

SYNTHESIS OF AZOLES WITH TWO PYRIDINE SUBSTITUENTS AT CARBON ATOMS AND THEIR USE IN COORDINATION CHEMISTRY. (REVIEW)

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Published data on the synthesis of azoles containing two pyridine substituents are analyzed in relation to the type of central five-membered ring. The applications of such molecules as ligands in coordination chemistry are discussed.

Keywords: isoxazoles, imidazoles, oxadiazoles, pyrazoles, pyridines, thiadiazoles, thiazoles, triazoles.

The design of coordination polymers having unique structures and valuable functional characteristics is one of the most rapidly developing regions of modern chemistry and materials science [1, 2]. Most of the employed *exo*-dentate ligands belong to the bipyridine class with the general formula Py–X–Py, where X is a conjugated disubstituted fragment. The parent of such ligands is 4,4'-bipyridine (X is absent), which has been widely used for a long time in the construction of coordination polymers [3]. The most widely used bridges X include double and triple carbon–carbon bonds, azo and imino groups, and benzene, pyridine, triazine, and tetrazine rings or combinations of these fragments [4].

One modern trend in the synthesis of coordination polymers is to use ligands of the Py–X–Py type, where X is a *meta*- or *ortho*-substituted azole. The interest in such compounds is due, first, to their electronic characteristics and, second, to the ability of the pyridine nitrogen atom of the azole ring to coordinate with the metal ion. This fact significantly extends the possibilities of the ligands in coordination, enhancing the practical characteristics of the complexes. At the moment the coordination characteristics of a small group of dipyridylazoles have been studied. It is important to emphasize that at this time there has been no systematic treatment of data on the design and synthesis of such compounds. In view of the foregoing it seemed to us important and timely to clarify some of the problems that arise in the synthesis of dipyridylazoles for the systems that are finding use in coordination chemistry.

It should be noted that in this paper we restrict ourselves to examination of the synthesis and coordination characteristics of azoles containing not less than one nitrogen atom of the pyridine type. Consequently, we do not consider five-membered donating heterocycles with one heteroatom. The second restriction is the fact that we decided to examine only azoles substituted by pyridine groups at carbon atoms, and the range of compounds studied does not therefore include tetrazoles.

The review is divided up according to the types of central five-membered heterocycles. In each section the synthetic aspects and questions concerning the use of specific ligands in coordination chemistry are examined.

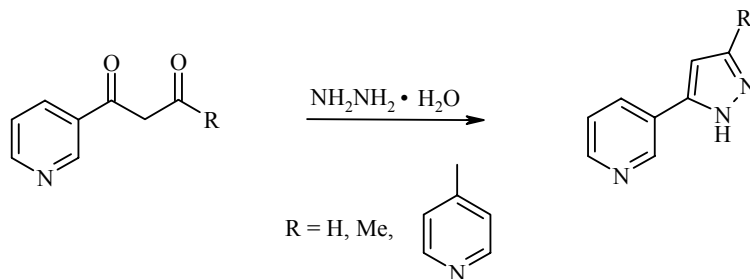
* Dedicated to Academician Nikolai Serafimovich Zefirov in honor of his seventieth birthday.

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In the review we use the name "pyridylazoles" so as to concentrate the reader's attention on the central ring of the studied molecules.

1. PYRAZOLES

3,5-Di(2-pyridyl)pyrazole was first obtained in the reaction of 1,3-di(2-pyridyl)propane-1,3-dione with hydrazine hydrate [5]. A series of mono- and di(4-pyridyl)-substituted pyrazoles were synthesized using the same approach [6]. 1,3-Diketones and keto aldehydes produced by the Claisen condensation were used as precursors, but unfortunately the product yields were not indicated.



A large volume of the research was done by the authors [7, 8], who synthesized a series of symmetrical and unsymmetrical 3,5-dipyridyl-substituted pyrazoles and also a few 3,5-dipyridyl-substituted isoxazoles (Table 1).

