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REVIEW

**Transition metal complexes with Girard reagents
and their hydrazones**

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Abstract: This is the first review dealing with the coordination chemistry of metal complexes with Girard reagents and their hydrazones. The short introduction indicates the chemical properties and significance of these organic compounds. The next section briefly describes synthetic methods for preparing complexes with Girard reagents, as well as the modes of coordination of these ligands. The last two extensive sections review the preparation, stereochemistry and structural characteristics of metal complexes with Girard hydrazones, including also some newer non-hydrazonic derivatives of Girard reagents.

Keywords: Girard reagents; hydrazones; metal complexes; synthesis; physico-chemical characteristics; X-ray crystallography.

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1. INTRODUCTION

There are a large number of organic compounds that are used as reagents for the identification of some other compounds, *i.e.*, their corresponding functional groups.^{1,2} Among them, Girard reagents form an important group (Fig. 1), which serve for the separation of carbonyl compounds from their complex mixtures, by forming water-soluble hydrazones.

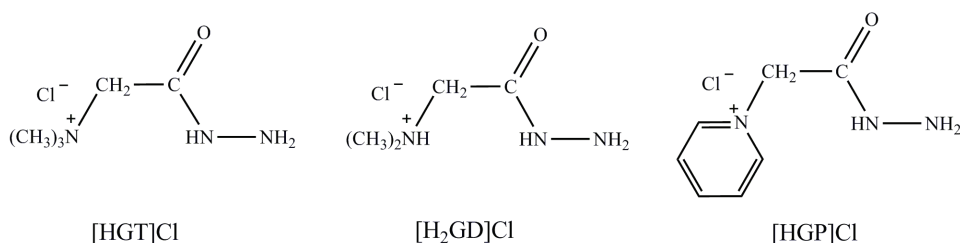


Fig.1. Structures of Girard reagents.

To these reagents, which may be considered as N-substituted glycine hydrazides, belong:

Girard-T (trimethylacetylhydrazide ammonium chloride), [HGT]Cl,

Girard-D (*N,N*-dimethylglycine hydrazide hydrochloride), [H₂GD]Cl and

Girard-P (pyridinioacetylhydrazide chloride), [HGP]Cl.

The Girard-T and Girard-P reagents were synthesized first by A. Girard and G. Sandulesco in 1936, by the reaction of ethyl chloroacetate with trimethylamine or pyridine, yielding quaternary ammonium esters, which in the reaction with hydrazine afforded the corresponding [HGT]Cl and [HGP]Cl Girard reagents.³ These two reagents are soluble in water and biological studies showed that they inhibit certain enzymes (histidine decarboxylase,⁴ acetylcholine esterase⁵ and aryl sulfatase⁶). [H₂GD]Cl was synthesized much later by the reaction of *N,N*-dimethylglycine ethyl ester and hydrazine hydrate with addition of *cc.* hydrochloric acid.⁷

The Girard-T and Girard-P reagents have been widely used to facilitate various separations^{1,2,8-10} and were recently utilized by Lehn *et al.*¹¹ as platforms for the slow release of fragrance aldehydes.

The Girard-T reagent is very soluble in water, less soluble in methanol, ethanol, 2-propanol, glycerol, 1,2-ethanediol and acetic acid, and insoluble in non-hydroxylic organic solvents.^{3,12,13} It is very hygroscopic and it decomposes in the presence of moisture and air, liberating an unpleasant odor. The crystals can be cleaned by washing with ethanol.¹⁴

The Girard-P reagent is less soluble in polar solvents and, in contrast to the Girard-T reagent, it is not hygroscopic.¹⁴

More recently, it was found that some Girard-T or Girard-P derivatives are good inhibitors of C-steel corrosion in acidic medium.^{20,21}

2. COMPLEXES OF GIRARD REAGENTS

As can be seen from their formulas (Fig. 1), Girard reagents have several atoms as potential donors, *viz.* two nitrogen of the hydrazine moiety and one oxygen atom, and in the case of neutral and monoanionic forms of the Girard-D reagent, also the amine nitrogen atom. As will be shown later, a common feature of all Girard reagents is that, in addition to the oxygen atom, the terminal hydrazine nitrogen atom participates in coordination, forming a five-membered metallocycle. To date, the largest number of complexes have been synthesized with the Girard-T reagent, whereas, to the best of our knowledge, no complexes with the Girard-P reagent have been reported.

Although these reagents are known since 1936, the first paper in the field of coordination chemistry dealing with Girard reagents, describing a copper(II) complex with the Girard-T reagent, was published in 1969.¹⁵ Thus, the reaction of aqueous solutions of CuSO_4 and this reagent, in the presence of a small amount of methanol, gave the blue bis(ligand) complex of the formula $[\text{Cu}(\text{HGT})_2](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$. The investigations showed that variation of the metal–ligand molar ratio from 1:2 to 1:4 always resulted in the bis(ligand) complex. Based on IR and UV spectral analyses, the authors¹⁵ proposed a bidentate NO coordination.

More recently, some new complexes of copper(II) and copper(I) and Girard-T reagent of the formulas $[\text{Cu}(\text{HGT})\text{Cl}_2(\text{H}_2\text{O})_2]\text{Cl} \cdot \text{H}_2\text{O} \cdot \text{EtOH}$, $[\text{Cu}(\text{GT})(\text{EtOH})_{3/2}]\text{Br}_2$, $[\text{Cu}(\text{HGT})\text{I}_2] \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{HGT})\text{I}]\text{I}$ were reported by Mostafa and Abdel-Rhman.²² The first was prepared by the reaction of ethanolic solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the Girard-T reagent in the molar ratio of 1:2, and the second one by the reaction of the first complex with KBr. It is interesting to note that this tribochemical reaction of preparation of the bromide salt is accompanied by the deprotonation of the organic ligand. For both complexes, a bidentate NO coordination of the Girard-T reagent was proposed. The iodido complexes were also prepared by the tribochemical reaction of the mentioned chlorido complex and CaI_2 or KI, and, due to the reducing properties of iodide, the product was a diamagnetic copper(I) complex. It is important to note that the newest evaluation of the biological activity of the above-mentioned chlorido complex showed that it is a promising antitumor agent.²³

The reaction of an ethanolic solution of the neutral Girard-D reagent with an aqueous solution of $\text{Cu}(\text{ClO}_4)_2$ gave a copper(II) complex of the formula $\text{Cu}(\text{GD})\text{ClO}_4 \cdot \text{H}_2\text{O}$. This reagent, with copper chloride or sulfate, also gave copper(II) complexes of analogous compositions.¹⁵ In all cases where the metal:ligand ratio was changed from 1:1 to 1:4, only monoligand complexes were obtained.

In the same paper, the authors also considered the possibility of a bidentate coordination of the monoanion of this reagent (Fig. 2), and proposed the most probable NO coordination (Fig. 2a), analogous to copper(II) coordination in dipeptides.²⁴

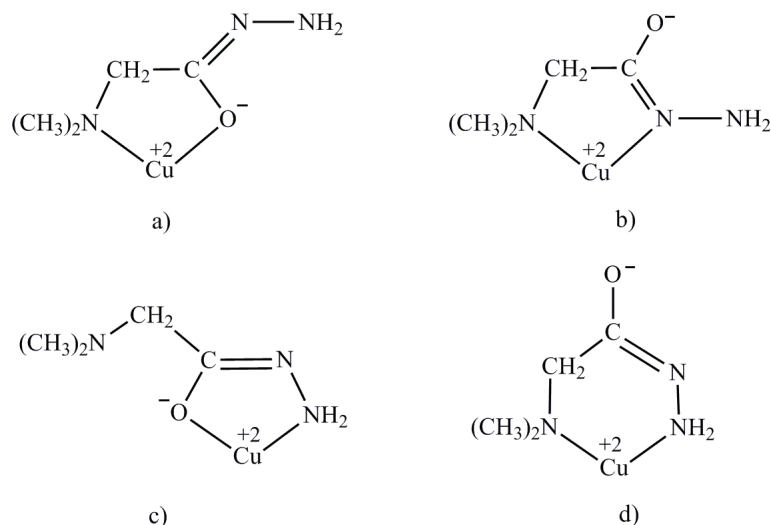
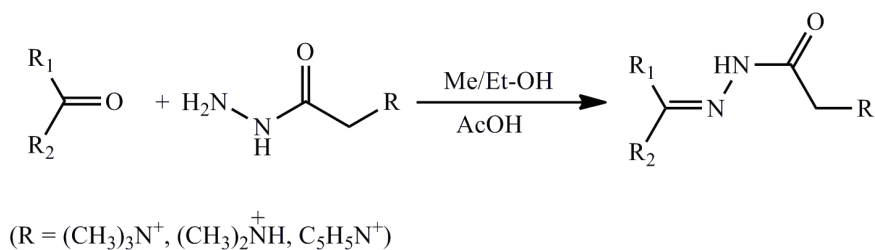


Fig. 2. Possible coordination modes of the Girard-D reagent monoanion.

3. HYDRAZONES OF GIRARD REAGENTS AND THEIR COMPLEXES

3.1. Preparation of Girard hydrazones

Girard reagents hydrazones are obtained in condensation usually of ethanolic or methanolic solutions of Girard reagents and carbonyl compounds in the presence of acetic acid (Scheme 2).



Scheme 2. Preparation of Girard hydrazones.

The mentioned mixtures were refluxed for 20–60 min in the case of aldehydes,³ and up to 12 h in the case of the less reactive ketones.²⁵

Solutions of Girard reagent hydrazones are stable in approximately neutral media (pH 6.5–7.0), whereas they undergo hydrolysis in acidic media.³

Up to now, a number of Girard reagent hydrazones of different mono- and poly-functional carbonyl compounds are known.^{15,21,26–38}

Apart from numerous hydrazone derivatives of Girard reagents, there are also some non-hydrazone Girard-T/P derivatives of the general formula $R-CH_2-C(=O)-NH-NH-C(=S)-NHR'$ ($R = -(CH_3)_3N^+Cl^-$, $-C_5H_5N^+Cl^-$; $R' = -C_2H_5$, $-CH_2CH=CH_2$, $-C_6H_5$). These compounds were obtained by Mostafa³⁹ by boiling under reflux the corresponding R' isothiocyanates and Girard-T/P reagents in absolute ethanol.

3.2. Complexes of Girard hydrazones

Girard hydrazones may have three or more potential ligand atoms; hence, they are also of interest to coordination chemists.

