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Nucleophilic additions to pseudohalides in the coordination sphere of transition metal ions and coligand isomerism

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Abstract

Coordinated pyrazoles exhibit a nucleophilic addition to the cyanate ligand inside the transition metal coordination sphere and new chelate complexes are formed; the new anionic ligand of the carbamoylpyrazolate type can be released. The conditions for such an addition were studied and established by selecting various central atoms and different *N*-donor heterocyclic ligands.

Some non-linear pseudohalides, namely $N(CN)_2^-$, $C(CN)_3^-$ and $ONC(CN)_2^-$, are also capable of such reactions but the addition proceeds under different conditions due to different electronic and steric requirements.

A new type of isomerism—coligand isomerism—has been discovered: one isomer is the usual complex of the $[MX_2(pzt)_2]$ type (pzt, pyrazole-type ligand) whereas in the second isomer $[M(pzt \cdot X)_2]$ a new anionic chelating ligand formed by nucleophilic addition is present.

Another type of nucleophilic addition, reaction of methanol with the $N(CN)_2^-$ specifically in the coordination sphere of Cu^{II} leads to the formation of a six-membered metallacycle. Nucleophilic addition of methanol to the $ONC(CN)_2^-$ anion in the transition metal coordination sphere results in formation of a five-membered metallacycle.

All nucleophilic additions studied have a common feature in a coordinative activation of the carbon β-site of the pseudohalides changing its hybridization and providing an unsaturated valency for a nucleophilic attack. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Nucleophilic additions; Pyrazole type ligands; Pseudohalides; Transition metals; Anionic chelate ligands; Metallacycles

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Nomenclature

bpy	2,2′-bipyridine
Br–pz	4-bromopyrazole
Cl–pz	4-chloropyrazole
DMF	dimethylformamide
dmpz	3,5-dimethylpyrazole
$(dmpz \cdot NCO)^-$	1-carbamoyl-3,5-dimethylpyrazolate
DMSO	dimethylsulfoxide
DTA	differential thermal analysis
$(ecoe)^-$	ethyl-2-cyano-2(hydroximino)ethaneimidate
en	1,2-ethanediamine, ethylenediamine
ESCA	X-ray photoelectron spectroscopy for chemical analysis
Et	ethyl
INDO	intermediate neglect of differential overlap
inz	indazole, benzopyrazole
I–pz	4-iodopyrazole
iz	imidazole
L	neutral monodentate ligand

$(mcoe)^-$	methyl-2-cyano-2(hydroximino)ethaneimidate
Me	methyl
$(mici)^-$	dimethylimidodicarbonimidate
mpz	3(5)-methylpyrazole
NH_2–pz	4-aminopyrazole
NO_2–pz	4-nitropyrazole
PEOE	partial equalization of orbital electronegativities
PPh_3	triphenylphosphine
py	pyridine
pyoxal	4,4-disubstituted 2-(2-pyridinyl)-2-oxazoline
pz	pyrazole
pzt	pyrazole-type ligand
$(pzt\cdot NCO)^-$	1-carbamoylpyrazolate-type ligand
$(pzt\cdot X)^-$	ligand resulting from nucleophilic addition
TCNE	tetracyanoethylene
TIP	temperature-independent paramagnetism
tmpz	3,4,5-trimethylpyrazole
X^-	pseudohalide ligand

1. Introduction

In the last decade, great attention was paid to the reactivity of coordinated ligands, because such understanding contributes to the solution of many practical and theoretical problems not only of coordination chemistry, but also of other chemical areas such as biochemistry and catalysis. The intramolecular reactions of ligands and the stabilization of labile molecules or ions by coordination provide much valuable information about the chemical properties and the structure of ligands. The importance of these reactions consists in the fact that bonding of the ligand to the central atom changes the reactivity of the former. In some cases its properties are varied to such an extent, that it undergoes quite different reactions when compared with its uncoordinated form [1–3]. This reactivity change is the reason for the efficiency of many complexes in biological processes and also as homogeneous catalysts in various reactions.

During studies of pseudohalide complexes with Cu^{II}, Ni^{II}, Co^{II} and occasionally other central atoms, the reaction course led to unexpected products in numerous cases. Into this category belong such types of nucleophilic additions, which result in the formation of new organic ligands. Simultaneously these reactions undergo ring closure including a central metal atom. In some cases, besides formation of complexes with new ligands formed by nucleophilic addition, normal pseudohalide complexes arose; the respective isomeric pairs were called coligand isomers.

In this review, the many complexes formed by nucleophilic addition in the central atom coordination sphere are presented. The chemical reactions, structures, spectral and magnetic properties of these coordination compounds are surveyed. Examples of coligand isomerism are discussed.

2. Experimental results demonstrating the reactions of pseudohalides in the transition metal coordination sphere

During the systematic research of cyanato–copper(II) complexes [4], two compounds of composition $Cu(NCO)_2 \cdot 2dmpz$ (α- and β-form) were isolated [5], the IR spectra of which differed substantially from those of the cyanate complexes. The most significant feature of the IR spectra of these compounds was the occurrence of a very strong band at about 1690 cm^{-1}, the shape of which is very similar to the $\nu_{as}(NCO)$ band. However, the usual very strong bands around 2200 cm^{-1}, corresponding to the $\nu_{as}(NCO)$ vibration [4], were absent. Upon dissolving these compounds in DMF, the bands at 1690 cm^{-1} disappear and the usual strong bands at around 2200 cm^{-1} emerge.

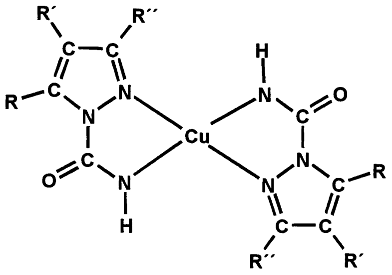
In the system $Cu^{II}–N(CN)_2^-–py–CH_3OH–H_2O$ the originally blue colour changed during several days into red–violet and finally violet–red crystals separated [6,7]. The analytical results and IR data excluded the formation of a dicyanamide complex. The CN stretching vibration is shifted by ca. 500 cm^{-1} towards lower frequencies, suggesting a drastic reduction of the bond order.

The yellow–green system $Ni^{II}–ONC(CN)_2^-–pz–CH_3OH–H_2O$ slowly changed into dark-red at room temperature (r.t.) and generated rose-red crystals, the analytical results of which indicated the composition $Ni\{ONC(CN)_2\}_2 \cdot 2pz \cdot 2CH_3OH \cdot 0.5H_2O$ [8]. Nitrosodicyanomethanide anions are absent from the Ni^{II} coordination sphere on the basis of IR data. A very intense band appears at about 1600 cm^{-1} and the bands of the C≡N stretching vibration lost significant intensity.

It is clear that the IR spectral data are neither able to elucidate the structure of the products mentioned above nor the chemical processes which led to formation of these compounds. Therefore, X-ray crystallographic analyses of single crystals of these unusual compounds were performed.