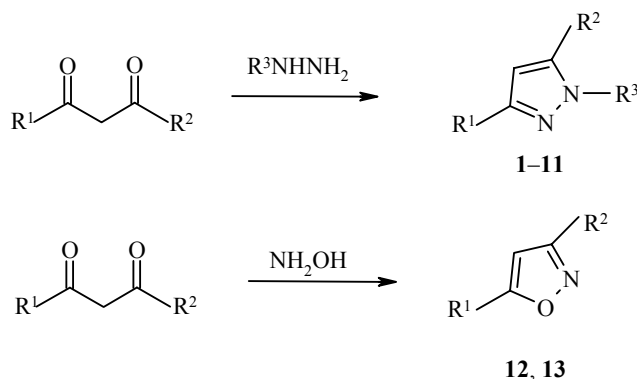


TABLE 1. Pyrazoles and Isoxazoles Obtained in [7, 8]

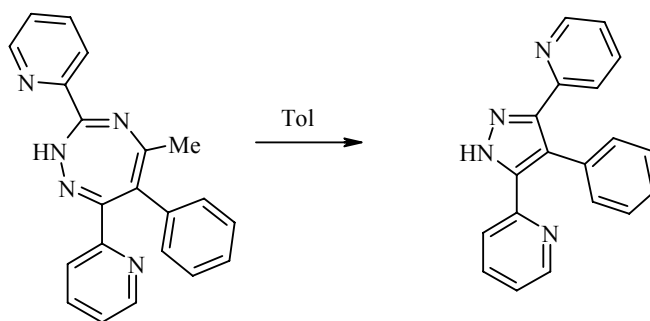
Compound	R ¹	R ²	Yield, %	Compound	R ¹	R ²	Yield, %
1	2-Pyridyl	2-Pyridyl	81	8	2-Pyridyl	3-Pyridyl	24
2	3-Pyridyl	3-Pyridyl	89	9	2-Pyridyl	4-Pyridyl	17
3	4-Pyridyl	4-Pyridyl	90	10	3-Pyridyl	3-Pyridyl	27
4	2-Pyridyl	3-Pyridyl	63	11	4-Pyridyl	4-Pyridyl	47
5	2-Pyridyl	4-Pyridyl	72	12	2-Pyridyl	2-Pyridyl	28
6	3-Pyridyl	4-Pyridyl	81	13	3-Pyridyl	3-Pyridyl	41
7	2-Pyridyl	2-Pyridyl	40				

* **1-6** R³ = H, **7-11** R³ = Ph.

The starting materials were 1,3-dipyridylpropanediones. The structures of all the compounds were proved unambiguously, and the yields are the preparatively useful. It is interesting that the authors obtained a series of N-phenyl-substituted pyrazoles. In all cases of the production of isoxazoles a single isomer was isolated, sometimes it is true with a very small yield. The structure of compounds **7-11** was additionally confirmed by the data from 2D-COSY ^1H - ^1H experiments.

The reaction of hydrazine hydrate with 1,3-diketones is also a method for the synthesis of symmetrical homologs of compound **1** containing methyl groups at both pyridine substituents [9, 10].

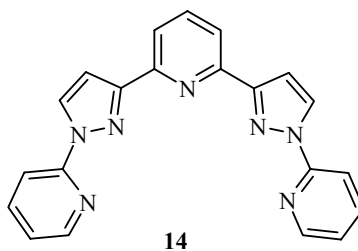
In [11] a triaryl-substituted pyrazole with 2-pyridine groups at positions 1 and 3 was obtained by heating the triazepine shown in the scheme, but the reaction mechanism and the composition of the elimination products were not discussed in detail. Certainly, such a method cannot be used for the production of a wide range of products.



2,2'-Dipyridylpyrazoles and their analogs exclusively have found use in coordination chemistry. Thus compound **1** and its dimethyl homologs were used in the synthesis of binuclear complexes based on Fe(II) [12], which are of interest from the standpoint of their magnetic characteristics and understanding the nature of the *spin-crossover* effect. Such bisbidentate ligands have been most widely used in the synthesis of mononuclear [13, 14] and binuclear [14, 15] complexes of Ru(II), which are interesting as subjects for studying intramolecular energy transfer.

In [15] it was found that the ligand present in a binuclear complex of ruthenium is capable of entering into nitration with nitrosonium tetrafluoroborate with a yield of 62%. Substitution takes place at position 4 of the coordinated pyrazole ring.