Although Girard hydrazones have been known for a very long time, the number of their complexes with metals is relatively small. In all the complexes described to date, the Girard hydrazones behave as mono-, di-, tri- and penta-dentate Schiff bases.

3.2.1. Complexes with Girard-T hydrazones

Most of the synthesized complexes with Girard hydrazones are with Girard-T hydrazone of various denticities. Thus, Mostafa *et al.*³⁵ in the reaction of equimolar amounts of diacetylmonoxime Girard-T hydrazone, $[(CH_3)_3N^+-CH_2-C(=O)NH-N=C(CH_3)-C(CH_3)=NOH]Cl$, $[HDMGT]Cl$, and $CuCl_2$ obtained complexes, which, in dependence of the nature of the solvent and pH, have different compositions, as well as different ligand denticity.³⁵ Namely, it was found that from an ethanolic solution, a square-planar mono(ligand) complex $[Cu(HDMGT)Cl_2]Cl \cdot H_2O$ crystallized, in which this, potentially tridentate, ligand is coordinated in a bidentate manner, involving the hydrazone and oxime nitrogen atoms (Fig. 3).

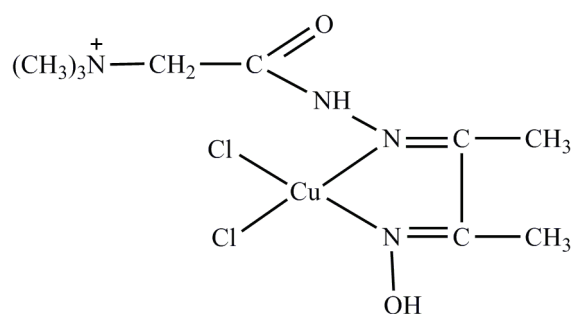


Fig. 3. Supposed square-planar structure of $[Cu(HDMGT)Cl_2]^+$.

If, however, the reaction is performed in an aqueous solution at pH 5, the result was an octahedral bis(ligand) complex $[Cu(HDMGT)_2Cl_2]Cl_2$, with the al-

ready mentioned NN coordination of the ligand. Finally, from an aqueous solution of pH 10, the octahedral mono(ligand) complex $[\text{Cu}(\text{DMGT})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{H}_2\text{O}$ crystallized. In this complex, the ligand is coordinated in a tridentate mono-deprotonated enol form, $[\text{DMGT}]$, through the hydrazine and oxime nitrogen atoms, as well as through the deprotonated oxygen atom of the enolised carbonyl group.³⁵

With anisaldehyde Girard-T hydrazone, $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OCH}_3]\text{Cl}$, $[\text{HAGT}]\text{Cl}$, two complexes were reported, *viz.* the square-planar copper(II) complex $[\text{Cu}(\text{HAGT})\text{Cl}_2]\text{Cl}$ and the square-pyramidal iron(III) complex $[\text{Fe}(\text{HAGT})\text{Cl}_3]\text{Cl}$.³⁷ Moreover, in the same paper, octahedral bis(ligand) complexes of manganese(II) and cobalt(II) of the general formula $[\text{M}(\text{HAGT})_2\text{Cl}_2]\text{Cl}_2$ were described. In these complexes, the ligand is coordinated bidentately, through the nitrogen atom of the azomethine group and the carbonyl oxygen atom.

With tridentate ONO salicylaldehyde Girard-T hydrazone, $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}]\text{Cl}$, $[\text{H}_2\text{SalGT}]\text{Cl}$, the first synthesized complexes were those of dioxovanadium(V) and dioxomolybdenum(VI) of the formulas $[\text{VO}_2(\text{SalGT})]^{28}$ and $[\text{MoO}_2(\text{SalGT})(\text{CH}_3\text{OH})]\text{I}$, respectively.⁴⁰ The complexes were obtained in the reactions of methanolic solutions of Et_4NVO_3 , and $\text{MoO}_2(\text{acac})_2$ (addition of I_2) with $[\text{H}_2\text{SalGT}]\text{Cl}$, respectively.

X-Ray analysis of these complexes showed that the ligand was coordinated as tridentate in the monoanionic form, *via* the oxygen atom of the deprotonated phenolic OH and the enolized carbonyl group, as well as *via* the azomethine nitrogen atom. It was found that the structure of the dioxovanadium(V) complex was a very deformed square pyramid (Fig. 4a).²⁸ On the other hand, the dioxomolybdenum(VI) complex had a deformed octahedral geometry in which, in addition to the two oxygen atoms of the dioxomolybdenum(VI) and the tridentate chelate ligand, the sixth coordination site was occupied by the methanol oxygen atom (Fig. 4b).⁴⁰

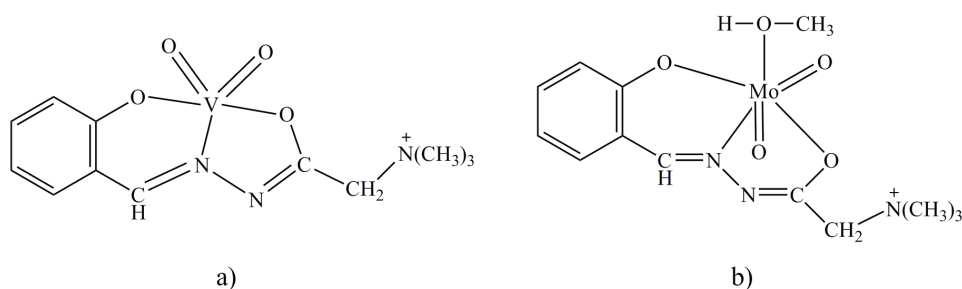


Fig. 4. Structures of the V(V) (a) and Mo(VI) (b) complexes with salicylaldehyde Girard-T hydrazone.

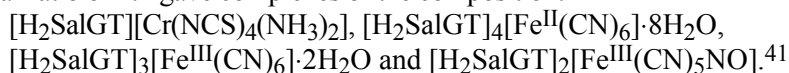
More recently, some new complexes of the same ligand were synthesized, and some of them, as well as the ligand itself, were characterized by X-ray structural analysis.^{31,41,42}

In its crystalline state, the ligand consists of the $[\text{H}_2\text{SalGT}]^+$ cation and Cl^- , and the donor atoms – the hydrazine nitrogen N(1), carbonyl oxygen O(1) and phenolic oxygen O(2), are mutually in a *cis*-position, *i.e.*, in the position that is favorable for coordination³¹ (*vide infra*). Otherwise, this is not the case with compounds of a similar class, such as the majority of semicarbazones,^{43,44} in which the carbonyl oxygen in the free ligand is in the *trans* position with respect to the hydrazine nitrogen.

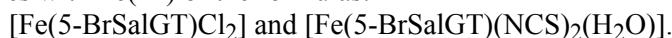
In the isostructural square-pyramidal complexes of copper(II) with the same ligand, of the formula $[\text{Cu}(\text{HSalGT})\text{X}_2] \cdot \text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), the tridentate ONO ligand is coordinated in its neutral, *i.e.*, monodeprotonated form, through the carbonyl oxygen, hydrazine nitrogen and the oxygen of the deprotonated phenolic hydroxyl.³¹

Apart from the mentioned copper(II) complexes, a zinc(II) complex of the formula $\text{Zn}(\text{SalGT})\text{Cl} \cdot 2\text{H}_2\text{O}$ ⁴² was prepared. It involves the monodeprotonated form of the ligand, as in the previously described complexes of dioxovanadium(V)²⁸ and dioxomolybdenum(VI).⁴⁰

Finally, there are also the complexes in which the ligand $[\text{H}_2\text{SalGT}]\text{Cl}$ plays the role of the cation, which is capable of precipitating some voluminous complex anions. Thus, the reaction of aqueous solutions of the ligand and $\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, or $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, in a molar ratio of 1:1 gave complexes of the composition:



Revenco *et al.*³³ synthesized and characterized the structure of a new ligand, a derivative of the Girard-T reagent and 5-bromosalicylaldehyde, $[(\text{CH}_3)_3\text{N}^+ - \text{CH}_2 - \text{C}(=\text{O})\text{NH} - \text{N} = \text{CH} - \text{C}_6\text{H}_3(\text{OH})(\text{Br})]\text{Cl}$, $[\text{5-BrH}_2\text{SalGT}]\text{Cl}$, and its complexes with Fe(III) of the formulas:



The chlorido complex was obtained in the reaction of an ethanolic solution of FeCl_3 and the ligand, while the thiocyanato one was formed in the reaction of an aqueous ethanolic solution of the chlorido complex and NH_4NCS .

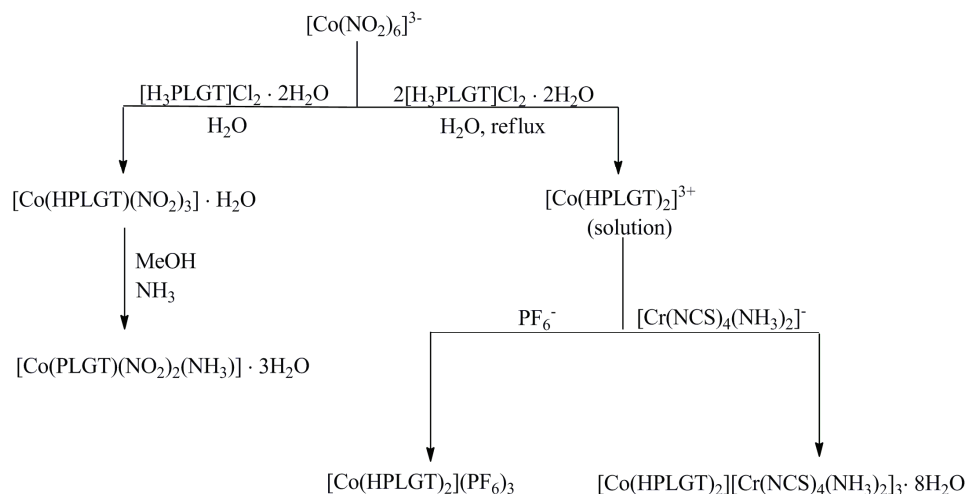
It was found that the Fe(III) in the chloride complex was in a distorted square-pyramidal environment, which was realized by ONO coordination of the doubly deprotonated Schiff base ligand and two chloride ligands. In the second complex, the octahedral surroundings of Fe(III), in addition to the ONO donor atoms of the organic ligand, were realized with two nitrogen atoms of the NCS^- and the oxygen atom of a water molecule. Both complexes were high-spin and were ordinary paramagnets down to 2 K.