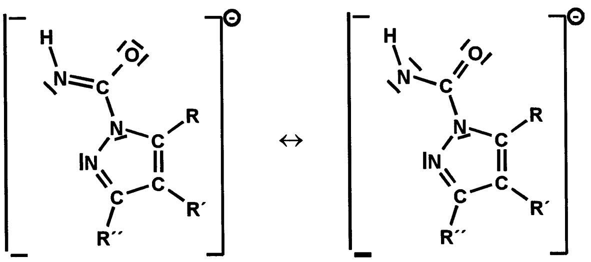
2.1. Fundamental X-ray crystallographic results

The structure of α-$Cu(NCO)_2 \cdot 2dmpz$ [5] consists of discrete molecules $[Cu(dmpz \cdot NCO)_2]$ (**1a**) (Fig. 1), which are almost planar and contain 1-carbamoyl-3,5-dimethylpyrazolate anions (**2a**), chelating with the Cu^{II} atoms by nitrogen atoms of the NCO groups and pyrazole rings; $R(Cu–N) = 1.908–1.990$ Å. The new anionic ligand **2a** arose by nucleophilic addition of the imine nitrogen of the pyrazole ring to the cyanate carbon. From indirect X-ray evidence the nitrogen atom of the NCO group carries a hydrogen atom.



1: [Cu(pzt.NCO)$_2$]

No.	pzt	R	R′	R′′
1a	dmpz	Me	H	Me
1b	pz	H	H	H

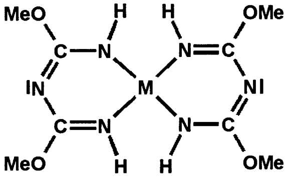


2: (pzt.NCO)$^-$

No.	pzt	R	R′	R′′
2a	dmpz	Me	H	Me
2b	pz	H	H	H
2c	mpz	Me	H	H
2d	tmpz	Me	Me	Me
2e	NH_2-pz	H	NH_2	H
2f	Br-pz	H	Br	H
2g	I-pz	H	I	H
2h	inz	H	[a]	[a]

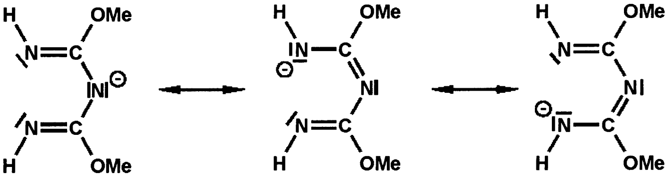
[a] inz = 4,5-benzopyrazole

The compound isolated from the dicyanamide system [6,7] is composed of discrete chelate molecules, [Cu(mici)$_2$] (**3a**) (Fig. 2), held together by van der Waals interactions and hydrogen bonds. The copper atom is located at the centre of symmetry and is coordinated in a square-planar fashion by four nitrogen atoms; R(Cu–N) = 1.942 or 1.948 Å. The anionic ligand, (mici)$^-$ (**4**)[1], forms a six-membered metallacycle with the Cu^{II} atom.



3: [M(mici)$_2$]

No.	M
3a	Cu
3b	Ni



4: (mici)$^-$

The compound Ni{ONC(CN)$_2$}$_2$·2pz·2CH$_3$OH·0.5H$_2$O [8] is built from discrete [Ni{NO(CN)CC(OCH$_3$)NH}$_2$(pz)$_2$] units, *cis*-[Ni(mcoe)$_2$(pz)$_2$] (**5a**) (Fig. 3), in which the central Ni atom appears to be octahedrally coordinated by six nitrogen donor atoms; R(Ni–N) = 2.050–2.101 Å. Two of them are tertiary nitrogen atoms of pyrazole molecules which are surprisingly arranged in *cis*-position. The remaining four nitrogen donors originate from two bidentate anionic chelate ligands, (mcoe)$^-$ (**6**).

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[1] In the previous papers the abbreviation of this ligand was (BMCA)$^-$.

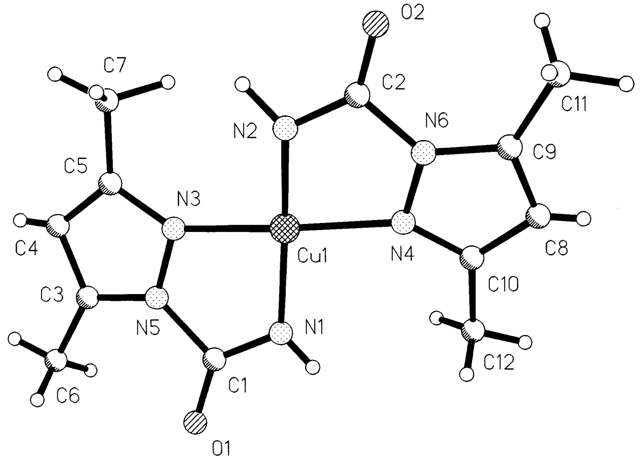
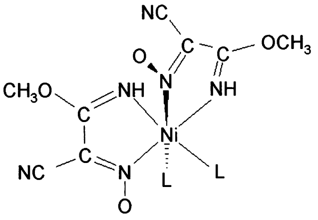
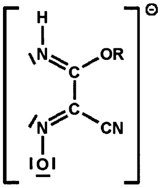


Fig. 1. Molecular structure of [Cu(dmpz·NCO)$_2$] (**1a**).



5: *cis*-[Ni(mcoe)$_2$L$_2$]

No.	L
5a	pz
5b	tmpz



6: (mcoe)$^-$

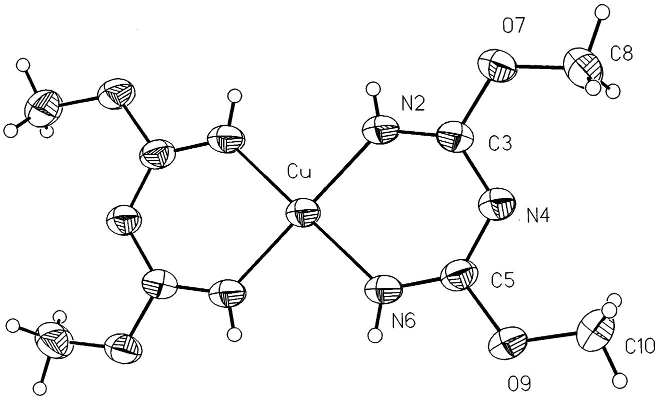


Fig. 2. Molecular structure of [Cu(mici)$_2$] (**3a**). Ellipsoids correspond to 50% probability levels; hydrogen atom radii are arbitrary.