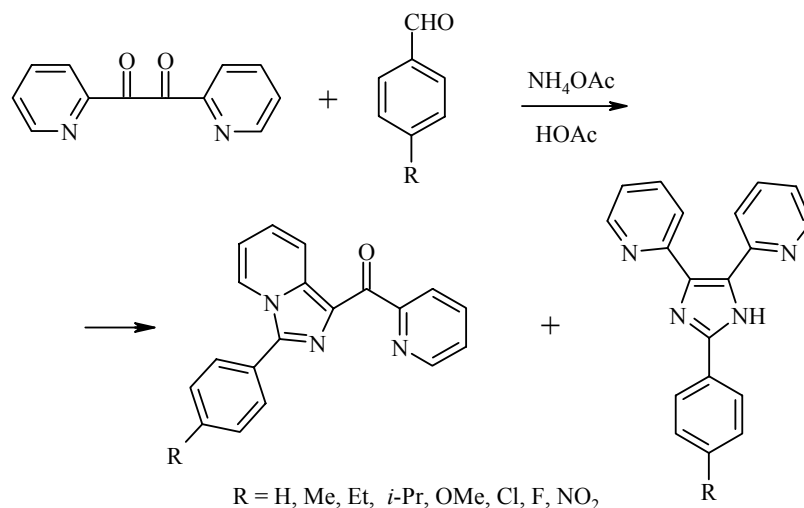
An interesting polydentate analog of compound **1** is the ligand **14**, produced by arylation of the dianion of 2,6-di(3-pyrazolyl)pyridine [16].



Compound **14** takes part in complexation with the Cu(II) ion as a bisbidentate ligand, used for binding the nitrogen atoms of the pyrazoles and the terminal pyridines with the metal ions [16]. In the case of the complex with Co(II) compound **14** represents a tridentate ligand, which bonds with the metal through the nitrogen atoms of the pyrazoles and the central pyridine ring [17].

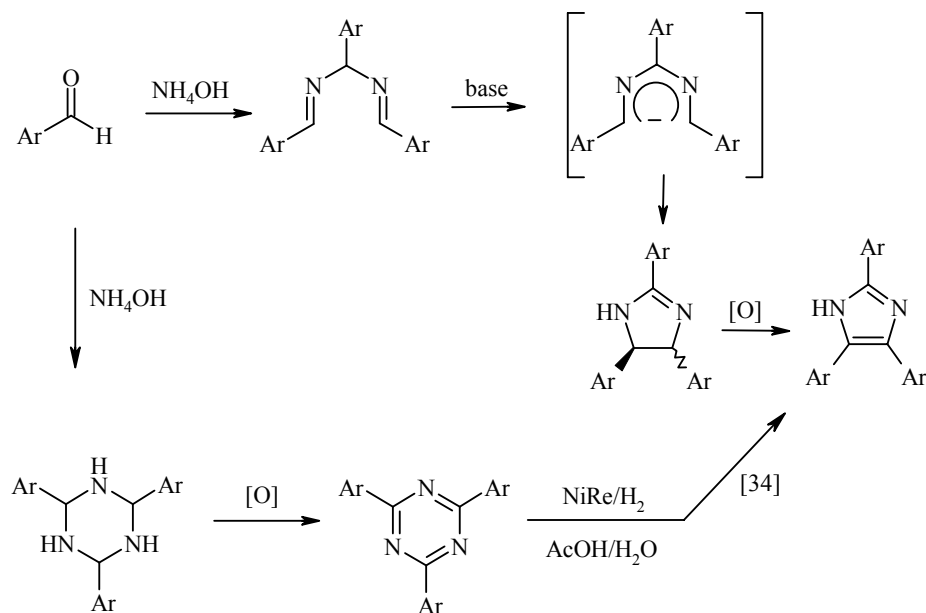
2. IMIDAZOLES AND THIAZOLES

One of the most convenient methods for the synthesis of 2,4,5-trisubstituted imidazoles is the reaction between 1,2-diketones and aldehydes. In the case of derivatives of imidazole with pyridine substituents, however, the use of this method is restricted by the availability of the respective diketones. Thus, only the production of 4,5-di(2-pyridyl)imidazoles from the commercially available 2,2'-bipyridyl has been described in the literature [18]. Here the imidazoles are obtained in a mixture with the corresponding imidazo[1,5-*a*]-pyridines:



The production of 2,4-dipyridylimidazoles was described in the patent [19]. This method is based on the reaction of acetylpyridines with the amidines of pyridine carboxylic acids.

