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Metal Complexes of Aroyl(acyl)benzoylhydrazones of Aromatic Aldehydes and Ketones: Coordination Modes and Properties

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Abstract—The data based on the X-ray diffraction analysis results obtained within the recent 20 years about the coordination modes of aroyl(acyl)hydrazones of aldehydes and ketones containing chelatophoric groups of atoms and their photoluminescence and magnetic properties and biological activity are reviewed and generalized. The most significant earlier studies of the metal complexes with the aroyl(acyl)hydrazone ligands are also considered. This review is fruitful for researchers specialized in the target synthesis of new metal complexes of the ligands of this class aimed at manufacturing practically important materials based on these complexes.

Keywords: aroyl(acyl)hydrazones, metal complexes, molecular structure, tautomerism, photoluminescence, magnetic properties, biological activity

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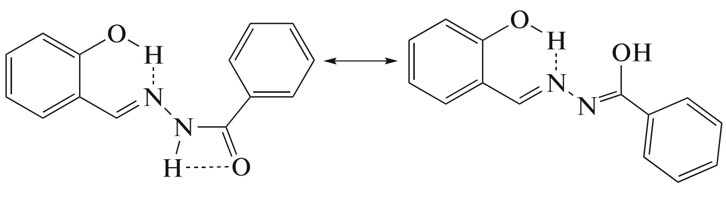
High scientific interest in hydrazones of aromatic aldehydes and ketones and their metal complexes is evoked by a wide range of their biological activity: antibacterial [1–5], antimicrobial [6–8], antiviral [9–14], antitumor [4, 15–18], cytotoxic [19], and antifungal [20, 21] activities. They also manifest the catalytic activity [22–26]. For example, these aroylhydrazone compounds are of high practical significance as efficient and selective catalytic systems for the oxidative functionalization of inert alkanes to more valuable organic products: the catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone used for nylon manufacturing [25, 27–32]. The examples of using these compounds as efficient antiwear additives in friction units are known [33–36].

Aroyl(acyl)hydrazones of aromatic aldehydes are polydentate organic ligands that form metal complexes of various compositions and structures (mono-, bi-, or polynuclear) depending on the synthesis conditions and nature of the metal. A large group of polynuclear complexes consists of the compounds bearing exchange-bound paramagnetic ions of transition metals. The key role for understanding the magnetic properties in these exchange clusters belongs to the elucidation of an interrelation of the exchange parameters and specific structures of similar complexes, which is significant for understanding magnetic interactions and magnetic structural correlations in the molecular systems [37–46]. The zinc and rare-earth metal complexes of 2-hydroxy- or 2-(*N*-tosylamino)benzaldehyde benzoylhydrazones manifest the photo- and electroluminescence properties. The efficient light emitting devices were fabricated using these compounds [47–50].

The main attention of researchers is given to the study of aroylÅhydrazones based on 2-hydroxybenzaldehyde and its analogs. The number of examples of the syntheses and studies of the physicochemical properties of aroylhydrazones based on 2-(*N*-tosylamino)-benzaldehyde, their metal complexes, and adducts with heterocyclic bases is much smaller [48–57].

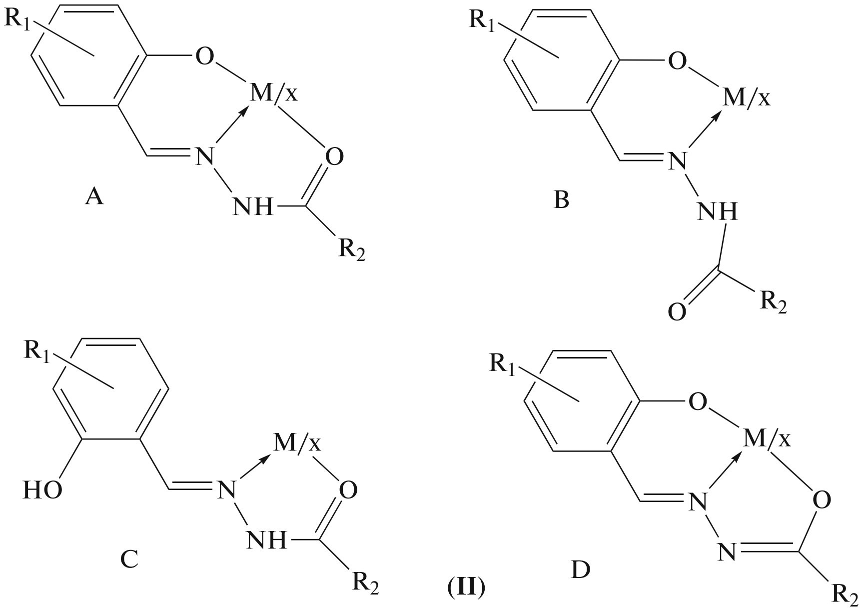
In this review, we generalized and systematized the data based on the X-ray diffraction analysis (XRD) results obtained within the recent 20 years about the coordination modes of aroyl(acyl)hydrazones of aldehydes and ketones bearing chelatophoric groups of atoms, their photoluminescence and magnetic properties, and biological activity.

Aroyl(acyl)hydrazones of aldehydes and ketones bearing the chelatophotic groups (–OH, –SH, –NH-Ts, and –COOH) represent a wide class of compounds evoking permanent scientific interest. It is shown [37, 48–50] that aroyl(acyl)hydrazones of 2-hydroxybenzaldehyde and its analogs can exist in at least two tautomeric forms: hydrazone (keto form **Ia**) or α-oxyazine (enol form) **Ib** (Scheme 1).


(Ia) **(Ib)**

Scheme 1.

According to the data of IR spectroscopy, ^{1}H NMR spectroscopy, quantum-chemical calculations, and XRD, aroyl(acyl)hydrazones of salicylaldehyde and its derivatives in the free state exist in the hydrazone (keto) tautomeric form **Ia**. For example, as shown in [58], the molecule of salicylaldehyde benzoylhydrazone is planar with the strong intramolecular hydrogen bond between the azomethine nitrogen atom and hydrogen atom of the hydroxyl group. The possibility of various tautomeric forms to exist in these systems provides a possibility (depending on the synthesis conditions and nature of the complexing metal) to synthesize from them metal complexes with different coordination modes of the indicated ligand systems [59–63]. According to [59–63], four main coordination modes of salicylaldehyde aroyl(acyl)hydrazones can exist in the metal complexes **(IIA–IID)** (Scheme 2).

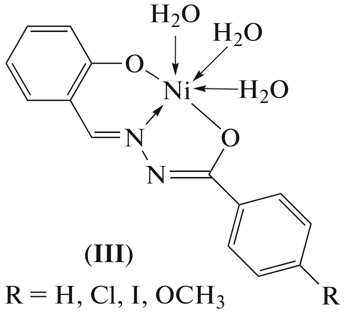


(II)

Scheme 2.

2-Hydroxybenzaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-oxyacetophenone, *o*-oxypropiophenone, and *o*-oxybenzophenone benzoylhydrazones with copper(II), nickel(II), manganese(II), and iron(II) acetates and vanadyl(II) acetylacetonate in neutral or weakly alkaline media form the complexes containing the enol **II**(D) or keto form of benzoylhydrazone of type **II**(A) [58, 64].

Structures of the metal complexes can be both mononuclear and binuclear. The compositions, structures, and coordination modes in the nickel(II) complexes of salicylaldehyde aroylhydrazones can change substantially depending on the synthesis conditions [65, 66]. The reactions of salicylaldehyde benzoyl-, *p*-chlorobenzoyl-, *p*-iodobenzoyl-, and *p*-methoxybenzoylhydrazones with nickel(II) acetate excess afford paramagnetic mononuclear complexes **III** (Scheme 3) with the coordination of the ligands in the enol tautomeric form of type **II**(D) (Scheme 2).



(III)

R = H, Cl, I, OCH_3

Scheme 3.

(IV)

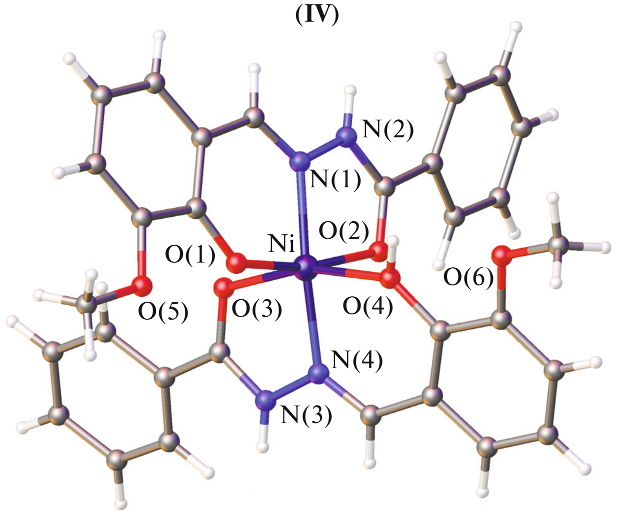
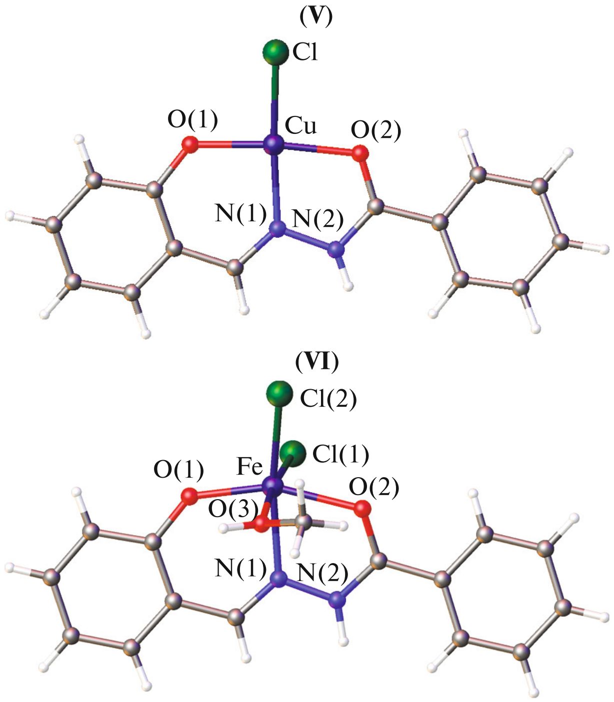


Fig. 1. Molecular structure of complex **IV** [67].

At the same time, octahedral nickel(II) complexes **IV** in which the ligand in the hydrazone (keto) form coordinates to the nickel atom were synthesized in several works [60–65, 67] (Fig. 1).

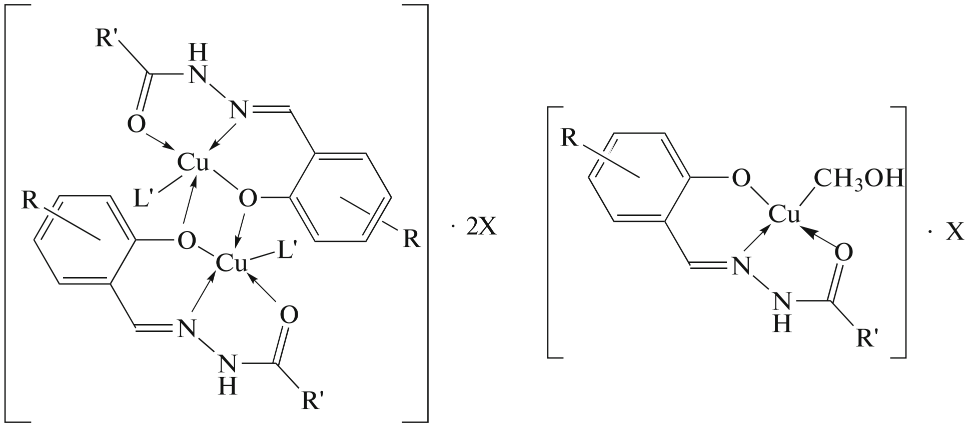
The hydrazone form of salicylaldehyde acylhydrazone coordinated via the tridentate mode is observed in the complexes of copper(II) chloride and bromide and iron(II) chloride of types **V** and **VI** (Fig. 2) [65, 66, 68–73]. The mononuclear structures of copper(II) and iron(II) complexes **V** and **VI** were determined by the XRD method [73].


(V)

(VI)

Fig. 2. Molecular structures of complexes **V** and **VI** [73].

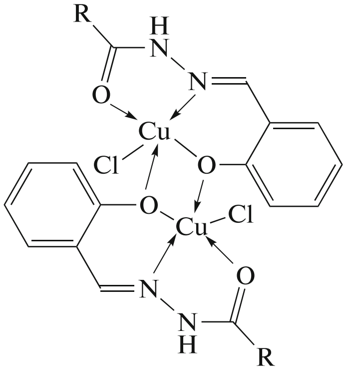
The reactions of salicylaldehyde acylhydrazones and aroylhydrazones with copper(II) nitrate and perchlorate afford the binuclear (**VII**) or mononuclear (**VIII**) complexes [74–77] with the coordination of the ligands in the hydrazone (keto) form (Schemes 4, 5).



(VII) **(VIII)**

R = H, 5-NO_2, 5-OCH_3, 5-CH_3, 5-Cl, 5-Br; R$'$ = CH_3; X = NO_3, ClO_4^-; L' = H_2O, CH_3OH, C_2H_5OH

Scheme 4.

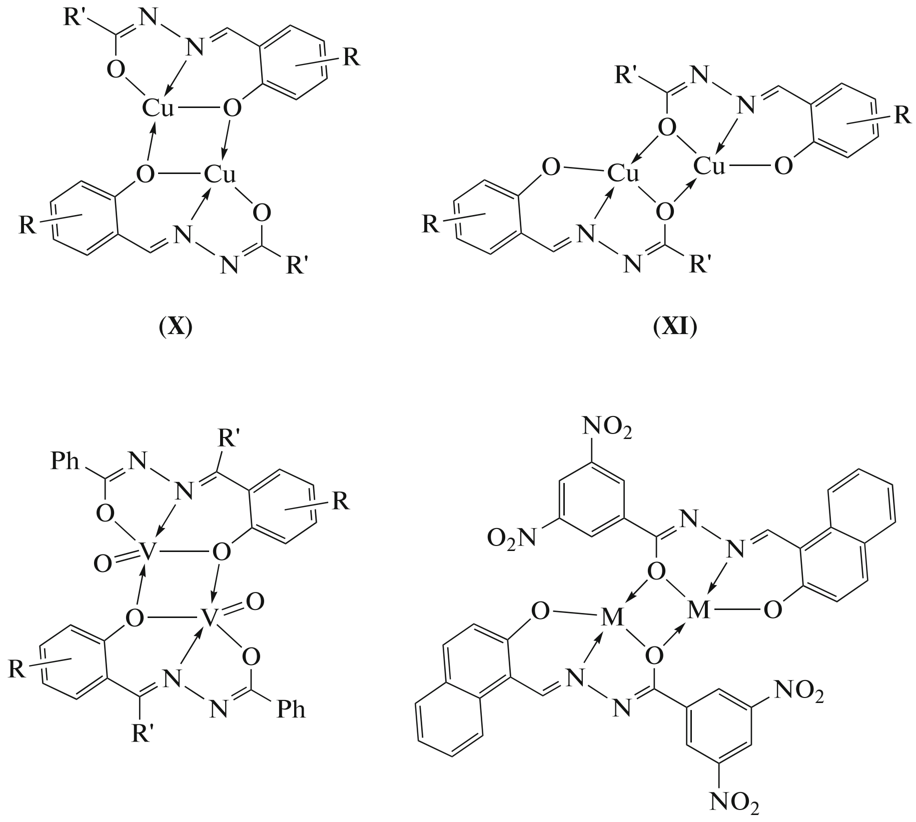


(IX)

R: Ph, $PhCH_3$, *p*-Tol, *t*-But

Scheme 5.