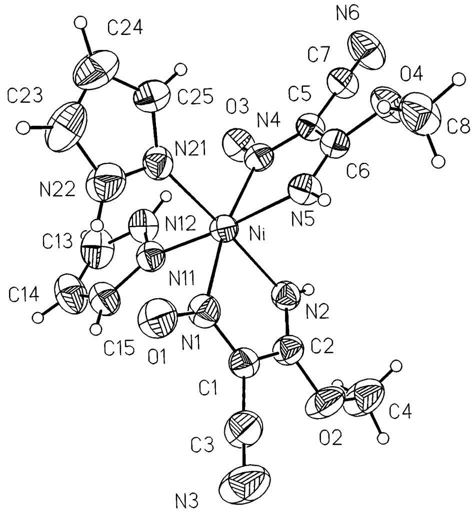
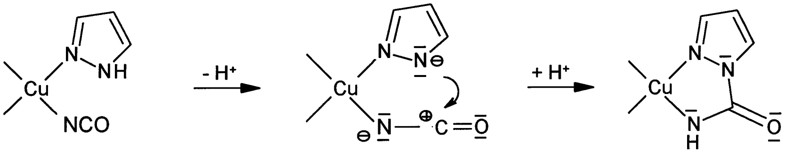
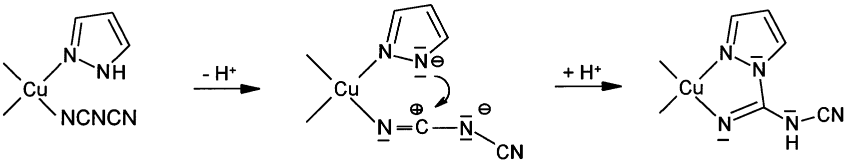


Fig. 3. Molecular structure of *cis*-[Ni(mcoe)$_2$(pz)$_2$] (**5a**). Ellipsoids correspond to 50% probability levels; hydrogen atom radii are arbitrary.



Scheme 1.



Scheme 2.

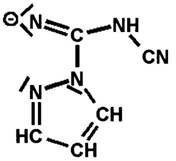
2.2. Formation of the anionic chelate ligands in the metal coordination sphere

The nucleophilic addition in the system Cu^{II}–NCO^-–pzt (formation of ligands of type **2**) is of relatively general character, because analogous reactions occur in many systems with different pyrazole ligands, non-linear pseudohalides, and in coordination spheres of other central atoms. On the other hand, the nucleophilic addition of methanol to dicyanamide yielding ligands of **4** is highly specific for copper(II). The third type of nucleophilic addition of methanol to nitrosodicyanomethanide can occur with various central atoms, producing ligands of type **6**.

In order to elucidate the formation of $[Cu(dmpz\cdot NCO)_2]$ (**1a**), a nucleophilic addition of a pz molecule to the positively charged carbon of the NCO group was supposed [5], as a result of which a new bond C–N(ring) arose. This is drawn in Scheme 1 for the formation of $[Cu(pz\cdot NCO)_2]$ (**1b**).

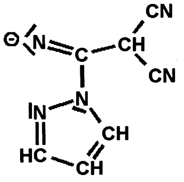
In order to ascertain the conditions under which this nucleophilic addition occurs, as well as the factors influencing this reaction, a great number of other systems was investigated, with different central atoms, non-linear pseudohalides and numerous pyrazole derivatives, with various electronic and steric properties. From many of these systems new compounds of the type $[M(pzt\cdot X)_2]$ were isolated which contain anionic chelate ligands of the carbamoylpyrazolate type **2**.

It was ascertained that the non-linear pseudohalide anions, dicyanamide $N(CN)_2^-$, tricyanomethanide $C(CN)_3^-$ and nitrosodicyanomethanide $ONC(CN)_2^-$ are also able to react with pyrazole ligands and form new anionic chelate ligands in the M^{II} coordination sphere. In the case of dicyanamide the imine nitrogen of the pyrazole ring attacks the more positively charged carbon of one of the cyano groups, and thus, a covalent bond C(CN)–N(ring) is formed yielding a derivative of **7**, the proton being transferred from the pyrazole nitrogen to the negatively charged amide nitrogen (Scheme 2) [9–11].



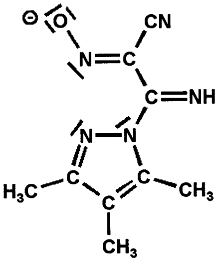
7: $\{pz.N(CN)_2\}^-$

With the tricyanomethanide, the chain –N=C–CH=(C≡N)$_2$ is present in the new anionic ligand **8** in place of the chain –N=C–NH–C≡N [12,13].



8: {pz.C(CN)$_3$}$^-$

In the case of nitrosodicyanomethanide, the formation of the chain –N(O)=C–C≡N is supposed for the new anionic ligand **9** on the basis of IR spectra [14].



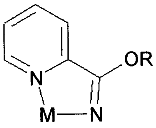
9: {tmpz.ONC(CN)$_2$}$^-$

An interesting reaction analogous to those described before, which proceeds in the coordination sphere of copper and is connected with a simultaneous redox reaction, was discovered by Ten Hoedt et al. [15].

The reaction of N(CN)$_2^-$ and ONC(CN)$_2^-$ with methanol can be classified as a metal-promoted nucleophilic reaction of a nitrile [16]. A model for the reaction pathway to form the chelate [Cu(mici)$_2$] was constructed using quantum chemical calculations ab initio [7].This reaction is promoted by coordinative activation of the carbon β-site of N(CN)$_2^-$ anion. The reaction can be divided into five steps: activation of dicyanamide (bonding and stretching) changing the β-carbon hybridization to sp^2, chelation leading to the complex [Cu{N(CN)$_2$}$_2$], addition of four molecules of methanol, release of ligand and its relaxation to an optimal geometry.

The activation of molecules containing the nitrile group upon their coordination to a metal atom has been exploited in addition reactions of nucleophiles such as water, alcohol and amines yielding amide [17], imino ether [18,19], or amidine [18] complexes.

As has previously been observed, the reaction of pyridine-2-carbonitrile with water or an alcohol in the presence of some metal(II) salts leads to formation of complexes which contain pyridine-2-carboxamide or O-alkylpyridine-2-carboximidate [20,21]. The crystal and molecular structures of [Ni(O-methylpyridine-2-carboximidate)$_3$]Br$_2 \cdot 4H_2O$ [22] and dimeric [CuCl$_2$(O-ethylpyridine-2-carboximidate)]$_2$ [21] were determined. The O-alkylpyridine-2-carboximidate molecules form *N*,*N*-coordinated bidentate chelate ligands as in **10**. The IR spectral data confirm this mode of ligand coordination for all Cu^{II}, Co^{II} and Ni^{II} complexes containing O-methylpyridine-2-carboximidate [22].



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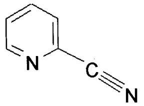
On the other hand, several Ni^{II} complexes of 2-pyridinyl-2-oxazolines **13a–c** have been isolated [23] from aqueous or alcoholic solutions of pyridine-2-carbonitrile **11** in the presence of the amino alcohols **12a–c**.



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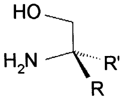

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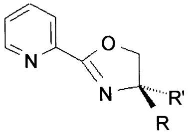

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No.		R	R'
12a	**13a**	CH$_2$OH	CH$_2$OH
12b	**13b**	CH$_2$OH	CH$_3$
12c	**13c**	CH$_3$	CH$_3$

3. Synthesis and structural characterization

3.1. Synthetic procedures

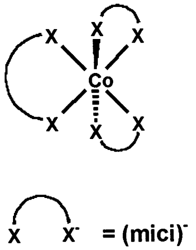
The complexes [M(pzt·X)$_2$] were obtained from systems containing M^{II} salts and potassium or sodium salts of the pseudohalides X$^-$ and ligands pzt of the pyrazole type, in short: systems M^{II}–X$^-$–pzt. A methanol + water mixture, or in special cases pure methanol, served as solvents. The synthetic methods, which are leading to the isolation of compounds [M(pzt·X)$_2$] can be divided into the following categories:

1. Direct isolation from the system M^{II}–X$^-$–pzt at r.t. [13,24].
2. Direct isolation from the system M^{II}–X$^-$–pzt at higher temperature [10,25].

