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The authors congratulate Academician V.I. Ovcharenko on the occasion of his 70th jubilee

Verdazyls in Coordination Chemistry

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Abstract—The present minireview describing the mono- and biradical structures of heterocyclic radicals (verdazyls) in the role of ligands and types of their metal complexes is based on an analysis of scientific literature published since 2000 to 2021. In the majority of cases, monoverdazyl radicals in the composition of the complexes are described as *N*,*N*-bidentate or *N*,*N*,*N*-tridentate redox-active ligands. The verdazyl-containing biradical systems are considered. Examples of other verdazyl compounds with metals are presented.

Keywords: verdazyl, oxoverdazyl, biradical, metal complex
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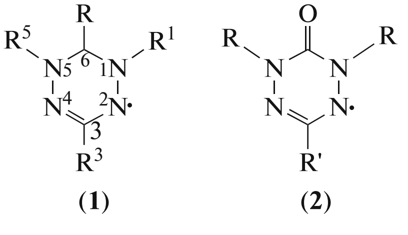
INTRODUCTION

π-Delocalized stable radicals became important structural elements of ultramodern materials for technological and biological application [1–3]. Among compounds of this type are heterocyclic radicals verdazyls differed in the nature of the group in position 6: Kuhn verdazyls (**1**) are presented by the radicals with the saturated carbon atom and oxoverdazyls (**2**) containing the carbonyl group (Scheme 1).



Scheme 1.

A high chemical stability, synthetic flexibility, and the ability to form metal complexes allow verdazyls to be attributed to the most attractive and large classes of stable radicals [4]. They find use in various fields of chemistry, physics, and biology as stabilizers, spin labels, and building blocks for manufacturing molecular magnets and organic materials with photoswitcheable or conduction properties. Rapt attention to metal complexes of these radicals is due to the possibility of developing from them new hybrid magnetic materials [5–8]. Several reviews are devoted to the chemistry of verdazyl radicals, including coordination chemistry [9–12]. The structures of verdazyls as ligands and the types of related metal complexes are considered in the present minireview.

MONOVERDAZYL LIGANDS AND RELATED METAL COMPLEXES

Bidentate ligands. The ability of verdazyl radicals to form metal complexes attracted attention of researchers significantly later than their other properties. 6-Oxoverdazyls are stable redox-active heterocyclic radicals possessing structural versatility due to various substituents and can be included directly into ligands of the polypyridyl type. They became a platform for the onrush of the coordination chemistry of verdazyls.

The introduction of N-containing heterocycles into position 3 of oxoverdazyl made it possible to obtain bidentate redox-active ligands for the synthesis of mono- and binuclear complexes. A series of the metal complexes (**3a**)–(**3k**) was synthesized from 1,5-*R*-6-oxo-3-(pyridin-2-yl)verdazyls. The structures of these complexes depend on the nature of the metal, anion X, synthesis conditions, and substituents in the ligand. The Zn(II) ((**3a**), (**3b**)) and Cd(II) ((**3c**), (**3d**)) complexes with the diamagnetic metals are characterized by the tetrahedral environment of the metal (Scheme 2) [13]. The complexes with the paramagnetic metals Mn(II) (**3e**) and Ni(II) (**3f**) have the mononuclear pseudooctahedral structures [14]. The Ru(II) complexes (**3j**) and (**3k**) with additional acetylacetonate (acac) and hexafluoroacetylacetonate (Hfac) ligands are close in structure to the octahedral

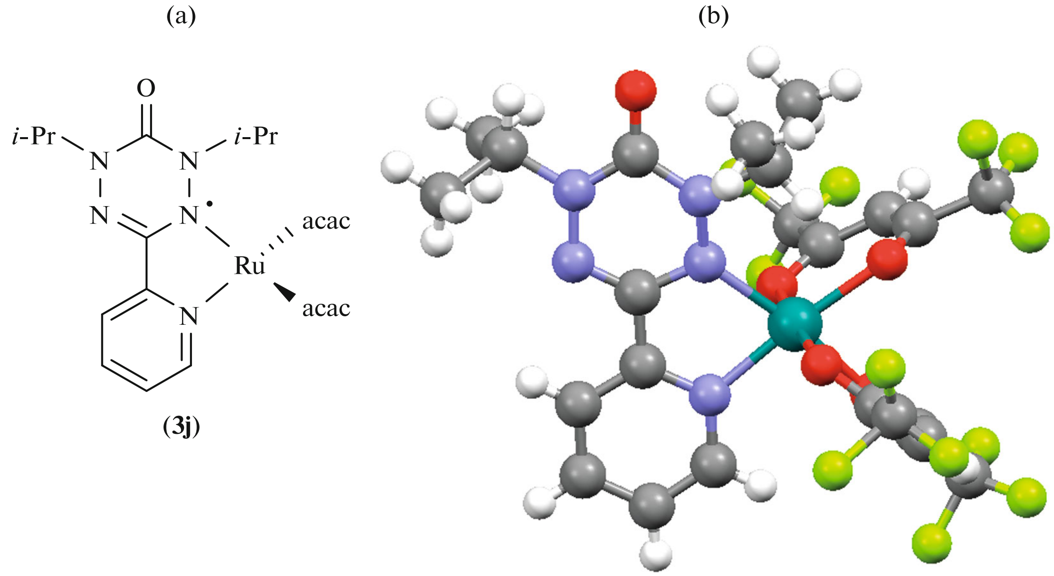
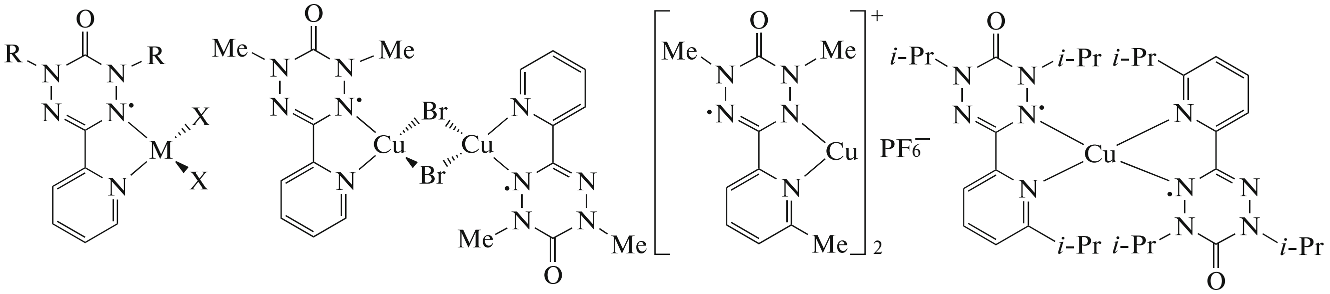


Fig. 1. (a) Chemical and (b) molecular structures of complex (**3j**) (CIF file CCDC no. 748432) [15].

coordination mode (Fig. 1) [15]. However, high differences in their EPR spectra and electrochemical properties show that the charge delocalization is very sensitive to the nature of the β-diketonate ligand. The environment of the metal in the Pd(II) (**3g**) and Pt(II) (**3h**) complexes is planar (Fig. 2) [16].



(3) **(4)** **(5)** **(6)**

(**3**): R = Me: Zn, Cl (**a**), Zn, I (**b**); Cd, Cl (**c**),
Cd, I (**d**); Mn, Hfac (**e**), Ni, Hfac (**f**);
R = *i*-Pr: Pd, Cl (**g**); Pt, Cl (**h**); Ru, Acac (**j**);
Ru, Hfac (**k**)

Scheme 2.

The dimeric structure (**4**) with a weak antiferromagnetic exchange between free radicals was determined for the complexes synthesized using CuBr [17]. The coordination polyhedron of the Cu(I) complex (**5**) based on 1,5-dimethyl-3-(6-methylpyridin-2-yl)-6-oxoverdazyl is a flattened pseudotetrahedron [18]. Complex (**4**) with 1,5-di(isopropyl)-3-(6-isopropylpyridin-2-yl)-6-oxoverdazyl was synthesized by the oxidation of the radical precursor (tetrazane) with benzoquinone in the presence of Cu(I) rather than from the radical itself [19]. The coordination node is a distorted tetrahedron, and the angle between the planes of the verdazyl ligands is 75°. The structures of complexes (**3**) with Zn, Cd, Mn, Ni, Pd, and Pt and complexes (**4**)–(**6**) were confirmed by X-ray diffraction (XRD) data.

A group of mononuclear metal complexes (**7**) was synthesized from 3-(imidazol-2-yl)-containing verdazyls, and their structures were studied using diverse methods, including XRD (Scheme 3) [20]. The Cu(II) complex with 1,5-di(isopropyl)-3-(*N*-methylimidazol-2-yl)verdazyl (**7f**) is characterized by the octahedral environment of the copper ion, and the nitrogen atoms of verdazyl bound to Cu occupy the axial positions. The Ni(II) (**7a**) and Mn(II) (**7b**) complexes with 1,5-dimethyl-3-(imidazol-2-yl)verdazyl are isostructural.