A specific feature of the dimeric complexes of this type is that both the phenoxyl oxygen atom of the aldehyde fragment (similarly to that in complexes **IX**) (Scheme 5, Fig. 3 [78]) and the hydrazone oxygen atom of ligands **X**, **XI**, **XII**, and **XIII** (Scheme 6) can perform the bridging function. Both possible methods for dimer formation are known in the literature. The dimeric structures with the bridging phenoxyl oxygen atoms were obtained for the copper(II), uranium(II), iron(III), chromium(III), cobalt(III), manganese(III), and vanadium(II) complexes [79–87], for example, of type **X** or with the hydrazone oxygen atom of types **XI** and **XIII** (Scheme 6). In all cases, the coordination in the dimeric complexes was concluded on the basis of the data of IR spectroscopy.



(X)

(XI)

(XII)

(XIII) M: Cu^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}

R: H, 5-NO_2, 5-OCH_3, 5-CH_3, 5-Cl, 5-Br

R': C_nH_{2n+1}, $n = 1–3, 5, 6, 11, 17$

Scheme 6.

All dimeric complexes of this type were characterized by the exchange interaction of the antiferromagnetic type between the paramagnetic metal ions, which was found by the method of temperature magnetochemistry. For the binuclear copper(II) complexes, the dimerization of monomeric objects via the phenoxyl oxygen atoms has a directed character caused by specific features of the structures of the ligand systems as shown in [38, 88, 89].

Hydrazones based on 2-(*N*-tosylamino)benzaldehyde **XIV** [90] (Scheme 7) are studied to a lower extent than hydrazones of salicylaldehyde and its derivatives.

(IX)

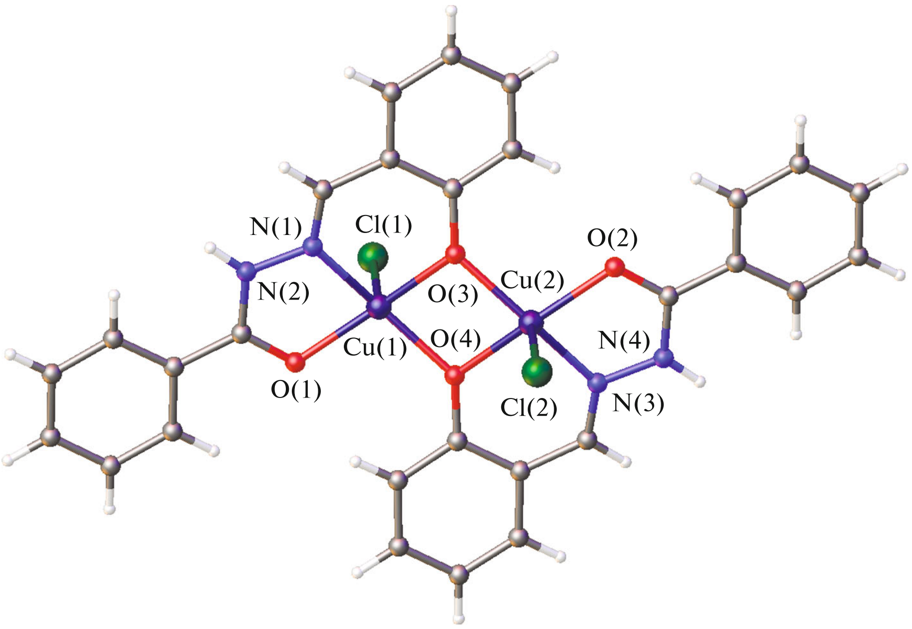
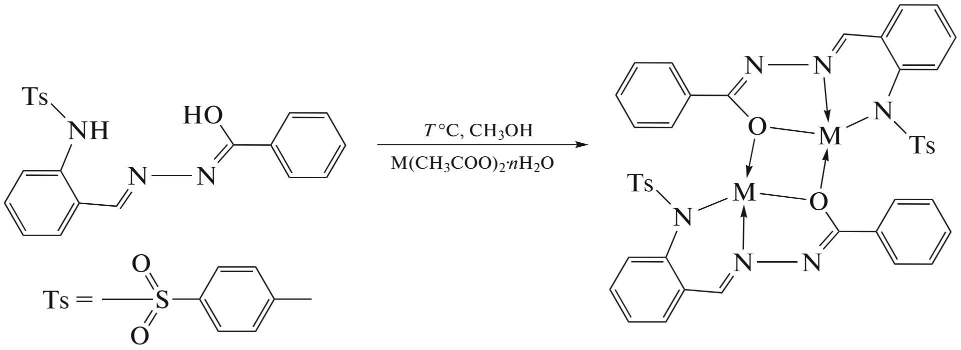


Fig. 3. Molecular structure of complex **IX** [78].



(XIV)

(XV)

Scheme 7.

A specific feature of these ligand systems is that the dimerization via the nitrogen atom of the aldehyde fragment is excluded for the binuclear complexes. The metal complexes of 2-(*N*-tosylamino)benzaldehyde benzoylhydrazones of type **XV** were synthesized (Scheme 7) [91, 92]. The coordination of the ligands in the doubly deprotonated enol form in complexes **XV** was confirmed by the data of IR spectroscopy and temperature magnetochemistry that showed the strong exchange interaction of the antiferromagnetic type. Dimerization in these complexes occurs via the single mode: through the oxygen atoms of the hydrazone fragments [91–93].

The lanthanide complexes with 2-(*N*-tosylamino)benzaldehyde benzoylhydrazones [48–50] are of high scientific interest. The erbium(III) (**XVI**), ytterbium(III) (**XVII** and **XVIII**), europium(III) (**XIX**), and lutetium(III) (**XX**) complexes of this ligand (Figs. 4–6) were synthesized and structurally characterized by the XRD method [49, 50].

According to the XRD data, in complexes **XVI**–**XIX**, one monodeprotonated ligand coordinates in the hydrazone (keto) form and another doubly deprotonated ligand coordinates in the enol form. In complex **XX**, two monodeprotonated ligands in the enol form coordinate to the metal. These complexes demonstrate efficient luminescence in the IR range with high quantum yields. The red boundary of the excitation spectrum reaches 450 nm, providing a possibility for the excitation of the complexes with the blue light,

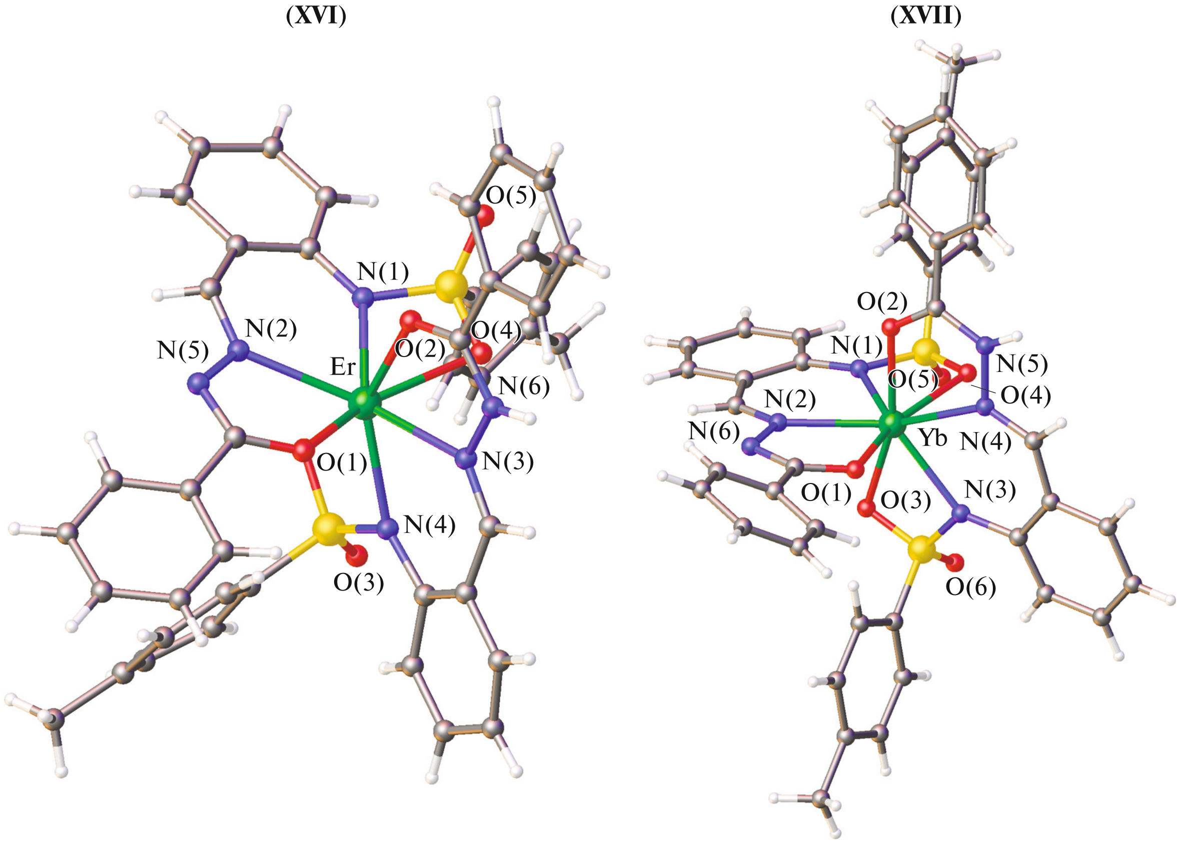
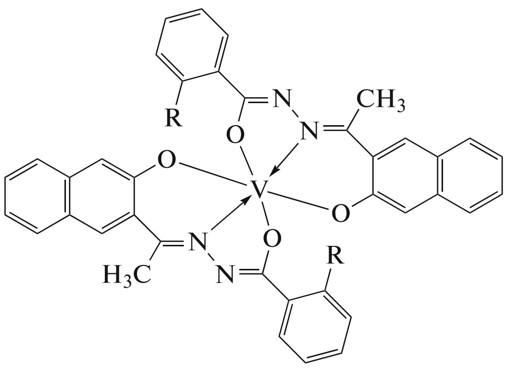


Fig. 4. Molecular structures of complexes **XVI** and **XVII** [49].

which is important for biovisualization. The ytterbium complex showed the record-breaking high efficiency as an emission material in OLED devices: 385 μW/W.

A series of adducts of the metal complexes of benzoyl- or salicyloylhydrazones of salicylaldehyde and its derivatives with pyridine; 2-, 3-, or 4-picolines; 1,10-phenanthroline; and 8-hydroxyquinoline was described [23]. In the adducts of the vanadium(II) complexes with the 8-hydroxyquinoline (**XXI**) or 1,10-phenanthroline (**XXII**) molecule (Fig. 7), the doubly deprotonated ligand salicylaldehyde salicyloylhydrazone [23] in the enol form coordinates to vanadium to form (together with additional molecules) a distorted octahedron environment of the metal atom. The hydroxy group of the benzoylhydrazone fragment is not involved in the coordination with the metal. Complexes **XXI** and **XXII** were studied as catalysts of alcohol oxidation to ketones.

The hexacoordinated mononuclear vanadium(IV) complexes of type **XXIII** were synthesized and structurally characterized [94] (Scheme 8).



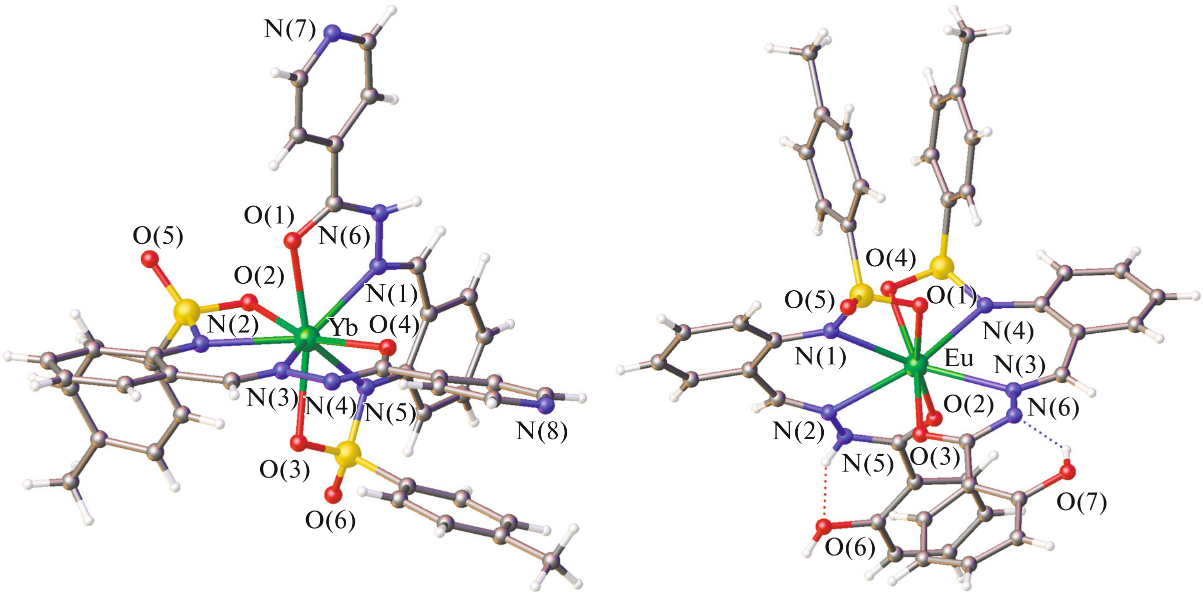
(XXIII)

R = NH$_2$ (a), OH (b), H (c)

Scheme 8.

The enol form of the ligand is observed in these complexes. Complexes **XXIIIa**–**XXIIIc** (Scheme 8) in vitro manifest the mimetic activity toward insulin and anticancer activity.

