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Molecular structures and spin-states of pseudohalide metal complexes with hydrazones of Girard's T reagent

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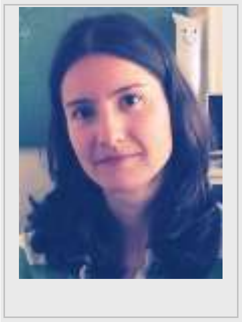
Abstract

The pseudohalide metal complexes with hydrazones of Girard's T reagent are reviewed with respect to their synthesis, characterization, structures (in both solution and solid state) and magnetic properties. This microreview can serve as a concise guide through chemistry of pseudohalide metal complexes with hydrazones of Girard's T reagent.

Keywords: metal complexes, pseudohalides, Girard's T reagent hydrazones, physico-chemical characteristics, X-ray crystallography.

Milica R. Milenković obtained her Ph.D. degree in Chemistry from University of Belgrade, working under the supervision of Prof. Katarina Anđelković. She worked as post-doc researcher in the group of Prof. Dr. Igor N. Shcherbakov at Southern Federal University, Russia. She is assistant professor at Faculty of Chemistry, University of Belgrade. Her researches are oriented towards investigations of structures and properties of hydrazone metal complexes.



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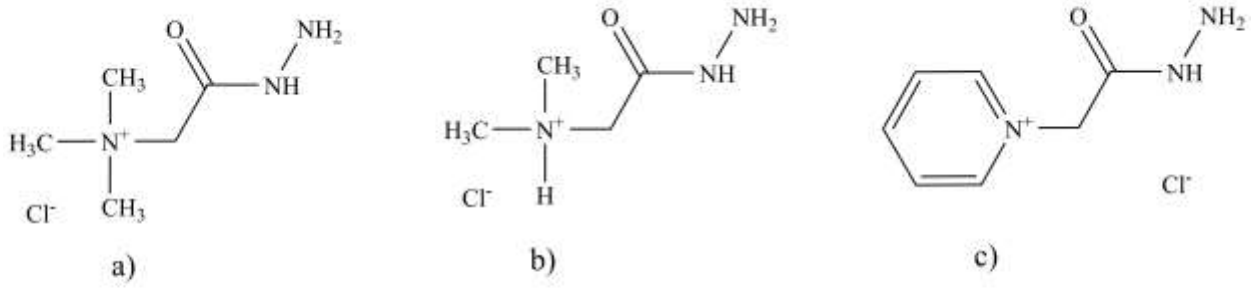
Božidar Čobeljić received his PhD in Chemistry in 2015 (Faculty of Chemistry, University of Belgrade, Serbia), in the study of magnetic properties and biological activity of hydrazone metal complexes. In 2014 he joined Ecostbio as an assistant in the team of prof Katarina Anđelković. In 2016 he continued his work with postdoctoral fellowship at Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia.

Katarina Anđelković is Full Professor at Faculty of Chemistry, University of Belgrade, Serbia. She is Chief of the Department of General and Inorganic Chemistry. Her main research interests are coordination and bioinorganic chemistry. The focus of her work in last years are investigations of structure-activity relationship of biological active metal complexes and their possible applications.

Iztok Turel is Professor of Inorganic Chemistry at the University of Ljubljana, Slovenia. He is (co)author of more than 110 publications, with Hirsch index of 35. His main research interests are coordination and bioinorganic chemistry. His group is dealing with interactions of biologically active ligands (quinolones, azoles, diketonates, hydrazones, hydroxyquinolines, pyrithione, etc) with metal ions. The focus of his work in last years are ruthenium complexes and their applications (biological activity, catalysis).

1. Introduction

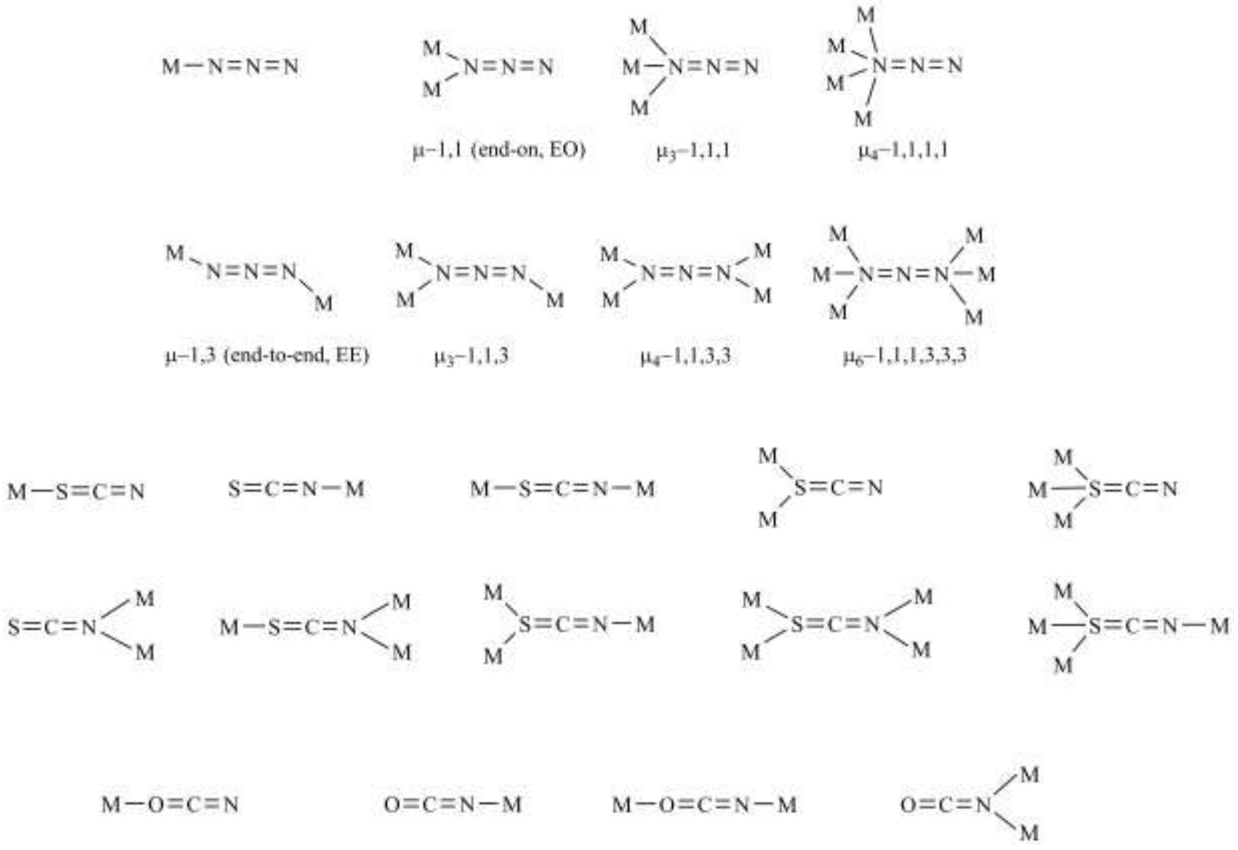
Girard’s reagents are *N*-substituted glycine hydrazides.[1, 2] The main application of Girard’s reagents is for the separation of carbonyl compounds from complex organic mixtures. In the reaction of Girard's reagents with carbonyl groups water soluble hydrazones are formed, which can be easily separated from mixtures soluble in non-polar solvents.[1–5] There are three different types of Girard’s reagent (Scheme 1): 1) Girard’s T (trimethylacetylhydrazide ammonium chloride) [6] 2) Girard’s D (*N*,*N*-dimethylglycine hydrazide hydrochloride) [7] 3) Girard’s P (pyridinioacetohydrazide chloride).[6]