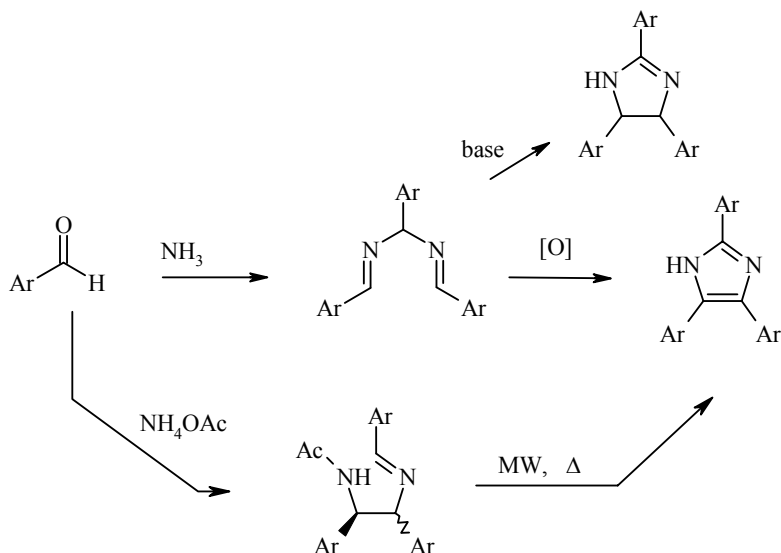
A method for the production of 2,4,5-*sym*-trisubstituted imidazoles is the reaction of aromatic or heteroaromatic aldehydes with ammonia [20]. The action of heat with an oxidizing agent on the intermediately obtained imidazoline in dimethyl sulfoxide leads to the formation of the imidazole.



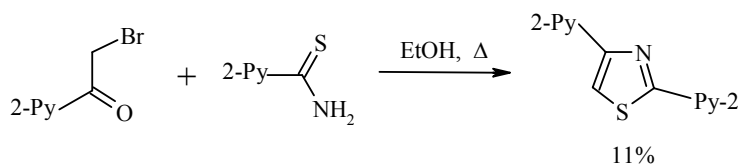
sym-1,3,5-Triazine is sometimes formed as side product. The method is very convenient but is restricted with regard to the structure of the product. Nevertheless, it is worth mentioning that this method was used to obtain 2,4,5-tris(2-pyridyl)imidazole. It is interesting that the corresponding aromatic 2,4,6-*sym*-triazene forms the same trispyridylimidazole with an excellent yield during hydrogenation at Raney nickel [21].

Tris(3-pyridyl)imidazole and tris(4-pyridyl)imidazole were obtained for the first time by thermolysis of the respective aldazines [22].

Original and accessible methods for the synthesis of imidazoles were proposed by Zefirov and coworkers [23, 24]. In addition to the synthesis questions concerning the selectivity in the production of the derivatives in relation to a series of factors are discussed.

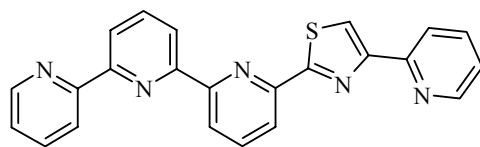


2,4-Di(2-pyridyl)thiazole was first obtained comparatively simply but with a low yield by the cyclocondensation of the thioamide of picolinic acid and an α -bromo ketone [25]. However, the authors were unable to demonstrate rigorously the absence of the isomeric 2,5-di(2-pyridyl) derivative.