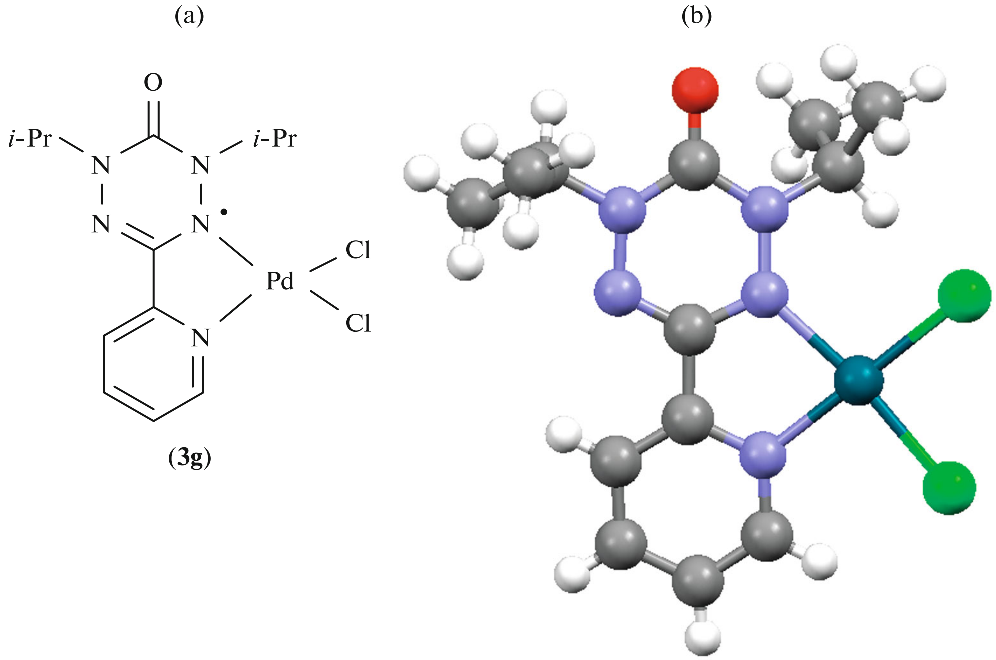
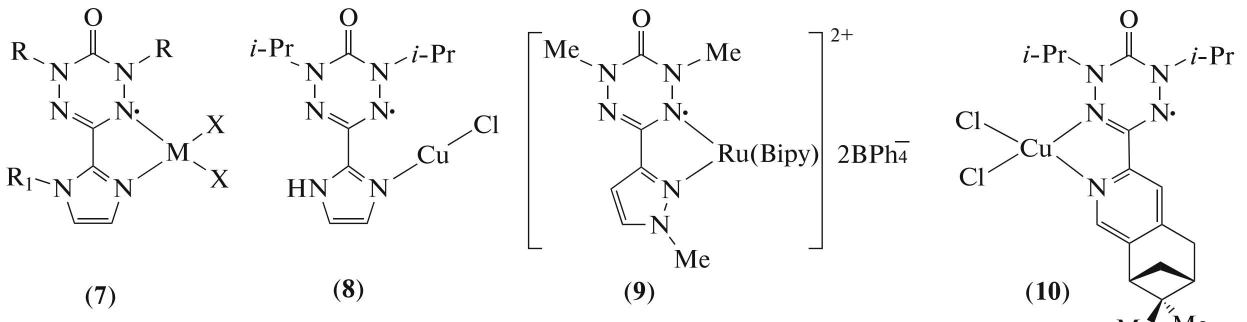


Fig. 2. (a) Chemical and (b) molecular structures of complex (**3g**) (CIF file CCDC no. 787980) [16].

The metal ion is linked to four oxygen atoms of the Hfac ligand and two nitrogen atoms of verdazyl to form the distorted octahedral structure (Fig. 3) [21]. The environment of the metal is planar in the Pd(II) (**7g**) and Pt(II) (**7h**) complexes based on 1,5-di(isopropyl)-3-(*N*-methylimidazol-2-yl)verdazyl [16]. In the crystal, the complexes form ensembles with the π-stacking architecture. The first lanthanide (Gd, Tb, Dy) complexes (**7c**)–(**7e**) were synthesized with 1,5-dimethyl-3-(imidazol-2-yl)verdazyl [22]. All of them are isomorphous and contain one-dimensional chains in which the verdazyl ligand is the bridge between two lanthanide ions.



(**7**): R, R_1 = Me, H: Ni, Hfac (**a**); Mn, Hfac (**b**);
Gd, Hfac (**c**); Tb, Hfac (**d**); Dy, Hfac (**e**);
R, R_1 = *i*-Pr, Me: Cu, Hfac (**f**); Pd, Cl (**g**); Pt, Cl (**h**)

Scheme 3.

Complex (**8**) was synthesized by the reaction of tetrazane with Cu(II) chloride [23]. The reaction includes the oxidation of tetrazane and reduction of copper. According to the XRD data, the structure of the complex is unusual and the copper ion is in the quasi-linear environment. In this case, verdazyl acts as a monodentate ligand. Ruthenium complex (**9**) was synthesized using 1,5-dimethyl-3(1-methylpyrazol-3-yl)-6-oxoverdazyl as the ligand [24]. The Cu(II) complex (**10**) was synthesized using enantiopure oxoverdazyl containing the (–)-pinene–pyridinyl substituent at C_3 [25]. According to the XRD data, the structure of this complex is similar to those of the previously described complexes of the Vd···$CuCl_2$ type (Vd is verdazyl). However, the long intermolecular Cu···N contact (3.889 Å) binds two molecules of complex (**10**)

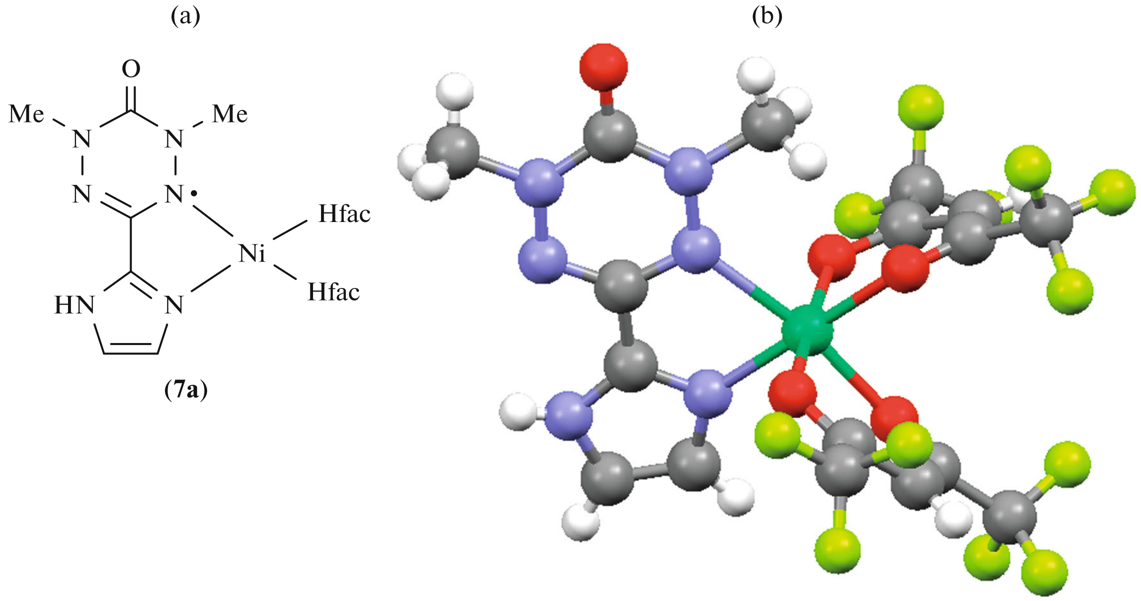
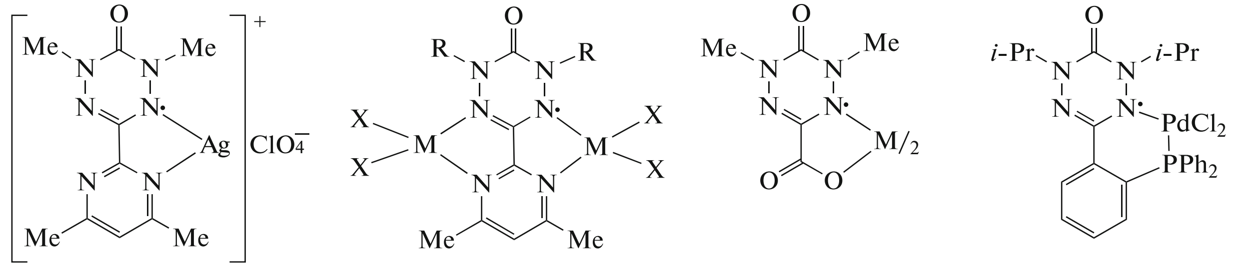


Fig. 3. (a) Chemical and (b) molecular structures of complex (**7a**) (CIF file CCDC no. 653518) [21].

into centrosymmetric dimers. The Cu atom exists in the pseudooctahedral coordination environment.