The condensation of 2-formylpyridine with the Girard-T reagent in MeOH yielded $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{CH}-\text{C}_5\text{H}_4\text{N}]\text{Cl}$, $[\text{H}(2\text{-PyGT})]\text{Cl}$.³⁴ This compound (DMF solution) reacted with iron(III) or copper(II) chloride to give the deformed octahedral complex $[\text{Fe}(2\text{-PyGT})\text{Cl}_3]$ (*vide infra*) and the deformed square-pyramidal complex $[\text{Cu}(2\text{-PyGT})\text{Cl}_2]\cdot\text{H}_2\text{O}$. In these complexes, the tridentate NNO organic ligand is formally a neutral species, but acts as a zwitterion, *i.e.*, the quaternary ammonium cationic group is compensated by a negative charge resulting from deprotonation of the enolic tautomer. As expected for mononuclear complexes, the small and negative Weiss constant of these compounds indicates that the spin carriers are only in very weak antiferromagnetic interactions in the crystal lattice.

The metal complexes with Schiff bases derived from pyridoxal (PL), *e.g.*, 3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carboxaldehyde (one of the forms of vitamin B6) and the Girard-T reagent was the subject of studies of Leovac *et al.*^{30,41,42,45,46} The dichloride salt of the ligand, pyridoxal Girard-T hydrazone dihydrate, $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{CH}-\text{C}_5\text{HN}^+\text{H}(\text{CH}_3)(\text{OH})-(\text{CH}_2\text{OH})]\text{Cl}_2$, $[\text{H}_3\text{PLGT}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$, was obtained by reaction of an ethanolic solution of the Girard-T reagent and pyridoxal hydrochloride. In $[\text{H}_3\text{PLGT}]\text{Cl}_2\cdot 2\text{H}_2\text{O}$, the pyridine nitrogen of the pyridoxal is protonated. Its first deprotonation step was the loss of the most acidic proton (of the phenolic hydroxyl), whereas the neutral form resulted from an additional deprotonation of the enolized form of the carbonyl group. To obtain a monoanionic form, it is necessary to extract additionally the least acidic proton bound to the pyridine nitrogen of pyridoxal, for which the presence of a proton acceptor, *e.g.*, ammonia, acetate, *etc.* is required.⁴⁷

The first structurally characterized complex with this ligand is the cobalt(III) complex $[\text{Co}(\text{HPLGT})(\text{NO}_2)_3]\cdot\text{H}_2\text{O}$,³⁰ which was obtained by the reaction of aqueous solutions of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ and the ligand in a molar ratio of 1:1 (Scheme 3). In this complex, the central atom is in an octahedral environment, which is realized by the meridionally arranged ONO atoms of the tridentate Schiff base and three monodentate N-bonded NO_2 groups (*vide infra*). The pyridoxal fragment is in a zwitterionic form, which in the case of the coordinated ligand is formed by deprotonation of the coordinated oxygen atom of the phenolic OH group and protonation of the pyridine nitrogen.

The crystallization of the bis(HPLGT) cobalt(III) complex with common small anions appeared to be unsuccessful,⁴¹ whereas the addition of more voluminous anions enabled the isolation of the complexes $[\text{Co}(\text{HPLGT})_2](\text{PF}_6)_3$,³⁰ and $[\text{Co}(\text{HPLGT})_2][\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]_3\cdot 8\text{H}_2\text{O}$.⁴¹ These complexes were prepared by the reaction of aqueous solutions of $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ and the ligand in a molar ratio of 1:2, in the presence of ammonium salts of PF_6^- , or $[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]^-$ (Scheme 3).



Scheme 3. Preparation of the Co(III) complexes with pyridoxal Girard-T hydrazone.

Finally, the reaction of the MeOH solution of the complex $[\text{Co}(\text{HPLGT})(\text{NO}_2)_3] \cdot \text{H}_2\text{O}$ ³⁰ with an excess of $\text{NH}_3(\text{aq})$ gave the non-electrolyte complex: $[\text{Co}(\text{PLGT})(\text{NO}_2)_2(\text{NH}_3)] \cdot 3\text{H}_2\text{O}$.^{41,45}

As can be seen from the formula, the replacement of one nitro ligand with an NH_3 molecule occurred, with the simultaneous deprotonation of the Schiff base, *i.e.*, of the pyridoxal ring. This is the first example of a complex in which the ligand is coordinated in its triply deprotonated form.

Isostructural, most probably square-pyramidal, complexes of $\text{Cu}(\text{HPLGT})\text{X}_2$ ($\text{X} = \text{Cl}$ or Br) were obtained in the reaction of CuX_2 ($\text{X} = \text{Cl}$ or Br) with $[\text{H}_3\text{PLGT}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.⁴² Starting from copper(II) nitrate, the authors obtained a complex $\text{Cu}(\text{HPLGT})\text{Cl}(\text{NO}_3)$.⁴¹ In two other complexes of this metal,⁴⁵ the ligand is coordinated in its triply deprotonated (monoanionic) and doubly deprotonated (neutral) form, giving the $[\text{Cu}(\text{PLGT})\text{N}_3]$ and the square-pyramidal $[\text{Cu}(\text{HPLGT})(\text{NCS})_2]$ complexes, respectively, the latter of which was characterized by X-ray structural analysis.

Here, it is important to stress that attempts to synthesize copper complexes that would, in addition to this ligand, contain also pyridine and its methyl derivatives, were unsuccessful, since the result was the mentioned complexes.⁴¹ Such a behavior of pyridoxal Girard-T hydrazone is in contrast to the behavior of the similar tridentate Schiff bases.

To date, two zinc complexes with this ligand are known, one of them being the chloride complex of composition $\text{Zn}(\text{HPLGT})\text{Cl}_2$,⁴² which in reaction with NH_4NCS gave $\text{Zn}(\text{HPLGT})(\text{NCS})_2 \cdot \text{H}_2\text{O}$.⁴⁵

In the reaction with ammonium metavanadate, pyridoxal Girard-T hydrazone gave gold-yellow crystals, the preliminary structural analysis of which showed

that the composition of the formed complex was $[\text{VO}_2(\text{PLGT})]\cdot\text{H}_2\text{O}$ (Fig. 5).⁴⁸ As can be seen from the formula, the complex contains the ligand in its monoanionic form, formed by deprotonation of the pyridine nitrogen atom, which could be expected since the reaction was performed in an ammoniacal medium. The complex has a pentacoordinated structure (deformed square-pyramid) with two oxo-ligands in the *cis* position. As mentioned above, there is another analogous complex with the salicylaldehyde ligand, $[\text{VO}_2(\text{SalGT})]$.²⁸

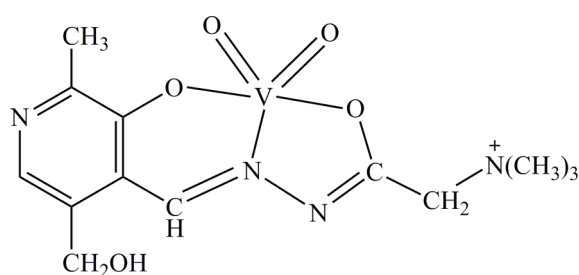
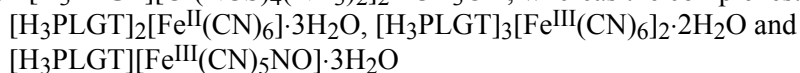


Fig. 5. Structure of $[\text{VO}_2(\text{PLGT})]$.

Finally, the reaction of pyridoxal Girard-T hydrazone with some anionic complexes of Cr(III) and Fe(II and III) gave complexes in which the hydrazone ligand plays the role of the outer-sphere counter ion $[\text{H}_3\text{PLGT}]^{2+}$. Thus, the reaction of a methanolic solution of the ligand and Reinecke salt, $\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$, in the mole ratio of 1:1 gave a complex of the composition $[\text{H}_3\text{PLGT}][\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]\cdot 2\text{CH}_3\text{OH}$, whereas the complexes:



were obtained by mixing a methanolic solution of the ligand with aqueous solutions of $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$, respectively, in a mole ratio of 1:1.⁴¹

In continuation of their study of the synthesis of new derivatives of the Girard-T reagent, Leovac *et al.* investigated the possibility of the preparation of the Schiff bases of this reagent and acetylacetone (Hacac), *i.e.*, of Hacac mono- and bis(Girard-T hydrazone).⁴⁵ To this end, they performed the reactions in methanolic solutions of the Girard-T reagent and acetylacetone in the molar ratios of 1:1 and 2:1 in the presence of acetic acid. To such solutions, they added methanolic solutions of CuCl_2 , which, instead of a complex with the desired Schiff base, resulted in a mixture of monocrystals: brown $[\text{Cu}(\text{acac})_2]\cdot 2[\text{Cu}(3,5\text{-Me}_2\text{pz})_2\text{Cl}_2]$ (3,5-Me₂pz = 3,5-dimethylpyrazole), green $[\text{Cu}(3,5\text{-Me}_2\text{pz})_2\text{Cl}_2]_2$, and blue $\text{Cu}(\text{acac})_2$, the identity and structural analysis of which were established by X-ray structural analysis, while the latter two complexes were previously characterized.^{49,50}

Here, a cyclization reaction occurred between the condensed hydrazide moiety of the Girard-T reagent and acetylacetone, resulting in the formation of a pyrazole derivative and elimination of the trimethylammoniumacetyl moiety in the presence of metal ions because of the weaker NH–CO bond due to the coordination. The formation of a complex with the above pyrazole derivative is not surprising since the reactions of acetylacetone and hydrazine derivatives are known to result in the corresponding pyrazole derivatives.⁵¹

Novaković *et al.*,⁴⁶ by reaction of a methanolic solution of 2,3,4-trihydroxybenzaldehyde Girard-T hydrazone with ZnCl₂ obtained white monocystals, the crystal structure of which contained the tetrachloridozincate ion and two Girard-T hydrazone cations.