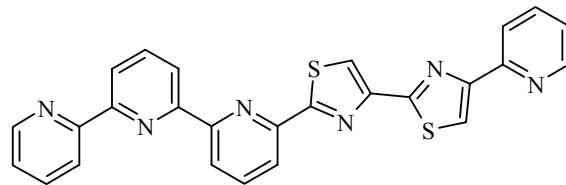


This compound and also its analogs have actually been used in coordination chemistry since 1964, when the synthesis and magnetic characteristics of chelate mononuclear complexes with the chlorides and perchlorates of Fe(II), Co(II), Ni(II), and Cu(II) were described [26]. The same authors described the production of mono- and binuclear complexes of Fe(II) [27]. In the seventies the binuclear complexes of 2,4-di(2-pyridyl)thiazole with Fe(II) were studied as models capable of exhibiting the *spin-crossover* effect [28]. This ligand has also attracted the attention of specialists in the study of the luminescent characteristics of lanthanides [29].

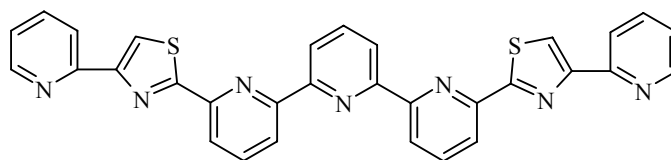
In recent years polydentate ligands capable of interacting with metal ions to form the so-called "helicates" have been actively studied. One type of such ligands is the structural analogs of 2,4-di(di-2-pyridyl)thiazole, such as compounds **15-17** [30, 31]. These polydentate ligands actually form helicate products during reaction with Cu(II) and Cd(II) ions.



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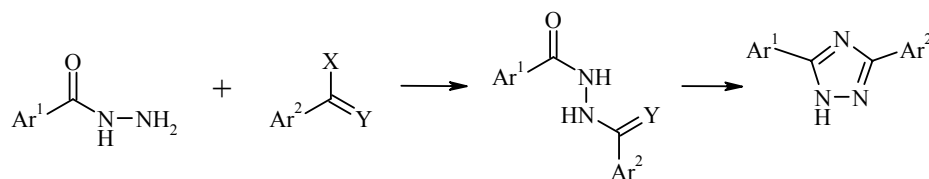
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3. TRIAZOLES, OXADIAZOLES, AND THIADIAZOLES

Five-membered heterocycles containing three heteroatoms can exist in the form of several isomers. In the case of triazoles 1,2,3- and 1,2,4-isomers are possible. The 1,2,3-triazoles contain a three-heteroatom fragment, in which the bipolar fragment of the azide group is immediately seen. Nevertheless, we were unable to find in the literature any data about the production of 1,2,3-triazoles containing two pyridine substituents.

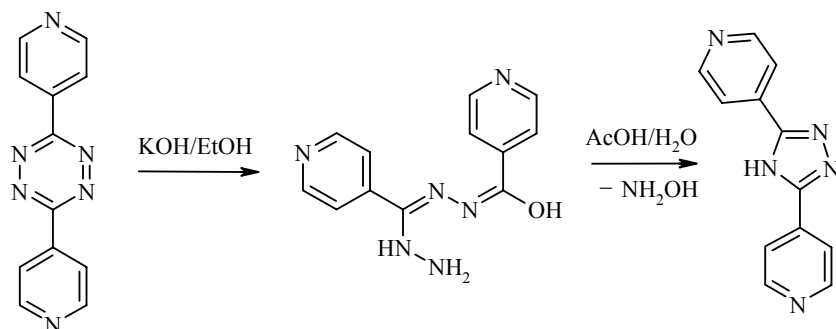
On the other hand 1,2,4-triazoles with pyridine substituents are compounds that have been known for a long time and are widely used in coordination chemistry. The first synthesized representative of this group of compounds was 3,5-di(4-pyridyl)-1,2,4-triazole, obtained by the deamination of 4-amino-3,5-di(4-pyridyl)-1,2,4-triazole. The latter was isolated as a side product of the reaction of isonicotinic acid with hydrazine hydrate [32, 33].