The introduction of the pyrimidine fragment into position 3 of oxoverdazyl made it possible to synthesize both mono- and binuclear complexes. The reaction of 1,5-dimethyl-3-(4,6-dimethylpyrimidin-2-yl)oxoverdazyl with Ag(I) perchlorate afforded mononuclear complex (**11**) (Scheme 4) [26]. According to the XRD data, complex (**11**) is built of cationic chains of silver ions that serve as bridges linking the bidentate ligands. This verdazyl with Mn(II) and Ni(II) ions forms binuclear complexes (**12**) with the octahedral structure of each metal ion [27]. Complexes (**12**) with Ru(II) based on 1,5-di(isopropyl)-3-(4,6-dimethylpyrimidin-2-yl)oxoverdazyl have similar structures [28].



(**11**) (**12**) (**13**) (**14**)

(**12**): R = Me: Mn, Hfac (**a**); Ni, Hfac (**b**); R = *i*-Pr: Ru, Acac (**c**); Ru, Hfac (**d**); (**11**): Ni (**a**), Co (**b**)

Scheme 4.

1,5-Dimethyl-3-carboxyl-6-oxoverdazyl was used as a bidentate N,O-ligand, whose deprotonated form is highly soluble in water, which makes it possible to synthesize the complexes in an aqueous medium, including the use of the hydrothermal method [29]. The Ni(II) and Co(II) complexes with this ligand (**13**) were synthesized by the reaction of the radical precursor with metal perchlorates in a water-alkaline medium. According to the XRD data, both complexes have a pseudooctahedral environment of the metal ion consisting of two N,O-chelating verdazyl ligands in the *anti*-configuration in the equatorial plane and two *trans*-aqua ligands in the axial positions.

Verdazyl containing the diphenylphosphine group was used as one more bidentate ligand for the synthesis of the Pd(II) complex (**14**) (Fig. 4) [30]. The XRD data show the nonplanar arrangement of the chelate node in this complex and a difference in the Pd–Cl bond lengths. The electrochemical properties of this complex differ from the properties of other Pd complexes with verdazyls. The ability of complex (**12**) to reversibly transform into the stable binuclear complex

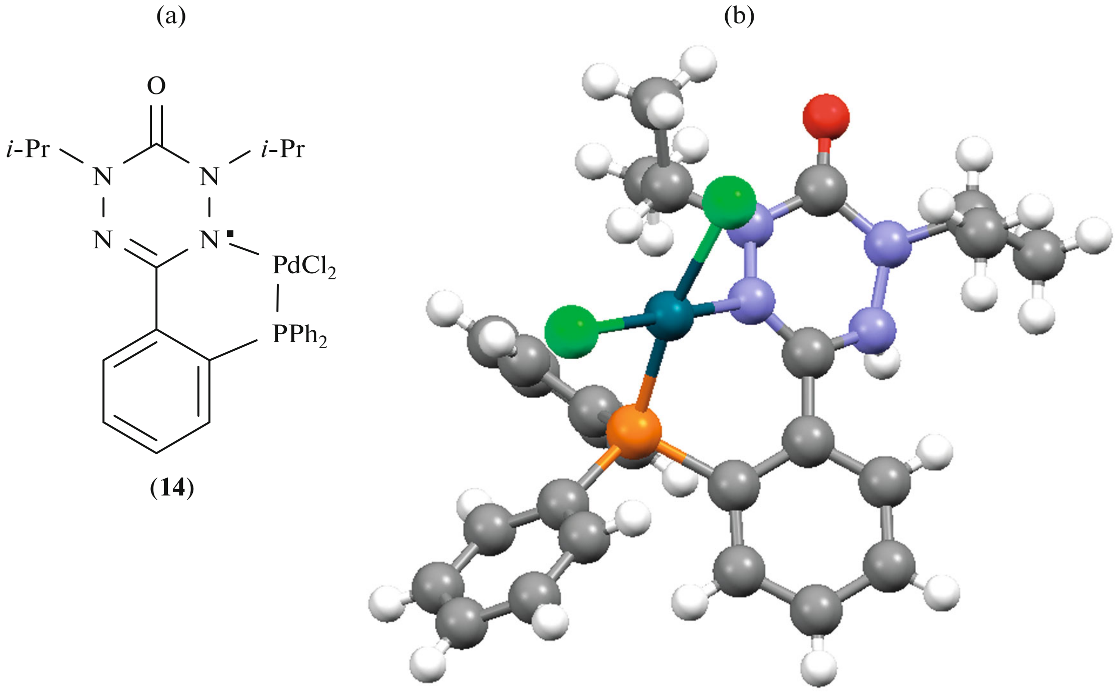
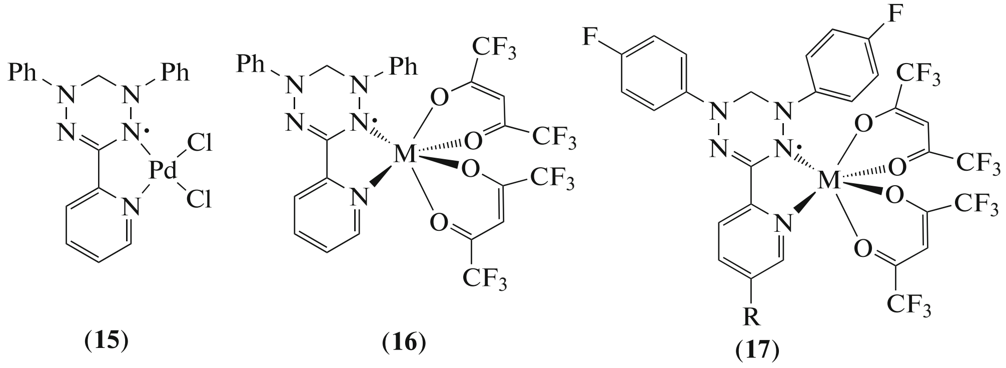


Fig. 4. (a) Chemical and (b) molecular structures of complex (**14a**) (CIF file CCDC no. 997842) [30].

$(VdP)_2Pd_2Cl_2$ under the reduction conditions was shown. The structure of the latter was determined by XRD. In this binuclear complex, two Pd(II) ions that exist in the planar square environment are linked by the chloride bridges.

Only oxoverdazyls were used for a long time in the synthesis of metal complexes. Using 3-(pyridin-2-yl)-1,5-diphenylverdazyl as an example, it was shown for the first time that the Kuhn radicals containing the sp^3-hybridized carbon atom in position 6 can coordinate metal ions similarly to oxoverdazyls. The reaction of this ligand with palladium chloride on heating in acetonitrile afforded complex (**15**) (Scheme 5) [31]. The structures and properties of this complex and similar complex based on 6-oxoverdazyl were studied in comparison. According to the XRD data, both complexes have the plane-planar metal–chelate node.

The Zn(II) and Mn(II) complexes (**16**) were synthesized later from 3-(pyridin-2-yl)-1,5-diphenylverdazyl (Scheme 5) [32]. The structures of the complexes were confirmed by the XRD data: they are isomorphous at room temperature, and the environment of the metal is octahedral. The diamagnetic fragment $Zn(Hfac)_2$ acts as a spacer between the verdazyl radicals, which results in the formation of the one-dimensional magnetic structure.



(**16**): M = Zn (**a**), Mn (**b**); (**17**): R = H: Zn (**a**), Mn (**b**); R = Cl: Zn (**c**)

Scheme 5.