Scheme 1: Girard’s reagents: a) Girard’s T (trimethylacetylhydrazide ammonium chloride) b) Girard’s D (*N*,*N*-dimethylglycine hydrazide hydrochloride) c) Girard’s P (pyridinioacetohydrazide chloride)

The Girard's T reagent was synthesized first by A. Girard and G. Sandulesco in 1936, in the reaction of ethyl chloroacetate with trimethylamine.[6] Among the Girard’s reagents the largest number of the complexes have been synthesized with the Girard’s T reagent. In the reported complexes Girard’s T reagent was coordinated to metal ions through terminal hydrazine nitrogen atom and carbonyl oxygen atom, forming a five-membered chelate ring.[8] Whereas the chemistry of acylhydrazone and semicarbazone metal complexes has been intensively studied, relatively small number of metal complexes with Girard’s reagents hydrazones have been synthesized until now. In the reported complexes, the Girard’s reagents hydrazones behave as mono-, di-, tri- and pentadentate ligands.[8–15] The Girard’s T reagent hydrazones exhibit keto-enol tautomerism and can coordinate metal ions in non-deprotonated positively charged form or deprotonated formally neutral zwitter-ionic form. The presence of the quaternary ammonium group in the metal complexes of Girard’s T reagent hydrazones increases their water solubility and has effect on their biological activity.[15]

Pseudohalide ligands (azide, cyanate and thiocyanate) exhibits versatile coordination modes. They can be coordinated as monodentates or as bridges between metal centers (Scheme 2).[16,17] Among pseudohalide ligands the homoatomic azide is the most used for the synthesis of polynuclear complexes in which it displays different bridging coordination modes: single and double $\mu_{1,3}$-N_3 (end-to-end, EE) and $\mu_{1,1}$-N_3 (end-on, EO), $\mu_{1,1,3}$-N_3, $\mu_{1,1,1}$-N_3, $\mu_{1,1,1,1}$-N_3, $\mu_{1,1,3,3}$-N_3, and $\mu_{1,1,1,3,3,3}$-N_3.[16] Azido bridges in such complexes mediate different types of magnetic exchange interactions, which magnitude depends on the distance between metal ions, dihedral angle between the planes containing metal ions and metal-bridging ligand bond lengths.[18] In most of the cases antiferromagnetic coupling is associated with end-to-end ($\mu_{1,3}$-N_3) coordination of azido ligand,[19–21] while end-on ($\mu_{1,1}$-N_3) coordination mode results in ferromagnetic coupling.[22–24] Ambidentate cyanate and thiocyanate ligands exhibit linkage isomerism and may coordinate through nitrogen or chalcogen (oxygen or sulfur donor atoms) as a monodentate or bridging ligand.[17]

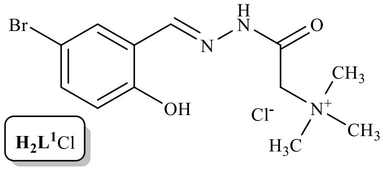
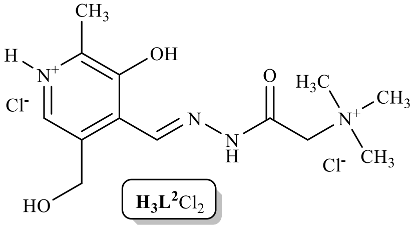
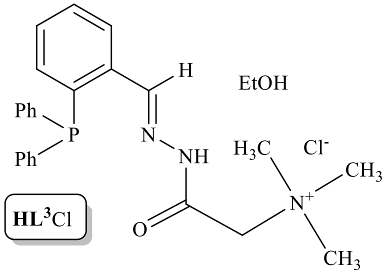


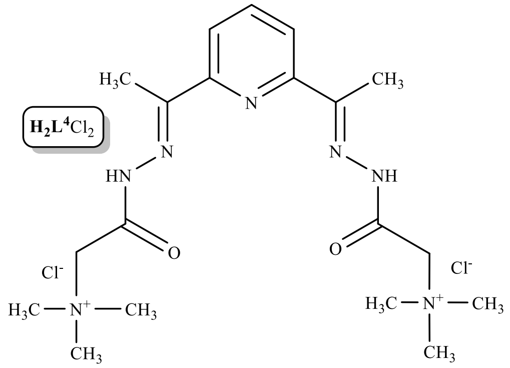
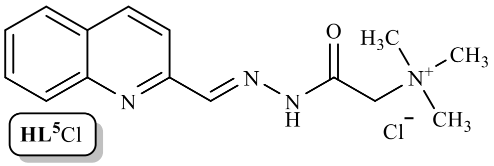
Scheme 2. Coordination modes of selected pseudohalide ligands (azido, thiocyanato/isothiocyanato, isocyanato/cyanato)

Spin as a fundamental property of molecules which originates from their unpaired electrons determine their electronic properties, structure, reactivity, magnetic and spectroscopic properties. The most of organic molecules have a closed-shell electronic structure with singlet ground state. Spin-states of transition metal ions in complexes are determined by occupation of their d-orbitals, which depend on the oxidation state of metal and its coordination surrounding.[25] In some complexes metal ion can exist in several spin states and small energy difference between these states allows that certain stimulus as light, heat or pressure can induce reversible switch of predominant population of two states.[26] Insight into spin states of metal ions in complexes can be obtained by spectroscopy, magnetic measurements and computational studies.[25,26]

In 2012. Leovac at all provided a detailed review about metal complexes with Girard's reagents and their hydrazones.[8] This review also covers some pseudohalide metal complexes with Girard’s T reagent hydrazones which were reported until 2012.[27,28] In recent years our two research groups (K. Anđelković and co-workers and I. Turel and co-workers) have given significant contribution in the research of coordination chemistry of pseudohalide metal complexes with Girard’s T reagent hydrazones.[29–39] The summary of pseudohalide metal complexes with Girard’s T reagent hydrazones, which are reported until now is given in Table 1. Their synthesis, characterization, structures (in both solution and solid state) and magnetic properties will be discussed in following sections.