3. Separation from the filtrate after isolation of the corresponding solid pseudohalide complex [10,11,26,27].
4. Substitution of a sterically hindered ligand L, e.g. 2,4-lutidine, in the polymeric compound $[Cu(NCO)_2L]$ [4] by treating with a pyrazole type ligand pzt in methanol solution at r.t. or at higher temperature [5,24,28]. The isomeric form of $[Cu(pzt \cdot NCO)_2]$ can sometimes be obtained by crystallization of the filtrate remaining after the product of the same composition was removed by suction filtration [28].
5. Transformation of the corresponding complex $[CuX_2(pzt)_2]$ by standing for a long time in the solid state [11,27,28].
6. Recrystallization of the corresponding complex $[CuX_2(pzt)_2]$ from hot methanol [28,29].
7. Attempted substitution of chloride ligands in a complex $[MCl_2(pzt)_2]$ ($M = Pd$, Pt) by treating with a silver pseudohalide AgX [$X = NCO$, $N(CN)_2$, $C(CN)_3$] [12].

Table 1 surveys the results which were obtained by study of numerous systems in which the possibility of nucleophilic addition was assumed. Thus, a variety of coordinated carbamoylpyrazolate ligands can be formed; good yields of pure copper chelates of the ligands **2a–h** can be obtained. In some of these systems the nucleophilic addition proceeds only partially and the formation of a mixture of compounds $[M(pzt \cdot X)_2]$ and $[MX_2(pzt)_2]$ was obtained.

When a solution of $[Cu(mici)_2]$ (**3a**) in dimethylsulfoxide was treated with cobalt sulphide at 50°C under reflux for 5 days, filtered, and left standing for 6 months, crystals of the composition $[Co(mici)_3]$ (**14**) deposited from solution [30]. This procedure was also used for obtaining red $[Ni(mici)_2]$ (**3b**).



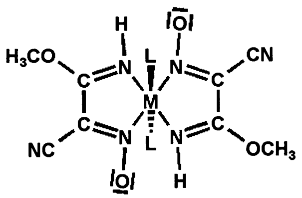
14: $[Co(mici)_3]$

Crystals of composition $[Ni(mcoe)_2(H_2O)_2]$ (**15a**) were prepared from the system $Ni^{II}–ONC(CN)_2^-–dmpz–CH_3OH–H_2O$ [31], whereas from the analogous systems with pz or tmpz, crystals of $[Ni(mcoe)_2(pz)_2] \cdot 0.5H_2O$ (**5a**) [8] and $[Ni(mcoe)_2(tmpz)_2]$ (**5b**) [30,32], respectively, were obtained. From the systems $Cu^{II}–ONC(CN)_2^-–B–CH_3OH–H_2O$, where $B = pz$, dmpz, tmpz, iz (the system also works without B), always the same product $[Cu(mcoe)_2(H_2O)_2]$ (**15b**) separated [32]. The compound $[Pd(mcoe)_2]$ (**15c**) was isolated from the system $Pd^{II}–ONC(CN)_2^-–CH_3OH–H_2O$ [32]. The compound $[Cu(ecoe)_2(H_2O)_2]$ (**15d**) was prepared by recrystallization of $[Cu\{ONC(CN)_2\}_2(py\}_2]$ from hot ethanol [33].

Table 1
Course of the nucleophilic addition of pyrazoles (pzt) to pseudohalides X^- in the coordination sphere of metal ions M^{IIa}

	NCO^-					$N(CN)_2^-$				$C(CN)_3^-$				$ONC(CN)_2^-$		
pzt/M^{II}	Cu^{II}	Ni^{II}	Co^{II}	Pd^{II}	Pt^{II}	Cu^{II}	Ni^{II}	Co^{II}	Pd^{II}	Cu^{II}	Ni^{II}	Co^{II}	Pd^{II}	Cu^{II}	Ni^{II}	Co^{II}
pz	+	−	±	+	+	+	+	−	+	+	−	−	+	−	−	−
mpz	+	−	−	0	0	−	0	0	0	−	0	0	0	+	−	−
dmpz	+	−	−	±	0	−	−	−	0	−	−	−	±	−	−	−
tmpz	+	+	−	0	0	−	−	−	0	−	−	−	0	−	−	+
inz	+	−	−	0	0	+	−	−	0	0	0	0	0	0	0	0
NH_2–pz	+	−	−	0	0	0	0	0	0	0	0	0	0	0	0	0
NO_2–pz	±	±	−	0	0	+	+	−	0	−	±	0	0	0	0	0
Cl–pz	−	±	−	0	0	+	±	−	0	−	−	0	−	0	0	0
Br–pz	+	±	±	0	0	+	−	−	0	−	−	−	0	0	0	0
I–pz	+	−	−	0	0	+	±	−	0	−	−	−	0	0	0	0

[a] +, nucleophilic addition runs; ±, nucleophilic addition runs partly and a mixed product is formed; −, nucleophilic addition does not run; 0, system was not investigated.



15: trans-$[M(mcoe)_2L_2]$

No.	M	L
15a	Ni	OH_2
15b	Cu	OH_2
15c	Pd	-
15d	Cu	OH_2[a]

[a]ecoe (**3**, R = C_2H_5) instead of mcoe

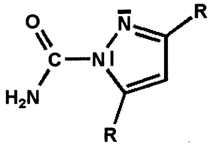
The compound $[Cu(mcoe)(bpy)N(CN)_2]$ (see Section 3.3.) was obtained by reaction of water solutions of $Cu(NO_3)_2$, $KN(CN)_2$ and $NaONC(CN)_2$ with a methanol solution of bpy [34].

3.2. Chemical aspects

By comparison with complexes $[MX_2(pzt)_2]$ which are soluble in many common organic solvents, chelates of the type $[M(pzt \cdot X)_2]$ are soluble only in dimethylformamide and dimethylsulfoxide. In these solvents the single C–N bond formed by nucleophilic addition is split and isomeric pseudohalide complexes arise.

By treating suspensions of the carbamoylpyrazolate complexes, e.g. $[Cu(pz \cdot NCO)_2]$ (**1b**), with H_2S, CuS precipitates and the acids $H(pzt \cdot NCO)$ (**16a**) corresponding to the anionic ligands **2** are formed.

The resulting carbamoylpyrazole **16b** was identified by elemental analyses and their IR spectra, which were in agreement with spectra of compound prepared by usual methods.