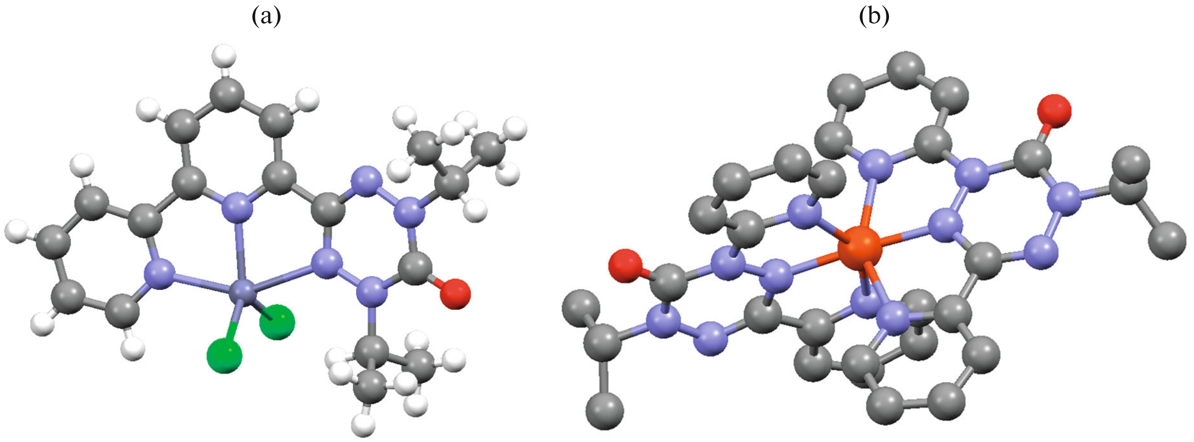
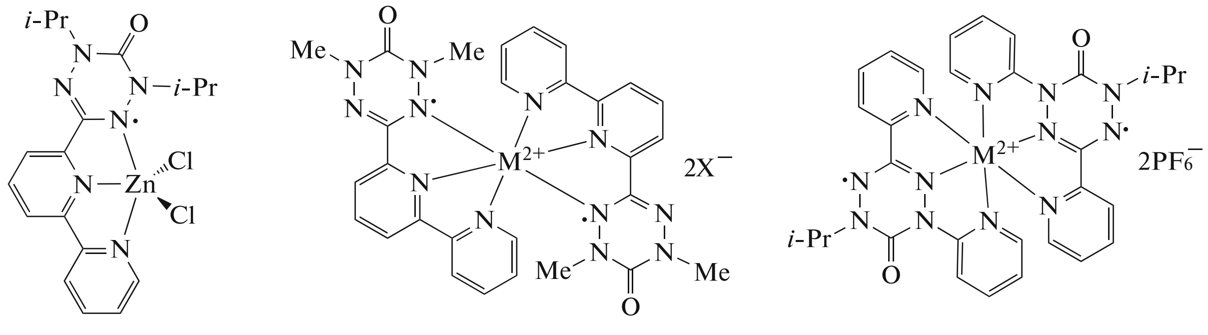


Fig. 5. Molecular structures of complexes (a) (**18**) (CIF file CCDC no. 809820 [36]) and (b) (**20b**) (CIF file CCDC no. 1824292) [40].

The Zn(II) ((**17a**), (**17b**)) and Mn(II) (**17c**) complexes have recently been synthesized (Scheme 5) using 3-(3-*R*-pyridin-2-yl)-1,5-di(4-F-phenyl)verdazyls as ligands and were studied by H. Yamaguchi and coauthors [33–35]. They obtained the XRD data for all complexes and discussed the crystal structures and magnetic properties on the basis of the quantum chemical calculations. The Zn(II) complex (**15b**) is presented as a model compound for the Heisenberg ferromagnetic chain $S = 1/2$ [33]. The antiferromagnetic honeycomb lattice with $S = 1/2$ consisting of the Zn(II) complex (**17a**) is presented [34]. The complex with the paramagnetic Mn(II) ion (**17c**) is antiferromagnetic with $S = 2$ [35]. The authors concluded that the molecular verdazyl complexes with transition 3*d* metals demonstrated that the strong bond between the spins of the metal and verdazyl resulted in the formation of a hybrid spin in the low-temperature ranges.

Tridentate ligands. Verdazyls as tridentate ligands were synthesized by the introduction of the bipyridinyl fragment into position C(3) or by the introduction of two pyridinyl residues into positions C(1) and C(3). For example, the Zn(II) complex (**18**) with the trigonal pyramidal coordination node (according to the XRD data) was synthesized on the basis of 3-(2,2'-bipyridin-2-yl)-1,5-diisopropyl)-6-oxoverdazyl (Scheme 6) (Fig. 5a) [36].

A series of complexes (**19**) with ions Mn(II), Ni(II), Cu(II), and Zn(II) was synthesized using 1,5-dimethyl-3-(2,2'-bipyridin-2-yl)-6-oxoverdazyl [37, 38]. In all cases, according to the XRD data, two verdazyl ligands are nearly perpendicular to each other in the meridional positions to form a pseudooctahedral complex. Metal–verdazyl intramolecular exchange interactions in these complexes depend on the metal nature.



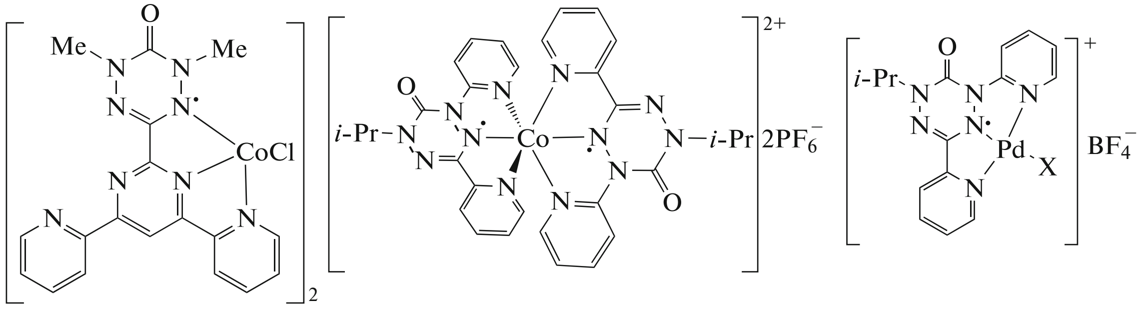
(**18**) (**19**) (**20**)

(**19**): M, X-: Mn, PF_6 (**a**), ClO_4 (**b**); Ni, PF_6 (**c**),
ClO_4 (**d**); Cu, PF_6 (**e**), ClO_4 (**f**);
Zn, PF_6 (**g**), ClO_4 (**h**);
(**20**): M: Ni (**a**), Fe (**b**)

Scheme 6.

Complex (**20a**) was synthesized from 5-isopropyl-6-oxo-1,3-di(pyridin-2-yl)verdazyl and Ni(II) triflate [39]. The Fe(II) complex (**20b**) was synthesized under the same conditions [40], but the authors showed that the results were more easily reproduced if the radical precursor tetrazine was used for the synthesis rather than the radical itself. Tetrazine is formed upon the partial oxidation of tetrazane. In complexes (**20**) with the MN_6 coordination node and pseudooctahedral structure, the metal–verdazyl bonds are shorter than those in the complexes with other radicals (Fig. 5b).

The synthesis of the Co(II) complex with 1,5-dimethyl-6-oxo-3-(4,6-bis(2-pyridyl)pyrimidin-2-yl)verdazyl (**21**) was described [41] (Scheme 7). An attempt to obtain the complex directly from the radical was unsuccessful because of an insufficient stability of the latter. The reaction of the corresponding tetrazane with cobalt chloride in oxygen-saturated methanol afforded complex (**21**). In this complex, the radical acts as a tridentate ligand for one metal ion only. The second tridentate coordination position of the radical remains vacant. An analysis of the crystal structure shows that the complex is dimeric and its cobalt ions are linked by the chloride bridges. The $CoCl_2$ node is asymmetrical and includes two short and two long Co–Cl bonds.



(**21**) (**22**) (**23**)

X = NCMe, Cl

Scheme 7.

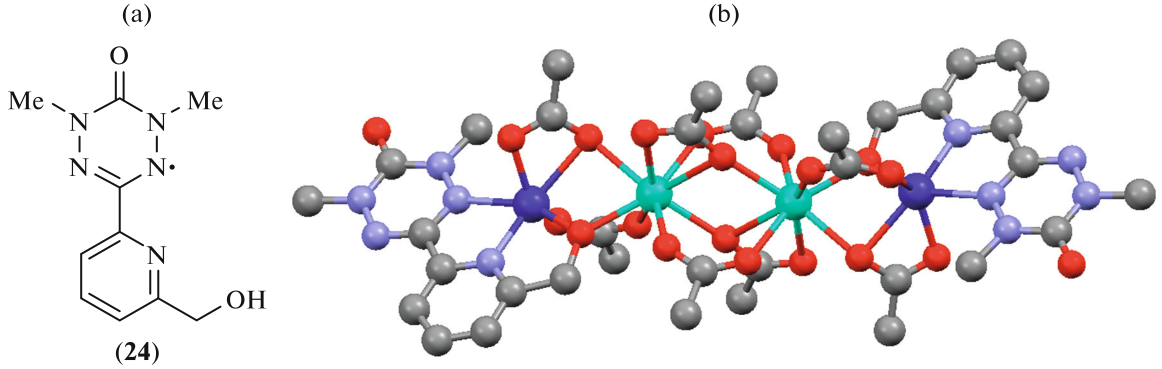
The complex formation of 5-isopropyl-6-oxo-1,3-di(pyridin-2-yl)verdazyl with Co(II) triflate was comprehensively studied [42]. The coordination of this verdazyl to cobalt is shown to result in dication (**22**), which can be described best of all in the solid state as the Co(II) ion with a high spin coordinated to two verdazyl ligands with $S = 3/2$ in the ground state. A single crystal corresponding to the earlier determined tetragonal unit cell was isolated. Its full XRD analysis confirmed the previously mentioned isomorphism and gave the metal–ligand bond lengths corresponding to the metal ion with a high spin. The Co(II) complex dissolved in acetonitrile is equilibrated with the Co(III) valence tautomer with $S = 1/2$ in the ground state. Switching between two tautomers in the solution and the presence of different forms in the solution at low temperatures as compared to the solid state indicate that changes in the molecular medium can strongly affect the equilibrium.