It is known that 2,6-diacetylpyridine is an excellent precursor for the synthesis of a number of bis(Schiff base) ligands in which they act as planar pentadentate ligands,⁵² promoting thus the formation of heptacoordinated pentagonal-bipyramidal complexes. A number of manganese(II) complexes have been synthesized in which bis(hydrazone) chelating agents may participate with different sets of donor atoms, including the N₃O₂ set,^{52–56} involved also in the title ligand. In a study⁵⁷ the ligands, 2,6-diacetylpyridine bis(Girard-T/P hydrazone) dichloride were obtained in the form of anhydrous salts, although they were recrystallized from water–ethanol systems. However, neither physico-chemical characterization of the given hydrazone Girard-T ligand nor elemental analysis data were given in the paper. The authors only showed that the listed ligands were suitable for chromatographic determinations of Ti(IV), U(VI), Fe(III) and V(V).⁵⁷ Leovac *et al.*³² described a simpler method for the synthesis of 2,6-diacetylpyridine bis(Girard-T hydrazone)dichloride ligand in the form of the tetrahydrate salt, $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{C}(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N}]\text{Cl}_2 \cdot [\text{H}_2\text{dap}(\text{GT})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$. This ligand was obtained in high yield by the reaction of a warm methanolic solution of the stoichiometric amounts of the Girard-T reagent and 2,6-diacetylpyridine, the result being white fibrous crystals, stable in air.

Yellow, plate-like single crystals of the $[\text{Mn}(\text{H}_2\text{dap}(\text{GT})_2)(\text{NCS})_2](\text{NCS})_2 \cdot \text{CH}_3\text{OH}$ ³² complex were obtained by mild heating of a MeOH solution of the ligand and MnCl₂ in a mole ratio of 1:1 in the presence of an excess of NH₄NCS. The complex had pentagonal-bipyramidal coordination geometry, with the pentadentate N₃O₂ ligand in the equatorial plane and two isothiocyanato groups in the axial positions (*vide infra*).

Finally, as examples of non-hydrazone Girard-T derivatives, 4-ethyl/benzoyl-1-[2-(trimethylammonio)acetyl]thiosemicarbazide chlorides, $[(\text{CH}_3)_3\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{NH}-\text{C}(=\text{S})\text{NH}-\text{R}]\text{Cl}$, (R = –C₂H₅ or –C(=O)C₆H₅; [H₂GTETS]Cl, [H₂GTBzIT]Cl, respectively) are mentioned. They are obtained in the reaction of the Girard-T reagent and ethyl/benzoyl isothiocyanate and gave several mono- and bi-nuclear complexes, which were characterized by spectroscopic me-

thods.^{58,59} Thus, $[\text{H}_2\text{GTETS}]\text{Cl}$ gave binuclear complexes of cobalt(II) and copper(II) of the formulas $[\text{Co}_2(\text{GTETS})(\text{OAc})(\text{OH})(\text{H}_2\text{O})_3]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH}$ and $[\text{Cu}_2(\text{HGTETS})(\text{OH})_3(\text{H}_2\text{O})]\text{Cl}\cdot 0.5\text{C}_2\text{H}_5\text{OH}$.⁵⁸ As can be seen from Fig. 6, one cobalt atom is situated in an octahedral and the other in a square-planar environment, and the bridging ONS ligand is coordinated in its thiol form. An identical coordination mode, but involving a thione form, was also found in the copper complex. In addition to these complexes, the same paper also describes a mononuclear octahedral complex of copper(II) with the formula $[\text{Cu}(\text{H}_2\text{GTETS})(\text{H}_2\text{O})_2\text{Cl}_2]\text{Cl}\cdot 1.5\text{H}_2\text{O}$, involving NS coordination of the ligand in its thione form, as well as a tetrahedral complex of cobalt(II) with the formula $[\text{Co}(\text{H}_2\text{GTETS})(\text{H}_2\text{O})\text{Cl}_2]\text{Cl}\cdot\text{C}_2\text{H}_5\text{OH}$, involving an S-coordination of the ligand.

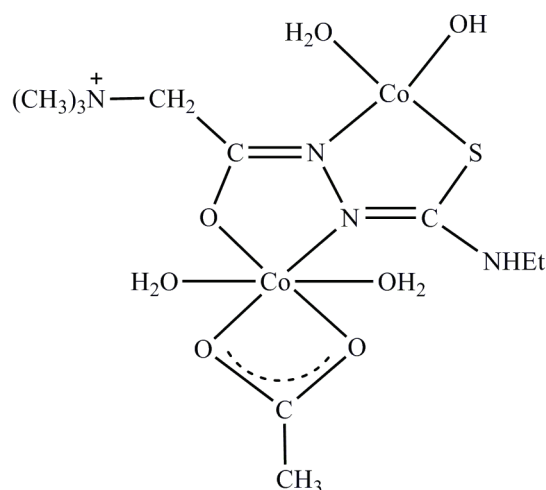


Fig. 6. Proposed structure for $[\text{Co}_2(\text{GTETS})(\text{OAc})(\text{OH})(\text{H}_2\text{O})_3]^+$.

In contrast to this ligand, in the case of the cation $[\text{H}_2\text{GTBzIT}]^+$, thanks to the presence of another oxygen atom as ligator, the IR spectra indicated that, apart from one nitrogen atom, both oxygen atoms were involved in the coordination.⁵⁹ Such a coordination mode was also found in the mononuclear $\text{Cr}(\text{HGTBzIT})\text{Cl}_3\cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{GTBzIT})\text{Cl}\cdot 5\text{H}_2\text{O}$, and $\text{Cd}(\text{H}_2\text{GTBzIT})\text{Cl}_3\cdot 3\text{H}_2\text{O}$ complexes, in the binuclear complex $\text{Co}_2(\text{GTBzIT})\text{Cl}_3\cdot 4\text{H}_2\text{O}$ and in the trinuclear complexes of Cu(II) and Zn(II) of the formula $\text{M}_3(\text{HGTBzIT})(\text{GTBzIT})\text{Cl}_5\cdot 3\text{H}_2\text{O}$. The only exception from such a coordination mode of $[\text{H}_2\text{GTBzIT}]^+$ that has hitherto been reported is the bis(ligand) complex $\text{Mn}(\text{H}_2\text{GTBzIT})_2\text{Cl}_4$, in which the bidentate coordination of the ligand involves the OS or NS ligator atoms.⁵⁹ In addition to the spectroscopic characterization of the above complexes, their stability in both the solid state and solution were also investigated.

3.2.2. Complexes with Girard-D hydrazones

Of the complexes with Girard-D hydrazones, to the best of our knowledge, only complexes with the diacetylmonoxime Girard-D hydrazone, $[(\text{CH}_3)_2\text{N}^+\text{H}-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{NOH}]\text{Cl}$, $[\text{HDMGD}]\text{Cl}$ have been reported. Thus, mono-ligand complexes $[\text{M}(\text{HDMGD})\text{Cl}_2]\text{Cl}$ ($\text{M}(\text{II}) = \text{Cd}$ or Hg), and bis(ligand) complexes $[\text{Cu}(\text{HDMGD})_2\text{Br}_2]\text{Cl}_2$ and $[\text{M}(\text{DMGD})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot n\text{H}_2\text{O}$, ($\text{M} = \text{Ni}(\text{II})$, $\text{Cu}(\text{II})$ or $\text{U}^{\text{VI}}\text{O}_2$) were synthesized by Mostafa *et al.*³⁶ In the complexes of cadmium(II) and mercury(II), NO bidentate coordination was ascribed to the hydrazone ligand, which was realized by coordination of the carbonyl oxygen atom and the azomethine nitrogen atom. In view of the participation of two chlorine atoms in the coordination, the authors supposed that these complexes had a tetrahedral geometry. For the octahedral bis(ligand) complexes $[\text{M}(\text{DMGD})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot n\text{H}_2\text{O}$, which were obtained in the presence of sodium acetate, the authors also supposed a bidentate coordination of the ligand, but with the participation of the oxygen atom of the enol form. In contrast to these complexes, in which this hydrazone ligand is coordinated bidentately, for the bis(ligand) complex of copper(II), $[\text{Cu}(\text{HDMGD})_2\text{Br}_2]\text{Cl}_2$, based on IR spectral analysis, monodentate ligand coordination was proposed, which involved two azomethine nitrogen atom of two HDMGD cations that, together with two bromine atoms, formed a square-planar environment around the copper(II).³⁶

3.2.3. Complexes with Girard-P hydrazones

In contrast to the Girard-P reagent, with which, to the best of our knowledge, no metal complexes have been reported up to now, several complexes of its hydrazones have been described. Thus, Wang *et al.*^{28,60} described the syntheses, spectroscopic properties and X-ray structures of the neutral square-pyramidal VO_2^+ and monocationic octahedral MoO_2^{2+} complexes with the ONO salicylaldehyde Girard-P hydrazone, $[\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}]\text{Cl}$, $[\text{H}_2\text{SalGP}]\text{Cl}$, of the formula $[\text{VO}_2(\text{SalGP})] \cdot \text{CH}_3\text{OH}$ and $[\text{MoO}_2(\text{SalGP})(\text{CH}_3\text{OH})]\text{Cl}$, respectively. In addition to the mentioned complexes, the same authors⁶¹ also synthesized and structurally characterized the square-pyramidal VO_2^+ complex with tridentate ONO benzoylacetone Girard-P hydrazone, of the formula $[\text{VO}_2(\text{BAGP})] \cdot \text{CH}_3\text{CH}_2\text{OH}$ ($\text{H}_2\text{BAGP} = \text{C}_5\text{H}_5\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{C}(=\text{O})-\text{C}_6\text{H}_5$) (*vide infra*). The complexes were obtained in reaction of alcoholic solutions of $\text{MoO}_2(\text{acac})_2$ or NEt_4VO_3 with the corresponding Schiff bases.

Several complexes of the general formula $[\text{M}(\text{SalGP})(\text{H}_2\text{O})]\text{Cl} \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ni}(\text{II})$, $\text{Co}(\text{II})$ or $\text{Zn}(\text{II})$), as well as the copper(II) complex $[\text{Cu}(\text{SalGP})_2]\text{Cl}_2$, involving the same ligand, have been described in the literature.⁶²

With a ligand similar to that above, *i.e.*, *o*-hydroxyacetophenone Girard-P hydrazone, $[\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{N}=\text{C}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OH}]\text{Cl}$, $[\text{H}_2\text{AFGP}]\text{Cl}$,

several complexes of the formula $M(\text{AFGP})(\text{H}_2\text{O})\text{Cl}$ ($M = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ or Zn(II)) have been reported.³⁷ In these complexes, in addition to the tridentate ONO coordination of the doubly deprotonated ligand, the fourth coordination site is ascribed to a water molecule. There appeared an interesting possibility of thermal dehydrohalogenation of these complexes. Namely, the results of differential thermal analysis showed the formation of stable complexes of non-electrolyte type, $[\text{M}(\text{AFGP}-\text{H})]\cdot\text{H}_2\text{O}$.