According to the XRD data, 2-hydroxypropiophenone salicyloylhydrazone coordinates in the keto form in the mononuclear copper(II) (**XXIV**) and manganese(II) (**XXV**) complexes (Fig. 8), whereas it is the enol form in binuclear zinc complex **XXVI** (Fig. 9)


(**XVIII**)

(**XIX**)

Fig. 5. Molecular structures of complexes **XVIII** and **XIX** [50].

(**XX**)

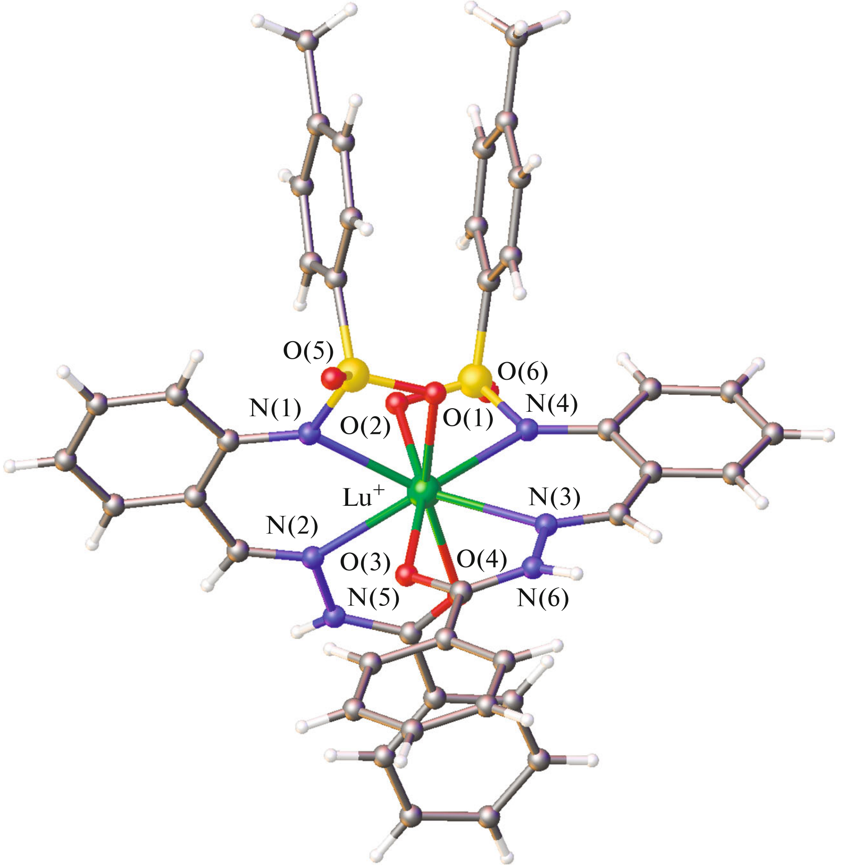


Fig. 6. Molecular structure of complex **XX** [49].

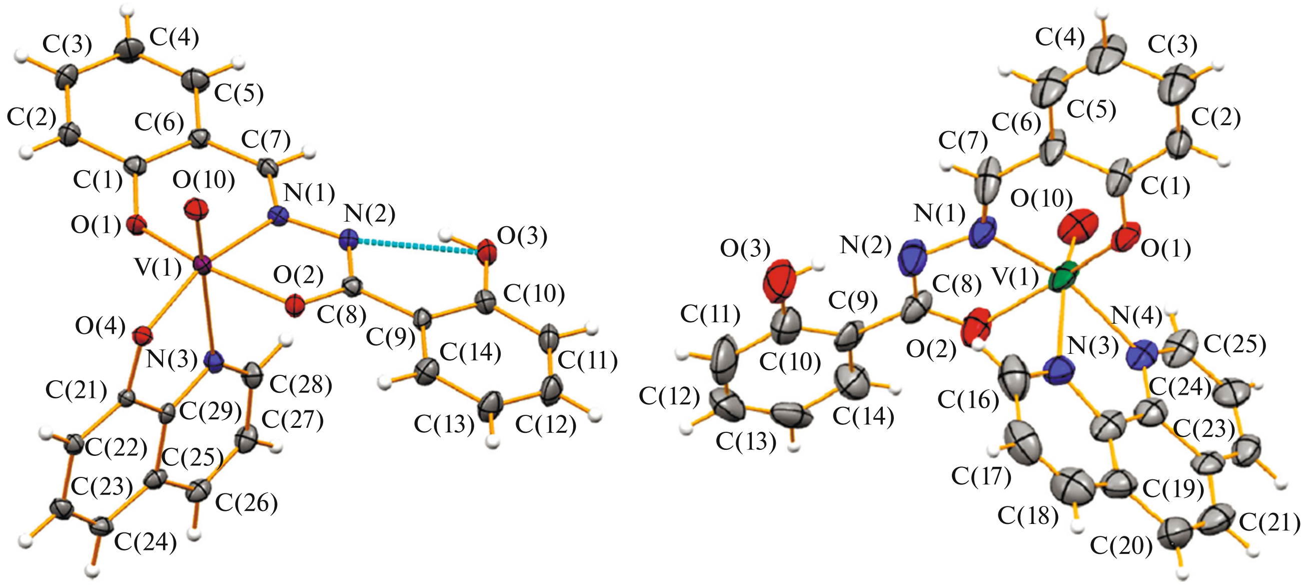

(XXI) (XXII)

Fig. 7. Molecular structures of complexes **XXI** and **XXII** [23].

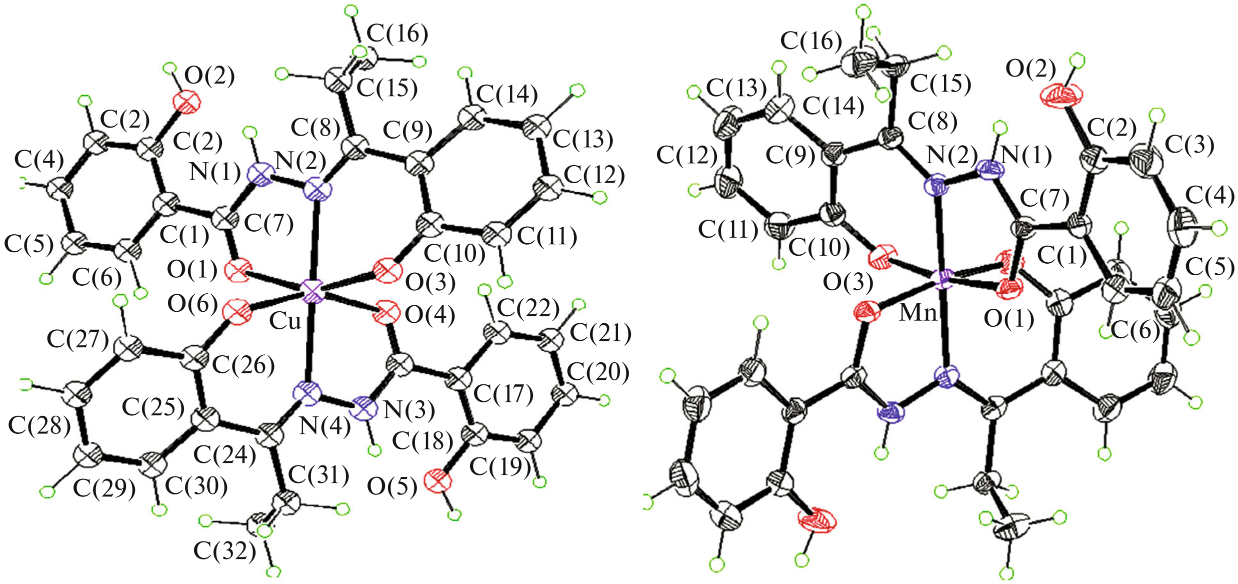

(XXIV) (XXV)

Fig. 8. Molecular structures of complexes **XXIV** and **XXV** [95].

[95]. Complexes **XXIV–XXVI** were studied as corrosion inhibitors.

The molecular structures of the copper(II) (**XXIV**) and manganese(II) (**XXV**) complexes are close and demonstrate a distorted octahedral geometry around the metal ion. In both complexes, the metal ion is coordinated by two monoanionic ligands through the carbonyl oxygen atom, azomethine nitrogen atom, and phenolate oxygen atom of each ligand.

The molecular structure of complex **XXVI** represents the phenoxy-bridged centrosymmetric dimer as a five-coordinate distorted pyramid in which the metal is bound through the azomethine nitrogen atom, carbonyl oxygen atom, and two bridging phenolate oxygen atoms of the ligands, and the sulfoxide oxygen atom of the DMSO molecule occupies the apical position. The hydroxy group of the salicyloylhydrazone fragment does not coordinate to the metal.

(XXVI)

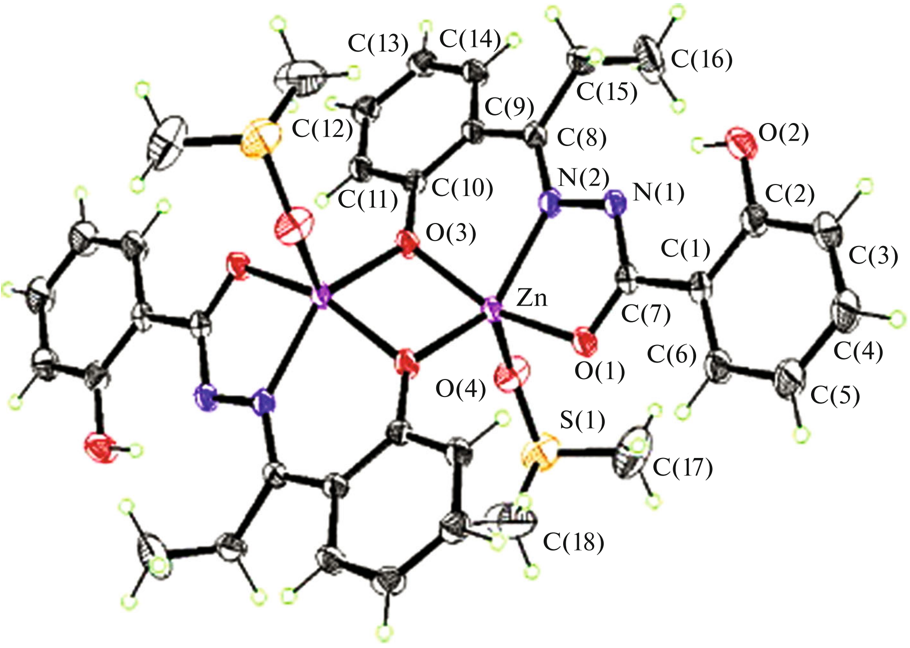


Fig. 9. Molecular structure of complex **XXVI** [95].

The reaction of salicylaldehyde 2-hydroxybenzoylhydrazone (H_2L) with vanadyl acetylacetonate in ethanol affords the oxoethoxovanadium complex [VO(OEt)L], with reacts with Lewis bases (L') to form complexes of the [VO(OEt)L'] type, where L' is pyridine, 2-picoline, 3-picoline, 4-picoline, 2-aminopyridine, imidazole, or 4-methylimidazole (**XXVII**) (Fig. 10). Complexes **XXVII** structurally characterized by XRD have a distorted octahedral coordination environment O_4N_2 around the vanadium(V) acceptor center due to the bond with the phenol oxygen atom, enol oxygen atom of the hydrazone fragment, and imine nitrogen atom of the tridentate ligand and the oxygen atom of the ethoxy group of the deprotonated ethanol molecule. Two axial positions are occupied by the oxo O atom of vanadyl and nitrogen atom of the secondary ligand L' [96].

In the case where L' is 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethylene, dimeric molecules $[VO(OEt)L]_2(L')$ are formed due to the coordination to vanadium of the nitrogen atom of 4,4'-bipyridine (in **XXVIIIa**) and 1,2-bis(4-pyridyl)ethylene (in **XXVIIIb**) [96] (Fig. 11). The OH group of the salicyloylhydrazone fragment does not participate in coordination with the metal but forms hydrogen bonds with the deprotonated nitrogen atom of the hydrazone fragment.

Similar products of the binuclear oxomolybdenum(VI) complexes were also synthesized and structurally characterized [97–99].

Two new oxovanadium(V) complexes, [$VOLL^1$] (**XXIX**) and [$VOLL^2$] (**XXX**), where L is the dianionic form of the hydrazone ligand of *N*'-(2-hydroxy-3-methoxybenzylidene)-3-methylbenzoylhydrazide (H_2L), were synthesized. Ligands L^1 and L^2, being the deprotonated forms of 3-hydroxy-2-methyl-4*H*-pyran-4-one (HL^1) and 3-hydroxy-2-ethyl-4*H*-pyran-4-one (HL^2), respectively, were synthesized and characterized by the XRD [100] method (Fig. 12). The vanadium(V) atoms in the complexes exist in the octahedral coordination environment, and the hydrazone ligand coordinates in the enol form with the metal atoms through the phenolate oxygen atom, imine nitrogen atom, and enolate oxygen atom of the benzoylhydrazone fragment, whereas the coordination

(XXVII)

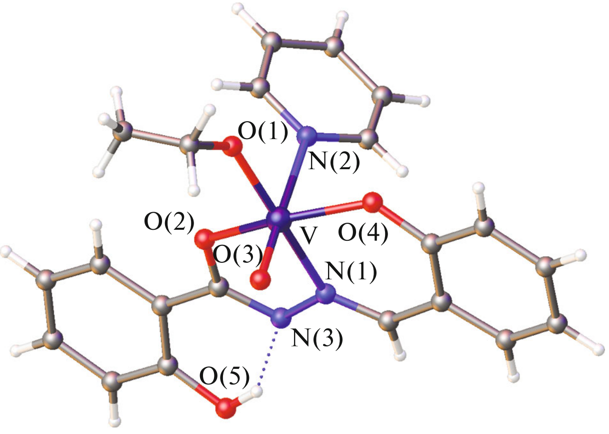
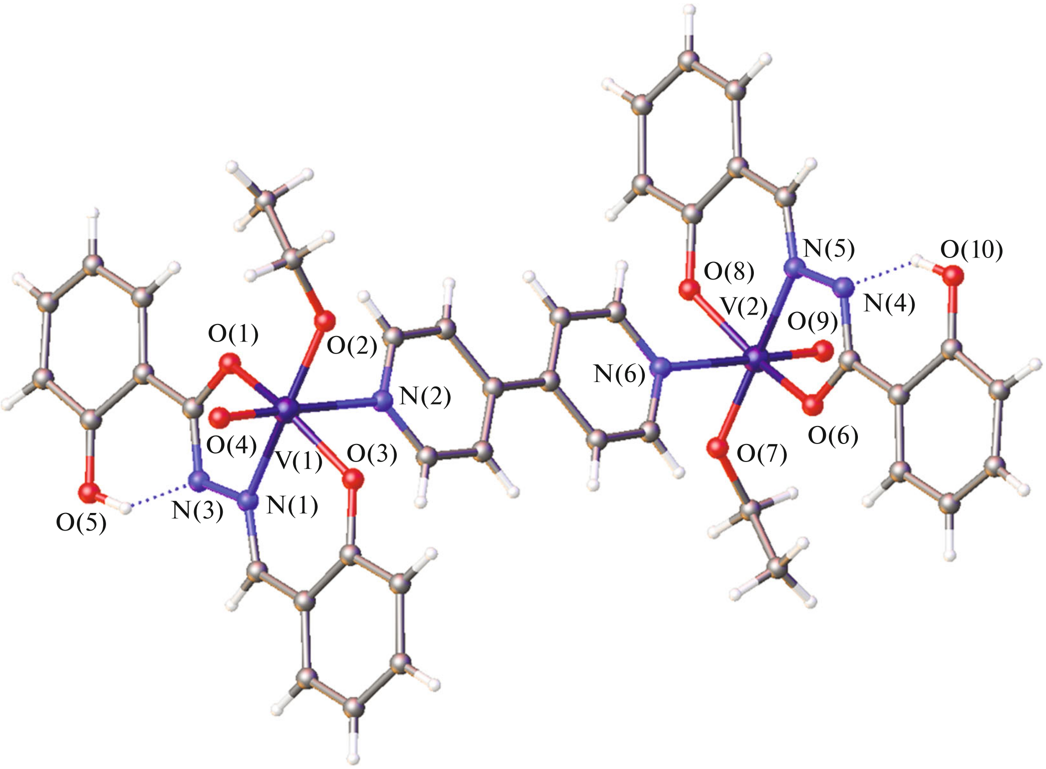


Fig. 10. Molecular structure of complex **XXVII** [96].