16: H(pzt)

No.	R
16a	H
16b	Me

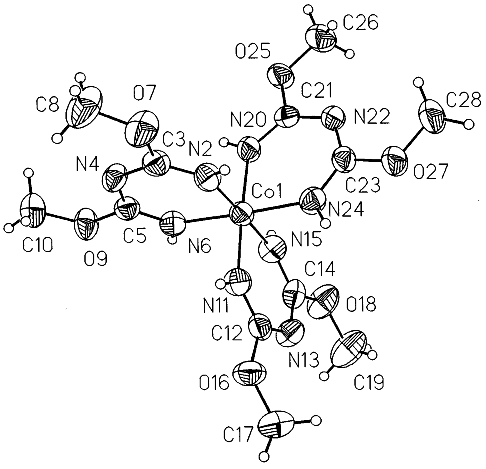


Fig. 4. Molecular structure of [Co(mici)$_3$] (**14**). Ellipsoids correspond to 50% probability levels; hydrogen atom radii are arbitrary.

3.3. *X-ray crystal structures of other compounds formed by nucleophilic addition*

The crystal structure of [Co(mici)$_3$] (**14**) consists of discrete molecules (Fig. 4) [30] in which the Co atom is octahedrally coordinated by six nitrogen atoms from three chelate anions (4); the Co–N distances vary between 1.883 and 1.899 Å. The metal–ligand moiety forms a six-membered metallacycle as in the analogous copper(II) complex (**3a**, Section 2.1) [6,7].

The crystal structure of *trans*-[Ni(mcoe)$_2$(H$_2$O)$_2$] (**15a**) [31] is built of discrete molecules (Fig. 5) in which the Ni atom is coordinated by four nitrogen atoms of two bidentate anionic chelate ligands and by two oxygen atoms of water molecules with R(Ni–N) = 2.032 or 2.093 Å and R(Ni–O) = 2.129 Å. The Ni atom forms five-membered planar rings by bonding with atoms N1 and N2. [Ni(mcoe)$_2$(pz)$_2$] (**5a**) [8] and *trans*-[Cu(mcoe)$_2$(H$_2$O)$_2$] (**15b**) are structurally rather

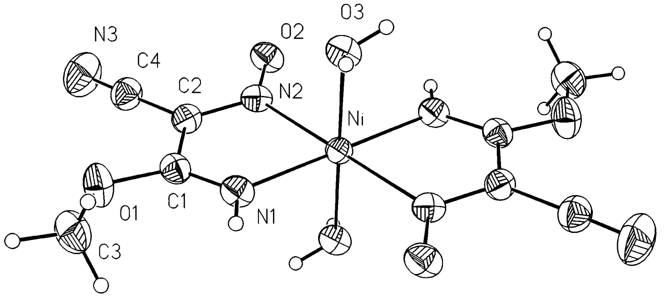


Fig. 5. Molecular structure of *trans*-[Ni(mcoe)$_2$(H$_2$O)$_2$] (**15a**). Ellipsoids correspond to 50% probability levels; hydrogen atom radii are arbitrary.

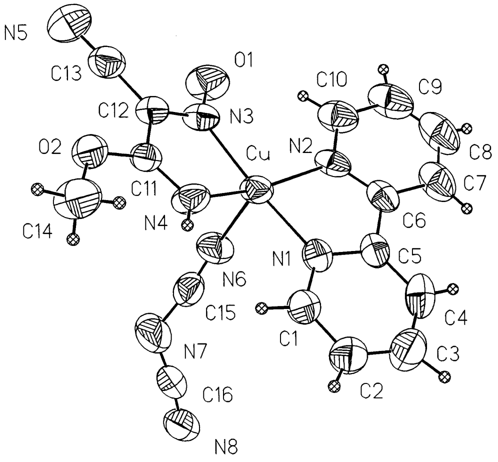


Fig. 6. Molecular structure of [Cu(mcoe)(bpy){N(CN)$_2$}] (courtesy of M. Dunaj-Jurčo). Ellipsoids correspond to 50% probability levels; hydrogen atom radii are arbitrary.

similar, but in the latter the water molecules occupy axial positions at long distances from Cu^{II}.

The crystal structure of [Cu(mcoe)(bpy){N(CN)$_2$}] consists of discrete molecules (Fig. 6) [34] in which the Cu atom is coordinated by five nitrogen atoms stemming from one mcoe$^-$ anion, one bipy molecule and one N(CN)$_2^-$ anion. There are two five-membered metallacycles in the equatorial plane and the coordination is completed in the apical position by a dicyanamide nitrogen atom to a distorted tetragonal pyramid with R(Cu–N equatorial) between 1.958 and 2.038 Å and R(Cu–N apical) = 2.188 Å.

Table 2
Characteristic IR frequencies (cm^{-1}) of the complexes [M(pzt·NCO)$_2$]

Compound	ν(C=O)	ν(C=N)	ν(C–N$_{ring}$)	γ(NCO)	Ref.
α-[Cu(pz·NCO)$_2$]	1726	1326	1215	514	[27]
α-[Cu(mpz·NCO)$_2$]	1704	1363, 1353	1195	503	[28]
α-[Cu(dmpz·NCO)$_2$]	1694	1357	1215	508	[5]
[Cu(tmpz·NCO)$_2$]	1691, 1680	1351, 1342	1252	506	[36]
[Cu(Br–pz·NCO)$_2$]	1716		1240		[24]
[Cu(I–pz·NCO)$_2$]	1717, 1680		1243		[24]
[Cu(NH$_2$–pz·NCO)$_2$]	1692, 1650		1242	507	[37]
[Cu(inz·NCO)$_2$]	1705	1333	1213	508	[25]
[Ni(tmpz·NCO)$_2$]	1691	1325	1250	527	[26]
[Ni(Cl–pz·NCO)$_2$]	1660, 1614				[38]
[Co(pz·NCO)$_2$·pz]	1665	1331	1209	527	[26]
[Pd(pz·NCO)$_2$]	1700		1211, 1204		[12]
[Pd(dmpz·NCO)$_2$]	1715, 1675		1220		[12]
[Pt(pz·NCO)$_2$]	1706		1214, 1207		[12]

Table 3
Systems M–X^-–pzt from which coligand isomer pairs were isolated

M	X	pzt
Cu	NCO	pz, mpz, dmpz, tmpz, Br–pz, I–pz, NH_2–pz, inz
	$N(CN)_2$	pz, inz, Br–pz
	$C(CN)_3$	pz
Ni	NCO	tmpz
	$N(CN)_2$	pz, NO_2–pz
Co	$ONC(CN)_2$	tmpz

The compound $[Cu(ecoe)_2(H_2O)_2]$ (**15d**) forms discrete molecules [33] which are similar to those of *trans*-$[Ni(mcoe)_2(H_2O)_2]$, but the pseudooctahedral coordination is considerably elongated with R(Cu–N) = 1.970 or 2.057 Å and R(Cu–O) = 2.535 Å.

The compound $[Co(mcoe)(en)_2](NO_3)_2 \cdot CH_3OH$ contains cationic chelate complexes in which the Co atom is *mer*-octahedrally coordinated by six nitrogen atoms of one $mcoe^-$ anion and two en molecules with R(Co–N) = 1.918 and 1.911 Å, respectively [35].

3.4. Infrared evidence of nucleophilic addition

The most important IR frequencies which characterize compounds of the type $[M(pzt \cdot NCO)_2]$ are listed in Table 2. The IR spectra of compounds isolated from the NCO^-–pzt systems can be unequivocally interpreted and used for confirmation of formation of chelate ligands **2**.

