interatomic distance ≈ 0.30 nm) with the nitrogen donor atoms of the ligand L it affects the bonding relations in the primary coordination sphere and thus also the mode of coordination of the remaining nonsubstituted thiocyanate ligand. The original S coordination of the thiocyanate ligands in complexes *X* and *XIII* is changed into an N coordination which, in the crystal structure of the compound *IX*, adopts a rather unusual bridging coordination solely through nitrogen atom. By substitution of one thiocyanate ligand in the compound *XV* by one perchlorate anion the compound *XIV* arises. In distinction to the previous cases, the perchlorate anion affects the mode of coordination of the remaining nonsubstituted thiocyanate ligand by its direct weak axial interactions with the central atom Cu(II). The original monodentate N coordination of this ligand in the compound *XV* is changed into bidentate bridging coordination, which, in the crystal structure of the compound *XIV*, is accompanied by formation of dimer structure units.

The mode of coordination of the thiocyanate ligand can be affected by other factors as well. Thus, *e.g.*, in compounds *XV, XVI, XVII* in which the tetradentate and tridentate chelate ligands lack any apparent π-acceptor capacity, the thiocyanate ligand is, against any expectation, coordinated by nitrogen atom. Similarly in

compounds *XVII* and *XVIII* (L = trien is linear isomeric form of L = triam) the mode of coordination of the thiocyanate ligand varies. In these compounds most probably the steric effects prevail [16] and for this reason instead of the expected coordination by sulfur atom the spatially less exigent bonding through nitrogen atom takes place.

ii) *The manifestation of the MIL on the bonding parameters of the thiocyanate ligand*

Infrared [131] and electronic [116] spectra of thiocyanate copper(II) compounds $[CuL_2(NCS)_2]$ (where L = pyridine and all isomeric forms of picolines and lutidines) furnished information on "static" consequences of the MIL in complexes of Cu(II).

.On the basis of electronic spectral data in the area of ligand field bands (Table 12) to the compounds $[CuL_2(NCS)_2]$ (except when L = 2,3-lutidine) pseudooctahedral configuration of ligands around the central atom was assigned,

Table 12

Electronic spectral data on thiocyanate complexes $[CuL_2(NCS)_2]$ in solid state (cm^{-1}) [116]

Compound with L	$\bar{v}_{max}$	
	$(d—d)$ band	CT band
py	15 600	24 400
2-pic	$\approx 13\ 000$ sh, 16 600	23 700
3-pic	17 100	24 500
4-pic	$\approx 13\ 400$ sh, 16 200	24 700
2,3-lut	14 100	$\approx 22\ 200$
2,4-lut	17 150	24 150
2,5-lut	16 600	24 000
2,6-lut	$\approx 14\ 500$ sh, 16 700, $\approx 19\ 700$ sh	23 600
3,4-lut	$\approx 13\ 100$ sh, 16 300	24 700
3,5-lut	$\approx 13\ 200$ sh, 16 300	24 800

sh — shoulder.

analogous to that in $[Cu(py)_2(—NCS—)_2]$ [54, 152, 181, 211, 116]. To the compound $[Cu(2,3-lut)_2(NCS)_2]$, in agreement with [97, 179, 212, 175] and by analogy to $[Cu(2-pic)_2Cl_2]$ [65] and $[Cu(2-pic)_2Br_2]$ [200], tetragonal pyramidal configuration was assigned.

Data on stretching frequencies of the central atom $v(Cu—N(L))$ and $v(Cu—NCS)$ for compounds $[CuL_2(NCS)_2]$ (Table 13) show that changed chemi-

Table 13

Wavenumbers of stretching vibrations v(Cu—N) in compounds [CuL$_2$(NCS)$_2$] in solid state (cm^{-1}) [131]

Compound with L	v(Cu—NCS)	v(Cu—N(L))	
py	321 s	257 s	
2-pic	331 s	253 sh, 242 s	
3-pic	312 s	270 s,	238 w^a
4-pic	321 s, 363 w^a	261 s,	250 sh
2,3-lut	324 s	244 s	
2,4-lut	336 s	266 mw, 248 m	
2,5-lut	331 s, 316 sh	254 m,	237 w
2,6-lut	345 s, 322 sh	248 s	
3,4-lut	323 s	256 s	
3,5-lut	307 s	251 s	

s — strong, m — medium, w — weak, sh — shoulder.
a) assignment of the band is not clear.

cal properties of pyridine ligands L affect not only v(Cu—N(L)) but also v(Cu—NCS). Then an interdependence of strength of ligand bonds in equatorial plane of the coordination polyhedron was observed.