3,5-Diaryl-1,2,4-triazoles are obtained by the cyclization of N^2 -aroylamidrazones. The method for the production of such linear derivatives is extremely simple; the acid hydrazide [34] is brought into reaction with an amide, thioamide, alkyl imidate, or imidoyl chloride. A whole series of dipyridyltriazoles were produced by such a method, and the methyl imidate was used as "electrophilic" component [26]. Unfortunately the authors did not make any correlations between the type of pyridine ring and the yield of the triazole.

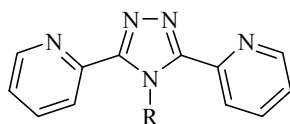


X, Y = NH₂, O; NH₂, S; OCH₃, NH; Hal, NH

An alternative method for the production of 3,5-di(4-pyridyl)-1,2,4-triazole was proposed in [35, 36]; the readily obtainable 3,6-di(4-pyridyl)-1,2,4,5-tetrazene was treated first with a base and then with an acid. Nucleophilic opening of the ring occurs initially, and this is then followed by rapid recyclization with the elimination of hydroxylamine.



The use of dipyridyl-1,2,4-triazoles in coordination chemistry is restricted to the use of the 2,2'-isomers, and at the present time more than 30 complexes have been synthesized. This reaction path has been described in detail in recent reviews [37, 38], and therefore here we will only give information on the ligands employed (Table 2).



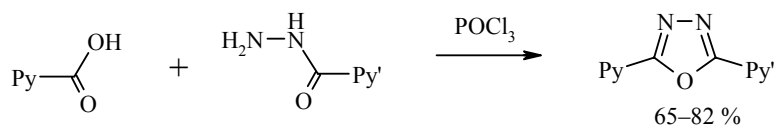
For oxadiazoles, in addition to the 1,2,3- and 1,2,4-isomers, two other isomers, 1,2,5- and 1,3,4-oxadiazoles, are also possible. The dipyridine derivatives of only last two isomers have been described in the literature.

One of the first methods for the synthesis of 2,5-di(3-pyridyl)-1,3,4-oxadiazole involved heating 1,2-dinicotinoylhydrazide with phosphorus oxychloride followed by treatment with ice and hydroxylamine and gave a yield of 23% [45]. The 4,4'-isomer was obtained similarly, but in this case the cyclization was carried out in concentrated sulfuric acid [35].

Another method for the synthesis of 1,3,4-oxadiazole involved generation of the diacylhydrazide *in situ*. The isomeric 2,5-dipyridyl-1,3,4-oxadiazoles were obtained in this way [46, 47]. The nature of the substituents in the initial compounds had little effect on the product yields.

TABLE 2. 4-Substituted 3,5-Di(2-pyridyl)-1,2,4-triazoles Used in the Synthesis of Coordination Compounds

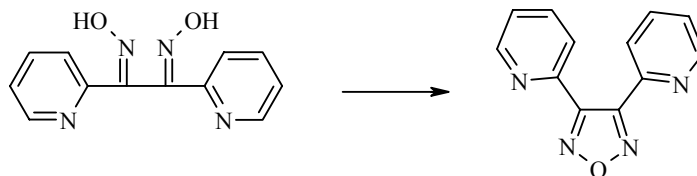
R	Precursor	Reference
H	Bispyridinoylhydrazine	[36]
NH ₂	2-Pyridinecarbonitrile	[40]
OH	3,5-Di(2-pyridyl)-1,2,4-triazole	[41]
2-Pyridyl	5-(2-Pyridyl)tetrazole	[42]
1-Pyrrolyl	4-Amino-3,5-di(2-pyridyl)-1,2,4-triazole	[43]
4-BrC ₆ H ₄	5-(2-Pyridyl)tetrazole	[44]



The modern version of this method, suitable for the synthesis of all symmetrical 1,3,4-oxadiazoles, uses aromatic acids, hydrazine dihydrochlorides, and a mixture of orthophosphoric acid with phosphorus oxide and phosphorus oxychloride [48]. The same authors proposed the use of microwave radiation for the production of dipyridyl-1,3,4-oxadiazoles [49].

During oxidation with sodium nitrite in an acidic medium the above-mentioned 3,6-di(2-pyridyl)tetrazene forms 3,5-di(2-pyridyl)-1,3,4-oxadiazole [36].