(**XXVIIIa**)



(**XXVIIIb**)

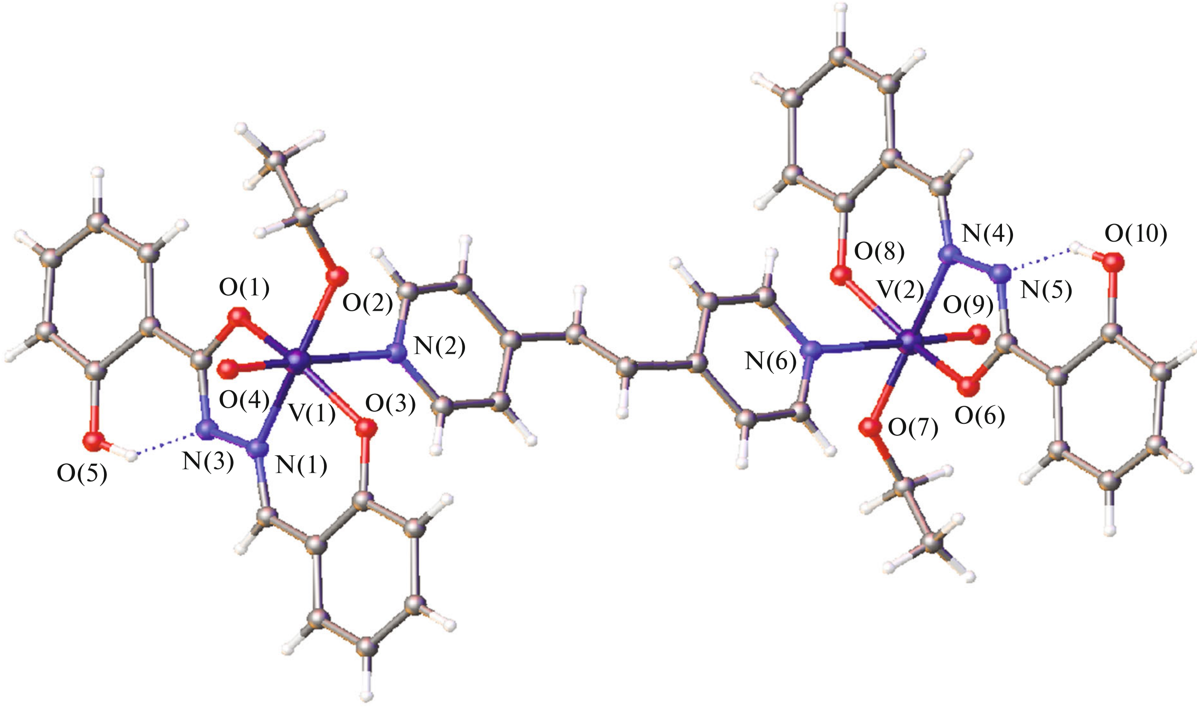


Fig. 11. Molecular structures of complexes **XXVIIIa** and **XXVIIIb** [96].

with the pyrone ligand occurs through the oxygen atoms of the carbonyl and hydroxyl groups. Both complexes are characterized by high antibacterial and antifungal activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* compared to the activities of free hydrazone.

(XXIX) **(XXX)**

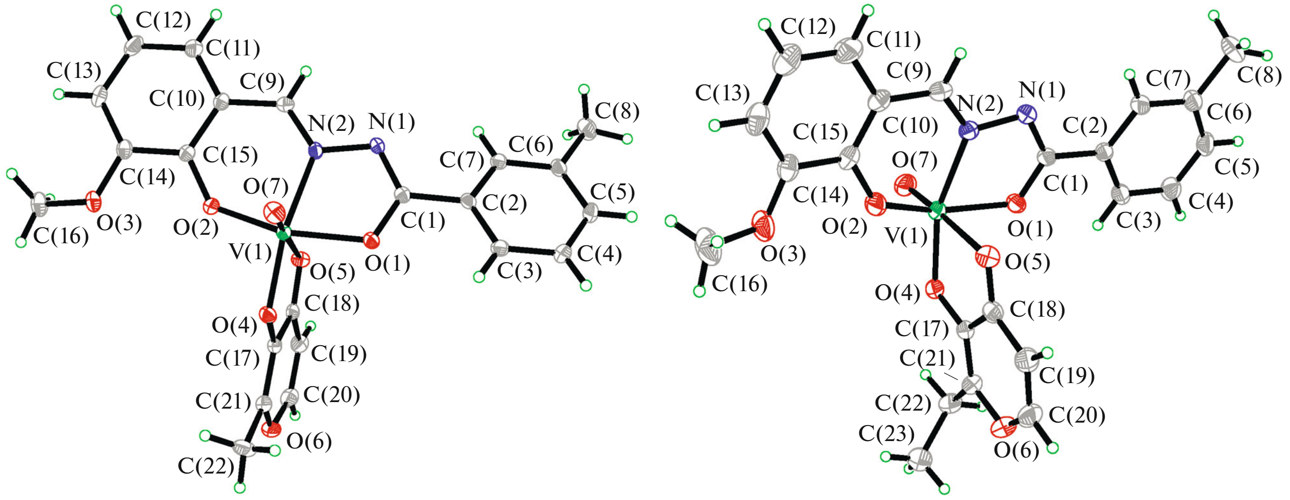
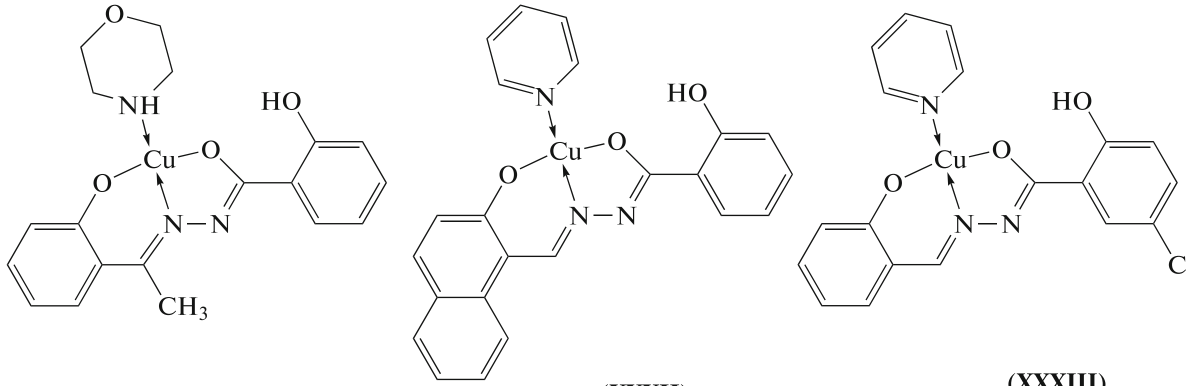


Fig. 12. Molecular structures of complexes **XXIX** and **XXX** [100].

2-Hydroxybenzaldehyde and 2-hydroxynaphthaldehyde salicyloylhydrazones in the adducts with morpholine **XXXI** [101] and pyridine (**XXXII** and **XXXIII**) [102, 103] coordinate in the enol form to the copper(II) ion (Scheme 9).



(XXXI) **(XXXII)** **(XXXIII)**

Scheme 9.

The Cu(II) ion in complex **XXXI** is coordinated by the oxygen atom of the hydrazone fragment of the ligands in the enol form, azomethine nitrogen atom, phenolate oxygen atom of the doubly deprotonated tridentate ligand, and the nitrogen atom of the morpholine molecule to form the distorted *trans*-CuN_2O_2 planar square geometry. A similar coordination environment of the Cu(II) ions is formed in complexes **XXXII** and **XXXIII** [102, 103].

In the dimeric copper adduct with DMF (**XXXIV**), 2-hydroxy-3-methoxy-5-bromobenzaldehyde 2-hydroxybenzoylhydrazone in the enol form coordinates to the formation of a distorted square pyramidal coordination geometry. The dimeric molecule is formed due to the axial oxygen atoms of the hydrazone fragments of the ligands [104] (Fig. 13).

The cytotoxicity of salicylidenebenzoylhydrazones and their copper(II) complexes **XXXV** against the human adenocarcinoma cell line was evaluated [18]. In some cases, the cytotoxicity of copper(II) complexes **XXXV** exceeds that of cisplatin by more than two times. In these complexes, the ligand in the keto form coordinates to the copper atom [21] (Scheme 10).

(XXXIV)

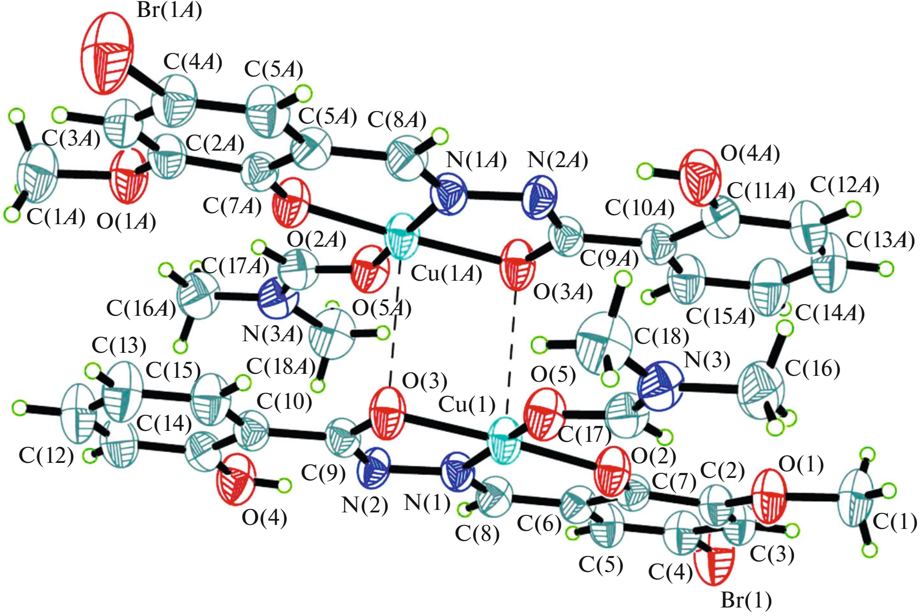
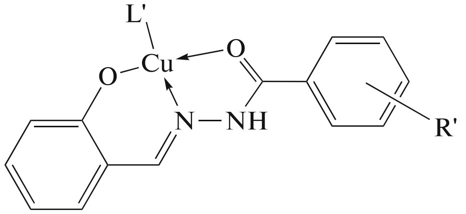


Fig. 13. Molecular structure of complex **XXXIV** [104].



(XXXV)

M = Cu^{2+}; R = H; 2-CH_3; 3-OCH_3; 5-OCH_3;
5-Cl; 5-NO_2; 5-CH_3; R' = H, 2-CH_3;
3-CH_3; 4-CH_3; 4-F; 4-Cl; 4-Br; 4-NO_2; 2-OH;
4-OH; 4-CH_3; 4-Cl; 4-NO_2; L' = Cl, NO_3

Scheme 10.

The following adducts of the copper(II) products were synthesized and structurally characterized [105, 106]: the binuclear adduct based on 5-bromosalicylbenzoylhydrazone with imidazole (**XXXVI**) and that of 5-bromosalicylal-3,5-dimethoxybenzoylhydrazone with 1,10-phenanthroline (**XXXVII**) (Fig. 14).

In complexes **XXXVI** and **XXXVII**, copper is coordinated by the ligand in the enol form and is additionally coordinated by the nitrogen atoms of the imidazole or 1,10-phenanthroline molecule. Complex **XXXVI** has a distorted planar square geometry, whereas complex **XXXVII** is characterized by a distorted square pyramidal geometry in which the N,N-donor atoms of 1,10-phenanthroline are axial equatorial. The oxygen atoms of the hydrazone fragment act as bridges in the dimeric structure of complex **XXXVI**. In both structures, the ONO-donor hydrazone ligand occupies the basal plane of the phenolate oxygen atom, imine nitrogen atom, and deprotonated oxygen atoms of the amide fragment.

The complexes (mono- and binuclear) of 2-hydroxy-4-octyloxybenzaldehyde and 4-formyl-3-hydroxyphenyl-4-octyloxybenzene pyridinoylhydrazone (**XXXVIII** and **XXXIX**, Fig. 15) having the photoluminescence properties [107] with high photoluminescence quantum yields were characterized by the XRD method.

The geometry of the coordination mode in complexes **XXXVIII** and **XXXIX** is square pyramidal or trigonal bipyramidal with pentacoordinated zinc(II) coordinated by the hydrazone O,N,O-ligand in the enol form and one or two pyridines. The ligands are elongated and nearly planar. The oxygen atoms of the phenol fragments in salicylaldehydes act as bridges in dimeric complex **XXXVIII**.

A number of mono- and binuclear zinc complexes **XLa** and **XLb** is characterized by the photoluminescence properties (Scheme 11, Fig. 16), and their structures determined by XRD [108] contain tridentate ligands coordinated to the zinc ion through two oxygen atoms and one nitrogen atom. The coordination sphere of the zinc ion is supplemented by one (**XLb**) or two (**XLa**) pyridine molecules. Binuclear complex **XLb** is formed via the bridging phenolate oxygen atoms of the aldehyde fragment.