The Pd(II) complexes (**23**) were synthesized by the reaction of 5-isopropyl-6-oxo-1,3-di(pyridin-2-yl)-verdazyl with $(MeCN)_4Pd(BF_4)_2$ or the leuco form of this radical with $(MeCN)_4PdCl_2$ [43]. According to the XRD data, the distorted square planar geometry around the metal (sum of angles around Pd 360.0°) corresponds to palladium(II). The authors studied the redox reaction of the verdazyl–palladium complexes.

The synthesis of new tetrazane ligand designed for the oxidation to the verdazyl form (**24**), which is capable of simultaneous binding with transition metal and lanthanide ions, was reported [44]. 1,5-Dimethyl-3-[6'-(hydroxymethyl)-2'-pyridine]-6-oxotetrazane was prepared by the condensation of 6-(hydroxymethyl)-2-pyridinaldehyde with bis(1-methylhydrazide)carboxylic acid. The reaction of tetrazane with the Co(II) and Dy(III) acetate salts in acetonitrile under aerobic conditions by self-assembling led to the formation of the molecular cluster $[(V\text{-}CH_2O)_2Co_2Dy_2Ac_8]$ (Ac = CH_3COO–) consisting of six spin centers. The structure of the cluster was determined by the XRD data (Fig. 6). The cluster has the properties of a monomolecular magnet.

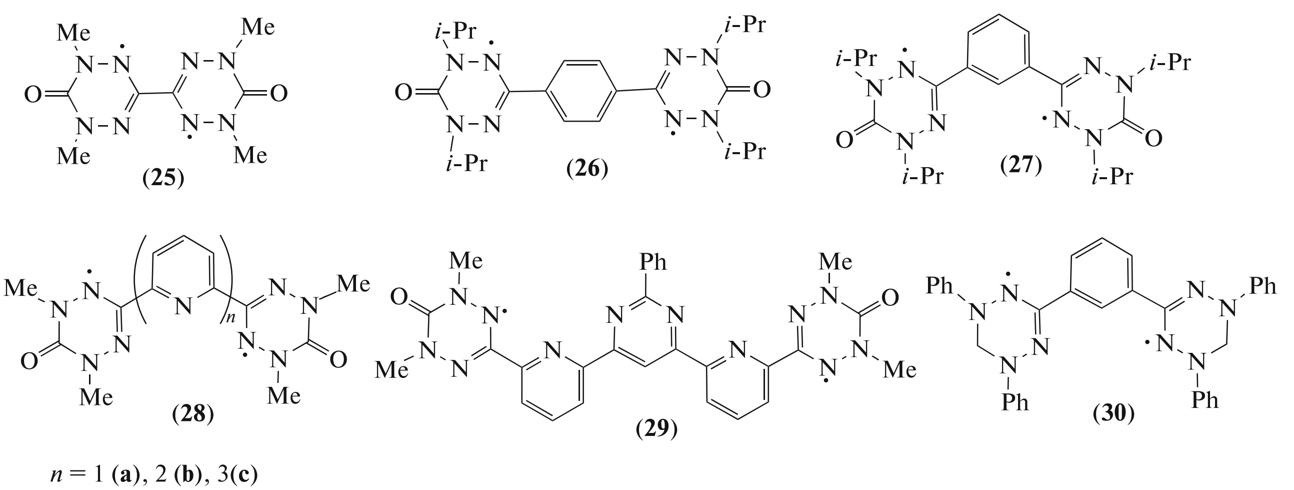
BIRADICAL SYSTEMS CONTAINING VERDAZYL

The ability to chelation of polydentate verdazyl radicals makes them efficient ligands for the formation of complexes with various metals. In order to prepare paramagnetic analogs of oligopyridine metal-containing supramolecular "building blocks," the biradicals were synthesized in which the 6-oxoverdazyl fragments are bound directly (**25**) [45] or through the spacer ((**26**)–(**29**)) (Scheme 8) [46, 47]. The Kuhn biradical (**30**) was obtained later as a high-purity crystal [48].



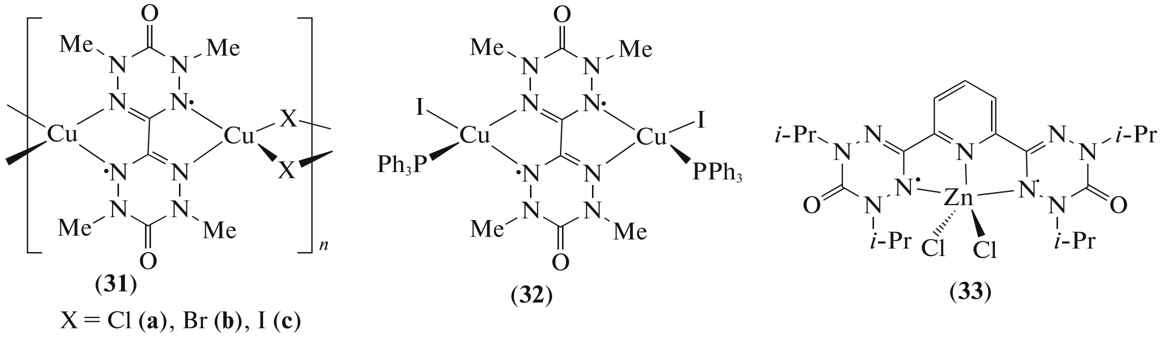
(24)

Fig. 6. (a) Structure of complex (**24**) and (b) view of the 2*p*–3*d*–4*f* cluster. Dysprosium, cobalt, carbon, nitrogen, and oxygen atoms are shown as green, pink, gray, blue, and red spheres, respectively (CIF file CCDC no. 1499890) [44].



Scheme 8.

The metal complexes with some biradicals were described. For example, the reactions of bis(verdazyl) (**25**) with Cu(I) halides gave complexes (**31**) (Scheme 9) [45]. The polymer structure was determined by XRD and is presented in Fig. 7a for bromide complex (**31b**) as an example. The bis(bidentate) molecule of the diradical is coordinated by two copper atoms, and these fragments are bound in the chain by the bromide bridges.



Scheme 9.

The Cu(I) complexes based on the same biradical but with the binuclear structure rather than the polymer structure (**32**) were synthesized and described for comparison [49].

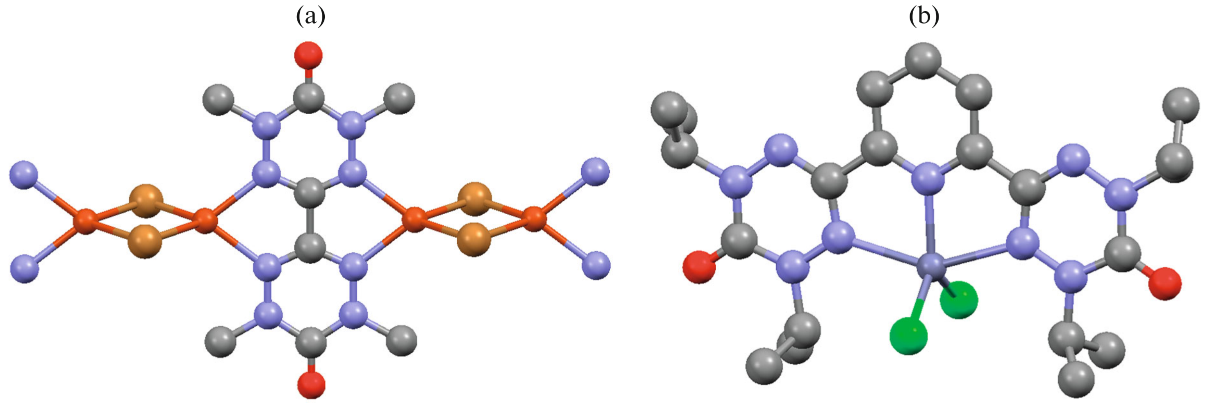
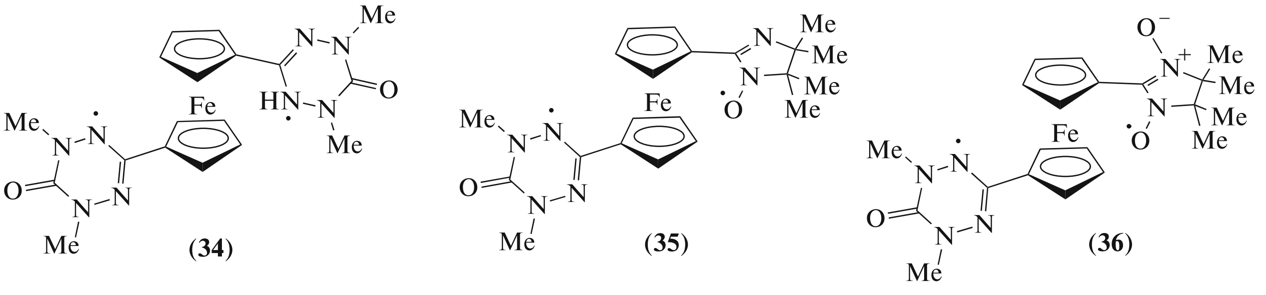


Fig. 7. Molecular structures of complexes (a) (**30b**) (CIF file CCDC no. 1216731) [45] and (b) (**33**) (CIF file CCDC no. 809822) [36].