Finally, a series of metal complexes with the derivatives of Girard-P reagent and 4-benzoylthiosemicarbazide, *i.e.*, with 4-benzoyl-1-(2-pyridinioacetyl)thiosemicarbazide chloride, $[\text{C}_5\text{H}_5\text{N}^+-\text{CH}_2-\text{C}(=\text{O})\text{NH}-\text{NH}-\text{C}(=\text{S})\text{NH}-\text{C}(=\text{O})-\text{C}_6\text{H}_5]\text{Cl}$, $[\text{H}_2\text{GPBzIT}]\text{Cl}$ have been described.⁶³ The IR spectra of the complex $\text{Mn}(\text{HGPBzIT})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$ showed that the ligand behaves as a bidentate chelate. It coordinates *via* CS in the thione form and the enolized carbonyl oxygen of the benzoyl moiety with the displacement of a hydrogen atom from the latter group. Furthermore, in the complexes, $\text{Cr}(\text{HGPBzIT})\text{Cl}_3\cdot\text{H}_2\text{O}$, $\text{Co}(\text{HGPBzIT})\text{Cl}_2$ and $\text{Zn}(\text{HGPBzIT})\text{Cl}_2\cdot 2\text{H}_2\text{O}$, the ligand $[\text{H}_2\text{GPBzIT}]\text{Cl}$ behaves as a tridentate chelate. In $\text{Ni}(\text{GPBzIT})\text{Cl}\cdot\text{H}_2\text{O}$, $\text{Cu}_2(\text{GPBzIT})\text{Cl}_3\cdot 2\text{H}_2\text{O}$ and $\text{Cd}_2(\text{GPBzIT})\text{Cl}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$, the ligand behaves as a tridentate chelate, involving the enolic oxygen of both CO groups and the nitrogen of the NH group. In addition to spectroscopic methods (IR and UV-Vis), the obtained complexes were also characterized by thermal analysis and by determination of the stability constants.

4. STRUCTURAL CHARACTERISTICS

The structural properties of the Girard reagent-based compounds are reviewed based on information available in the Cambridge Structural Database (CSD).⁶⁴ The CSD search revealed only 22 such compounds, of which 14 were complexes the crystal structures of which were characterized by X-ray structural analysis. Out of all the reported crystal structures, 19 are derivatives of the Girard-T reagent, while only three are Girard-P reagent-based compounds. To the best of knowledge, no structural data concerning the Girard-D reagent are available. An overview of the compounds and their selected structural parameters is given in Tables I and II. The general atom-numbering scheme of the moieties of the Girard reagents employed in this work was retained from the reports of Leovac *et al.*^{30-32,45,46} (see Fig. 7a).

The crystal structures reported can be divided into four groups:

- Non-coordinated Girard-T reagent,¹⁰ both unmodified or with the substituted amino H, all present as cations with the bulky $[\text{BPh}_4]^-$ as a counterion (structures **1-3**);
- Non-coordinated Schiff bases Girard-T hydrazones. Hitherto, the Schiff bases of salicylaldehyde (**4**),³¹ 5-bromosalicylaldehyde (**5**),³³ indole-2,3-dione

(**6**),⁶⁵ 2,3,4-trihydroxybenzaldehyde (**7**),⁴⁶ as well as of isobutyraldehyde (**8**),¹⁰ have been reported;

- Coordination compounds with Girard-T hydrazones (**9–19**);^{28,30–34,40,45}
- Coordination compounds with Girard-P hydrazones (**20–22**).^{28,60,61}

TABLE I. Selected bond distances (Å) in the crystal structures of Girard-based compounds

Compound	C1–O1	N1–N2	N2–C1	C1–C10	N3–C10	M–O1	M–N1	M–X	Ref.
[H ₂ GT]BPh ₄ (1)	1.21	1.43	1.34	1.50	1.50	–	–	–	10
[PhNHCO-HGT]BPh ₄ (2)	1.21	1.38	1.34	1.51	1.49	–	–	–	10
[CH ₃ CO-HGT]BPh ₄ (3)	1.22	1.37	1.33	1.52	1.50	–	–	–	10
[H ₂ SalGT]Cl (4)	1.22	1.37	1.34	1.52	1.50	–	–	–	31
[5-BrH ₂ SalGT]Cl (5)	1.22	1.38	1.35	1.53	1.51	–	–	–	33
[Indole-2,3-dione GT]Cl (6)	1.21	1.36	1.36	1.51	1.50	–	–	–	65
[C ₁₂ H ₁₈ N ₃ O ₄] ^a ₂ [ZnCl ₄]·CH ₃ OH (7) ^b	1.21	1.37	1.35	1.51	1.49	–	–	–	46
	1.20	1.37	1.35	1.52	1.51	–	–	–	–
[<i>i</i> -BuGT]BPh ₄ (8)	1.21	1.38	1.34	1.51	1.50	–	–	–	10
[Cu(HSalGT)Cl ₂]·H ₂ O (9)	1.28	1.35	1.29	1.50	1.50	2.05	1.98	1.90	31
[Cu(HSalGT)Br ₂]·H ₂ O (10)	1.24	1.38	1.32	1.51	1.51	2.03	1.97	1.91	31
[VO ₂ (SalGT)] (11)	1.29	1.40	1.28	1.49	1.53	2.00	2.13	1.90	28
[MoO ₂ (SalGT)(CH ₃ OH)]I (12)	1.31	1.46	1.23	1.56	1.54	2.00	2.22	1.92	40
[Fe(5-BrSalGT)Cl ₂] (13)	1.29	1.41	1.30	1.51	1.52	1.98	2.09	1.91	33
[Fe(5-BrSalGT)(NCS) ₂ (H ₂ O)] (14)	1.31	1.41	1.30	1.51	1.48	2.00	2.08	1.93	33
[Co(HPLGT)(NO ₂) ₃]·H ₂ O (15)	1.28	1.40	1.30	1.51	1.50	1.89	1.88	1.86	30
[Cu(HPLGT)(NCS) ₂] (16)	1.26	1.39	1.31	1.53	1.48	1.96	1.92	1.91	45
[Fe(2-PyGT)Cl ₃] (17) ^a	1.28	1.38	1.32	1.50	1.51	2.01	2.12	2.17	34
	1.29	1.38	1.30	1.52	1.48	2.02	2.12	2.16	–
[Cu(2-PyGT)Cl ₂]·H ₂ O (18)	1.28	1.38	1.33	1.51	1.52	2.01	1.94	2.03	34
[Mn(H ₂ dap(GT) ₂ (NCS) ₂)-(NCS) ₂ ·CH ₃ OH (19) ^a	1.23	1.37	1.23	1.51	1.49	2.31	2.32	–	32
	1.24	1.37	1.24	1.52	1.51	2.31	2.30	2.29	–
[VO ₂ (SalGP)]·CH ₃ OH (20)	1.30	1.41	1.29	1.50	1.48	1.97	2.14	1.89	28
[MoO ₂ (SalGP)(CH ₃ OH)]Cl (21)	1.34	1.41	1.29	1.48	–	2.02	2.24	1.91	60
[VO ₂ (BAGP)]·CH ₃ CH ₂ OH (22)	1.27	1.41	1.30	1.51	1.46	1.98	2.13	1.98	61

^a[C₁₂H₁₈N₃O₄]⁺ = 2,3,4-trihydroxybenzaldehyde Girard-T hydrazone cation; ^bthe structure contains two Girard reagent fragments or two independent molecules

In the solid state, all non-coordinated ligands appeared as cations, with the positive charge located on the quaternary ammonium group. The fragment C2–N1–N2H–C1(O1)–C10–N3 within the Schiff base is planar or slightly deviating from planarity. In fact, in the case of **4** (Fig. 7a) and its 5-bromo derivative **5**, all atoms of the structure, except for two methyl groups attached to the terminal N3, lie in the mirror plane. In most of the structures, the carbonyl O1 atom is placed *cis* to the azomethine N1 (*Z* configuration with respect to the C–N bond). The exceptions are the structures **6** (Fig. 7b) and **8**, in which the *trans* position of these atoms was observed (*E* configuration). As previously explained for the case of the Schiff bases of thiosemicarbazide,⁴³ the configuration of the

ligands is mostly influenced by the formation of intramolecular hydrogen bonds. Thus, in the case of **4** (Fig. 7a), the *Z* configuration is stabilized by the interaction of the phenolic hydroxyl and the azomethine N1, while in **6**, in the *E* configuration (Fig. 7b), an intramolecular interaction between the carbonyl O2 and the hydrazine N2H group could be expected. The *Z* configuration of the Girard hydrazones provides a suitable arrangement of the donor atoms for coordination to metal ions. Therefore, in all reported complexes, the Girard-T or Girard-P fragments coordinate *via* the azomethine N1 and carbonyl O1 atoms. In most of the structures, the Girard-based hydrazones coordinate as tridentate ligands involving the third donor atom from the condensed carbonyl moiety. The exception is the pentadentate ligand 2,6-diacetylpyridine bis(Girard-T hydrazone) in the Mn(II) complex **19**, which is, up to now, the only reported crystal structure comprising a Girard reagent-based ligand with a denticity larger than three.