Thus, *e.g.*, in comparison with [Cu(py)$_2$(—NCS—)$_2$], for compounds with methyl substituent in position 2 or 6 of the pyridine ring, the vibration frequencies v(Cu—N(L)) are shifted towards lower energy ranges, and the vibration frequencies v(Cu—NCS) are shifted in the opposite direction. The presence of methyl substituents in position 2, probably in consequence of steric effects, causes a decrease of strength of the bond Cu—N(L), which on the other hand makes the bonds Cu—NCS stronger. For remaining compounds interactions of equatorial bonds of the thiocyanate ligand were also observed, anyway there are many factors involved. For [Cu(3-pic)$_2$(NCS)$_2$], *e.g.*, shifts of stretching vibrations of the central atom opposite to those in the first group were observed. In the case of [Cu(3,5-lut)$_2$(NCS)$_2$] the frequency ranges of both stretching vibrations are shifted in the direction to lower energy ranges and for [Cu(4-pic)$_2$(—NCS—)$_2$], [Cu(3,4-lut)$_2$(NCS)$_2$] the frequencies of both vibrations change very little in comparison with [Cu(py)$_2$(—NCS—)$_2$].

Information on changed bonding properties of the thiocyanate ligands induced by changes of ligands L can be obtained for the group of compounds under investigation by interpretation of ultraviolet electronic spectral data (Table 12). In this range the compounds [CuL$_2$(NCS)$_2$] have broad, in the range of higher frequencies asymmetric bands of charge transfer (CT bands). In agreement with [132, 146, 147, 15], these bands were assigned to electron transitions from molecular σ orbitals of the thiocyanate ligand into d orbitals of the central atom.

On comparison of peak frequencies of the charge transfer band for the investigated group of compounds with those for $[Cu(py)_2(—NCS—)_2]$ two groups of compounds can be distinguished. The first consists of compounds with methyl substituents in position 2 or 6 of the pyridine ring and in it the frequencies of peaks are shifted towards the lower energy ranges. In this group the electron transfer from the thiocyanate ligand to the central atom is energetically more favourable than in $[Cu(py)_2(—NCS—)_2]$. The chemical consequence of such transfer will be an easier reduction of the central atom [172]. For these compounds an easy reduction of Cu(II) in the course of their preparation and a short stability on their storage was observed [117]. X-ray spectral data confirmed lowered oxidation-reduction stability of these compounds [118].

For the remaining compounds the frequency peak of the charge transfer band is shifted, in comparison to that of $[Cu(py)_2(—NCS—)_2]$, towards higher energy range and consequently this electron transfer is regarded as less favourable.

Since the methyl and dimethyl pyridines are stronger bases [4] and weaker π acceptors [37] than pyridine, an analogous trend of electron transfer from the thiocyanate ligand to the Cu(II) atom could be expected. Actually, on comparison with pyridine, compounds with 2-substituted position in the ligand L behave differently from the others. In 2-substituted pyridine ligands their steric effect is decisive [98, 99], since it causes weakening of the Cu—L bond and thus facilitates the electron transfer (NCS) $\rightarrow$ Cu(II). In compounds with derivatives of pyridine without steric hindrance their basicity is probably the determinative factor which leads to the increase of electron density round Cu(II) and thus hinders the electron transfer.