Table 1. The pseudohalide metal complexes with Girard's T reagent hydrazones

Ligand	Complexes	Geometry	Magnetic data	ref.
 **H_2L^1**Cl	[Fe(**L**^{1})(NCS)$_2$(H$_2$O)] (**1**)	OC-6	μ_{eff}=5.81 μ_B	[27]
 **H_3L^2**Cl$_2$	[Cu(**HL**^{2})(NCS)$_2$] (**2**) [Zn(**HL**^{2})(NCS)$_2$]·H$_2$O (**3**) [Cu(**L**^{2})N$_3$] (**4**)	SP-5 TB-5 SP-4	μ_{eff}=1.75 μ_B diamagnetic μ_{eff}=2.13 μ_B	[28]
 **HL^3**Cl	[Ni(**HL**^{3})(NCS)$_3$]·H$_2$O (**5**) [Ni(**L**^{3})(NCS)]BF$_4$·2H$_2$O (**6**) [Ni(**L**^{3})(NCS)]SCN·H$_2$O (**7**) [Ni(**L**^{3})(NCO)]BF$_4$ (**8**) [Ni(**L**^{3})N$_3$]BF$_4$ (**9**)	OC-6 SP-4 SP-4 SP-4 SP-4	μ_{eff} = 3.1 μ_B diamagnetic diamagnetic diamagnetic diamagnetic	[29–31]

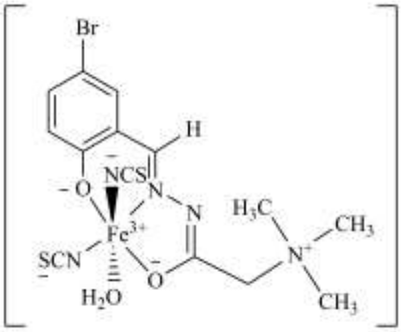
 $\mathbf{H_2L^4}Cl_2$	$[Mn(\mathbf{H_2L^4})(NCS)_2](SCN)_2\cdot CH_3OH$ (**10**)	PBPY-7	$\mu_{eff} = 5.89\ \mu_B$	[32–35]
	$[Co(\mathbf{H_2L^4})(NCS)_2](SCN)_2\cdot 2H_2O$ (**11**)	PBPY-7	$\mu_{eff} = 4.98\ \mu_B$	
	$[Co(\mathbf{H_2L^4})(NCS)_2][Co(NCS)_4]\cdot 2H_2O$ (**12**)	PBPY-7, T-4	$\mu eff = 2.65 \mu_B$	
	$[Ni(\mathbf{H_2L^4})(NCS)_2](SCN)_2\cdot 2H_2O$ (**13**)	PBPY-7	$\mu_{eff} = 3.04\ \mu_B$	
	$[Zn(\mathbf{H_2L^4})(NCS)_2][Zn(NCS)_4]\cdot 2H_2O$ (**14**)	PBPY-7, T-4	diamagnetic	
	$[Cd(\mathbf{H_2L^4})(NCS)_2][Cd(NCS)_4]\cdot 2H_2O$ (**15**)	PBPY-7, T-4	diamagnetic	
	$[Fe(\mathbf{L^4})(NCS)_2](SCN)\cdot 2H_2O$ (**16**)	PBPY-7	n.d.	
	$[Fe(\mathbf{L^4})(NCS)_2][Fe(NCS)_5(H_2O)]\cdot 4H_2O$ (**17**)	PBPY-7, OC-6	n.d	
 $\mathbf{HL^5}Cl$	$[Ni_2(\mathbf{L^5})_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\ H_2O\cdot CH_3OH$ (**18**)	OC-6	$\mu_{eff} = 3.16\ \mu_B\ (J = +12.0(2)\ cm^{-1})$	[36–39]
	$[Co(\mathbf{HL^5})(N_3)_3]$ (**19**)	OC-6	$\mu_{eff} = 1.65\ \mu_B$	
	$[Co_2(\mathbf{L^5})_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (**20**)	OC-6	n.d	
	$[Zn(\mathbf{L^5})(N_3)_2]$ (**21**)	SP-5	diamagnetic	
	$[Zn(\mathbf{L^5})(NCO)_2]$ (**22**)	SP-5	diamagnetic	
	$[Cd(\mathbf{L^5})(NCO)_2]$ (**23**)	SP-5	diamagnetic	

n.d.- not determined, SP-4 – square-planar, T-4 – tetrahedral, TB-5 – trigonal-bipyramidal, SP-5 – square-pyramidal, OC-6 – octahedral, PBPY-7 – pentagonal-bipyramidal

2. Pseudohalide metal complexes with Girard's T reagent hydrazones

2.1. Pseudohalide metal complexes with the condensation product of 5-bromosalicylaldehyde and Girard's T reagent

Isothiocyanato iron(III) complex [Fe(**L**^{1})(NCS)$_2$(H$_2$O)] (**1**) (Scheme 3) with the condensation product of Girard's T reagent and 5-bromosalicylaldehyde (**H$_2$L^1**Cl) was synthesized in the reaction of an aqueous ethanolic solution of the chlorido iron(III) complex with the same hydrazone ligand [Fe(**L**^{1})Cl$_2$] and NH$_4$NCS. In the isothiocyanato iron(III) complex the octahedral surrounding of Fe(III) consists of ONO donor atoms of doubly deprotonated hydrazone ligand, two nitrogen atoms of the NCS$^-$ and the oxygen atom of a water molecule. In complex **1** Fe(III) is in high-spin state (μ_{eff} = 5.81 μ_B) and acts as ordinary paramagnet down to 2 K.[27]

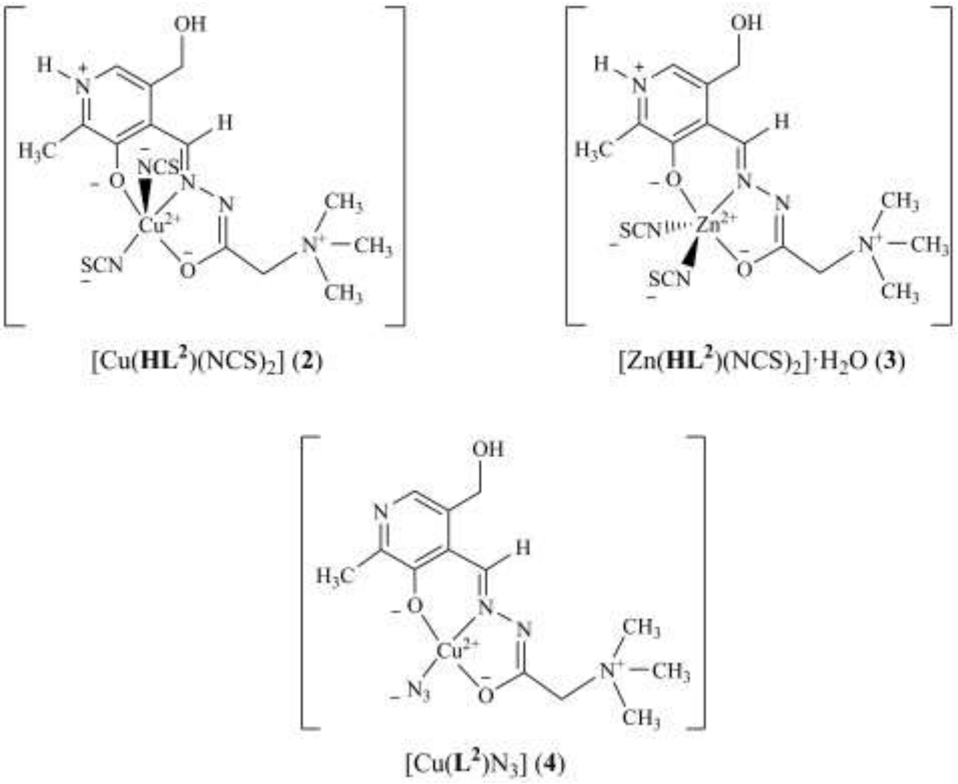


[Fe(**L**^{1})(NCS)$_2$(H$_2$O)] (**1**)

Scheme 3. Structure of isothiocyanato iron(III) complex [Fe(**L**^{1})(NCS)$_2$(H$_2$O)] (**1**) with the condensation product of Girard's T reagent and 5-bromosalicylaldehyde (**H$_2$L^1**Cl)