TABLE II. Selected bond angles (°) and torsion angles (°) for crystal structures of the Girard reagent-based compounds (T1 = O1–C1–C10–N4; T2 = N1–N2–C1–O1; T3 = C1–N2–N1–C2; T4 = C1–O1–M–N1; T5 = X–M–N1–C2)

Compound	O1–M–N1	N1–M–X	T1	T2	T3	T4	T5	Ref.
1	–	–	20.9	8.8	–	–	–	10
2	–	–	13.0	–1.6	–72.8	–	–	10
3	–	–	–59.6	–4.7	–163.9	–	–	10
4	–	–	8.9	169.3	–173.7	–	–	31
5	–	–	0.0	0.0	0.0	–	–	33
6	–	–	0.0	0.0	0.0	–	–	65
7	–	–	–0.49	–175.3	175.3	–	–	46
			21.6	4.5	–170.1	–	–	
8	–	–	–17.8	2.0	174.4	–	–	10
9	79.6	90.9	82.7	–2.0	178.6	–9.3	–2.5	31
10	79.8	90.8	–80.6	4.9	–179.9	9.9	4.2	31
11	73.5	82.2	89.5	0.2	179.4	4.1	6.3	28
12	73.6	79.4	73.4	–7.1	–176.8	–3.7	–13.7	40
13	75.4	85.1	–	–	–	–	–	33
14	76.6	86.2	–	–	–	–	–	33
15	83.2	94.8	–93.3	0.2	177.8	–1.6	1.9	30
16	80.8	91.0	–71.1	0.2	–176.5	5.9	4.6	45
17	75.0	73.6	82.2	–0.8	–176.6	–5.0	–4.7	34
	73.8	73.8	–11.6	–1.1	–179.9	2.2	1.4	
18	78.8	81.1	78.5	–5.1	179.9	–11.6	–3.9	34
19	68.5	67.8	–63.0	2.3	179.8	12.4	5.1	32
	66.2	68.3	–41.0	–2.9	178.3	7.4	6.8	
20	73.6	82.3	177.5	–0.4	177.8	–4.9	–29.1	28
21	73.5	81.9	–	–	–	–	–	60
22	73.5	82.0	–162.7	2.5	–178.3	11.3	15.6	61

It is worth mentioning that within the extracted complexes, the Girard reagent-based ligands behave as:

- neutral – in which the positive charge of the quaternary ammonium group is neutralized by deprotonation of the H atom belonging to the condensed carbonyl moiety (**9** and **10**), or by the deprotonation of the enolic H atom, formally belonging to the hydrazine N2H group (**17** and **18**), or both (**15** and **16**);
- negatively charged (–1) – in which the H atom belonging to the condensed carbonyl moiety and the enolic H atom are both dissociated (**11–14** and **20–22**);
- positively charged (+2) – in which only a positive charge exists that is located on the quaternary ammonium fragments (**19**).

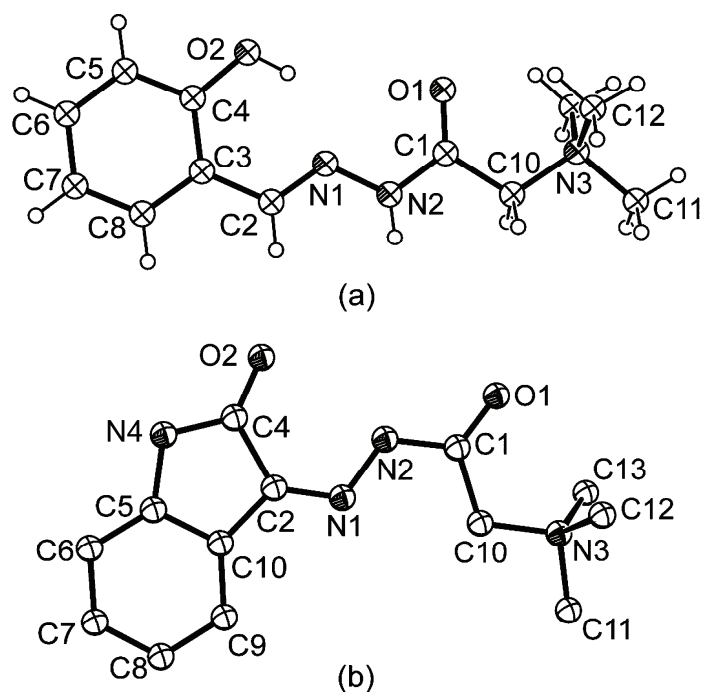


Fig. 7. The molecular structure of ligands a) $[\text{H}_2\text{SalGT}]\text{Cl}$ (**4**) and b) $[\text{indole-2,3-dione GT}]\text{Cl}$ (**6**) displaying *Z* and *E* configuration, respectively (the CIF file does not contain information concerning the H atoms in compound **6**).

Up to now, metal complexes with salicylaldehyde Girard-T and Girard-P hydrazones as ligands represent the largest family of compounds. These Schiff bases can coordinate in the neutral form *via* the deprotonated phenolic O2, azomethine N1 and carbonyl O1 (**9** and **10**) or as an anion, where the latter atom participates in the deprotonated enol form (**11**, **12**, **20** and **21**). The crystal structures of the two isostructural complexes **9** and **10** with the neutral HSalGT ligand have been reported (Fig. 8).³¹ The Cu(II) ion is here located in a square-pyramidal en-

vironment (the τ values are 0.20 and 0.19 in **9** and **10**, respectively) formed by the chelating ligand, one halogen atom in the basal plane and the second halogen in the apical position.

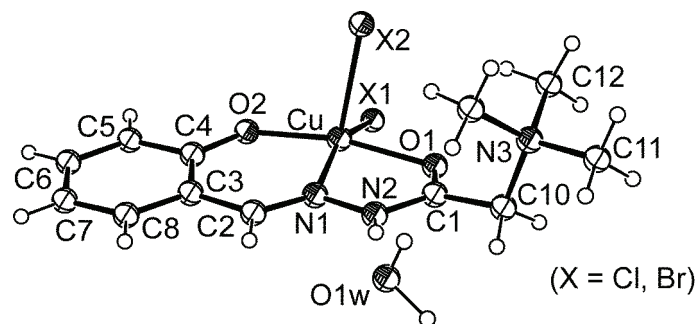


Fig. 8. The molecular structure of complexes $[\text{Cu}(\text{HSalGT})\text{Cl}_2] \cdot \text{H}_2\text{O}$ (**9**) and $[\text{Cu}(\text{HSalGT})\text{Br}_2] \cdot \text{H}_2\text{O}$ (**10**).

The same (ONO) coordination mode of the ligand, but involving the carbonyl O1 in a deprotonated enol form, was reported for the dioxovanadium(V) complex²⁸ **11** and dioxomolybdenum(VI) complex⁴⁰ **12**, as well as for their Girard-P analogues, **20**²⁸ and **21**.⁶⁰ According to the τ value of 0.44, the geometry of the VO_2^+ complex **11** can be described as very deformed square-pyramidal or trigonal-bipyramidal. The analogue complex **20**, on the other hand, displays a more regular, square-pyramidal configuration, with a τ value of 0.08. The cationic MoO_2^{2+} complex **12** and the analogous complex **21** have a similar octahedral geometry, where the oxygen atoms of the Schiff base occupy the axial positions while the azomethine N1 takes one of the equatorial sites.

Similarly to the VO_2^+ complex **20**, which is one of the three complexes with Girard-P hydrazones characterized by X-ray crystallography, complex **22** has square-pyramidal geometry⁶¹ ($\tau = 0.12$) (Fig. 9). In this complex, the monoanionic ligand benzoylacetone Girard-P hydrazone is coordinated *via* the enolized carbonyl O1 and O2 atoms, and the azomethine N1 atom. Revenco *et al.*³³ reported the crystal structures of Fe(III) complexes with the tridentate ONO 5-bromo derivative of the $[\text{H}_2\text{SalGT}]\text{Cl}$ ligand (**13** and **14**), which also coordinates to the metal as a monoanion. The coordination polyhedron of complex **13** was described as a much distorted square-pyramid ($\tau = 0.38$), while complex **14** has an octahedral structure. The increase in the coordination number in **14** in comparison with **13** has been explained by the smaller steric hindrances of the NCS compared to the Cl anions which allowed additional coordination of the water molecule.³³

The pyridoxal Girard-T hydrazone represents a specific ligand which can coordinate in a twice-deprotonated, and yet neutral form, as found in the case of the Co(III) (Fig. 10) and Cu(II) complexes.^{30,45} This tridentate ligand coordinates

through the deprotonated carbonyl O1, the azomethine N1 and the oxygen of the deprotonated phenolic hydroxyl, forming, as above, fused five- and six-membered chelate rings. The negative charge is neutralized by the positive charges located on the quaternary ammonium and pyridoxal fragments. In the octahedral Co(III) complex **15**, the three donor atoms of the chelate ligand, together with the N-coordinated nitro group, form the equatorial plane of the polyhedron.³⁰ In the Cu(II) complex **16**, the chelate ligand, together with one NCS anion, forms the basal plane of a distorted square pyramid ($\tau = 0.11$).⁴⁵

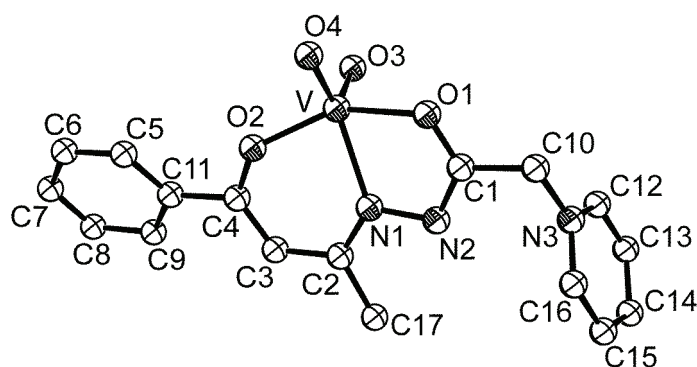


Fig. 9. The molecular structure of the complex $[\text{VO}_2(\text{BAGP})] \cdot \text{CH}_3\text{CH}_2\text{OH}$ (**22**) (the disordered molecule of the solvent is excluded for the sake of clarity; the CIF file does not contain information concerning the H atoms).

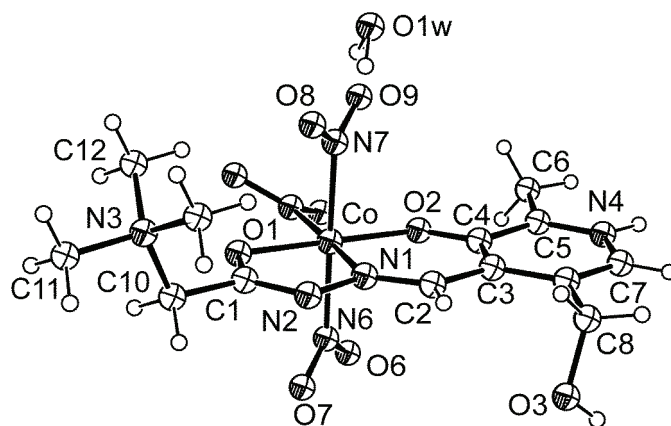


Fig. 10. The molecular structure of complex $[\text{Co}(\text{HPLGT})(\text{NO}_2)_3] \cdot \text{H}_2\text{O}$ (**15**).

Unlike the above Schiff bases, whose coordination results in the fused five- and six-membered chelate rings, the NNO coordination of the 2-pyridinecarboxaldehyde Girard-T hydrazone results in the formation of two five-membered rings.³⁴ Until now, two complexes comprising this neutral tridentate ligand have

been reported, the octahedral Fe(III) complex **17** (Fig. 11) and the square-pyramidal Cu(II) complex **18** ($\tau = 0.15$).