The changed chemical properties of pyridine ligands L in the group of compounds $[CuL_2(NCS)_2]$ apart from affecting the chemical interaction central atom—ligand L, will, through the central atom, affect also the electron transfers thiocyanate ligand—central atom and the bond energy of the coordinated thiocyanate ligands. Similar findings of the MIL deduced from infrared spectral data were reported several years ago [224].

iii) The manifestation of the MIL on chemical changes of the thiocyanate ligand

Thermal properties of compounds $[CuL_2(NCS)_2]$, where L = pyridine and all isomeric forms of picolines and lutidines, show that the changed chemical properties of ligands L will affect the temperature of decomposition of the investigated compounds and the types of thermal decomposition of the thiocyanate ligands [125, 118]. Thermal decomposition of the compounds $[Cu(py)_2(—NCS—)_2]$ and $[Cu(3,5-lut)_2(NCS)_2]$ (Figs. 11 and 12) can be described as follows
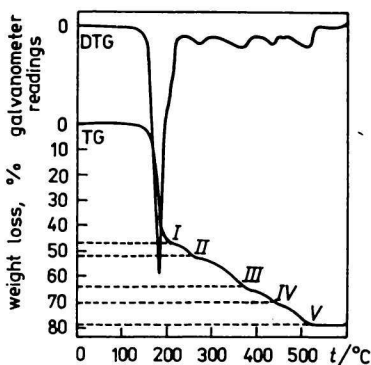
Fig. 11. Thermogram of the complex [Cu(py)₂(—NCS—)₂] [118].
I. CuNCS·NCS; *II.* Cu₂S₃(CN)₄; *III.* CuNCS; *IV.* Cu₂S(CN)₂; *V.* Cu₂S.
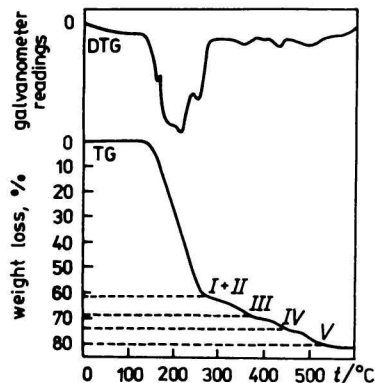
Fig. 12. Thermogram of the complex [Cu(3,5-lut)₂(NCS)₂] [118].
I, II. Cu₂S₃(CN)₄; *III.* CuNCS; *IV.* Cu₂S(CN)₂; *V.* Cu₂S.

$$[Cu(py)_2(-NCS-)_2] \xrightarrow[\text{I}]{-2py} [Cu(NCS)] \cdot NCS \xrightarrow[\text{II}]{-0.5\,S} \Big\}$$

$$[Cu(3,5\text{-lut})_2(NCS)_2] \xrightarrow[\text{I+II}]{-2\,(3,5\text{-lut})\, -0.5\,S} \Big\} \Big\} [CuS_{1.5}(CN)_2]$$

$$[CuS_{1.5}(CN)_2] \xrightarrow[\text{III}]{-CN\ -0.5\,S} [Cu(NCS)] \xrightarrow[\text{IV}]{-0.5\,S} [CuS_{0.5}(CN)] \xrightarrow[\text{V}]{-CN} CuS_{0.5}$$
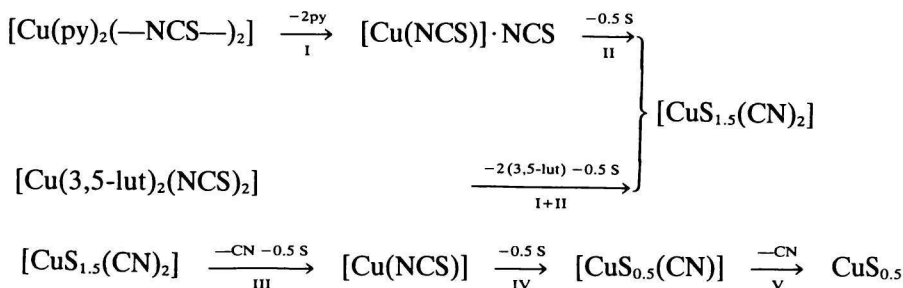
The thermal decomposition of [Cu(py)₂(—NCS—)₂] begins with the release of pyridine molecules and continues with decomposition and polymerization reactions of the thiocyanate ligands which take place in several discrete steps. From among the investigated compounds only for [Cu(3,5-lut)₂(NCS)₂] the thermal decomposition of thiocyanate ligands is similar to that in [Cu(py)₂(—NCS—)₂]. Decomposition and polymerization reactions of thiocyanate ligands take place at lower temperatures and partly overlap the release of molecules of 3,5-lutidine. Thermal stability of thiocyanate ligands of the remaining thiocyanate compounds was so lowered that their decomposition and polymerization reactions occur at ≈300°C and completely coincide with release of molecules of heterocyclic bases (Fig. 13).