2.2. Pseudohalide metal complexes with the condensation product of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde and Girard's T reagent

Isothiocyanato Cu(II) and Zn(II) complexes (Scheme 4) with the condensation product of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde and Girard's T reagent (**H$_3$L^2**Cl$_2$) i.e. [Cu(**HL**^{2})(NCS)$_2$] (**2**) and [Zn(**HL**^{2})(NCS)$_2$]·H$_2$O (**3**) were obtained in the reaction of the corresponding chlorido [M(**HL**^{2})Cl$_2$] complexes with excess of NH$_4$NCS. X-ray analysis of complex **2** showed the square-pyramidal coordination surrounding of Cu(II) which consists of two N coordinated NCS$^-$ monodentate ligand and doubly-deprotonated hydrazone coordinated through enol-form of deprotonated carbonyl oxygen, azomethine nitrogen and oxygen of deprotonated phenol hydroxyl. On the basis of IR spectra the same coordination mode of hydrazone ligand was suggested for complex **3**. In the IR spectra of complex **3** only one band was observed in the ν(CN) vibration range of NCS^{-} group indicating almost equivalent position of both NCS^{-} groups coordinated through nitrogen. Azido Cu(II) complex with triply-deprotonated condensation product of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde and Girard's T reagent $[Cu(\mathbf{L^2})N_3]$ (**4**) (Scheme 4) was synthesized in the reaction of $[Cu(\mathbf{HL^2})Cl_2]$ complex with excess of NaN_3. The values of effective magnetic moments for complexes **2** and **4** (μ_{eff} = 1.75 μ_B and μ_{eff} = 2.13 μ_B, respectively) correspond to unchanged oxidation state of Cu(II) in both complexes. In DMF solution complexes **3** and **4** are non-electrolytes. Contrary to them, complex **2** is 1 : 1 electrolyte in DMF solution due to dissociation of weakly coordinated apical NCS^{-} ligand. The molar conductivity values for complexes **2**, **3** and **4** in water indicate that complete dissociation of pseudohalide ligands occurred.[28]



$[Cu(\mathbf{HL^2})(NCS)_2]$ (**2**)

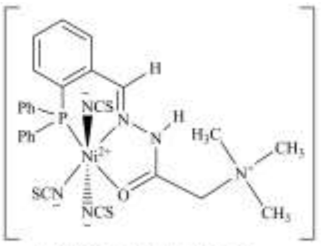
$[Zn(\mathbf{HL^2})(NCS)_2]\cdot H_2O$ (**3**)

$[Cu(\mathbf{L^2})N_3]$ (**4**)

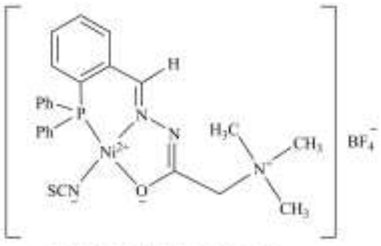
Scheme 4. Structures of pseudohalide metal complexes with the condensation product of 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde and Girard's T reagent

2.3. Pseudohalide metal complexes with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent

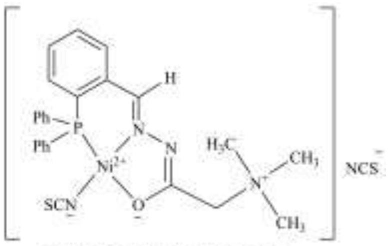
Octahedral [Ni(**HL**^{3})(NCS)$_3$]·H$_2$O (**5**) and square-planar [Ni(**L**^{3})(NCS)]BF$_4$·2H$_2$O (**6**), [Ni(**L**^{3})(NCS)]SCN·H$_2$O (**7**) isothiocyanato complexes of Ni(II) with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent (**HL**^{3}Cl EtOH) (Scheme 5) were synthesized and structurally characterized. Stoichiometry and geometry of these complexes depend on the source of Ni^{2+} and NCS$^-$ ions used in the reaction. In the reaction of hydrazone ligand (**HL**^{3}Cl EtOH), Ni(BF$_4$)$_2$·6H$_2$O and KSCN in molar ratio 1 : 1: 3 in methanol, the neutral octahedral complex [Ni(**HL**^{3})(NCS)$_3$]·H$_2$O (**5**) was obtained. In complex **5** the hydrazone ligand is coordinated as tridentate through phosphorus, imine nitrogen and carbonyl oxygen atoms, while the remaining three coordination positions are occupied with *mer* N-coordinated thiocyanate anions. In the reaction of hydrazone ligand **HL**^{3}Cl EtOH, Ni(BF$_4$)$_2$·6H$_2$O and NH$_4$SCN square-planar [Ni(**L**^{3})(NCS)]BF$_4$·2H$_2$O (**6**) complex was formed. The cationic complex in compound **6** consisted of one molecule of deprotonated ligand coordinated in a tridentate PNO fashion to Ni(II) and a thiocyanate anion coordinated through nitrogen atom. Reaction of Ni(AcO)$_2$·4H$_2$O, **HL**^{3}Cl EtOH ligand and KSCN in molar ratio 1 : 1 : 3 in methanol gives square-planar Ni(II) [Ni(**L**^{3})(NCS)]SCN·H$_2$O (**7**) complex (Scheme 5). In this compound the same cationic complex as in compound **6** is counterbalanced with a thiocyanate anion.



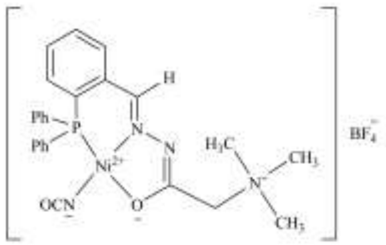
[Ni(**HL**^{3})(NCS)$_3$]·H$_2$O (**5**)



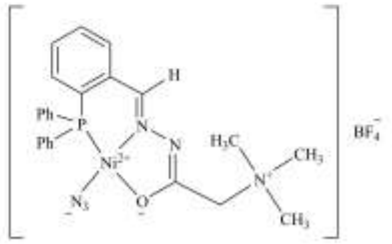
[Ni(**L**^{3})(NCS)]BF$_4$·2H$_2$O (**6**)



[Ni(**L**^{3})(NCS)]SCN·H$_2$O (**7**)



[Ni(**L**^{3})(NCO)]BF$_4$ (**8**)



[Ni(**L**^{3})N$_3$]BF$_4$ (**9**)

Scheme 5. Structures of pseudohalide Ni(II) complexes **5**–**9** with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent (**HL^3**Cl EtOH)