The IR spectra of compounds of the type $[M\{pzt \cdot N(CN)_2\}_2]$, $[M\{pzt \cdot C(CN)_3\}_2]$ or $[M\{pzt \cdot ONC(CN)_2\}_2]$ (chelates of the ligands **7–9**) also provide evidence for formation of these species. Bands appearing in a relatively broad range between 1705 and 1530 cm^{-1} are assigned to the C=N stretching vibrations, while bands of variable intensity between 1270 and 1190 cm^{-1} are assigned to the C–N(ring) stretching vibrations, as in the case of similar carbamoylpyrazolate compounds. Unlike these, bonds of the C≡N stretches (in the range between 2250 and 2150 cm^{-1}) are also present.

In the IR spectrum of $[Cu(mici)_2]$ (**3a**) [6], the very strong bands with maxima at 1606 cm^{-1} (and shoulders at 1614 cm^{-1}) and at 1375 cm^{-1} are assigned to the ν(C=N) and ν(C–N) vibrations, respectively. The complexes $[Co(mici)_3]$ (**14**) and $[Ni(mici)_2]$ (**3b**) have similar IR spectra to **3a**.

The IR spectrum of *cis*-$[Ni(mcoe)_2(pz)_2] \cdot 0.5H_2O$ (**5a**) [8] and related complexes *trans*-$[Cu(mcoe)_2(H_2O)_2]$ (**15b**), *trans*-$[Ni(mcoe)_2(H_2O)_2]$ (**15a**), *cis*-$[Ni(mcoe)_2(tmpz)_2]$ (**5b**) [31], $[Pd(mcoe)_2]$ (**15c**) and $[Co(mcoe)_3]$ [32] also exhibit vibrations characteristic of the same anionic chelate ligand.

4. Coligand isomerism

4.1. General remarks

From the systems $M^{II}–X^{-}–pzt$ [M = Cu, Ni, Co; X = NCO, $N(CN)_2$, $C(CN)_3$, $ONC(CN)_2$] arise the products of nucleophilic addition, but the usual pseudohalide complexes were also isolated. Thus, isomeric pairs arose which were called coligand isomers [36,39]. One isomer (henceforth called complex) contains pseudohalide groups and pyrazole type molecules as ligands, whereas the second one (henceforth called chelate) exhibits chelate ligands of carbamoylpyrazolate or analogous type.

A survey of the systems $M–X^{-}–pzt$, from which coligand isomers of the type $[M(pzt\cdot X)_2]$ (chelates) and $[MX_2(pzt)_2]$ (complexes) were isolated until now, is given in Table 3. These isomeric compounds can be unequivocally distinguished by means of their IR spectra. The spectra of the chelates $[M(pzt\cdot X)_2]$ show bands characteristic of the non-linear chain bonded to the pyrazole ring, as well as the bands connected with the C–N(ring) bond. On the other hand, the spectra of the complexes $[MX_2(pzt)_2]$, show bands typical of the pseudohalide ligands X^{-} [4,40,41].

4.2. The relative stability and thermal transformations of coligand isomers

In the coligand isomer pairs $[MX_2(pzt)_2]$ and $[M(pzt\cdot X)_2]$, the pseudohalogeno complexes $[MX_2L_2]$ are generally less stable and, in the solid state, more or less slowly are transformed into the more stable chelates $[M(pzt\cdot X)_2]$. A molecular-orbital study (quasirelativistic INDO/1 method) [42] performed in the case of coligand isomer pair $[Cu(dmpz)_2(NCO)_2]$ [43] and $[Cu(dmpz\cdot NCO)_2]$ [5] rationalizes this behaviour and maps the reaction pathway of the hydrogen transfer over the molecular skeleton. A similar study [42] carried out for another coligand isomer pair $[Cu(pz)_2(NCO)_2]$ and $[Cu(pz\cdot NCO)_2]$ [27] led to analogous results.

The thermal decomposition of the compounds $[Cu(NCO)_2(pzt)_2]$ and $[Cu(pzt\cdot NCO)_2]$, where pzt = pz, dmpz, tmpz and inz, were studied [44]. The DTA curves of the cyanate compounds exhibit an exothermic peak caused by the intramolecular nucleophilic addition somewhat below the decomposition temperature (90–160°C). The ΔH values, determined for these reactions by the DSC

Table 4
Values of ΔH and temperatures of exothermic excursion maxima for the isomerization $[Cu(NCO)_2(pzt)_2] \rightarrow [Cu(pzt\cdot NCO)_2]$

Compound	ΔH (kJ mol^{-1})	T_{max} (K)
$[Cu(NCO)_2(pz)_2]$	-12.80 ± 0.58	385.8
$[Cu(NCO)_2(dmpz)_2]$	-8.15 ± 0.64	377.3
$[Cu(NCO)_2(tmpz)_2]$	-19.49 ± 0.66	388.9
$[Cu(NCO)_2(inz)_2]$	-11.59 ± 0.72	431.8

Table 5
Calculated PEOE charges (me) for the three types of structures

	C1s		N1s			$Cu2p_{3/2}$
	Ring	–N=C=O	N1	N2	–N=C=O	
Ligands	−8 to +62		−286	−184		
Cyanate	−29 to +17	+313	−321	−287	−252	+799
Chelate	−28 to +31	+322	−228	−279	−335	+765

method, are given in Table 4. These values are considerably lower than the energy of C–N bond formation of the chelate. Apparently the major part of the energy released is used for the reorganization of the crystal and molecular structure.

The stoichiometry of thermal decomposition of $[Cu(NCO)_2(pzt)_2]$ and $[Cu(pzt \cdot NCO)_2]$ (**1**) is due to the exothermic isomerization $[Cu(NCO)_2(pzt)_2] \rightarrow [Cu(pzt \cdot NCO)_2]$. The bonding and steric properties of the pzt ligand influence strongly the ΔH values for these isomerization reactions and also the decomposition stoichiometries of the compounds under study.

DTA curves of $[Cu\{N(CN)_2\}_2(pz)_2]$, $[Cu\{C(CN)_3\}_2(pz)_2]$ and $[Ni\{C(CN)_3\}_2(pz)_2]$ have also been recorded and exothermic peaks of about 190°C were observed.

4.3. Study of the coligand isomers by the ESCA method

The N1s, C1s and Cu2p spectra were studied and analyzed for a series of coligand isomers of the type $[Cu(NCO)_2(pzt)_2]$ and $[Cu(pzt \cdot NCO)_2]$ (**1**), where pzt = pz, mpz, dmpz, tmpz [45] (Table 5).

All the spectra recorded allow clear distinctions to be made between cyanato complexes and chelates based upon their N1s peaks. One of the most striking observations is that the binding energy of the pyrazole nitrogen atoms is systematically lower in the complex than in the free ligand and both N1 and N2 will have similar binding energies. The global result is that the three different nitrogen atoms in the cyanato complex have very similar N1s energies and thus compose a rather narrow peak.