The individual ligands L affect the thermal decomposition of thiocyanate ligand in a specific way in dependence on the position of methyl substituents on the pyridine ring [120]. In cases of picolines as ligands L, the methyl substituents in individual positions on the pyridine ring are responsible for thermal decomposition
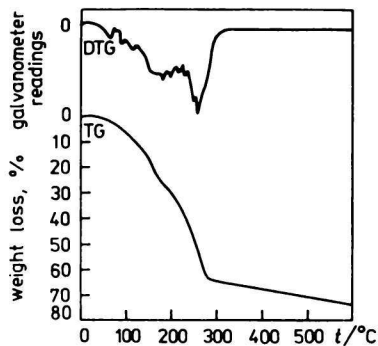
Fig. 13. Thermogram of the complex [Cu(2,4—lut)₂(NCS)₂] [118].
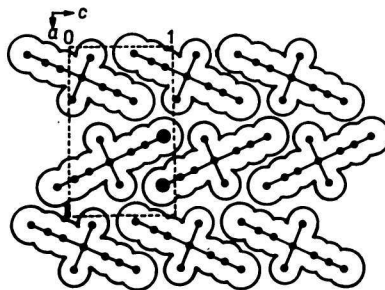
Fig. 14. Schematic representation of planar structure units of [Cu(NH₃)₂(—NCS)(—NCS—)] in the planes (020) [123].

processes which differ from each other. When lutidine is the ligand L then it is the methyl substituent in position 4 which determines the course of thermal decomposition of the thiocyanate ligand. The methyl substituent in position 3 or 5 on the pyridine ring has a decisive influence also when the other substituent occupies position 2. Methyl substituents in positions 2 or 6 also affect the process of thermal decomposition, their influence, however, when compared with that of methyl substituents in other positions of the pyridine ring, is the weakest one.

From the study of the MIL in compounds [CuL₂(NCS)₂], where L = pyridine and all isomeric forms of picolines and lutidines, following conclusions regarding the specific effects of methyl substituents on properties of thiocyanate ligands were drawn:

— the methyl substituent in position 2 decreases the bond strength of the bonds Cu—N(L) and favours thus the electron transfer thiocyanate ligand—central atom,

— π-acceptor capacity of the ligand (decreased as a consequence of the influence of methyl substituents especially in positions 3 and 5) affects the mode of coordination of thiocyanate bridges,

— the methyl substituent in position 4 affects most intensively the chemical transformation of the thiocyanate ligand in the course of thermal decomposition.

IV. Properties of the thiocyanate ligand in the thiocyanate copper(II) distortion isomers

The thiocyanate ligand is capable to reflect also changes in distortion of the coordination polyhedron in complexes of Cu(II). Changes in deformation of the

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coordination polyhedron of Cu(II) which are characteristic of distortion isomers [92, 95, 96, 197] are accompanied in thiocyanate copper(II) complexes by certain changes in properties of the thiocyanate ligands. Thus *e.g.* for distortion isomers [Cu(NH₃)₂(—NCS)(—NCS—)] changes in its geometry and for [Cu(py)₂(—NCS—)₂] changes in its chemical transformation were observed.

a) *Changes in symmetry of thiocyanate ligands in distortion isomers* [Cu(NH₃)₂(—NCS)(—NCS—)]

In the crystal structure of [Cu(NH₃)₂(—NCS)(—NCS—)] [81, 82, 53, 79, 80, 122] the central atom is planar coordinated by four nitrogen atoms from *trans*-coordinated thiocyanate ligands and ammonia molecules. In the crystal structure the planar structure moieties are arranged in planes (020) (Fig. 14). The reciprocal orientation of the planar moieties in contiguous planes (020) determines the complementing coordination of Cu(II) by sulfur atoms in the axial positions of the coordination polyhedron. The thiocyanate ligands are not equivalent as regards their coordination function, one of them is monodentate, coordinated only through nitrogen atom, the other forms a bridge, with one coordination bond to central atom *via* nitrogen and two coordination bonds *via* sulfur atom.