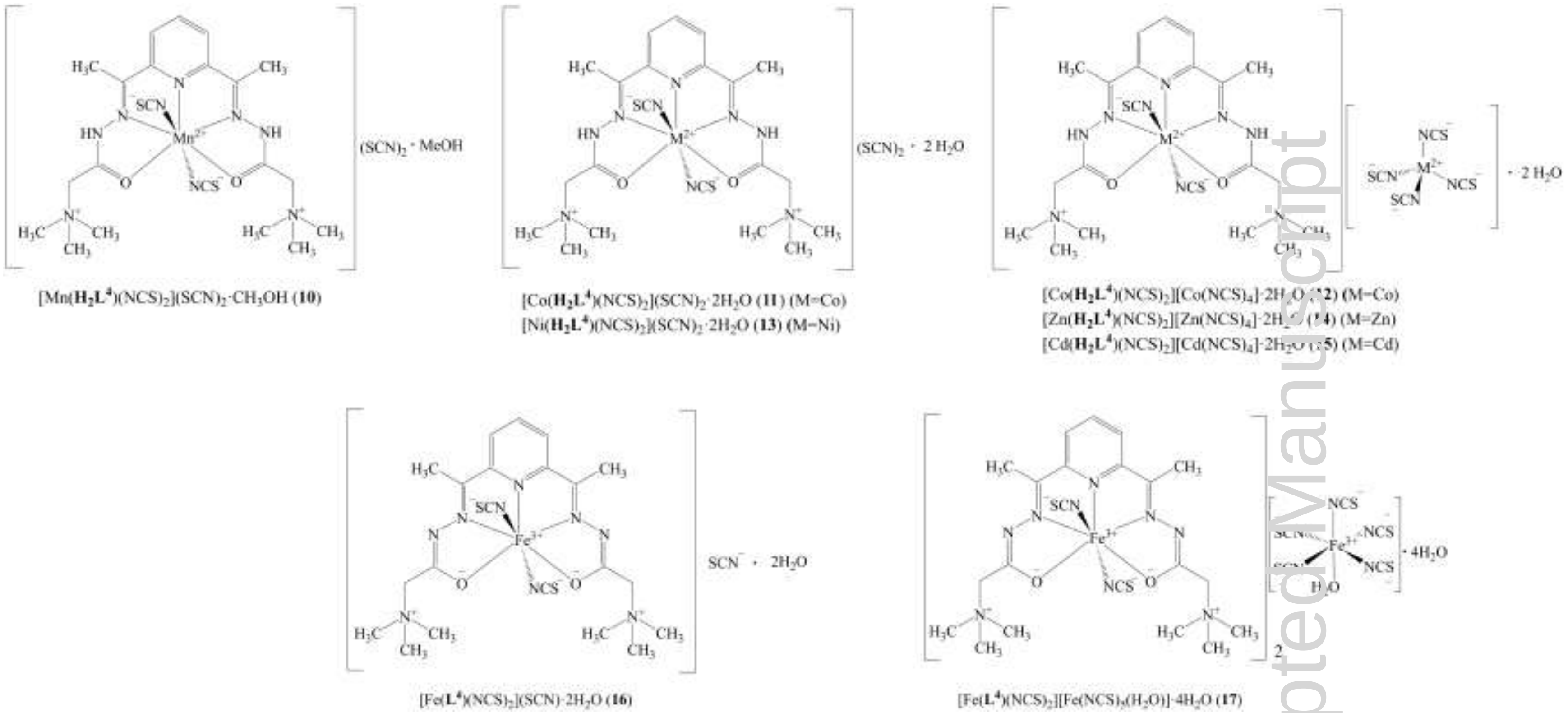
The effective magnetic moment of complex **5** μ_{eff} = 3.1 μ_B, is slightly higher than the spin-only value for Ni^{2+} ion (μ_{eff} = 2.82 μ_B), but it is in a good agreement with literature data for Ni^{2+} in octahedral environment. Reaction energetics and ligand field splittings of Ni(II) complexes with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent were studied by means of density functional theory (DFT). The trends in calculated electronic energies, reaction enthalpies and Gibbs free energies indicate that the formation of the octahedral complex with non deprotonated hydrazone ligand, is much more favorable than with the deprotonated one. The results of the analysis of the ligand field splitting in complexes with protonated and deprotonated forms of hydrazone ligand show that deprotonated form of the ligand produces a stronger orbital splitting both in square-planar and in octahedral environment. The results of theoretical calculations are in accordance with the experimental results, since the low spin square-planar structures **6** and **7** that require the stronger ligand field are isolated only with the deprotonated ligand, while the high-spin octahedral structure **5** is found with the protonated form. The reaction of **HL^3**Cl EtOH ligand with $Ni(BF_4)_2{\cdot}6H_2O$ and KSCN in methanol is favored due to the precipitation of insoluble KBF_4, which shifts the reaction equilibrium towards formation of octahedral complex **5**. Also, formation of an infinite chain of complex and water molecules connected by hydrogen bonds stabilizes octahedral structure of compound **5** in solid state.[29]

Isocyanato ([Ni(**L^3**)(NCO)]BF_4 (**8**)) and azido ([Ni(**L^3**)N_3]BF_4 (**9**)) complexes of Ni(II) with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent (**HL^3**Cl EtOH) (Scheme 5) were synthesized in the reaction of **HL^3**Cl EtOH, $Ni(BF_4)_2{\cdot}6H_2O$ and excess of NaOCN or NaN_3, respectively. In both of the complexes **8** and **9** square-planar surroundings of Ni(II) ion in complex cation consist of the deprotonated zwitterionic acylhydrazone ligand coordinated as a tridentate through phosphorus, imine nitrogen and carbonyl oxygen atoms and monodentate pseudohalide ligand in the fourth coordination place.[30,31] In electronic absorption spectra of square-planar nickel(II) complexes **6**–**9** in water and DMSO solutions the bands related to the d–d electronic transition ($d_{x2-y2} \leftarrow d_{xy}$), at 17000–22000 cm^{-1} or 600–450 nm region were not observed, so it is possible that change in the geometry to octahedral occurs, because the characteristic bands in electronic spectra of octahedral Ni(II) complexes are in the

Vis–NIR region (25000–4000 cm^{-1} or 400–250 nm). NMR spectra of square-planar Ni(II) complexes **6**–**9** in DMSO give additional support for change of geometry, since line broadening and loss of hyperfine splitting occurred, due to the presence of paramagnetic Ni(II) species in DMSO solution.[31]

2.4. Pseudohalide metal complexes with the condensation product of 2,6-diacetylpyridine and Girard's T reagent

Isothiocyanato complexes of Mn(II) ([Mn($\mathbf{H_2L^4}$)(NCS)$_2$](SCN)$_2$·CH$_3$OH) (**10**), Co(II) ([Co($\mathbf{H_2L^4}$)(NCS)$_2$](SCN)$_2$·2H$_2$O (**11**) and [Co($\mathbf{H_2L^4}$)(NCS)$_2$][Co(NCS)$_4$]·2H$_2$O (**12**)), Ni(II) ([Ni($\mathbf{H_2L^4}$)(NCS)$_2$](SCN)$_2$·2H$_2$O (**13**)), Zn(II) ([Zn($\mathbf{H_2L^4}$)(NCS)$_2$][Zn(NCS)$_4$]·2H$_2$O (**14**)) and Cd(II) ([Cd($\mathbf{H_2L^4}$)(NCS)$_2$][Cd(NCS)$_4$]·2H$_2$O (**15**)) with the condensation product of 2,6-diacetylpyridine and Girard's T reagent ($\mathbf{H_2L^4}$Cl$_2$) (Scheme 6) were obtained in the reaction of dihydrazone ligand, NH$_4$SCN and corresponding metal(II) salts (chloride in the case of Mn(II) (**10**), Ni(II) (**13**), Co(II) (**11** and **12**) and Zn(II) (**14**) complexes or nitrate in the case of Cd(II) complex (**15**)). X-ray analysis of Mn(II) (**10**), Ni(II) (**13**), Zn(II) (**14**) and both Co(II) complexes (**11** and **12**) showed the pentagonal-bipyramidal (PBPY-7) coordination surrounding of metal(II) which consist of dihydrazone ligand symmetrically coordinated through N$_3$O$_2$ donor atoms in equatorial plane and two N coordinated NCS$^-$ monodentate ligand in axial positions.[32–35] Contrary to complexes **10**, **11** and **13** in complexes **12**, **14** and **15** the counter ion of PBPY-7 complex cation is anionic tetrahedral [M(NCS)$_4$]$^{2-}$ instead of two SCN$^-$ ligands.[32–34]