The pentagonal-bipyramidal Mn(II) complex **19** (Fig. 12) is, to our knowledge, the only structurally characterized complex involving a pentadentate Girard reagent-based ligand.³² This is also the only complex where the ligand is coordinated as a cation. Through the symmetric coordination, the pentadentate ligand forms two pairs of fused five-membered chelate rings, which define the equatorial plane. The pentagonal-bipyramidal coordination geometry around the Mn(II) is completed by two NCS groups that occupy the axial positions, while two remaining NCS anions, out of the coordination sphere, neutralize the complex cation.

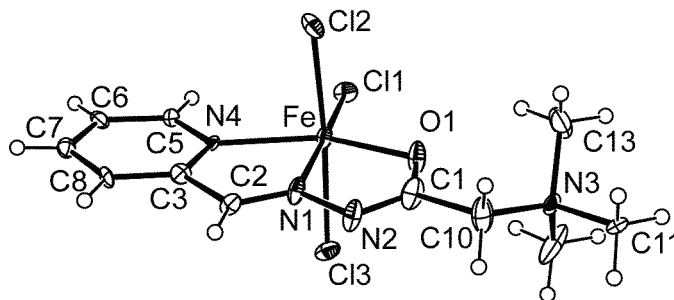


Fig. 11. The molecular structure of complex $[\text{Fe}(2\text{-PyGT})\text{Cl}_3]$ (**17**) (one of the two independent molecules).

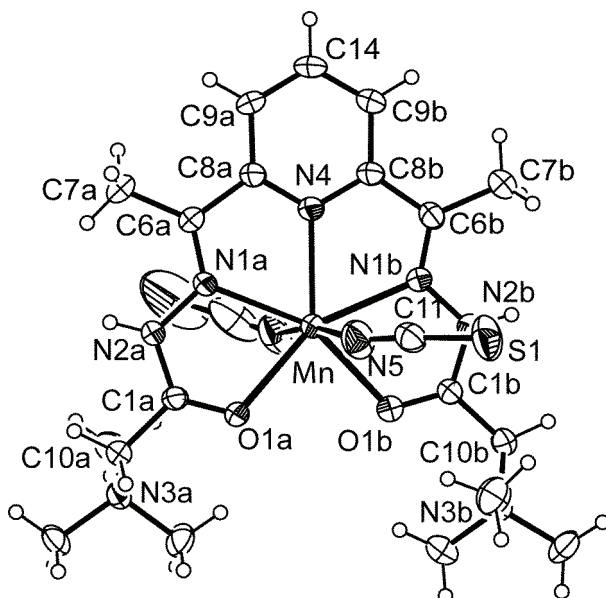


Fig. 12. The molecular structure of complex $[\text{Mn}(\text{H}_2\text{dap}(\text{GT})_2)(\text{NCS})_2](\text{NCS})_2 \cdot \text{CH}_3\text{OH}$ (**19**).

It is difficult to observe the straightforward differences between the geometries of the Girard reagent-based ligands when they coordinate as neutral, positively or negatively charged. As can be seen from Table I, the C1–O1 bond lengths in the free positively charged ligands have an average value of 1.22 Å, indicating a pronounced double bond character. As expected, the involvement of the O1 in coordination to the metal ion causes a noticeable elongation of the C1–O1 bond. The finer changes are most obvious if we compare the behavior of the ligand within the largest set of compounds *i.e.* the complexes of salicylaldehyde Girard hydrazones (Table I). Namely, the C1–O1 bond in the complexes with a neutral ligand (**9** and **10**), is noticeably shorter (C1–O1_(av.) = 1.26 Å) compared to the same bond in the complexes with an anionic ligand (C1–O1_(av.) = 1.30 Å). The similar length of the C1–O1 bond for anionic ligands can be observed in the complexes of the mononegative salicylaldehyde Girard-P (C1–O1_(av.) = 1.32 Å) and 5-bromosalicylaldehyde Girard-T (C1–O1_(av.) = 1.30 Å) hydrazones. In contrast to these examples, the pentadentate 2,6-diacetylpyridine bis(Girard-T hydrazone) is up to now the only ligand coordinated as a cation, where the keto form of the carbonyl O1 ligator is preserved.³² This is evidenced by the shortest lengths of the corresponding C1–O1 bonds (1.24 Å), which are closer to those found in the free ligands. Based on the data listed in Table I, it is possible to suggest that the N1–N2 bond is also affected by the deprotonation of the ligand. Namely, the average bond length in the complexes containing neutral or positively charged ligands (1.38 and 1.37 Å, respectively) is somewhat shorter than in the complexes with anionic ligands (1.41 Å). As regards the coordination sphere, it can be observed that in complexes **9**, **10** and **19**, containing the ligand in its keto form, the length of the M–N1 coordination bond is shorter or similar to that of the M–O1 (Table I). In the complexes containing the ligand in the deprotonated enolic form (**11–14**, **17**, **18** and **20–22**) the coordination bond M–N1 becomes noticeably longer than the M–O1. However, the different nature of the central metal ions should be born in mind. The coordination angles O1–M–N1 and N1–M–X in most of the cases deviate significantly from 90° (Table II), which can be a consequence of the tendency of ligand to form fused chelate rings.

A most common feature of all the Girard reagent-based ligands, either neutral or charged ones, is the delocalization of the electron density within the C2–N1–N2–C1(O1) fragment. This is evidenced by the values of the bond lengths that are between the values for single and double ones (Table I). Taking into account that in most of the cases the condensed carbonyl compound represents a part of some aromatic system, the delocalization often extends to the whole hydrazone moiety. The remaining C1–C10 and C10–N3 bonds are, on the other hand, practically single bonds and thus allow for free rotation of the quaternary ammonium fragment (this important property will be described later in more detail). In accordance with the mentioned delocalization, the most of non-hydrogen

atoms in the free and coordinated ligands are approximately coplanar. As described, the coordination of the Girard reagents-based ligands result in fused chelate rings. The planarity of these rings is evidenced by the values of the T2 and T3 torsion angles (Table II, **9–22**), which are rather uniform and do not exceed $|7.1|$ and $|176.5|^\circ$, respectively. Somewhat higher twisting, and thus deformation from the planar form, can be observed from the torsion angles T4 and T5, which include the coordination bonds. The largest torsion angle ($T5 = -29.1^\circ$) is found in compound **20**, in which the strong hydrogen bond existing between the complex molecule and the solvent contributes to the deformation of the chelate rings. In the analogous Girard-T derivative (**11**), which crystallizes without solvent, the value of T5 is 6.3° . The least deformation of the fused rings can be observed in the Co(III) complex with the pyridoxal Girard-T hydrazone (**15**).

Among the listed torsion angles, the largest variation in the values can be found for T1, which describes the position of the quaternary ammonium or pyridinium fragment with respect to the chelate rings. The $N(CH_3)_3^+$ group can easily change its position by rotating around the C1–C10 and C10–N3 bonds. It is important to remember that in the crystal structure of the free ligand, such as $[H_2SalGT]^+$ (Fig. 7a), the N3 atom is coplanar to the rest of the molecule, with the T1 torsion angle equal to 0° . This position of the $N(CH_3)_3^+$ group is supported by the intramolecular C–H...O1 interactions which involve the quaternary methyl groups.³¹ In the corresponding complexes **9** and **10** (Fig. 8), in which the O1 atom is engaged in coordination, the $N(CH_3)_3^+$ group shifts out of the plane of the ligand and orients toward the axially bonded ligand to form the corresponding C–H...X2 intramolecular interactions (T1 is equal to 82.7 and -80.6° in **9** and **10**, respectively). Due to these interactions, the O1–Cu–X2 angle appears smaller than the other X2-coordination angles.³¹ A similar, nearly orthogonal, orientation of the $N(CH_3)_3^+$ group ($T1 = -93.3^\circ$), is found in the crystal structure of **15**, in which a very strong intramolecular hydrogen bond is formed between the methyl groups of the $N(CH_3)_3^+$ fragment and the axial NO_2 ligand.³⁰ It should be noted, however, that the intermolecular interactions can also affect the position of the $N(CH_3)_3^+$ group. This is the most obvious in the case of **17**, which crystallizes with two independent molecules in the unit cell.³⁴ The $N(CH_3)_3^+$ groups in these molecules display rather different orientations (the T1 values are 82.2 and -11.6°), which can be explained by the differences in their intermolecular interactions. Significant differences were also found in the orientation of the two $N(CH_3)_3^+$ groups of the symmetrically coordinated $H_2dap(GT)_2^{2+}$ in complex **19**.³² In contrast to the Girard-T reagent-based complexes, in which the quaternary ammonium N3 atom significantly deviates from the rest of the chelate ligand, the data available for the two Girard-P reagent-based complexes (**20** and **22**) show that the corresponding quaternary pyridinium N3 atom remains more coplanar with the chelate rings (the T1 values are 177.5 and -162.7° , respecti-

vely). The pyridinium ring, however, can form different dihedral angles with respect to the nearest, five-membered chelate ring (62.3 and 83.0° in **20** and **22**, respectively), which suggests free rotation of the pyridinium fragment under the influence of the intermolecular interactions.

In general, the crystal structures of the reported Girard reagents-based compounds display extensive and diverse intermolecular interactions. In the complex compounds, the Girard reagents-based ligands have several potential hydrogen bonding binding sites. The most frequently engaged are the atom N2 (which can act as a donor or as an acceptor, depending on the deprotonation), the atom O1 (which upon coordination retains its acceptor abilities) and the possible binding sites from the condensed carbonyl moiety. In addition, as the chelate rings, together with the condensed carbonyl moiety, form extensive π -delocalized systems, the Girard reagent ligands can also engage in $\pi\cdots\pi$ and C–H $\cdots\pi$ interactions. The most specific fragments of these ligands, the quaternary ammonium and pyridinium groups, are highly interactive and prefer the surroundings of the strongest hydrogen bonding acceptors, such as O, N, Cl, Br and S.

5. CONCLUSIONS

Although Girard reagents have been known for more than 70 years, the first paper in the field of the coordination chemistry of these compounds, involving the Girard-T reagent, was published 33 years after the synthesis of this reagent. Nowadays, complexes with this reagent are most numerous, whereas complexes with the Girard-P reagent are, to the best of our knowledge, unknown.