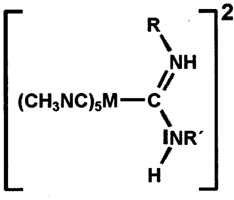
In the chelate the variation of N1s energies of the different nitrogen atoms cause a triplet structure of the corresponding peak. The correlation between PEOE charge density and experimental binding energy N1s is quite linear.

The binding energies for Cu levels decrease on going from the cyanato complex to the chelate type bonding, in accord with the PEOE charges. The PEOE method gives very similar positive charges for the cyanate carbon atoms in both coligand isomers.

4.4. Examples of coligand isomers in systems derived from isonitriles or various organic nitriles

Nucleophilic additions occur not only with coordinated pseudohalides but also with some other coordinated unsaturated systems, e.g. nitriles and isonitriles, and at the same time produce coligand isomers.

Balch et al. [46] have shown that addition of methylamine to $[Fe(CNCH_3)_6]^{2+}$ runs in two steps: first, complex **17** is formed which then changes into the coligand isomer **18** (R = R′ = Me). This reaction has turned out to be general in character [47]. For M = Ru; R = Me, R′ = Et and R = Et, R′ = Me, the formation of isomer **17**, for M = Fe; R = R′ = Me the formation of **18** predominates.



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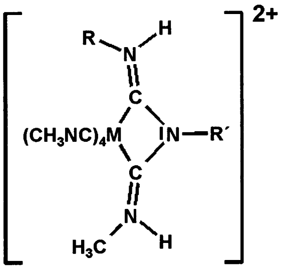
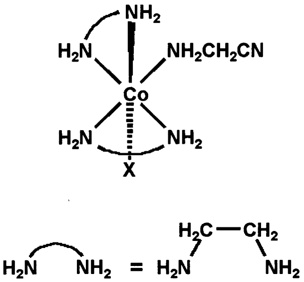


18

Sargeson et al. [48] showed that the aminoacetonitrile complexes *cis*-$[Co(en)_2(NH_2CH_2CN)X]^{2+}$ (X = Cl, Br) (**19**), react in nearly neutral or basic solution to give isomers with the constitution $[Co(en)(NH_2CH_2C(NH_2){=}NCH_2CH_2NH_2)X]^{2+}$ (**20**), i.e. amidine complexes, where one end of the bidentate ethylenediamine ligand is added to the bound NH_2CH_2CN moiety. The structure of the addition product **20** which is a coligand isomer of the complex **19** was solved by X-ray crystallography. Nolan and Hay [49] investigated the kinetics of the transformation of these aminoacetonitrile complexes **19** into the amidine complexes **20** in aqueous solutions.



X = Cl, Br

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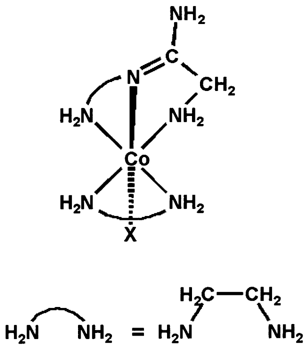
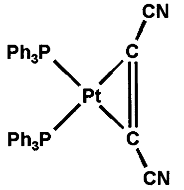


X = Cl, Br

20

Cases of photochemical isomerization, leading to formation of coligand isomers, are also known [50]. Baddley et al. [51] observed new bands in the IR spectrum of complex **21** some years after preparation, which they assigned to the isomeric complex **22**. The structure of **22** was proven by X-ray study of an aged sample of **21**.



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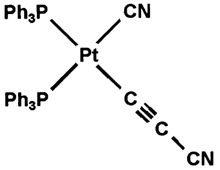

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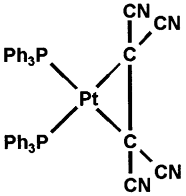
By irradiation of a chloroform solution of [Pt(PPh_3)$_2$(TCNE)] (**23**) at 313 nm Traverso et al. [52] obtained a new isomeric complex to which the structure **24** was assigned on the basis of IR spectra.



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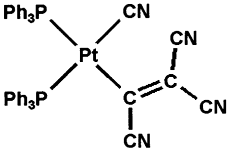

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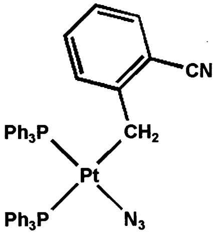
Ros et al. [53] established that addition of NaN_3 to *cis*-[Pt(O-$CH_2C_6H_4CN$)(PPh_3)$_2$](BF_4)$_2$ gives a stable complex, *cis*-[Pt(N_3)($CH_2C_6H_4CN$)(PPh_3)$_2$] (**25**), which by heating undergoes a intramolecular 1,3-cycloaddition forming its coligand isomer, a tetrazolate complex **26**. Analogous coligand isomers were observed with Pd^{II}, only instead of PPh_3 ligands bidentate diphosphine ligand is presented [54].

Coligand isomers also function as intermediates in the course of proposed mechanisms for reactions connected with a nucleophilic attack on suitable centres; reactions which have been reported include Bercaw et al. [55], Fischer [56], as well as Schrock et al. [57,58].



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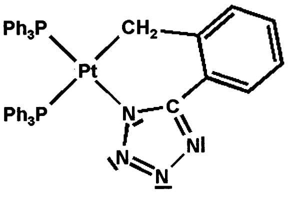

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From the examples presented, coligand isomerism has some general importance in transition metal chemistry.

5. Factors influencing the course of nucleophilic additions with pseudohalides

The nucleophilic addition of the pyrazole type ligand to the pseudohalide in the metal coordination sphere is influenced by the character of the central ion, of the pseudohalide as well as of the neutral ligand.

The coordination sphere of copper(II) provides the best conditions for the course of the nucleophilic addition, which is caused by its plasticity [59]. Similarly, the coordination spheres of palladium(II) and platinum(II) support the addition apparently owing to their tendency to form square planar species, without any axial interaction [12]. In the Pd^{II} and Pt^{II} systems, unlike other central ions, isomeric pseudohalogeno complexes are not formed. In the coordination sphere of nickel(II), however, the nucleophilic addition proceeds only rarely, and even more rarely in the case of cobalt(II) [9,10,26]. This is very likely connected with the ability of these central atoms to form monomeric complexes $[MX_2L_4]$, in which unfavorable conditions for nucleophilic addition exist. In the case of cobalt(II) with its inclination to form monomeric tetrahedral species $[CoX_2L_2]$ the nucleophilic addition is also prevented.

The reactivity (see Table 1) towards the pyrazole type ligands decreases in the following order: $NCO^- > N(CN)_2^- > C(CN)_3^- > ONC(CN)_2^-$.

The steric properties of the pseudohalides are also important, especially in the case of non-linear anions. Thus the tricyanomethanide and nitrosodicyanomethanide ions with their large steric requirements are less reactive.

With neutral ligands two aspects controlling the course of nucleophilic addition must be considered, viz. the electron density in the pyrazole ring and the steric effect of the ligands. The influence of the pyrazole electron density is definitely revealed in systems of Cu^{II} and NCO^- [5,13,24,26,28,36,37].