[Mn($\mathbf{H_2L^4}$)$(NCS)_2$]$(SCN)_2\cdot CH_3OH$ (**10**)

[Co($\mathbf{H_2L^4}$)$(NCS)_2$]$(SCN)_2\cdot 2H_2O$ (**11**) (M=Co)
[Ni($\mathbf{H_2L^4}$)$(NCS)_2$]$(SCN)_2\cdot 2H_2O$ (**13**) (M=Ni)

[Co($\mathbf{H_2L^4}$)$(NCS)_2$][Co$(NCS)_4$]$\cdot 2H_2O$ (**12**) (M=Co)
[Zn($\mathbf{H_2L^4}$)$(NCS)_2$][Zn$(NCS)_4$]$\cdot 2H_2O$ (**14**) (M=Zn)
[Cd($\mathbf{H_2L^4}$)$(NCS)_2$][Cd$(NCS)_4$]$\cdot 2H_2O$ (**15**) (M=Cd)

[Fe($\mathbf{L^4}$)$(NCS)_2$](SCN)$\cdot 2H_2O$ (**16**)

[Fe($\mathbf{L^4}$)$(NCS)_2$][Fe$(NCS)_5(H_2O)$]$\cdot 4H_2O$ (**17**)

Scheme 6. Structures of pentagonal-bipyramidal isothiocyanato complexes of Mn(II) (**10**), Co(II) (**11** and **12**), Ni(II) (**13**), Zn(II) (**14**) Cd(II) (**15**) and Fe(III) (**16** and **17**) with the condensation product of 2,6-diacetylpyridine and Girard’s T reagent ($\mathbf{H_2L^4}Cl_2$)

The values of effective magnetic moments for complexes **10**, **13** and **11** measured at room temperature (μ_{eff} = 5.89 μ_B, μ_{eff}= 3.94 μ_B and μ_{eff}= 4.98 μ_B, respectively) correspond to high-spin state of metal(II) in the complexes.[32, 33] The electronic absorption spectra of complexes **11** and **12** showed the presence of pentagonal-bipyramidal complex cation. In the spectrum of complex **12** the absorption maximum at 625 nm which corresponds to tetrahedral $[Co(NCS)_4]^{2-}$ was not observed, due to its low stability in water. Low stability of tetrahedral $[Co(NCS)_4]^{2-}$ was also confirmed on the basis of molar conductivity values for complexes **11** and **12** in water, which corresponds to 1 : 2 electrolytes. These results indicate that transformation of complex **12** presented with equation 1 occurs in aqueous solution.[33]

$$[Co(\mathbf{H_2L^4})(NCS)_2][Co(NCS)_4] \rightleftharpoons [Co(\mathbf{H_2L^4})(NCS)_2]^{2+} + [Co(H_2O)_6]^{2+} + 4SCN^- \qquad (1)$$

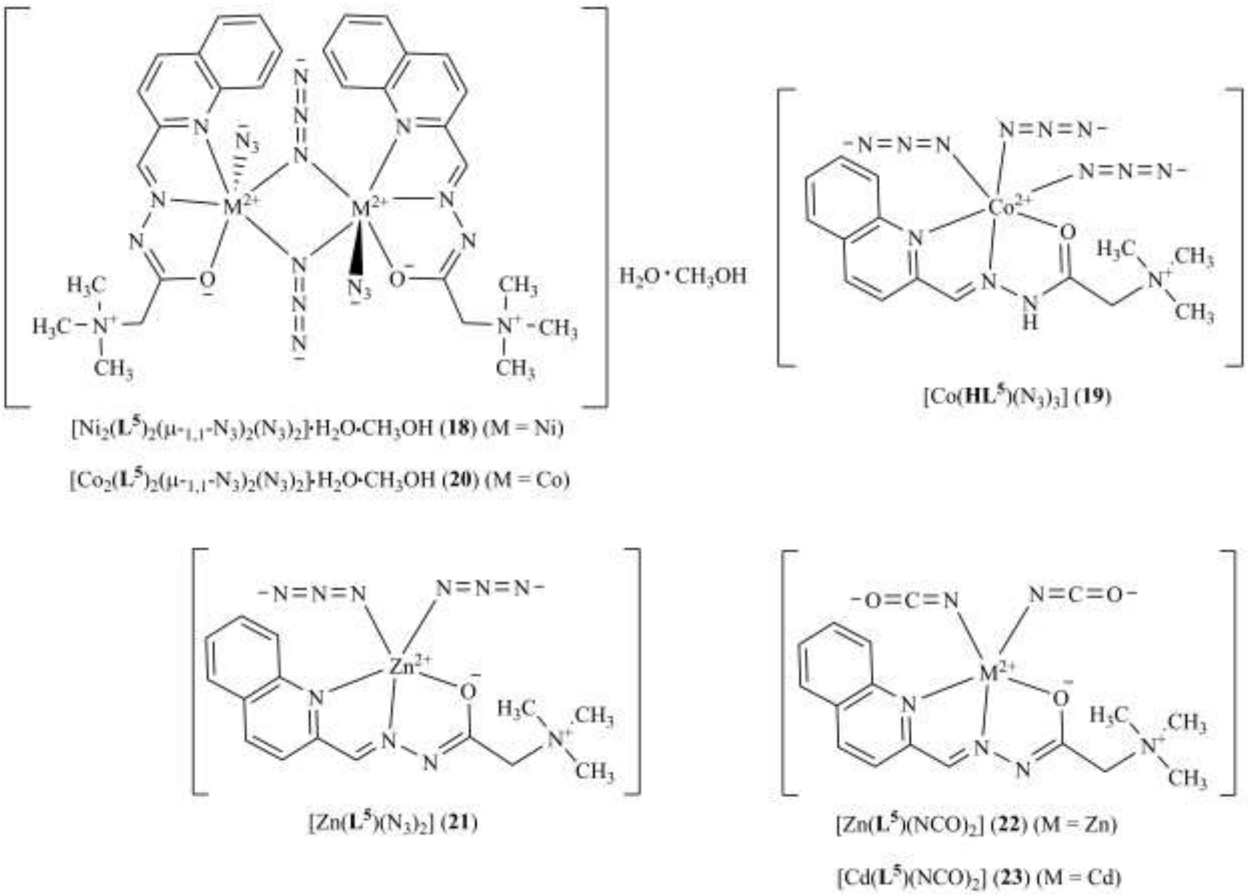
The structure of $[Cd(\mathbf{H_2L^4})(NCS)_2][Cd(NCS)_4]\cdot 2H_2O$ (**15**) complex was determined by elemental analysis, IR and NMR spectroscopy. The X-ray structure of complex **15** was not determined, due to low quality of obtained crystals. Since ambidentate thiocyanate could be coordinated through nitrogen or sulfur donor atoms DFT calculations of the molecular structures and the relative stabilities of linkage isomers of the PBPY-7 Cd(II) complex cation were performed. The results showed that the isomer with N–Cd–N coordination of SCN^- is the most stable.[34] Complexes **14** and **15** are not stable in solution. Two series of signals (ratio 3.4 : 1 in the spectrum of complex **14** and 4.5 : 1 in the spectrum of complex **15**) which appeared in their ^1H NMR spectra in DMSO-d^6 indicate substitution of thiocyanate ligands with solvent.[34]