Despite of the fact that a series of the Girard hydrazones are known, the number of their metal complexes is relatively small. In the complexes, Girard hydrazones behave as mono-, bi-, tri- or penta-dentate Schiff bases. Among the complexes of the Girard hydrazones, those with the tridentate Girard-T hydrazones are the most numerous.

In the crystal structures, the Girard reagents-based ligands, either free or coordinated, behave as highly delocalized systems and display considerable coplanarity of most of the constitutive atoms. The exceptions are quaternary ammonium and pyridinium groups, which can display different orientations under the influence of intra- and inter-molecular hydrogen bonds.

Since the assumptions on the different coordination modes and denticities of the non-hydrazonic Girard-T/P ligands were made based on their IR spectra,^{58,59,63} it would be of interest to confirm these data by the X-ray structural analysis of the complexes.

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ИЗВОД

КОМПЛЕКСИ ПРЕЛАЗНИХ МЕТАЛА СА ЖИРАРОВИМ РЕАГЕНСИМА
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Ово је прва ревија која описује координациону хемију комплекса метала са Жираровим реагенсима и њиховим хидразонима. У краћем уводу приказане су хемијске особине и значај ове групе органских једињења. Следећа, такође врло кратка, секција описује методе синтезе комплекса и начине координације самих Жирарових реагенаса. Последње две најопширније секције посвећене су препаратацији, стереохемији и структурним карактеристикама комплекса метала са хидразонима Жирарових реагенаса, укључујући и неке њихове нехидразонске деривате.

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REFERENCES

1. O. H. Wheeler, *Chem. Rev.* **62** (1962) 205
2. O. H. Wheeler, *J. Chem. Educ.* **45** (1968) 435
3. A. Girard, G. Sandulesco, *Helv. Chim. Acta* **19** (1936) 1095
4. N. G. Watson, *Br. J. Pharmacol.* **11** (1956) 119
5. F. Huidobro, *Bol. Soc. Biol. Santiago Chile* **5** (1948) 6
6. K. S. Dogson, B. Spenver, K. Williams, *Biochem. J.* **61** (1955) 374
7. M. Viscontini, J. Meier, *Helv. Chim. Acta* **33** (1950) 1773
8. S. Kim, H. Ko, S. Kim, T. Lee, *J. Comb. Chem.* **4** (2002) 549
9. W. Holstein, D. Severin, *Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem.* **32** (1979) 487
10. M. D. Soutullo, C. I. Odom, E. A. Salter, A. C. Stenson, R. E. Sykora, A. Wierzbicki, J. H. Davis Jr., *J. Comb. Chem.* **9** (2007) 571
11. B. Levrand, Y. Ruff, J.-M. Lehn, A. Herrmann, *Chem. Commun.* (2006) 2965
12. O. H. Wheeler, V. S. Gaiind, O. Rosaldo, *J. Org. Chem.* **26** (1961) 3537
13. F. S. Sterrett, *The Essential Oils*, vol. II, E. D. Guenther, Ed., Vab Nostrand Co., New York, 1949, p. 814
14. A. Petit, S. Tallard, *Rev. Chim. Ind. (Paris)* **48** (1939) 226
15. M. Masui, H. Ohmori, *J. Chem. Soc., A* (1969) 153
16. J. Heer, K. Miescher, *Helv. Chim. Acta* **34** (1951) 359
17. D. F. Godbois, J. M. Mendelsohn, L. J. Ronsivalli, *Anal. Chem.* **37** (1965) 1776
18. W. P. McKinley, *Science* **121** (1955) 139
19. E. Lederer, M. Lederer, *Chromatography*, Elsevier, New York, 1953, p. 113
20. A. A. El-Shafei, M. N. H. Moussa, A. A. El-Far, *Mater. Chem. Phys.* **70** (2001) 175
21. M. N. H. Moussa, A. A. El-Far, A. A. El-Shafei, *Mater. Chem. Phys.* **105** (2007) 105
22. M. M. Mostafa, M. H. Abdel-Rhman, *Spectrochim. Acta, A* **56** (2000) 2341
23. A. M. A. El-Sokkary, M. M. El-Naggat, A. F. Abdel-Aziz, *Appl. Organomet. Chem.* **24** (2010) 439
24. S. P. Datta, R. Leberman, B. R. Rabin, *Trans. Faraday Soc.* **55** (1959) 1982

25. A. Petit, S. Tallard, *Ind. Parf.* **3** (1948) 75
26. M. Masui, H. Ohmori, *Chem. Pharm. Bull.* **12** (1964) 877
27. M. Masui, H. Ohmori, *J. Chem. Soc., B* (1967) 762
28. X. Wang, X. M. Zhang, H. X. Liu, *Inorg. Chim. Acta* **223** (1994) 193
29. S. P. Rao, T. A. S. Reddy, *Z. Anal. Chem.* **277** (1975) 127
30. Lj. S. Vojinović, V. M. Leovac, S. B. Novaković, G. A. Bogdanović, J. J. Csanádi, V. I. Češljević, *Inorg. Chem. Commun.* **7** (2004) 1264
31. V. M. Leovac, G. A. Bogdanović, V. I. Češljević, Lj. S. Jovanović, S. B. Novaković, Lj. S. Vojinović-Ješić, *Struct. Chem.* **18** (2007) 113
32. Lj. S. Vojinović-Ješić, V. I. Češljević, G. A. Bogdanović, V. M. Leovac, K. Mészáros Szécsényi, V. Divjaković, M. D. Joksović, *Inorg. Chem. Commun.* **13** (2010) 1085
33. M. D. Revenco, P. N. Bourosh, O. V. Palamarciuc, J. Lipkowski, M. Gdaniec, Yu. A. Simonov, *Russ. J. Inorg. Chem.* **54** (2009) 1581
34. O. V. Palamarciuc, P. N. Bourosh, M. D. Revenco, J. Lipkowski, Yu. A. Simonov, R. Clérac, *Inorg. Chim. Acta* **363** (2010) 2561
35. M. M. Mostafa, S. M. Hassan, G. M. Ibrahim, *J. Inorg. Nucl. Chem.* **42** (1980) 285
36. M. M. Mostafa, M. A. Khattab, K. M. Ibrahim, *Transition Met. Chem.* **8** (1983) 212
37. M. E. M. Emam, M. A. H. Hafez, M. N. H. Moussa, *J. Thermal. Anal.* **37** (1991) 1005 and references therein
38. M. M. Abou Sekkina, M. R. Salem, *J. Thermal. Anal.* **48** (1997) 841 and references therein
39. M. M. Mostafa, *Spectrochim. Acta, A* **66** (2007) 480 and references therein
40. X. Wang, X. M. Zhang, H. X. Liu, *J. Coord. Chem.* **33** (1994) 223
41. Lj. S. Vojinović, *Ph. D. Thesis*, Faculty of Science, University of Novi Sad, 2005 (in Serbian)
42. V. M. Leovac, K. Mészáros-Szécsényi, Lj. S. Vojinović-Ješić, V. I. Češljević, S. Markov, T. Wadsten, *J. Therm. Anal. Cal.* **86** (2006) 379
43. J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **209** (2000) 197
44. G. Di Maio, S. Li, G. Portalone, *Acta Crystallogr., C* **50** (1994) 635
45. Lj. S. Vojinović-Ješić, G. A. Bogdanović, V. M. Leovac, V. I. Češljević, Lj. S. Jovanović, *Struct. Chem.* **19** (2008) 807
46. S. B. Novaković, B. M. Drašković, Lj. S. Vojinović-Ješić, V. I. Češljević, V. M. Leovac, *Acta Crystallogr.* **E66** (2010) m328
47. V. M. Leovac, V. S. Jevtović, Lj. S. Jovanović, G. A. Bogdanović, *J. Serb. Chem. Soc.* **70** (2005) 393
48. Lj. S. Vojinović-Ješić, V. M. Leovac, V. I. Češljević, unpublished results
49. Z. A. Starikova, E. A. Shugam, *Zh. Strukt. Khim. (Russ.)* **10** (1969) 290
50. V. Chandrasekhar, S. Kingsley, A. Vij, K. C. Lam, A. L. Rheingold, *Inorg. Chem.* **39** (2000) 3238
51. A. I. Vogel, A. R. Tatchell, B. S. Furnis, A. J. Hannaford, P. W. G. Smith, *Vogel's text-book of practical organic chemistry* 5th ed., Longman, London, 1989
52. S. Naskar, D. Mishra, S. K. Chattopadhyay, M. Corbella, A. J. Blake, *J. Chem. Soc. Dalton Trans.* (2005) 2428 and references therein
53. G. J. Palenik, D. W. Wester, *Inorg. Chem.* **17** (1978) 864
54. C. Lorenzini, C. Pelizzi, G. Pelizzi, G. Predieri, *J. Chem. Soc., Dalton Trans.* (1983) 721

55. M. R. Bermejo, A. Sousa, M. Fondo, A. M. González, O. L. Hoyos, R. Pedrido, M. A. Maestro, J. Mahia, *Z. Anorg. Allg. Chem.* **626** (2000) 506
56. K. B. Gudasi, S. A. Patil, R. S. Vadavi, R. V. Shenoz, M. Nethaji, S. W. A. Bligh, *Inorg. Chim. Acta* **359** (2006) 3229
57. M. V. Main, J. S. Fritz, *Anal. Chem.* **61** (1989) 1272
58. N. M. El-Metwally, I. M. Gabr, A. M. Shallaby, A. A. El-Asmy, *J. Coord. Chem.* **58** (2005) 1145
59. U. El-Ayaan, I. M. Kenawy, Y. G. Abu El-Reash, *J. Mol. Struct.* **871** (2007) 14
60. H. X. Liu, X. M. Zhang, X. Wang, *Polyhedron* **13** (1994) 441
61. H. X. Liu, W. Wang, X. Wang, *J. Coord. Chem.* **33** (1994) 347
62. R. M. El-Bahnasawy, *J. Therm. Anal.* **45** (1995) 1547
63. U. El-Ayaan, I. M. Kenawy, Y. G. Abu El-Reash, *Spectrochim. Acta, A* **68** (2007) 211
64. F. H. Allen, *Acta Crystallogr., B* **58** (2002) 380. The data were recovered from the August 2010 update release of the CSD (version 5.31)
65. Y.-Q. Sun, R.-S. Yang, H.-H. Zhang, R.-Q. Sun, Q.-Y. Yang, *Chin. J. Struct. Chem.* **20** (2001) 310.