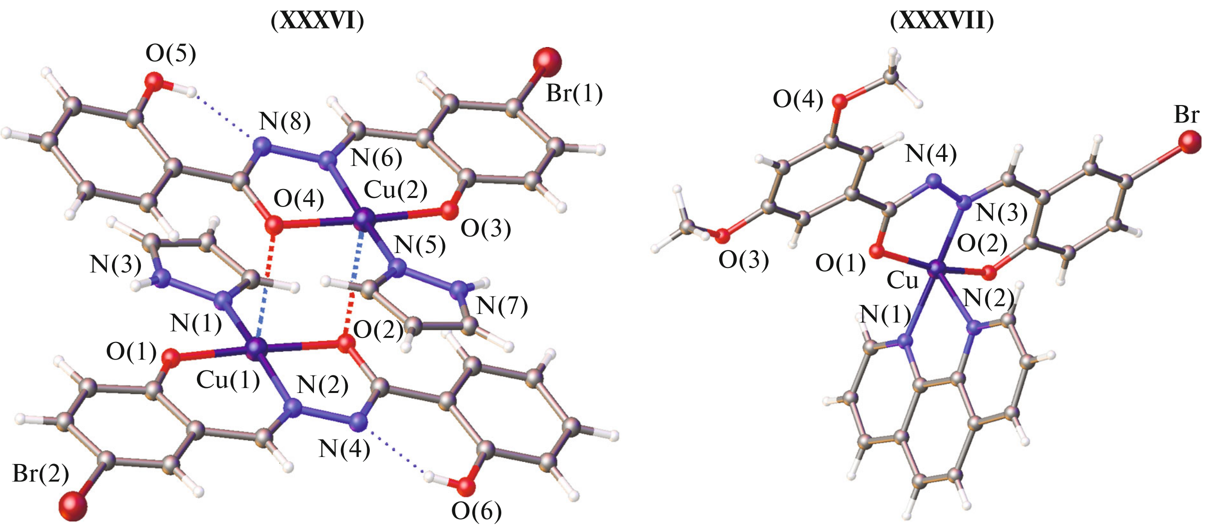

(XXXVI) (XXXVII)

Fig. 14. Molecular structures of complexes **XXXVI** [105] and **XXXVII** [106].

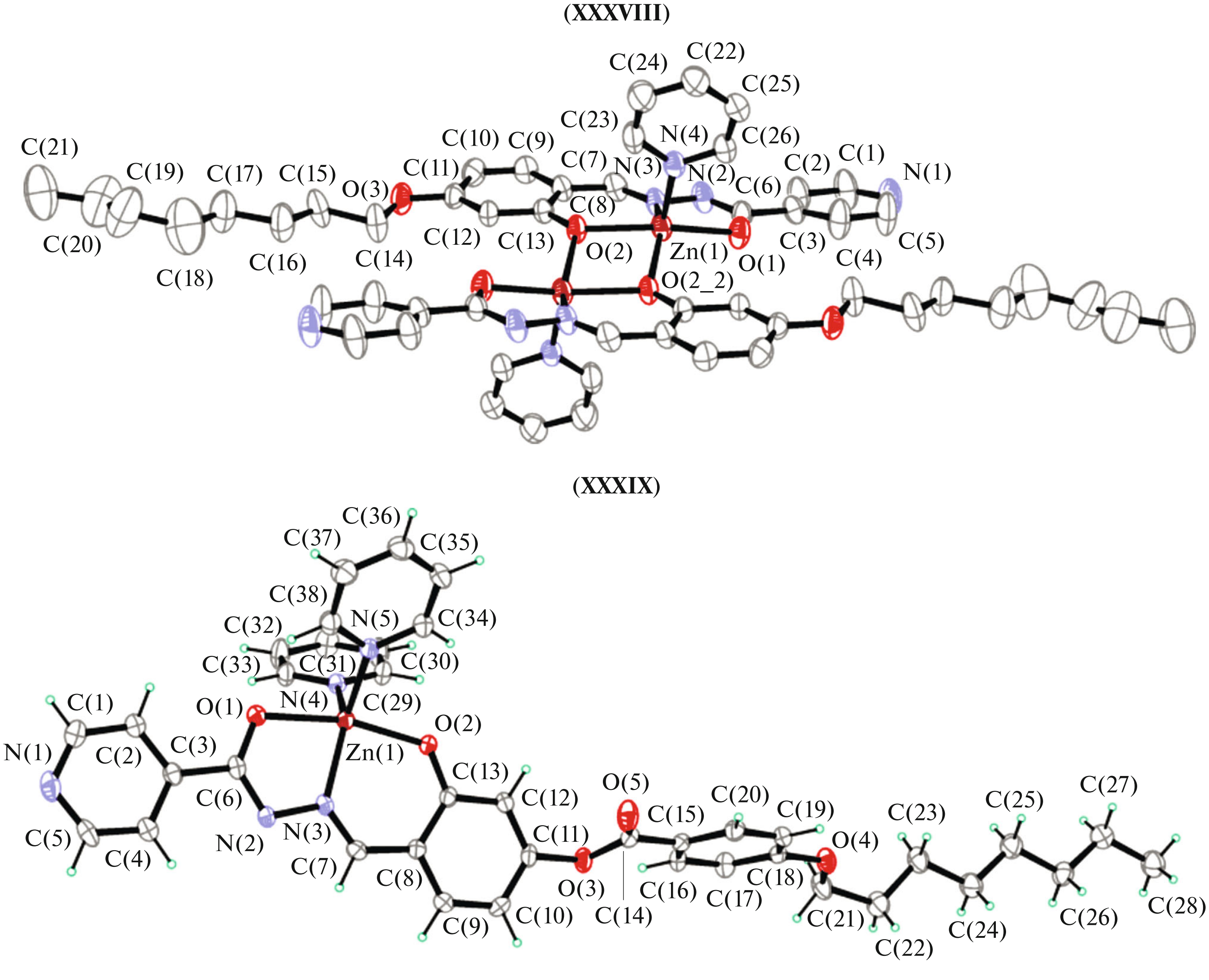
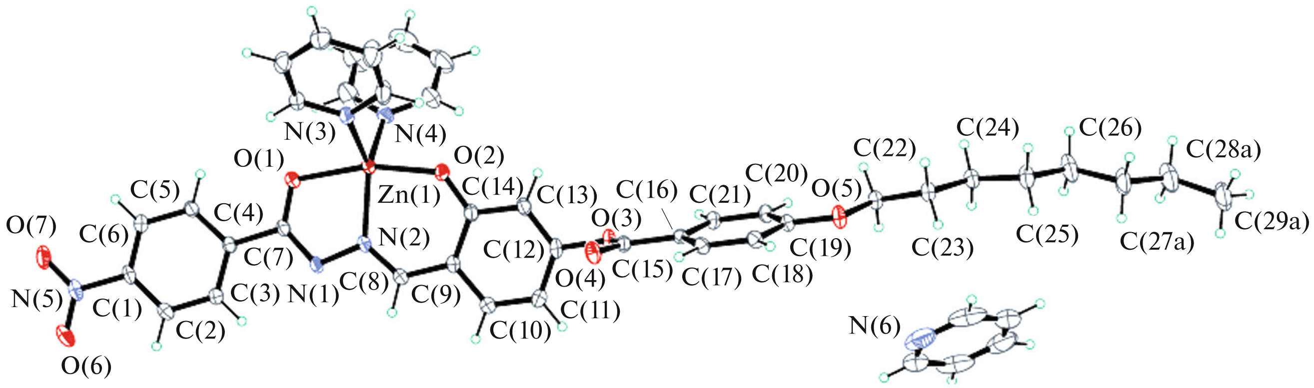

(XXXVIII) (XXXIX)

Fig. 15. Molecular structures of complexes **XXXVIII** and **XXXIX** [107].

(XLa)



(XLb)

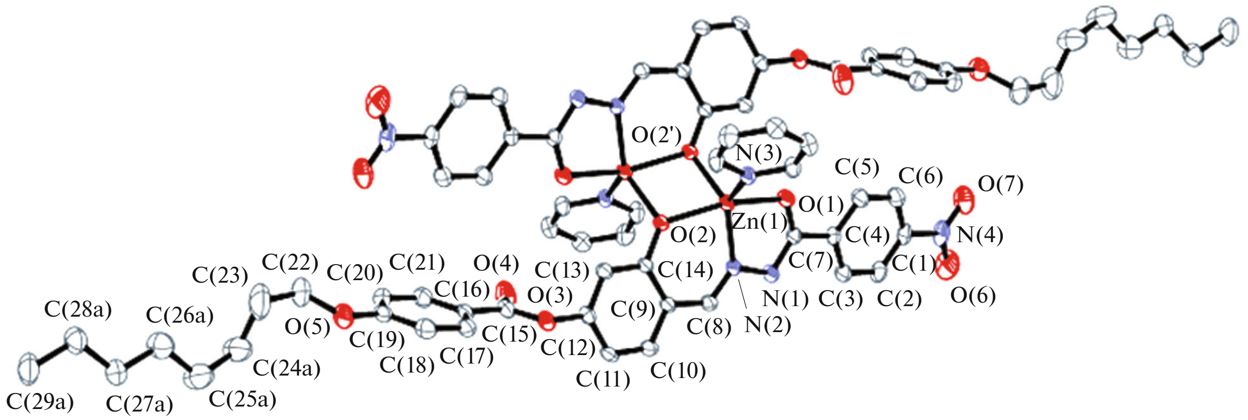
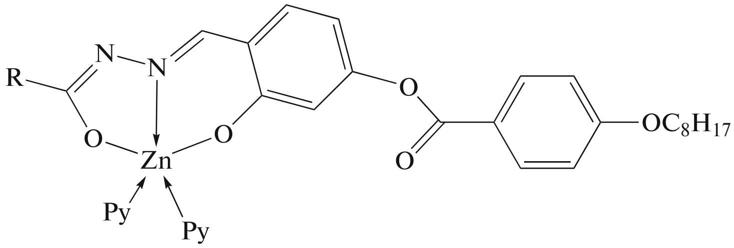


Fig. 16. Molecular structures of complexes **XLa** and **XLb** [108].



(XLa)

R = $-C_6H_4-4\text{-F}$, $-C_6H_4-4\text{-CN}$,
$-C_6H_4-4\text{-NO}_2$, 4-benzothiazole
Scheme 11.

Note that the ligands in the enol tautomeric form coordinate to the zinc atoms in complexes **XLa** and **XLb**.

Two mononuclear zinc(II) and manganese(II) compounds were synthesized: [ZnL_2] (**XLIa**) and [MnL(HL)]ClO_4 (**XLIb**) (Fig. 17), where L is the monoanionic form of *N*'-(1-(pyridin-2)-yl)ethylidene)isonicotinohydrazide (HL), and were characterized by the XRD method [109]. Compound **XLIa** contains the neutral complex molecule [ZnL_2], and complex **XLIb** contains the complex cation [MnL(HL)]$^+$ and one perchlorate anion. The metal atoms in the complexes exist in the octahedral coordination environment. The hydrazone ligands coordinate to the metal atoms through the pyridine nitrogen atom, imine nitrogen atom, and enolate oxygen atoms. The high antimicrobial activity of these compounds

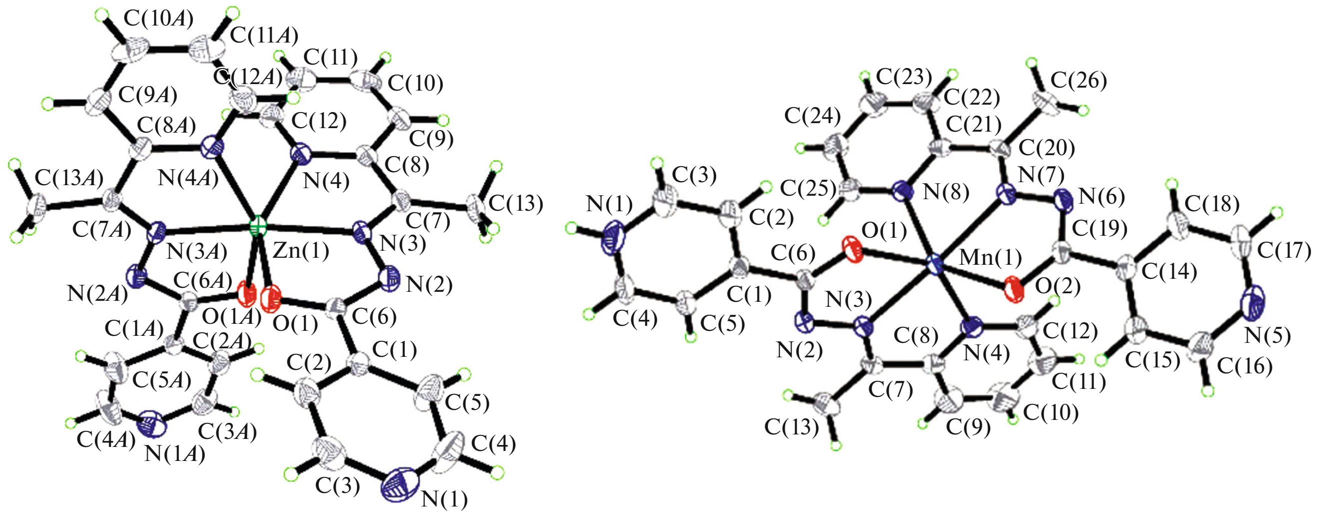

(XLIa) **(XLIb)**

Fig. 17. Molecular structures of complexes **XLIa** and **XLIb** [109].

against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* was shown [109, 110].

In the zinc complex with 2-hydroxy-3,5-dibromobenzaldehyde 2-hydroxybenzoylhydrazone, the ligand in the enol form also coordinates to the metal to form bipyridine adduct **XLII** (Fig. 18), where the coordination center has a distorted trigonal bipyramidal geometry [111].

The binuclear complexes of type **XLIII** (Scheme 12) with the ligand coordinated in the enol form and dimerization through the oxygen atoms of the aldehyde fragment were synthesized [112–114] by the reaction of 2-hydroxybenzaldehyde 2-hydroxybenzoylhydrazone with zinc acetate. The morpholine, pyridine, or methylpyridine molecules act as axial ligands.