The reaction of bis[1,5-di(isopropyl)-6-oxo-3]-2,6-pyridine-bound verdazyl with zinc chloride afforded the trigonal pyramidal complex (**33**) in which the Zn–N bonds with verdazyl are longer than those with pyridine (Fig. 7b) [36].

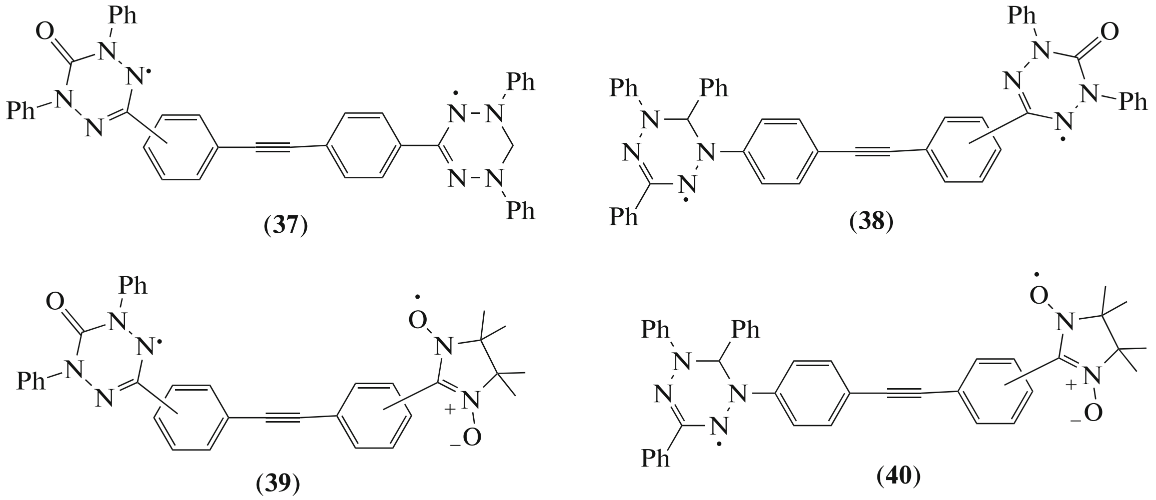
1,1'-Bis(verdazyl)ferrocene (**34**), the structure of which is shown in Fig. 8, is one of the most interesting compounds in the series of the synthesized biradicals of the verdazyl class [50]. According to the XRD data, in the solid state the verdazyl cycles are arranged nearly ideally above each other, indicating the formation of the intramolecular π dimer. In the crystal, verdazyl is diamagnetic, which indicates spin binding. However, in solution this biradical is not π dimer, because the exchange interaction is very weak. Biradical (**34**) and two low-energy isomers of this biradical obtained by the rotation of one of the verdazyl fragments along the Cp–Fe–Cp axis (Cp is cyclopentadienyl) by 19° (34') and by 144° (34") were later studied theoretically [51]. The unique two-electron eight-center bond was found in biradical (**34**) by these studies. According to the experimentally detected and theoretically calculated absorption spectra of three biradicals, biradical (**34**) is capable of transforming in the solution into isomer (**34"**) with two "separated" radical fragments.

The analogs of biradical (**34**) containing the verdazyl and iminonitroxide (**35**) or nitronyl nitroxide (**36**) radical fragments were described, and all the three biradicals were studied by the quantum chemical method [52]. The influence of the oxidation state of the iron atom in ferrocene on the magnetic interactions was considered. In authors' opinion [52], the studied biradical systems can be of interest as molecular magnets (Scheme 10).



Scheme 10.

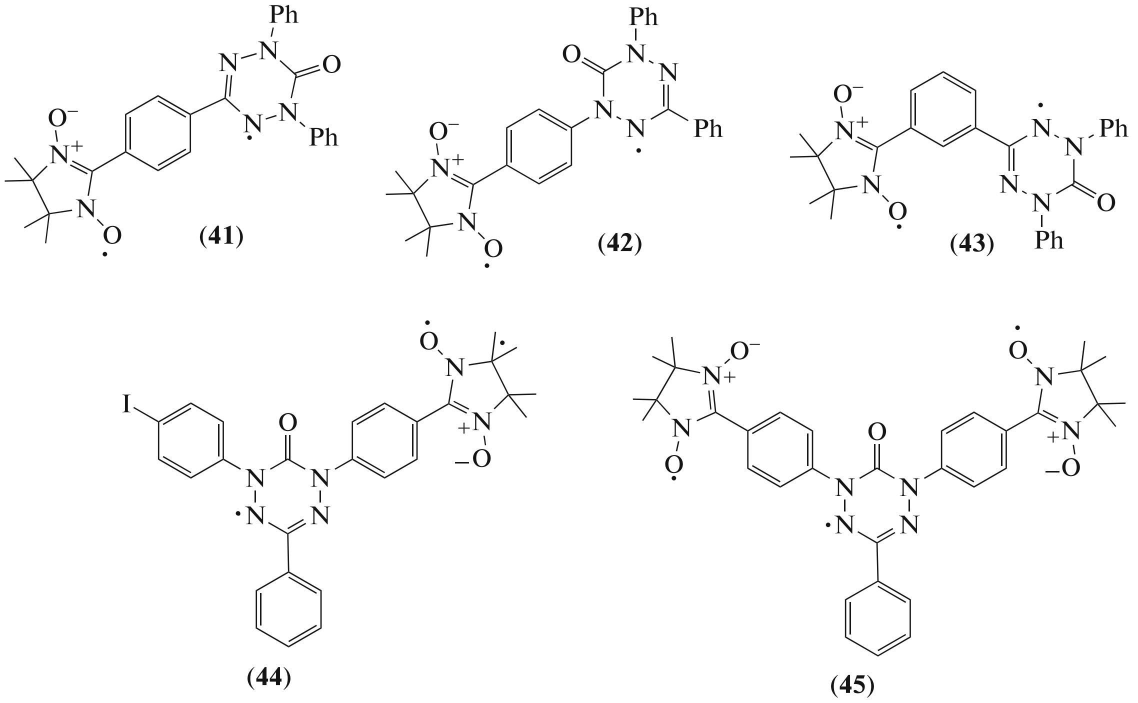
The heterospin biradical systems containing the verdazyl fragment are presented [53–56]. An approach was developed to the synthesis of tolane-bonded biradicals (**37**)–(**40**), containing two verdazyl radicals or verdazyl and nitronyl nitroxide radicals, and the verdazyl radical can be N- or C-bonded (Scheme 11) [53, 54]. The method is based on the Sonogashira cross-coupling of iodine-substituted radicals with ethynyl-containing building blocks. A combination of verdazyls and nitroxides can be promising for the synthesis of multispin molecules and possible materials for two-dimensional 2D- and 3D-ordered triplon excitations of spin dimers in the crystalline lattice.



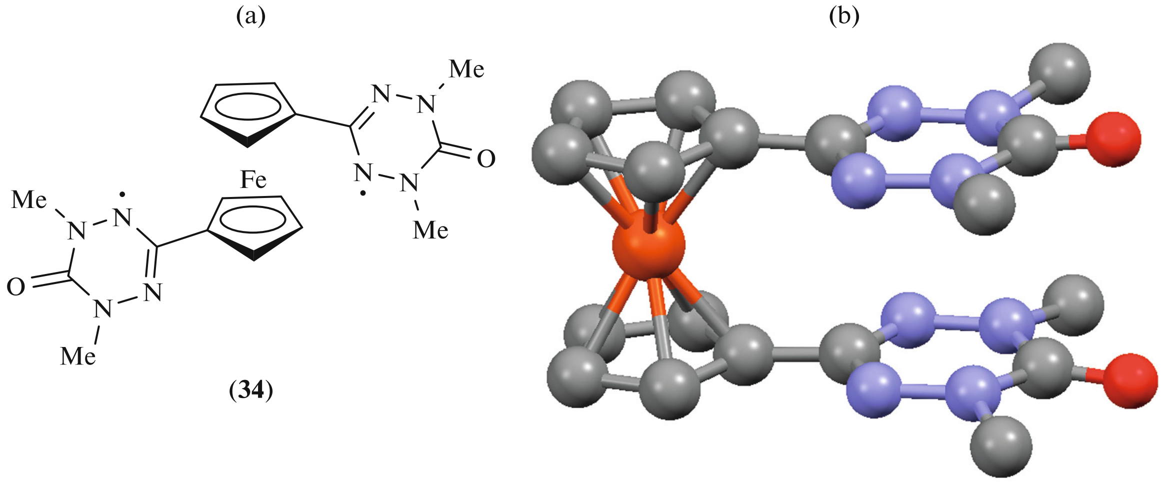
Scheme 11.