Until recently 3,4-di(2-pyridyl)-1,2,5-oxadiazole was unknown. The synthesis of this compound, which is at present the only known oxadiazole with pyridine substituents, was published in 2002 [50]. The production of this compound was based on the well known cyclocondensation of 1,2-dioximes:



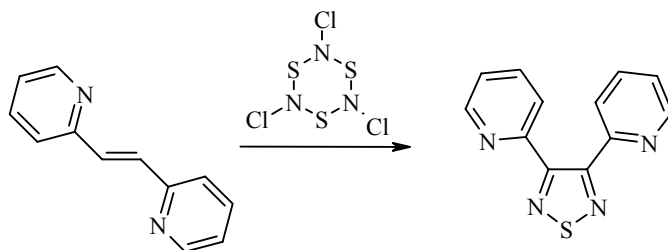
As in the case of indazoles, the development of this method for the synthesis of 1,2,5-oxadiazoles with a wide set of pyridine substituents was delayed by the lack of suitable methods for the synthesis of 1,2-dipyridyl-1,2-diones.

In contrast to triazoles, the coordination chemistry of oxadiazoles mainly involves the use of *exo*-dentate 3- and 4-pyridine ligands. A vigorous outburst of investigations into the complexes of oxadiazoles occurred at the beginning of the millennium. This was due to the fact that the rise of interest in coordination polymers, on the one hand, coincides with the development of convenient methods for the synthesis of the respective ligands, on the other. No small role is also played by the fact that most of the "classical" ligands had already been studied quite fully.

Due to the limited volume of this publication, we only present recent examples of the use of *exo*-dentate dipyridyloxadiazoles in the synthesis of coordination polymers, networks, and three-dimensional structures. At the present time compounds based on Co(II) [51], Cu(II), Cd(II) [52], Ag(I) [53], Mn(II) [54], and Zn(II) [55] have been obtained.

As in the case oxadiazoles, only the 1,3,4- and 1,2,5-isomers are known for thiadiazoles with pyridine substituents. Symmetrical dipyridyl-1,3,4-thiadiazoles (the 2,2', 3,3', and 4,4'-isomers) were first obtained by heating the corresponding bishydrazides with phosphorus pentasulfide in the presence of tertiary amines [56]. 2,5-Di(2-pyridyl)-1,3,4-thiadiazole was also obtained by the reaction of the thioamide of picolinic acid with the hydrazide of picolinic acid [36].

The only example of a dipyridyl-1,2,5-thiadiazole found in the literature was in the already cited paper [50]. The authors obtained 3,4-di(2-pyridyl)-1,2,5-thiadiazole by the reaction of 1,2-di(2-pyridyl)ethylene with $S_3N_3Cl_3$:



The coordination chemistry of dipyridylthiadiazoles has not so far been investigated as actively as the analogous chemistry of oxadiazoles. There are, nevertheless, data on the production of mononuclear chelate complexes of 2,5-di(2-pyridyl)-1,3,4-thiadiazole with Cu(II) , Ni(II) , and Co(II) salts [57]. Recently papers have also appeared on the synthesis of polymeric complexes of 2,5-di(4-pyridyl)-1,3,4-thiadiazole with Co(II) , Cu(II) , and Cd(II) [51, 52].

On the basis of the information presented above it is possible to reach the following conclusions about the current state of the organic and coordination chemistry of dipyridylazoles.

1. This region of chemistry is on the rise and in a state development and is timely from the standpoint both of organic and inorganic synthesis and the application of coordination polymers in materials science.

2. In spite of the great advances in the region of synthesis, many groups of dipyridylazoles have either not been obtained or are poorly accessible compounds. This applies primarily to the unsymmetrical derivatives both with respect to the position of substitution in the azole ring and with respect to the combination of various pyridine substituents.

3. The future of dipyridylazoles is involved with their ever increasing use as *exo*-dentate ligands. But this, in turn, dictates the need for active study of the applied characteristics of coordination polymers.

4. In the present work we have not strived to cover the whole field of the chemistry of dipyridylazoles. In particular it is necessary to mention the small numbers of theoretical and computational papers. It is undoubtedly necessary to move forward in this direction, since the established application of one or the other ligand demands considerable theoretical consideration.

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