(XLII)

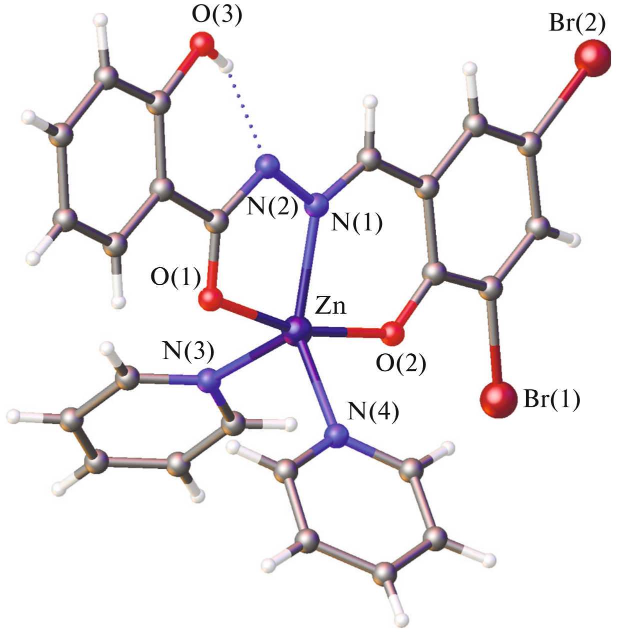
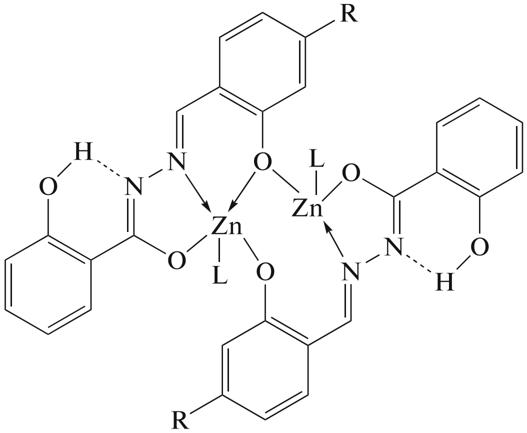


Fig. 18. Molecular structure of complex **XLII** [111].



(XLIII)

R = H, OH; L = morpholine, pyridine, methylpyridine

Scheme 12.

In dimeric complex **XLIV** (Fig. 19) synthesized from 2,4-dihydroxybenzaldehyde 2-hydroxybenzoylhydrazone and $Zn(OAc)_2 \cdot 2H_2O$, the ligand coordinates in the enol form, where the oxygen atoms of the aldehyde fragments act as bridges with the additional coordination of two pyridine molecules and two DMF molecules. All Zn(II) atoms are coordinated by three oxygen atoms and two nitrogen atoms to form a distorted tetragonal pyramidal geometry because of different Zn–O and Zn–N distances. Three oxygen

(XLIV)

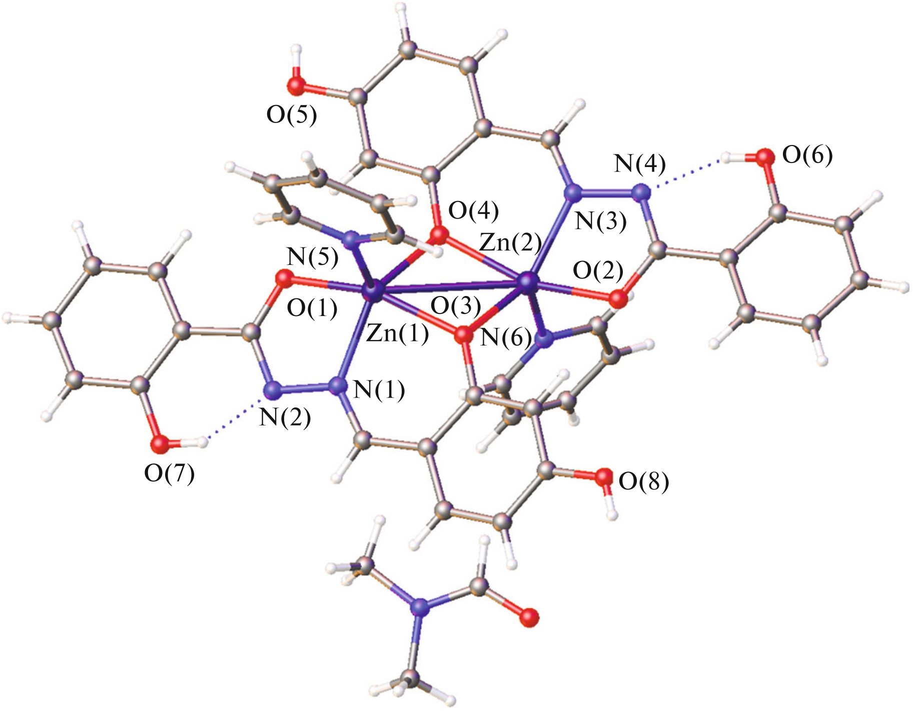


Fig. 19. Molecular structure of complex **XLIV** [115].

atoms and one nitrogen atom of ligands L are arranged in the basal plane of the distorted square pyramid, and the nitrogen atom belonging to the pyridine molecule occupies the apical position [115].

The XRD data for monomeric zinc complex **XLV** (Fig. 20) synthesized by the reaction of 2-methoxybenzaldehyde 2-hydroxybenzoylhydrazone with Zn(OAc)$_2$· 2H$_2$O, where the ligand in the enol form coordinates to the zinc atom, are presented [116]. The zinc(II) ion lying at the symmetry center has an octahedral environment and is coordinated by four oxygen atoms and two nitrogen atoms of two anionic 2-hyd-roxy-*N*-(2-methoxybenzylidene)benzoylhydrazide li-gands.

(XLV)

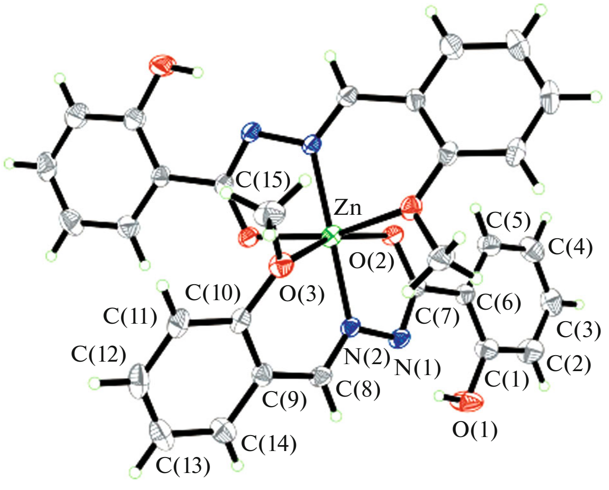
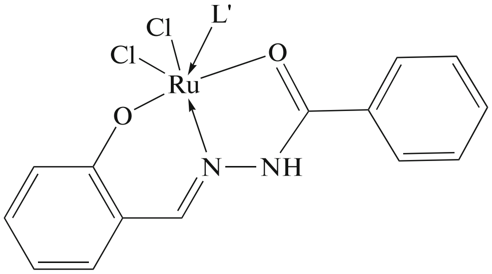


Fig. 20. Molecular structure of complex **XLV** [116].

Nickel adduct **XLVI** (Fig. 21) with three pyridine molecules and ligand in the enol form was structurally characterized [117]. The nickel(II) ion is surrounded by one nitrogen atom and two oxygen atoms of the Schiff base and three nitrogen atoms of three pyridine molecules. This coordination mode (NiN$_4$O$_2$) forms a distorted octahedral geometry.

The reactions of salicylaldehyde benzoylhydrazone with ruthenium(II) chloride in the presence of pyridine, 2-picoline, 3-picoline, and 4-picoline afford octahedral complexes **XLVII** (Scheme 13) in which, according to the IR spectral data, the ketone form of the ligand takes place [118].



(XLVII)

L' = pyridine, 2-picoline, 3-picoline, 4-picoline

Scheme 13.

(XLVI)

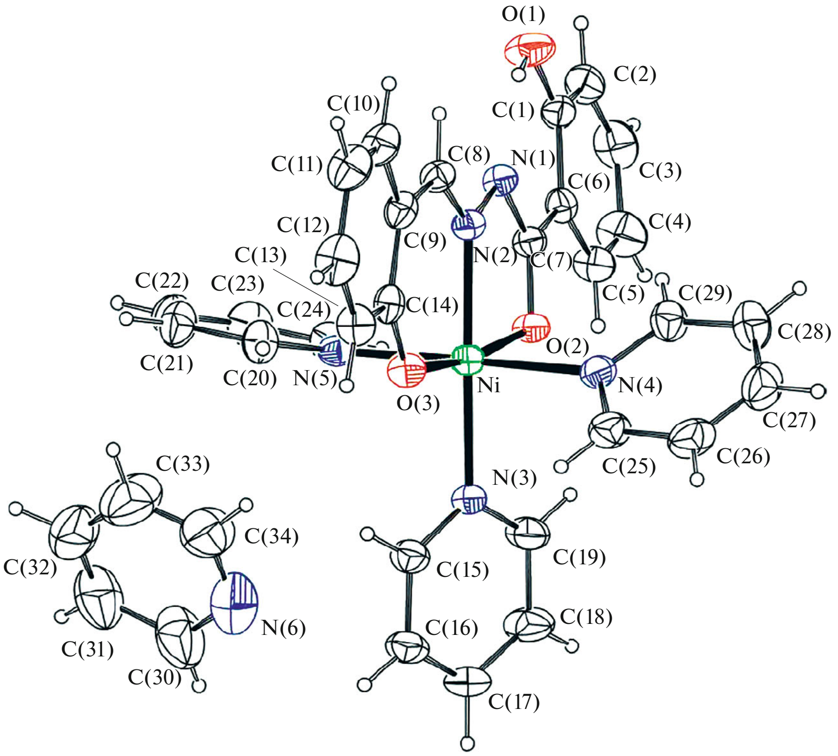


Fig. 21. Molecular structure of complex **XLVI** [117].

The octahedral ruthenium(II) complexes of the derivatives of 2-acetylpyridine benzoylhydrazone (**XLVIII**) (Fig. 22) with the catalytic activity in the reduction of aldehydes to alcohols were structurally characterized [119]. The ligand in the enol form coordinates in the ruthenium(II) complex. The *N*,*N*,*O*-benzoylhydrazone ligand coordinates to the ruthenium(II) ion through the pyridine and azomethine nitrogen atoms and deprotonated amide oxygen atom with the formation of two five-membered condensed chelate rings.

Three copper(II), zinc(II), and vanadium(V) complexes, $[CuL(HL)]ClO_4$ (**XLIX**), $[ZnL_2]$ (**L**), and $[VO_2L]$ (**LI**) (Fig. 23), where L is the anionic form of 3-methyl-*N*'-(1-(pyridin-2-yl)ethylidene)benzohydrazide (HL), where synthesized and characterized by the XRD method. All complexes are highly active against different bacterial strains *B. subtilis*, *S. aureus*, and *E. coli* [120].

The coordination geometry around the copper(II) ion in complex **XLIX** (Fig. 23) is distorted octahedral with one neutral and one anionic tridentate hydrazone ligands. The hydrazone ligands coordinate to the copper(II) ion through the pyridine nitrogen atoms, imine nitrogen atoms, and carbonyl and enolate oxygen atoms O(2) and O(1), respectively.

The coordination geometry around the zinc(II) ion in **L** (Fig. 23) is also distorted octahedral with the tridentate anionic hydrazone ligands in the enol form. The hydrazone ligands coordinate to the zinc ion through the pyridine nitrogen atoms, imine nitrogen atoms, and enolate oxygen atoms.

The coordination geometry around the vanadium(V) ion in complex **LI** can be described by a trigonal bipyramid with the imine nitrogen atom of the tridentate hydrazone ligand and two oxo O atoms in the enol form.

Pyridine adduct **LII** is formed by the reaction of benzaldehyde *N*-(4-oxo-4-phenylbutan-2-ylidene)benzoylhydrazone in the enol form with copper(II) chloride (Fig. 24) [121]. The central Cu(II) atom has a distorted planar square coordination geometry formed by two oxygen atoms, one nitrogen atom of the ligand molecule, and one nitrogen atom of the pyridine molecule.

The binuclear structure of complex **LIII** [122] (Fig. 25) in which the ligand in the enol form coordinates to the copper(II) ion with the additional coordination of the pyridine molecule was synthesized and structurally characterized. The copper(II) ion has an N_2O_2 square pyramidal environment, where the bridging oxygen atoms of the ligand occupy the axial positions.

(XLVIII)

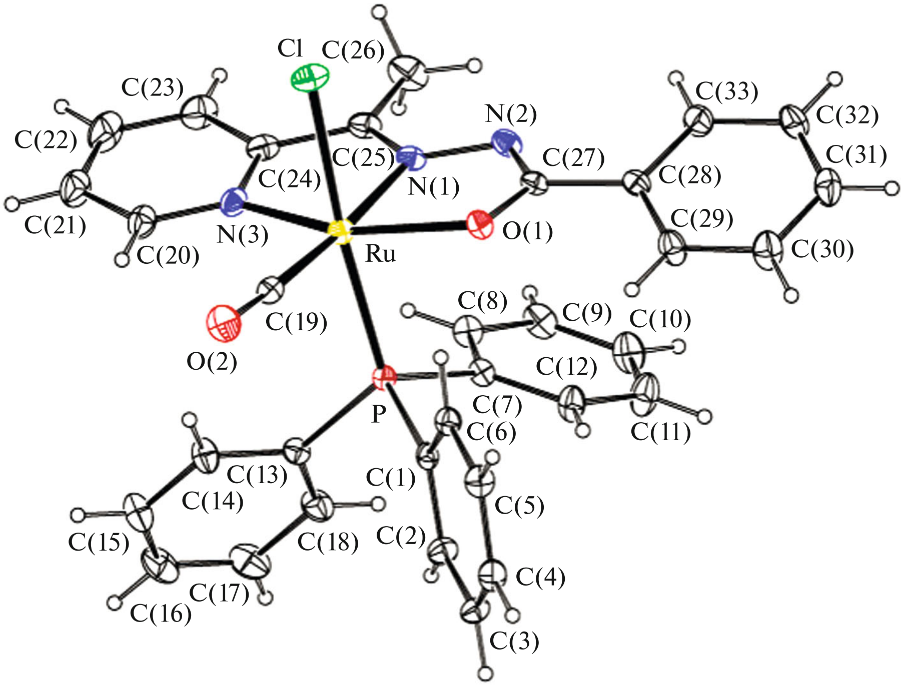
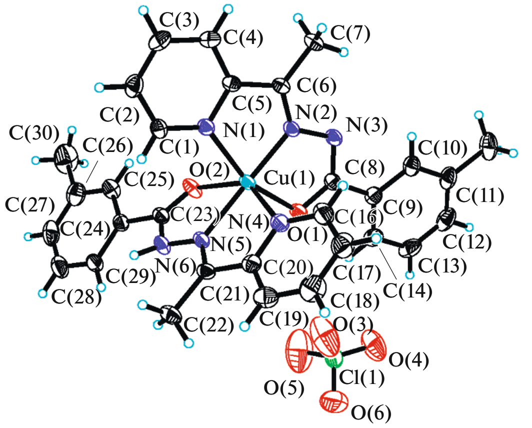
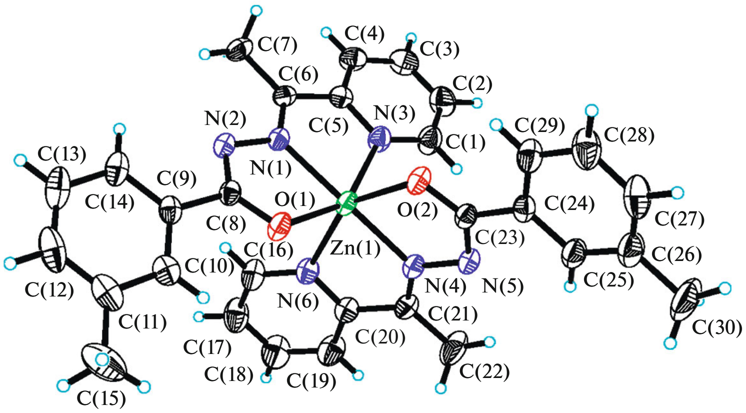


Fig. 22. Molecular structure of complex **XLVIII** [119].