Another situation, however, was observed in systems of non-linear pseudohalides. In these cases the pyrazole electron density is not explicitly manifested, whereas the steric bulk of the pyrazoles as well as of the pseudohalide ligands apparently play a more important role in the nucleophilic attacks.

Further, the nucleophilic addition proceeds only with five-membered rings in which the tertiary nitrogen is situated in an *ortho*-position to the imine group. The second *ortho*-position is occupied with a CH group.

Whereas the nucleophilic addition of pyrazole ligands to pseudohalides is fairly general, the reaction of methanol with dicyanamide proceeds exclusively in the coordination sphere of copper(II) (already at r.t.), perhaps due to the plasticity of the Cu^{II} coordination sphere [59].

6. Electronic properties

According to their d–d spectra the chelate complexes $[Cu(pzt\cdot NCO)_2]$ are often square-planar without any significant or with only relatively weak axial interaction [5,24,25,27,28,36,38]. Such axial interaction may occur through weak bonding to the Cu^{II} ions by carbamoyl oxygens of adjacent $[Cu(pzt\cdot NCO)_2]$ molecules and thus, the copper coordination number is enhanced to $4+2$ (tetragonal bipyramid) or $4+1$ (tetragonal pyramid). On the other hand, the corresponding isomeric cyanato complexes $[Cu(NCO)_2(pzt)_2]$ are mostly pseudooctahedral (in some cases tetragonal pyramidal) showing axial interaction of the Cu^{II} ions with oxygen or—more rarely—nitrogen atoms of the cyanate groups which are *N*-coordinated in neighbouring moieties [4]. This general difference between the structures of the two groups of isomeric complexes is a consequence of the equatorial–axial influence displayed in copper(II) complexes [60]. Similar structural differences appear in the coligand isomer pair $[Ni(tmpz \cdot NCO)_2]$ and $[Ni(NCO)_2(tmpz)_2]$ [26]. Some isomers of the $[Cu(pzt \cdot NCO)_2]$ complexes [5,36] exhibit distortion of their coordination polyhedra (distortion isomerism) [59].

From ligand field spectra, the chelates $[M(ptz \cdot X)_2]$, where $X = N(CN)_2$, $C(CN)_3$, exhibit square-planar chelate systems such that each M^{II} central ion forms one or two axial bonds of various length with cyano nitrogen atoms of adjacent moieties, so that the donor arrangement is elongated octahedral or octahedral [10,11,13,14,29].

The square-planar structure determined for $[Cu(mici)_2]$ (**3a**) remains unchanged in DMSO, DMF and py solutions according to its d–d band [7], indicating that the complex is essentially inert to ligation in axial sites.

The ligand field spectra of the nickel(II) bis-chelates $[Ni(mcoe)_2L_2]$ for L = pz, tmpz or H_2O [8,31] indicate an octahedral donor arrangement, established in two cases by X-ray crystallography (see Sections 2.1 and 3.3). The d–d spectra indicate, that the $(mcoe)^-$ chelates of Cu^{II}, Co^{II} and Pd^{II} show elongated pseudooctahedral, approximately octahedral, and square-planar geometry, respectively [32].

The EPR spectra of the solid copper(II) compounds are of normal axial type in most cases [5,7,11,14,29,36], more rarely they are isotropic or pseudoisotropic [27,28], exceptionally orthorhombic [28].

The EPR spectrum of $[Cu(mici)_2]$ (**3a**), measured in frozen (100 K) toluene solution [7], shows two parallel components of the Cu hyperfine structure, each split into superhyperfine lines from four equivalent ^{14}N nuclei. The perpendicular part of the spectrum is more complex.

The magnetic properties of $[Cu\{pz \cdot N(CN)_2\}_2]$ [11], $[Cu\{pz \cdot C(CN)_3\}_2]$ [29], $[Cu(mici)_2]$ [61] and *trans*-$[Ni(mcoe)_2(H_2O)_2]$ (**15a**) [62,63] were studied in more detail. For the first compound, a definite, but slight magnetic interaction ($|J| < 0.5$ cm^{-1}) was ascertained between its structure units. In $[Cu\{pz \cdot C(CN)_3\}_2]$ polymeric chains were assumed within and between which magnetic interaction operates.

In the case of *trans*-$[Ni(mcoe)_2(H_2O)_2]$ (**15a**), a numerical procedure gives the optimum set of magnetic parameters $g_x = g_y$, g_z, D, E, zJ and TIP.

7. Concluding remarks

A new type of chemical reaction was discovered—the nucleophilic addition of pyrazole moieties to cyanate groups in the coordination sphere of a transition metal ion. This reaction leads to formation of new anionic chelate ligands of the carbamoylpyrazolate type, which can be released from the coordination sphere in neutral form, and thus the corresponding organic compounds can be isolated. The conditions of the nucleophilic addition were studied and determined by selection of various central ions as well as different nitrogen heterocyclic ligands.

Replacing the cyanate group by non-linear pseudohalide groups, $N(CN)_2^-$, $C(CN)_3^-$ or $ONC(CN)_2^-$, nucleophilic addition under suitable conditions also takes place and anionic chelate ligands of cyanamido-, dicyanomethanido- or nitrosocyanomethanido-carbamoylpyrazolate type arise. The conditions in this case are distinctly different in comparison with the cyanate case because of electronic and especially steric properties of the non-linear pseudohalides.

A new type of isomerism has been discovered, namely coligand isomerism. One isomer contains pseudohalide (X^-) and pyrazole (pzt) ligands, whereas the other exhibits anionic chelate ligands $(pzt \cdot X)^-$ formed by a nucleophilic addition of X^- to pzt.

Another type of nucleophilic addition of the methanol oxygen atom to the cyano nitrogen atoms of the dicyanamide anion forms a new anionic chelate ligand, dimethylimidodicarbonimidate, $mici^-$. This ligand closes a stable six-membered metallacycle with a Cu^{II} ion, the skeleton of which is isoelectronic with β-diketonates. The reaction is highly specific for copper(II).

Substitution of Cu^{II} by Ni^{II} and Co^{II} ions leads to complexes $[Ni(mici)_2]$ and $[Co(mici)_3]$, respectively; in the latter case, oxidation of Co^{II} to Co^{III} took place.

A third type of nucleophilic addition in the transition metal coordination sphere was observed in systems with nitrosodicyanomethanide. The methanol oxygen atom is linked to a carbon of one cyano group of the nitrosodicyanomethanide anion and a new anionic chelate ligand arises. This ligand forms a strictly planar five-membered metallacycle with a central ion. This nucleophilic addition was observed in systems with Ni^{II}, Cu^{II}, Co^{II} (with oxidation to Co^{III}), and also Pd^{II}. An analogous nucleophilic addition was also established with ethanol.

A common feature of these transformations is coordinative activation of the carbon β-site of the pseudohalide, NCO^-, $N(CN)_2^-$, $C(CN)_3^-$ and $ONC(CN)_2^-$. We assume that bending of the linear $N{-}C_\beta{-}X$ arm of the pseudohalide (sp hybridized carbon) is caused by *N*-coordination and the carbon β-site becomes sp^2 hybridized, with an unsaturated valency, and thus becomes susceptible to nucleophilic attack.

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