In the distortion isomers [Cu(NH₃)₂(—NCS)(—NCS—)] the mode of coordination of the central atom Cu(II) and the arrangement of structural moieties in crystal structure are identical [124, 123, 114] but there is a difference in deformation of the coordination polyhedron around the central atom (Fig. 15). Also changes of bonding angles S—C—N in coordinated thiocyanate ligands were observed accompanied by displacement of sulfur atoms from the plane (020).

In most thiocyanate compounds the thiocyanate ligand is linear or there are relatively small deviations of the bonding angles S—C—N from 180°. Cases in which the bonding angle is known to reach the value ≈ 160° are rather exceptional. In this connection it is remarkable that an analogous decrease of the bonding angle S—C—N was observed also in another thiocyanate compound, [Cu(en)-(—NCS)(—NCS—)] [78]. In this compound, similarly as in the compound [Cu(NH₃)₂(—NCS)(—NCS—)] analogous σ-bonding properties of ligands L and analogous nonequivalent coordination modes of both thiocyanate ligands were observed. The smallest value found for the bonding angle S—C—N in four symmetrically independent thiocyanate ligands in the compound [Cu(en)-(—NCS)(—NCS—)] is 154.7° (±4.9°).

Different properties of thiocyanate ligands in distortion isomers [Cu(NH₃)₂(—NCS)(—NCS—)] were observed in infrared spectra on the stretching frequency band v(CN) [119, 158]. Splitting of the stretching frequency band v(CN) indicates the presence of two coordinatively nonequivalent thiocyanate ligands in this complex. Analysis of the band (in the range 2120—2130 cm⁻¹) for
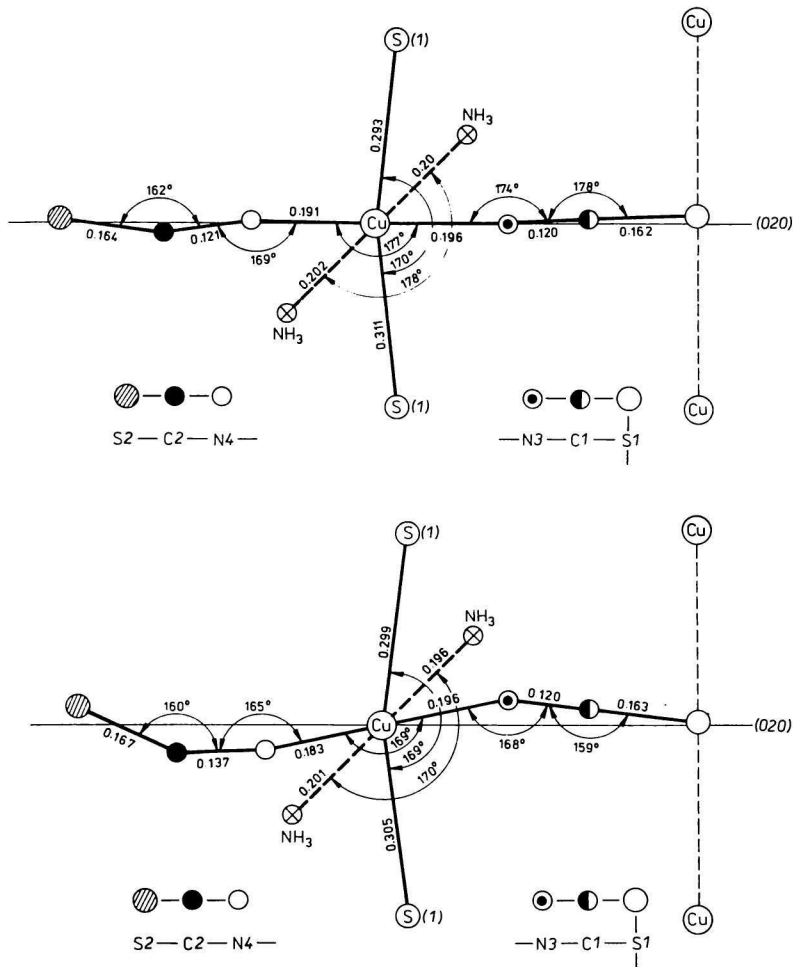
Fig. 15. Schematic representation of structural differences between distortion isomers
[Cu(NH₃)₂(—NCS)(—NCS—)] [114].