Iron(III) complexes $[Fe(\mathbf{L^4})(NCS)_2](SCN)\cdot 2H_2O$ (**16**) and $[Fe(\mathbf{L^4})(NCS)_2][Fe(NCS)_5(H_2O)]\cdot 4H_2O$ (**17**) (Scheme 6) were obtained in the reaction of dihydrazone ligand $\mathbf{H_2L^4}Cl_2$, $FeCl_3\cdot 6H_2O$ and NH_4SCN. The complexes were characterized by X-ray analysis, IR spectroscopy, elemental analysis and conductometric measurements. The same pentagonal-bipyramidal complex cation is present in both Fe(III) complexes, while the nature of their anions depends on mole ratio of NH_4SCN and $FeCl_3\cdot 6H_2O$ used in reaction. In PBPY-7 complex cation four fused five-membered chelate rings are formed in equatorial plane by N_3O_2 coordination of deprotonated dihydrazone ligand to Fe(III) ion, while N-coordinated SCN^- occupy axial positions. Complex **16** is 1 : 1 electrolyte in DMSO solution. The value of molar conductivity for complex **17** in DMSO solution indicates solvolysis of complex anion $[Fe(H_2O)(NCS)_5]^{2-}$ whereby one or two coordinated SCN^- ligands are replaced with molecules of solvent.[35]

2.5. Pseudohalide metal complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent

A dinuclear double end-on azido bridged Ni(II) complex, with composition $[Ni_2(\mathbf{L^5})_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]$ $H_2O{\cdot}CH_3OH$ (**18**) (Scheme 7), was obtained in the reaction of the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent (**HL⁵**Cl) with $Ni(BF_4)_2{\cdot}6H_2O$ and NaN_3. X-ray analysis of complex **18** reveals a neutral dimeric unit where two Ni(II) ions are bridged by two azido ligands in an end-on mode. Each Ni(II) ion is octahedrally coordinated by quinoline and azomethine nitrogen atoms and enol-form of deprotonated carbonyl oxygen from one hydrazone ligand, one nitrogen atom from one terminal azido ligand and two nitrogen atoms from two azido bridging ligands. The terminal azido ligands are coordinated *trans* to each other. Magnetic data for complex **18** showed very intensive intra-dimer ferromagnetic coupling between Ni^{2+} ions (J = +12.0(2) cm^{-1}) and inter-dimer antiferromagnetic interaction (δ = –0.8(3) cm^{-1}). The determined value of effective magnetic moment μ_{eff} = 3.16 μ_B, is slightly higher than the spin-only value for Ni^{2+} ion (μ_{eff} = 2.82 μ_B). Magnetic exchange interactions for complex **18** were modeled within broken symmetry approach (DFT-BS) using three formulas that are used to extract exchange parameter *J*, i.e. spin-projected formula by Noodleman, non-spin projected formula of Ruiz and Yamaguchi formula which is considered to be a ‘‘compromise” between first two. The calculation were performed using B3LYP, B3LYP*, TPSSh and PBE0 functionals and 6-311G(d,p) basis set. All considered methods predict the ferromagnetic type of exchange interaction in complex **18**. Yamaguchi and spin-projected formulas give almost the same values which are noticeable higher than experimentally determined value. The values obtained with Ruiz formula are in reasonably good agreement with the experimental data. Among the used DFT functionals the value of *J* parameter obtained with B3LYP* functional is the closest to experimentally determined. The ferromagnetic exchange coupling in complex **18** is determined by small magnetically active SOMOs of the metal centers overlap and their minor delocalization towards nitrogen atoms of the bridging azide anions.[36]

A mononuclear octahedral azido Co(II) complex [Co(**HL⁵**)$(N_3)_3$] (**19**) (Scheme 7) was synthesized in the reaction of the ligand **HL⁵**Cl with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 2 in methanol/acetonitrile mixture. The same complex was obtained as the main product in the reaction of **HL⁵**Cl with $Co(BF_4)_2 \cdot 6H_2O$ and NaN_3 in molar ratio 1 : 1 : 4 in the same mixture of solvents, together with a traces of dinuclear double end-on azido bridged Co(II) complex [Co_2(**L⁵**)$_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2$] $H_2O \cdot CH_3OH$ (**20**) (Scheme 7). X-ray analysis showed that in complex **19** quinoline nitrogen, azomethine nitrogen and carbonyl oxygen atoms from hydrazone ligands together with three monodentately coordinated azido ligands in a meridional alignment form octahedral environment of Co(II) ion. In complex **20** each of the two Co(II) centers is six coordinated with NNO donor atoms of deprotonated hydrazone ligand, one monodentate azido ligand and two end-on azido bridges. Obtained results of magnetic measurements for complex **19** (μ_{eff} = 1.65 μ_B) showed that Co(II) cation is in the low-spin state with $t_{2g}^6 e_g^1$ (S = 1/2) configuration. Magnetic exchange interactions in binuclear complex **20** were modeled within broken symmetry approach (DFT-BS) using Yamaguchi formula with B3LYP functional and TZVPP/TZV basis set for Co atoms and one set of first polarization functions (SVP basis set) for N, C, H and O atoms. DFT-BS calculations anticipated ferromagnetic type interaction between paramagnetic centers (J = 53 cm^{-1}).[37]



$[Ni_2(\mathbf{L^5})_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (**18**) (M = Ni)

$[Co_2(\mathbf{L^5})_2(\mu\text{-}_{1,1}\text{-}N_3)_2(N_3)_2]\cdot H_2O\cdot CH_3OH$ (**20**) (M = Co)

$[Co(\mathbf{HL^5})(N_3)_3]$ (**19**)

$[Zn(\mathbf{L^5})(N_3)_2]$ (**21**)

$[Zn(\mathbf{L^5})(NCO)_2]$ (**22**) (M = Zn)

$[Cd(\mathbf{L^5})(NCO)_2]$ (**23**) (M = Cd)

Scheme 7. Structures of pseudohalide metal complexes with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent

Azido ($[Zn(\mathbf{L^5})(N_3)_2]$ (**21**)) and isocyanato ($[Zn(\mathbf{L^5})(NCO)_2]$ (**22**)) Zn(II) complex with the condensation product of 2-quinolinecarboxaldehyde and Girard's T reagent (**HL**^{5}Cl) (Scheme 7) were obtained in the reaction of hydrazone ligand **HL**^{5}Cl with $Zn(BF_4)_2\cdot 6H_2O$ and corresponding pseudohalide NaN_3 or NaOCN. Structures of the Zn(II) complexes **21** and **22** in solid state and solution were determined by elemental analysis, IR and NMR spectroscopy and X-ray analysis. In both complexes Zn(II) is five coordinated with quinoline nitrogen atom, azomethine nitrogen atom and carbonyl oxygen atom from deprotonated hydrazone ligand and two N-coordinated monodentate ligands. There are no differences between the structures of complexes determined by X-ray crystallography and NMR spectroscopy indicating their stability in DMSO solution.[38]