(XLIX)



(L)



(LI)

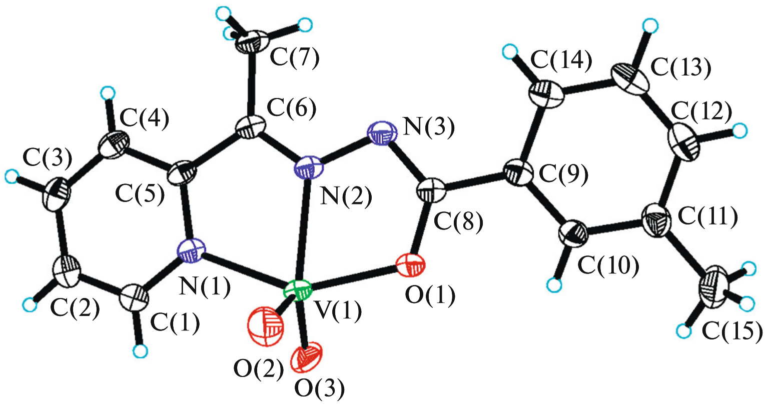


Fig. 23. Molecular structures of complexes **XLIX**, **L**, and **LI** [120].

(LII)

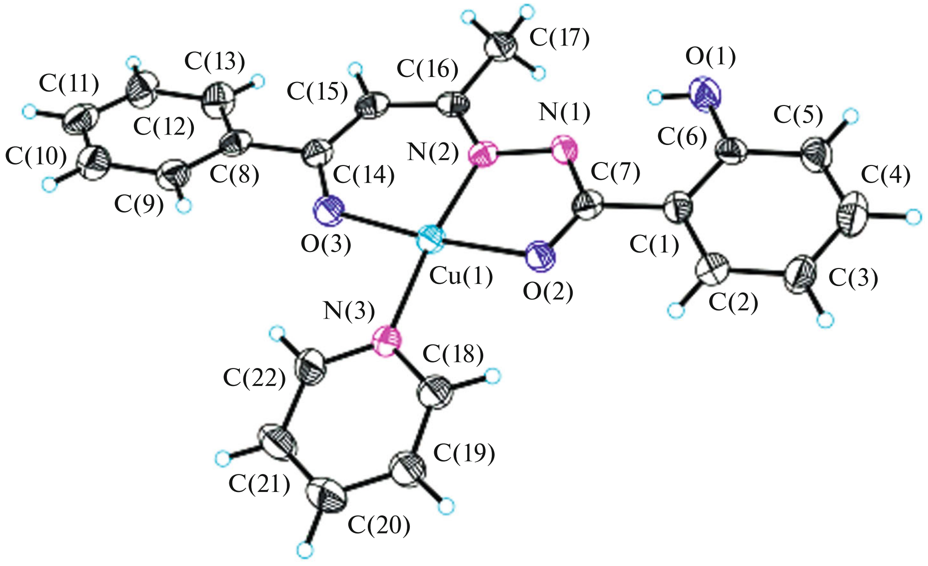


Fig. 24. Molecular structure of complex **LII** [121].

(LIII)

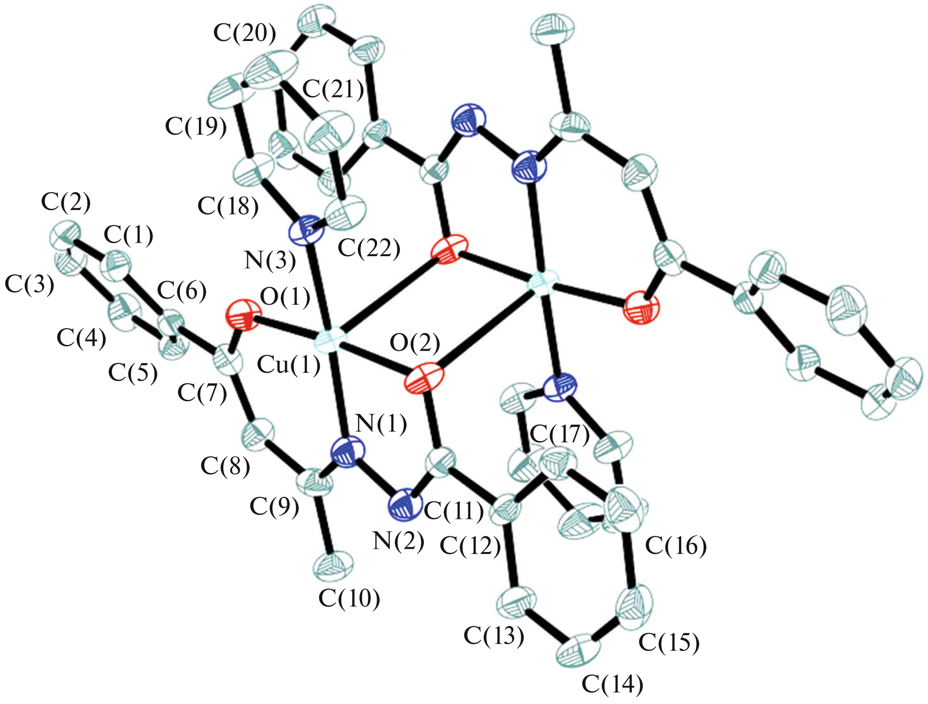
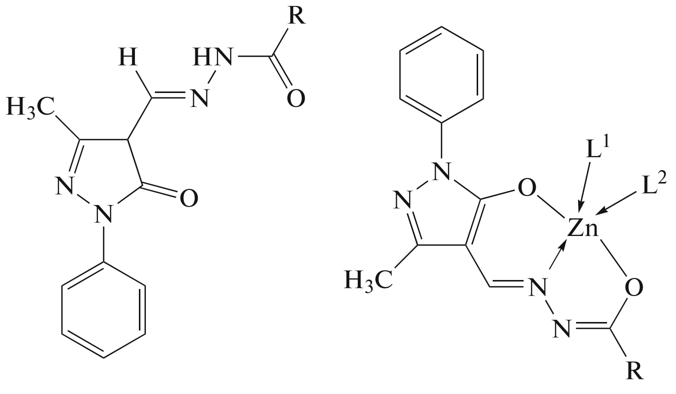


Fig. 25. Molecular structure of complex **LIII** [122].

The photoluminescent zinc complexes of 3-methyl-4-formylpyrazol-5-one aroyl(acyl)hydrazones (H_2L) (**LIVa**–**LIVf**) with the quantum yields from 10 to 64% (Scheme 14) were described and structurally characterized [47].



(H_2L) (**LIVa**–**LIVf**)

$L^1 = H_2O$, pyridine, $L^2 =$ COOCH

(**a**) $R = C_6H_5$
(**b**) $R = p\text{-}CH_3OC_6H_4$
(**c**) $R = C_6H_5CH_2$
(**d**) $R = p\text{-}CH_3C_6H_4$
(**e**) $R = p\text{-}ClC_6H_4$
(**f**) $R = C_6H_5CH_2CH_2$

Scheme 14.

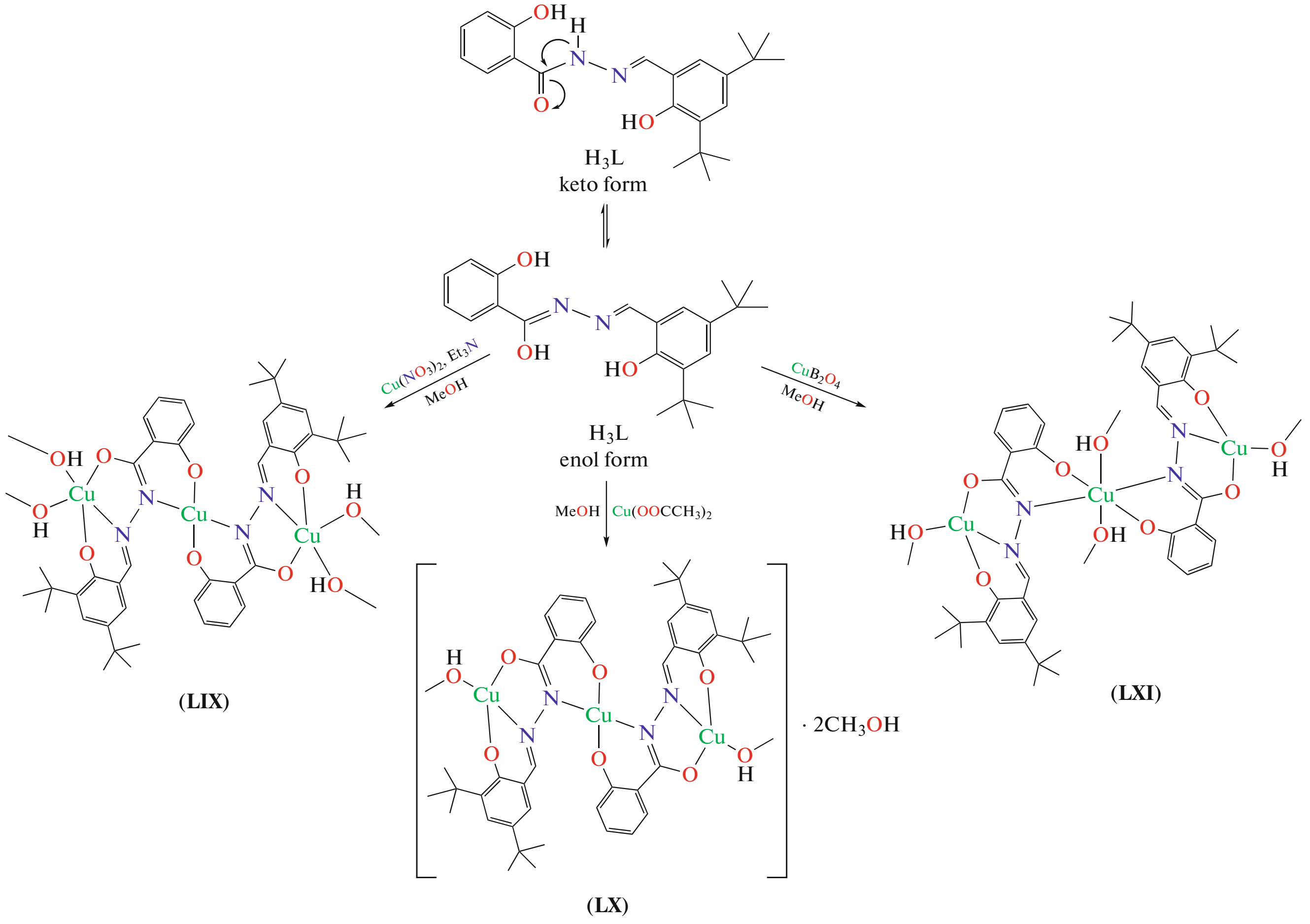
The coordination sphere of the zinc(II) ion is formed by one nitrogen atom, oxygen atoms of the pyrazole fragment of the ligand and carboxyl group of hydrazone (in the keto form), and oxygen atoms of the acetate anion coordinated via the monodentate mode and water (**LIVc**) or nitrogen atom of the pyridine molecule (**LIVe**) (Fig. 26). The coordination polyhedron in complexes **LIVc** and **LIVe** has the geometry of a trigonal pyramid.

The binuclear dysprosium(III) complex of 2-hydroxy-3-methoxybenzaldehyde 2-hydroxybenzoylhydrazone $[Dy_2(L)_2(DBM)_2(DMF)_2]\cdot 2DMF$ (**LV**), where H_2L is 2-hydroxy-*N*'-(2-hydroxy-3-methoxybenzylidene)benzohydrazide and HDBM is dibenzoylmethane (Fig. 27), was synthesized and structurally characterized [123] in order to study magnetism dynamics controlling in molecular magnets using guest solvent molecules. The magnetic properties of complex **LV** were studied in a wide temperature range to 2 K. In the dimeric molecule, the ligand in the keto form coordinates to dysprosium(III).

The structure of complex **LV** is presented by the neutral dimer in which two Dy(III) ions coordinate two ligands of the dianionic Schiff base (L^{2-}), two bidentate monoanionic ligands DBM^-, and two axial ligands of the DMF solvent. The dysprosium(III) ions are linked by two phenoxyl groups of two ligands.

The bimetallic mononuclear (**LVI**) and tetranuclear copper(II) (**LVII**) and gadolinium(III) (**LVIII**) complexes (Fig. 28) of 2-hydroxy-*N*'-[(2-hydroxy-3-methoxyphenyl)methylidene]benzohydrazide (LH_3), where the ligands in the enol form coordinate to the metal ions, were synthesized [124]. Heterometallic cubane complex **LVIII** consists of two Cu–Gd pairs bonded by the dihydroxo Gd–Gd bridge in which the Cu(II) and Gd(III) ions are linked by the nonsymmetric phenoxohydroxo bridge.

The trinuclear isomeric Cu(II) complexes $[Cu_3(L)_2(MeOH)_4]$ (**LIX**), $[Cu_3(L)_2(MeOH)_2]\cdot 2MeOH$ (**LX**), and $[Cu_3(L)_2(MeOH)_4]$ (**LXI**) (Fig. 29) were synthesized [125] by the reactions of the Schiff base (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H_3L) with copper(II) nitrate, acetate, or metaborate (Scheme 15). In these compounds, ligand L in the enol form exhibits the dianionic (HL^{2-} in complex **LIX**) or trianionic (L^{3-} in complexes **LX** and **LXI**) pentadentate coordination modes. The measurements of the magnetic susceptibility at various temperatures (2–300 K) showed a strong antiferromagnetic interaction between the copper(II) ions in all the three complexes.