the "Lorentz" components indicates three components for both distortion isomers which differ in position and intensity [158].

b) *Chemical changes of the thiocyanate ligands in the distortion isomers* [Cu(py)₂(—NCS—)₂]

Similarly as the MIL, also the changes in deformation of the coordination polyhedron of Cu(II) cause the differences in chemical transformation of the thiocyanate ligands [149].
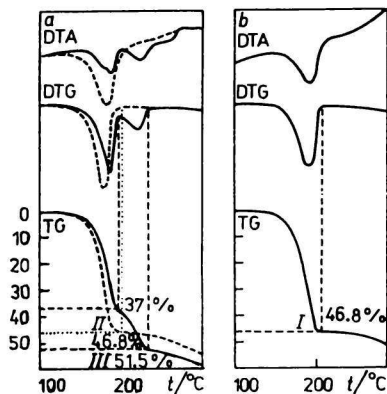
Fig. 16. Thermograms of distortion isomers
$[Cu(py)_2(—NCS—)_2]$ [149].

a) α-$[Cu(py)_2(—NCS—)_2]$: ——— decomposition in the air; – – – – decomposition under nitrogen.

b) β-$[Cu(py)_2(—NCS—)_2]$: ——— decomposition in the air and nitrogen.

I. $CuSCN \cdot SCN$-*I*; *II.* $CuSCN \cdot SCN$-*II*; *III.* $Cu_2S_3(CN)_4$.

Both distortion isomers $[Cu(py)_2(—NCS—)_2]$ give under nitrogen identical thermograms (Fig. 16). In the first phase of the thermal decomposition they release pyridine. Intermediate products of thermal decomposition of these distortion isomers have different properties and different degree of polymerization of the thiocyanate group in the structure $[Cu(—NCS—)]$. For convenience they are designated as $Cu(—NCS—) \cdot NCS$-*I* and $Cu(—NCS—) \cdot NCS$-*II*.

On thermal decomposition in air the distortion isomers yield curves different from the above mentioned. β isomer releases first pyridine molecules and .the properties of the intermediate product are identical with those of the product of thermal decomposition under nitrogen. In α isomer, simultaneously with releasing of pyridine molecules a partial decomposition of thiocyanate ligands takes place and elementar sulfur is released.

It has been found [121] that the different thermal stability of the thiocyanate ligands in distortion isomers $[Cu(py)_2(—NCS—)_2]$ is preserved even when under the action of pyridine vapours the two distortion isomers are transformed into tetrapyridine derivatives.

V. Conclusion

Analysis of bonding properties of thiocyanate ligand performed for more than hundred crystal structures of thiocyanate compounds allows to form conclusions on enormous coordination ability of this ligand and on great variability of its modes of bonding.

The great coordination ability of this ligand is exemplified by the existence of 38 "coordination types" which differ from each other in their mode of coordination or in the positions of the thiocyanate ligands in crystal structures. Variability of the bonding properties is due to the fact that for coordination the thiocyanate ligand uses one or two coordination bonds on nitrogen atom and one, two or three bonds on sulfur atom. From theoretically eleven possible modes seven have been observed.

Chemical approach to analysis of bonding possibilities of the thiocyanate ligand showed that the many variable modes of coordination of the thiocyanate ligand do not arise at random. The coordination modes of the thiocyanate ligands are influenced by the chemical properties of the central atoms and by other ligands in coordination spheres. This problem has been studied for cases of monodentate coordination of the thiocyanate ligand. Their N or S coordination was explained by cooperative effects of other ligands present in the coordination sphere. There was in literature an attempt for generalization of these findings to all transition metals. However, the contributions of the individual central atoms through which these cooperative effects take place were not considered in a sufficient measure.