In the reaction of **HL**^{5}Cl with $Cd(NO_3)_2\cdot 4H_2O$ and NaN_3 a chlorido Cd(II) complex $[Cd(\mathbf{L^5})Cl_2]$ was obtained, instead of the expected azido Cd(II) complex. In this reaction the presence of excess of basic N_3^- caused deprotonation of **HL⁵**Cl ligand, while Cl^- originating from **HL⁵**Cl coordinates to Cd(II). The reaction of **HL⁵**Cl with $Cd(NO_3)_2·4H_2O$ and excess of NaOCN results in formation of isocyanato Cd(II) complex ([Cd(**L⁵**)$(NCO)_2$] (**23**)) (Scheme 7). The crystal structure of chlorido Cd(II) complex was determined. Both complexes were characterized by elemental analysis, IR and NMR spectroscopy. In chlorido Cd(II) complex coordination surrounding of Cd(II) consists of quinoline nitrogen, azomethine nitrogen and carbonyl oxygen atom from deprotonated hydrazone ligand and two monodentate chlorido ligands. The structure of isocyanato Cd(II) complex **23** was proposed on the basis of its elemental analysis, molar conductivity, IR and NMR spectroscopy data. Tridentate NNO coordination of hydrazone ligand in complex **23** was proposed from similarity of its IR and NMR spectral data with corresponding data for chlorido Cd(II) complex. The presence of OCN^- in complex **23** is confirmed from its IR and ^{13}C NMR spectra. The molar conductivity values of complexes [Cd(**L⁵**)Cl_2] and [Cd(**L⁵**)$(NCO)_2$] correspond to non-electrolyte complexes stable in DMSO. In complex **23** Cd(II) is pentadentately coordinated with quinoline nitrogen, azomethine nitrogen and carbonyl oxygen atoms from deprotonated hydrazone ligand and two monodentate OCN^- ligands. Since, the ambidentate OCN^- ligand can be coordinated through nitrogen or oxygen donor atoms, DFT calculations of the molecular structures and the relative stabilities of linkage isomers of complex **23** were performed to give theoretical evidence about mode of its coordination. The results showed that N–Cd–N coordination of OCN^- is the most stable, the next in stability is N–Cd–O isomer (ΔE = 8.37 kcal/mol) and the most destabilized is O–Cd–O isomer (ΔE = 14.55 kcal/mol).[39]

3. Conclusion

In the present Microreview, we have summarized results of the experimental and computational studies on molecular structures and spin-states of pseudohalide metal complexes with hydrazones of Girard's T reagent. In described complexes Girard's T hydrazones behave as tri- or penta-dentate Schiff bases. Pseudohalide ligands are coordinated as monodentates or act as bridges between metal centers in dinuclear complexes. Spatial rearrangement and sequence of donor atoms in Girard’s T reagent hydrazones are similar to corresponding semicarbazones and acylhydrazones, and in many cases analogy in their coordination mode is observed.[40–52] In some cases deprotonation of Girard’s T reagent hydrazones has significant influence on geometry and stoichiometry of complexes and spin-state of their metal ions as it was observed in the case of isothiocyanato Ni(II) complexes with the condensation product of 2-(diphenylphosphino)benzaldehyde and Girard's T reagent.[29] This microreview illustrates versatility of structures and spin-states of pseudohalide metal complexes with hydrazones of Girard's T reagent, which is however only a small part of fascinating chemistry of pseudohalide metal complexes.

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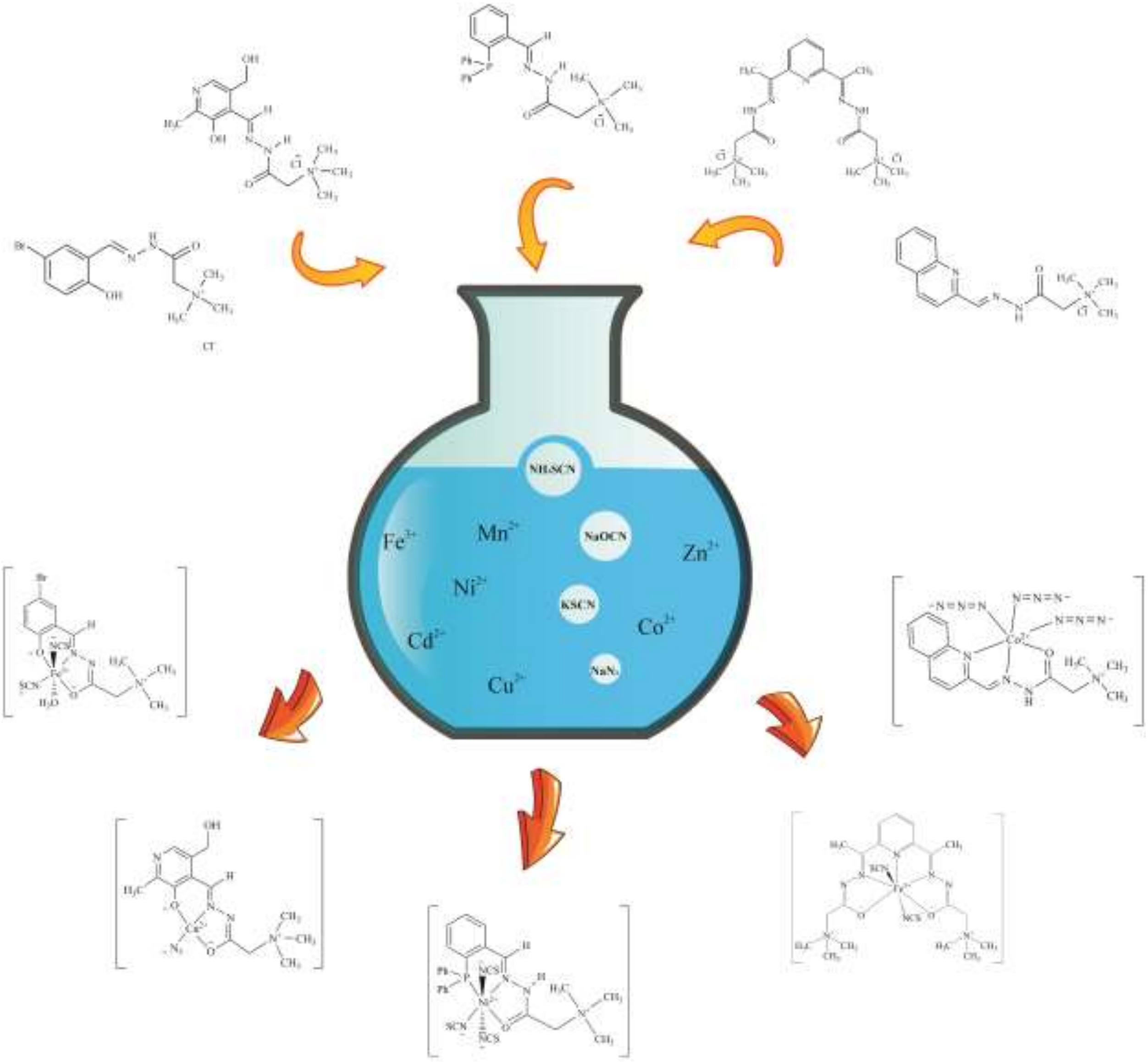

Structural versatility of pseudohalide metal complexes with Girard's T hydrazine is summarized in this microreview, with the special foxus on their spin-states and magnetic properties.