Oxoverdazyl–nitronyl nitroxide biradicals (**41**)–(**43**) with the shortened *para*- or *meta*-phenylene bridge were described [55] (Scheme 12). These compounds were prepared by the Pd-catalyzed cross-coupling of iodine-substituted verdazyls with the Au(I) complex of nitronyl nitroxide. Biradical (**44**) and triradical (**45**) were synthesized by the same method and studied [56].

Although biradicals (**37**)–(**45**) are not ligands for the synthesis of stable complexes, here we present these compounds. All of them are characterized by a high stability (especially triradical compounds) and provide new prospects for further functionalization. It is not surprising that metal complexes based on similar compounds would be prepared in the nearest future.



Scheme 12.



(34)

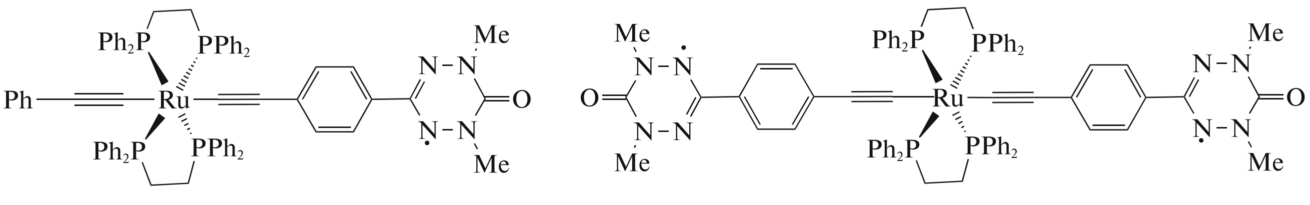
Fig. 8. (a) Chemical and (b) molecular structures of verdazyl (**34**) (CIF file CCDC no. 297792) [50].

OTHER VERDAZYL COMPOUNDS WITH METALS

As mentioned above for complex (**8**), the metal that is not always coordinated in the verdazyl complex is directly bound to the tetrazinyl cycle on which the unpaired electron is distributed. The reaction of 1,5-dimethyl-3-(imidazol-2-yl)-6-oxoverdazyl with Ln(Hfac)$_3$ afforded complexes (**46**) (Fig. 9) [22]. All complexes are isomorphous and contain one-dimensional chains in which the verdazyl ligand binds two lanthanide ions via the bridging mode. The structure of the Dy(III) complex taken as an example was confirmed by the XRD data (Fig. 9).

The Kuhn verdazyls containing the pyridine residue as a substituent were used for the synthesis of the complexes in which the donor centers for binding with the metal were specially remote from the tetrazinyl cycle. The Cu(II) complex (**47**) based on 1,5-diphenyl-6-oxo-3-(pyridin-4-yl)verdazyl was synthesized and structurally characterized (Fig. 10) [57]. The magnetic properties were studied in a wide temperature range and showed antiferromagnetic exchange interactions between the radicals in the crystal structure. The exchange interactions between the radical and Cu(II) are low as compared to strong intramolecular Cu···Cu antiferromagnetic interactions.

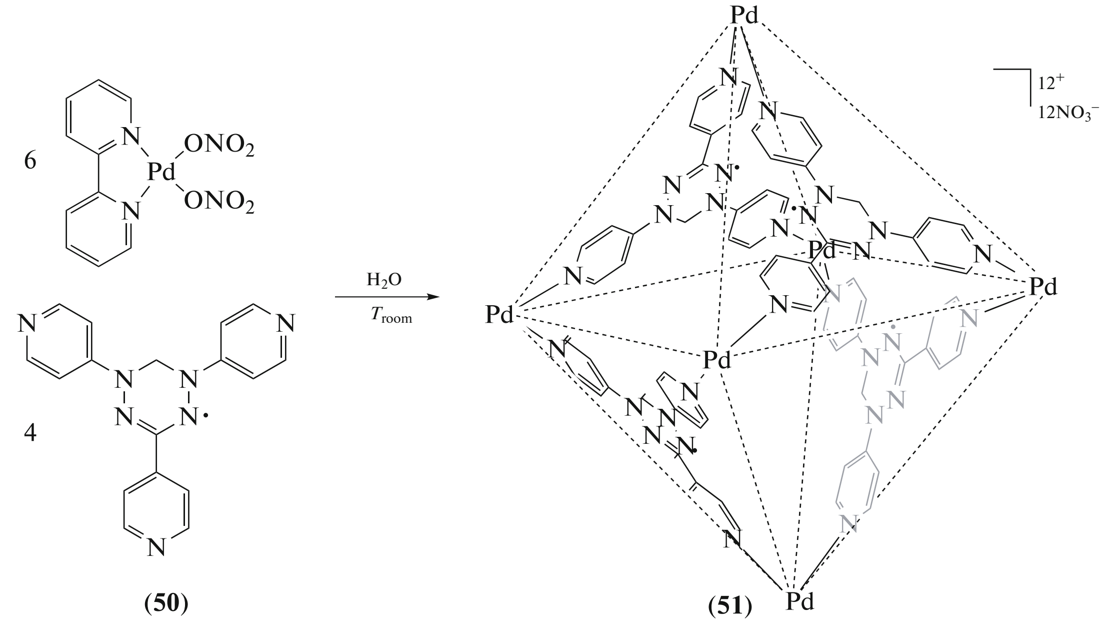
The nonsymmetrical (**48**) and symmetrical (**49**) (alkynyl)ruthenium verdazyl complexes were described [58] (Scheme 13). Compound (**48**) was synthesized by the reaction of [Ru=C=CHPh(Dppe)$_2$]-[OTf] (Dppe is 1,2-bis(diphenylphosphino)ethane) with 1,5-dimethyl-6-oxo-3-(4-ethynylphenyl)verdazyl. Complex (**49**) was synthesized from *cis*-[RuCl$_2$(Dppe)$_2$] and the same verdazyl containing the acetylene group. Ruthenium complexes (**48**) and (**49**) can be considered as systems with the redox-active metal center linking the spin blocks.



(48) **(49)**

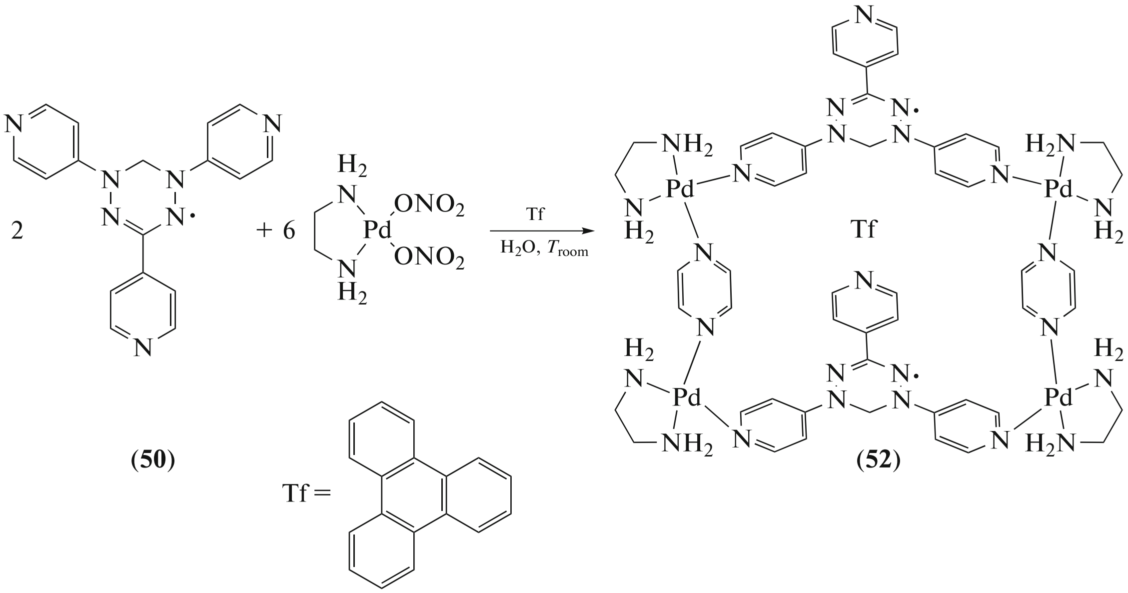
Scheme 13.