From among the known seven modes of coordination of the thiocyanate ligand six were observed for the central atom Cu(II). The high number of modes of coordination of this ligand in copper(II) complexes can be related also with the plasticity of the coordination polyhedron, its adaptability and availability of all six bonding possibilities of the central atom.

For thiocyanates it was shown for the first time in the present paper that the change of π-acceptor capacity of other ligands present in the coordination sphere brings about also change of the bridging coordination of the thiocyanate ligand.

Evaluation of bonding properties of the thiocyanate ligand in thiocyanate copper(II) complexes with regard to the mutual influence of ligands (MIL) showed that a change of chemical properties of other ligands present in the coordination sphere will affect the thiocyanate ligand in several ways, not only by change of its mode of coordination.

List of abbreviations and symbols

aep	2-(2-aminoethyl)pyridine
aebg	1-(2-aminoethyl)guanidino(guanyl)
an	aniline
AsPh$_3$	triphenylarsine
AsPh$_4$	tetraphenylarsonium
bipy	2,2'-bipyridyl
bispictn	1,7-bis(2-pyridyl)-2,6-diazaheptane
quin	quinoline

den	di(2-aminoethyl)amine
dena	N,N-diethylnicotinamide
dion	1,3-diphenylpropane-1,3-dionate
dpt	di(3-aminopropyl)amine
en	ethylenediamine
etu	ethylenethiourea
Et$_4$N	tetraethylammonium
2,3-lut	2,3-dimethylpyridine
2,4-lut	2,4-dimethylpyridine
2,5-lut	2,5-dimethylpyridine
2,6-lut	2,6-dimethylpyridine
3,4-lut	3,4-dimethylpyridine
3,5-lut	3,5-dimethylpyridine
N$_3$As	N,N-bis(2-diethylaminoethyl)-2-diphenylarsinoethylamine-N,N,N
n-Bu$_4$N	tetrabutylammonium
nitr	nitron
pep	2,15-dimethyl-3,7,10,14,20-pentazabicyclo[14,3,1]-eikosa-1(20),2,14,16,18--pentaene
py	pyridine
2-pic	2-methylpyridine
3-pic	3-methylpyridine
4-pic	4-methylpyridine
pyc	2-pyridinecarboxylate
phen	phenantroline
pop	2,13-dimethyl-3,6,9,12,18-pentazabicyclo[12,3,1]-octadeca-1(18),2,12,14,16--pentaene
PEt$_3$	triethylphosphine
PPh$_3$	triphenylphosphine
PPh$_4$	tetraphenylphosphonium
PPh$_2$Bu	(3,3-dimethylbutinyl)diphenylphosphine
PPh$_2$Et	1,2-bis(diphenylphosphino)ethane
PPh$_2$Me	methyldiphenylphosphine
PPHN	diphenyl(2-dimethylaminoethyl)phosphine
PPr$_3$	tri n-propylphosphine
π-C$_3$H$_5$	π-allyl
π-C$_4$H$_7$	π-2-methylallyl
sal	N'-pyridylmethylene-N''-salicyloylhydrazinate-N,N',O
SbPh$_3$	triphenylstibine
tam	triacetamide
thiosem	thiosemicarbazide
tn	1,3-diaminopropane
top	1,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12,3,1]octadeca--1(18),2,12,14,16-pentaene
triam	2,2',2''-triaminotriethylamine
tripyam	tri-2-pyridylamine

trien	triethylenetetramine
tricyclo	tricyclohexylphosphine
tu	thiourea
tetraxa	tetraoxo-1,7,10,16-diaza-4,13-cyclooctadecane

(Abbreviations of ligands were, in most cases, taken over from original literature.)

In formulae the following designations of coordination modes of thiocyanate ligands are used:

(—NCS)	monodentate N-bonded group
(—SCN)	monodentate S-bonded group
(—NCS—)	bridging group
(ÑCŠ)	linkage isomers
(NCS)	coordination mode is not specified

Since appropriate terminology is not available, the mode of coordination of the group (NCS) is not reflected in the nomenclature of the compounds and the term thiocyanate ligand or anion is used in all cases.

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