The self-assembling of the Pd(II) complex (**51**) with the M$_6$L$_4$ composition was carried out under the conditions where a mixture of 1,3,5-tri(pyridin-4-yl)verdazyl (**50**) and [Pd(Bipy)(NO$_3$)$_2$] was stirred in water at room temperature (Scheme 14) [59]. In this case, the ligand is the building block for the construction of a “spin-cage” with four spin centers. The hexanuclear structure of complex (**49**) was characterized by XRD.



Scheme 14.

Another example of the successful self-assembling of the Pd(II) complex (**52**) using the same verdazyl (**50**) (Scheme 15) was described [60].



Scheme 15.

According to the XRD data, complex (**52**) consists of two parallel radical fragments linked "face to face" by the palladium atoms and pyrazine molecules with the inclusion of triphenylene (Tf) as a guest. The EPR data show an interaction between the radicals in this complex. The planar copper(II) complexes were encapsulated into this "spin-cage," which enlarged possibilities for the observation of spin-spin interactions through the space.

The synthesis of salts with charge transfer ((**53a**), (**53b**)) in which verdazyl exists in the radical-cation form is described (Scheme 16) [61, 62]. These compounds were synthesized by the methylation of 1,5-diaryl-3-(pyridin-2-yl)verdazyls with methyl iodide at room temperature followed by the treatment of the obtained iodides with 1-butyl-3-methylimidazolium tetrachloroferrate. The crystal structures of salts (**53a**) and (**53b**) and their magnetic properties were studied. The salts are characterized by spin $S = 1/2$ on the verdazyl radical cation and spin $S = 5/2$ on the anion $FeCl_4^-$. The ab initio calculations made it possible to propose the model for compound (**53a**) including exchange interactions of three types in the layer

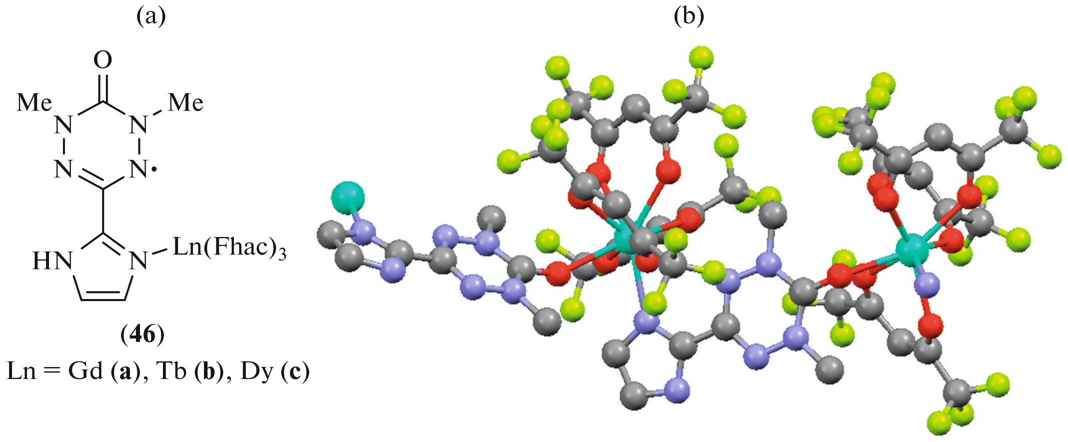
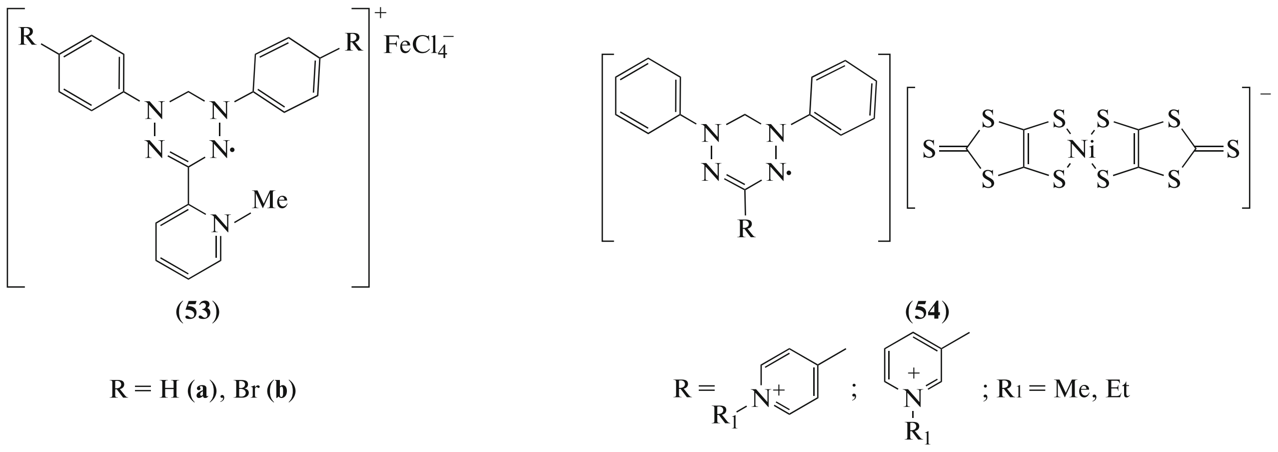


Fig. 9. (a) Chemical and (b) molecular structures of complex (**46c**) (CIF file CCDC no. 699837) [22].

(whose structure resembles honeycombs) formed by the radical cations and two types of interactions of the layer sites with the ion $FeCl_4^-$. Based on a broad range of the obtained magnetic data, the authors assert that heterospin compound (**53b**) with the three-dimensional network of nonequivalent antiferromagnetic interactions is unique, since this compound exhibits the classical properties of a magnet in a weak field and the quantum behavior upon a strong field application [61].

Salts (**54**) consisting of the verdazyl cation and anion of the $Ni(Dt)_2$ complex (Dt is 1,3-dithiol-2-thione-4,5-dithiolate) were described [63–66]. An analysis of the crystal structure of the salt shows the formation of dimers of $Ni(Dt)_2$ anions and dimers of the sandwich type between two verdazyl cations with the formation of the magnetically linear tetramer. The conductivity of the salts was measured, and they were shown to be molecular paramagnetic semiconductors.



Scheme 16.

The brief analysis performed for published data shows that interest in verdazyl radicals remains high. One of the reasons for attention to these radicals is that they have the delocalized π-electron spin density in the nonplanar molecular structure. Flexibility of molecular orbitals in the verdazyl radical makes it possible to tune intermolecular magnetic interactions using the molecular design principles. The introduction of a metal atom into the verdazyl structure allows the magnetic behavior of the ligand to be changed significantly with the formation of systems with new properties. Additional donor centers can rather easily be introduced into the verdazyl structure, which results in bi- and tridentate ligands and stable complexes with different environments of the metal–chelate node. The synthesis of the homo- and heterospin biradical systems provides prospects for the further functionalization, including the introduction of additional centers for the coordination and synthesis of multispin structures as molecular magnets.

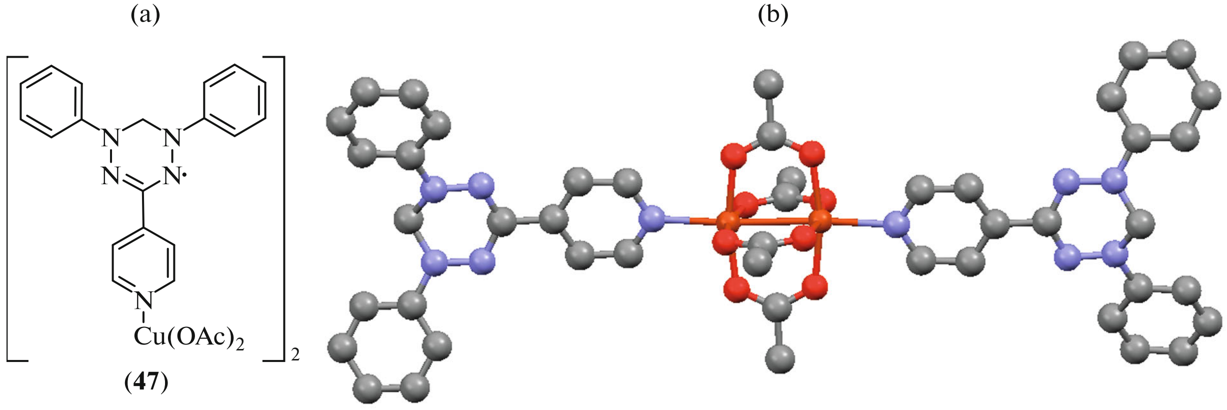


Fig. 10. (a) Chemical and (b) molecular structures of complex (**47**) (CIF file CCDC no. 686542) [57].

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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