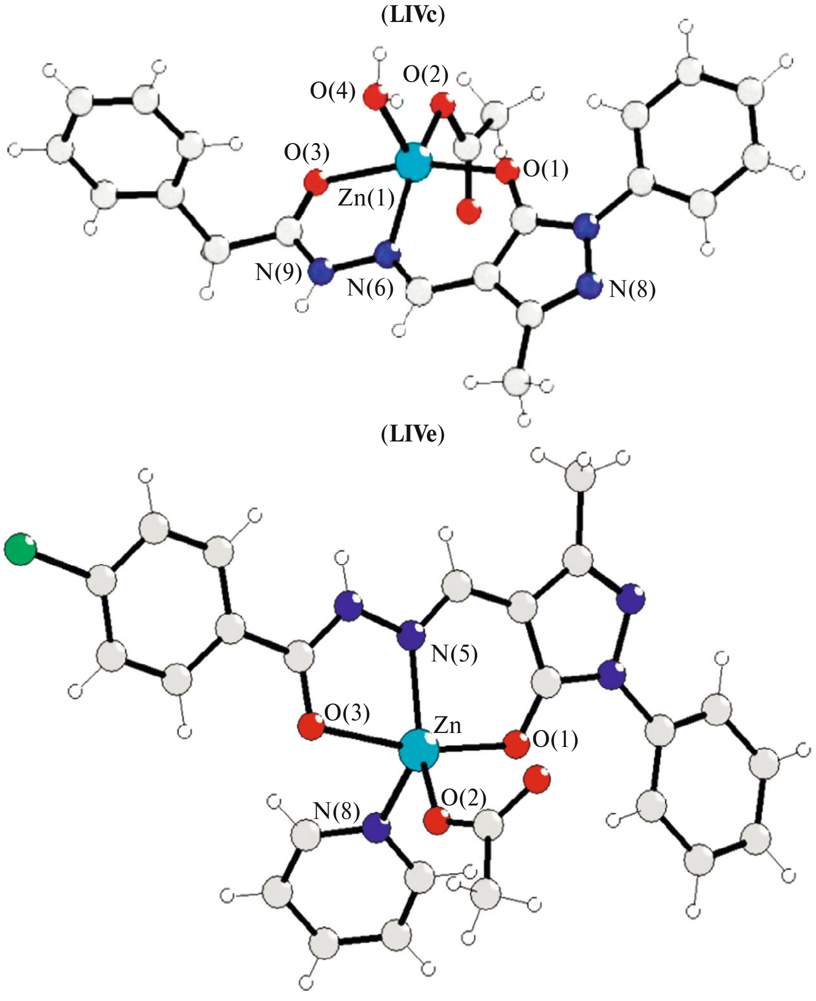


Scheme 15.

In some cases, the ligands in the enol and keto forms simultaneously coordinate to the metal ion. The Fe(III) and Co(III) complexes, $[Fe(L^1)(HL^1)]$ (**LXII**) and $[Co(L^2)(HL^2)]$ (**LXIII**) based on (3,5-di-*tert*-butyl-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (H_2L^1) and (3,5-di-*tert*-butyl-2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H_2L^2), were synthesized [126] (Fig. 30). The structural studies showed the presence of both the keto and enol tautomeric forms of the ligand in complexes **LXII** and **LXIII**. Both metal cations in these compounds are characterized by the octahedral geometry including two nonequivalent tridentate ligands and leading to the coordination modes N_2O_4.

The mononuclear zinc(II) complex $[Zn(HL)_2H_2O]$ (**LXIV**) was synthesized from the 2-hydroxy-*N*'-(1-oxoacenaphthylen-2(1*H*)idene benzohydrazide ligand (H_2L) [127] (Fig. 31). The ligand chelates with the metallic center by two nitrogen atoms of the imino group and two oxygen atoms of the enol group. The complex has a distorted trigonal bipyramidal geometry around the zinc(II) ion with the oxygen atoms lying in the equatorial plane, the nitrogen atoms of the imino groups in the axial direction, and additional oxygen atom of water.

New Zn(II), Cd(II), Ni(II), and Co(II) complexes with 3,5-di-*tert*-butylbenzoquinone-1,2 3-hydroxynaphthoylhydrazone were synthesized [128]. The structure of zinc complex **LXV** was determined by the XRD method (Fig. 32). Two organic ligands, namely, monodeprotonated 3,5-di-*tert*-butylbenzoquinone-



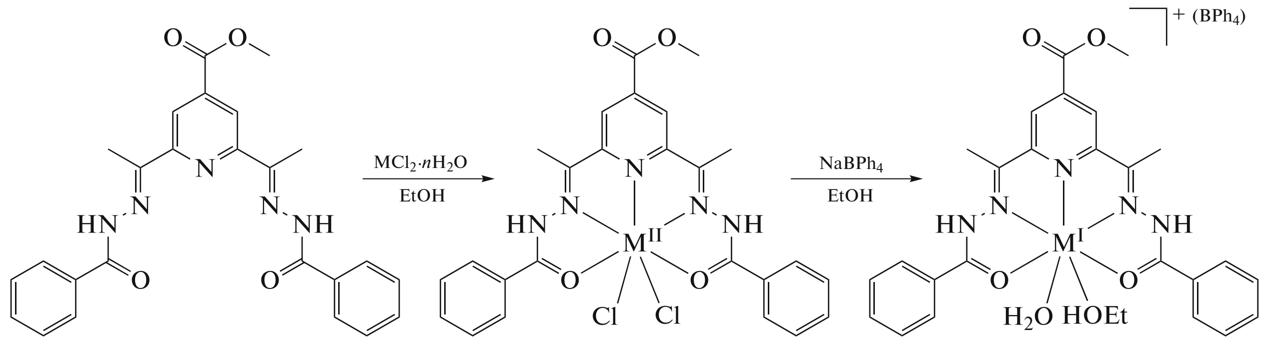
(LIVc)

(LIVe)

Fig. 26. Molecular structures of complexes **LIVc** and **LIVe** [47].

1,2 3-hydroxynaphthoylhydrazone in the enol form, are coordinated to the Zn atom in the complex via the tridentate mode. The coordination polyhedron of the zinc atom in complex **LXV** is a distorted octahedron formed by two nitrogen atoms and four oxygen atoms.

The Mn(II) and Co(II) complexes of the functionalized donor ligand $N_3O_2H_2L^2$, where H_2L^2 is 2,6-diacetyl-4-carboxymethylpyridine bis(benzoylhydrazone), were synthesized, and their structures were studied [129] (Scheme 16, Fig. 33).



H_2L^2

(LXVI) M = Mn(II)
(LXVII) M = Co(II)

(LXVIII) M = Mn(II)
(LXIX) M = Co(II)

Scheme 16.

(LV)

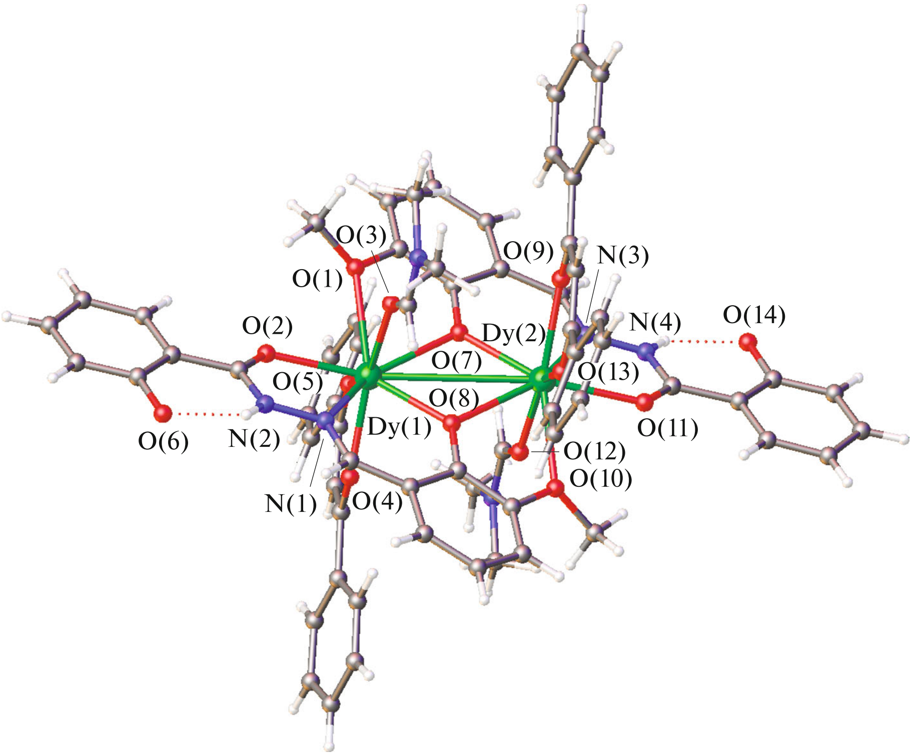
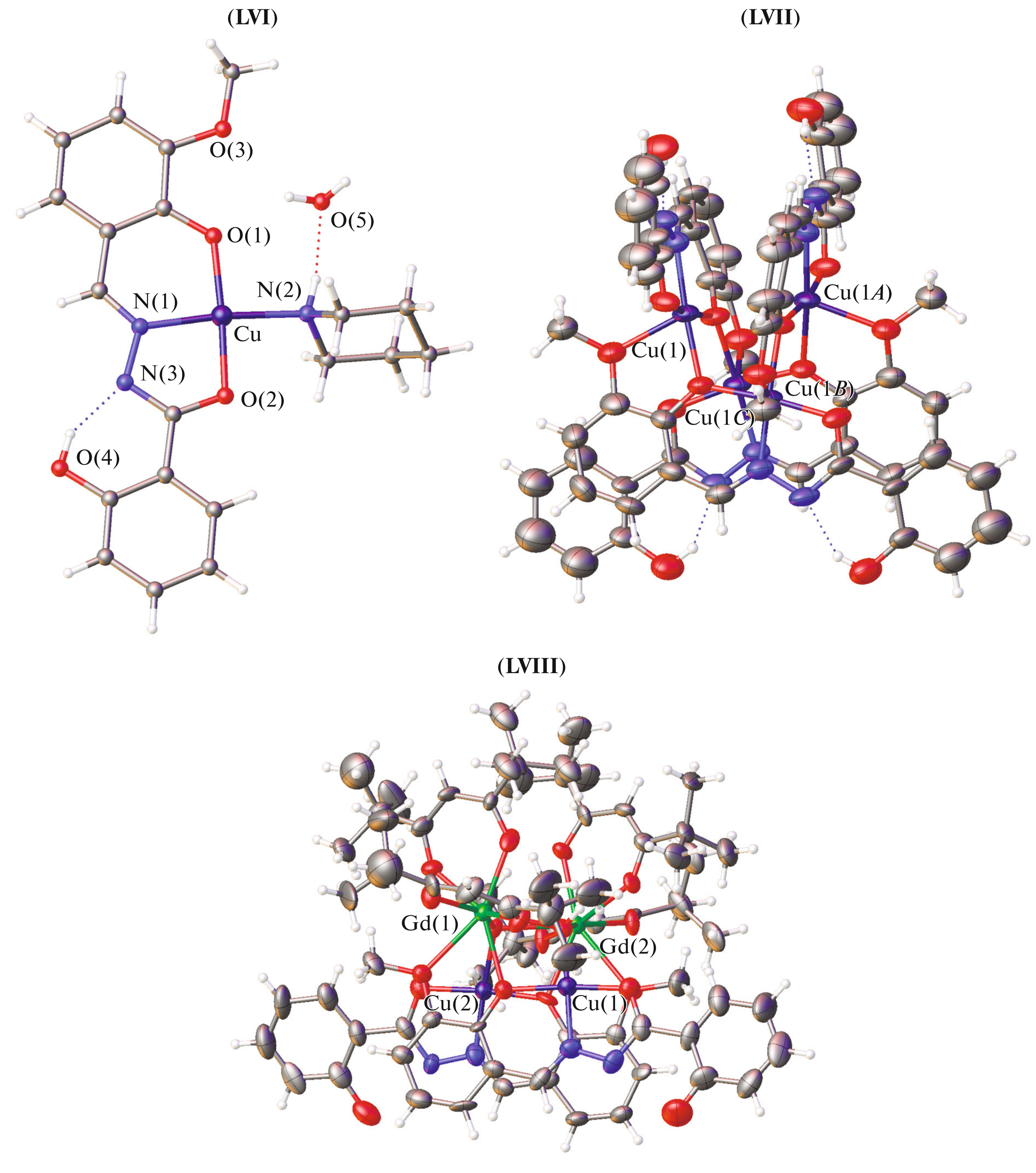


Fig. 27. Molecular structure of complex **LV** [123].

Ligand H_2L^2 in the keto form is shown to coordinate with the formation of the complexes $[M(H_2L^2)(Cl_2)]$ (M = Mn(II) (**LXVI**), Co(II) (**LXVII**)), whereas the keto and enol forms of the ligand are simultaneously observed in the complexes $[M(HL^2)(H_2O)(EtOH)BPh_4]$ (M = Mn(II) (**LXVIII**), Co(II) (**LXIX**)). The structures of complexes **LXVIII** and **LXIX** were determined by the XRD method. They are isostructural with distorted pentagonal bipyramidal coordinated manganese(II) and cobalt(II) ions and additional coordination modes of the H_2O and EtOH molecules in the axial positions.

At the same time, the copper(II) and nickel(II) complexes with diacetylpyridine bis(hydrazones) (H_2L) were described [130–132]. In these complexes, two organic ligands coordinate with two metal ions as hexadentate bridges instead of pentadentate coordination to one ion, which is usual for similar systems. The pyridine nitrogen atom performs the bridging function, which is unusual. The structure of complex **LXX** with diacetylpyridine bis(isonicotinoylhydrazone) Cu_2L_2 [132] is shown in Fig. 34.

There is a significant volume of structural data on the complexes of transition and rare-earth metals with the so-called ligands of the Robson type: 2,6-diformyl-4-R-phenol bis(azomethines) and bis(-hydrazones), whose structures assume the formation of binuclear complexes [133]. Two Schiff bases (H_3L^1 and H_5L^2) prepared from 2,6-diformyl-4-chlorophenol hydrazides and their complexes with some lanthanides (Y, La, Nd, Sm, Dy, and Er) (Fig. 35) were synthesized [134]. The XRD analysis of single crystals of two complexes $[La_2(H_2L^1)_3(C_2H_5OH)_2]$-$(Cl)(NO_3)_2$-$((CH_3)_2CO)_2(H_2O)_2$ (**LXXI**) and $[Er_2(H_4L^2)_3]$-$(SCN)_3(H_2O)$ (**LXXII**) revealed that the ligands in the keto form coordinated to the lanthanide(III) ions. The metal ions are linked by intramolecular bridges of three phenol oxygen atoms to form the binuclear complexes. The lanthanum(III) ions in complex **LXXI** are decacoordinated and bind three imine nitrogen atoms, three neutral oxygen atoms of hydrazone, three phenolate oxygen atoms of three ligand molecules, and one neutral oxygen atom of ethanol. The erbium(III)


(LVI)

(LVII)

(LVIII)

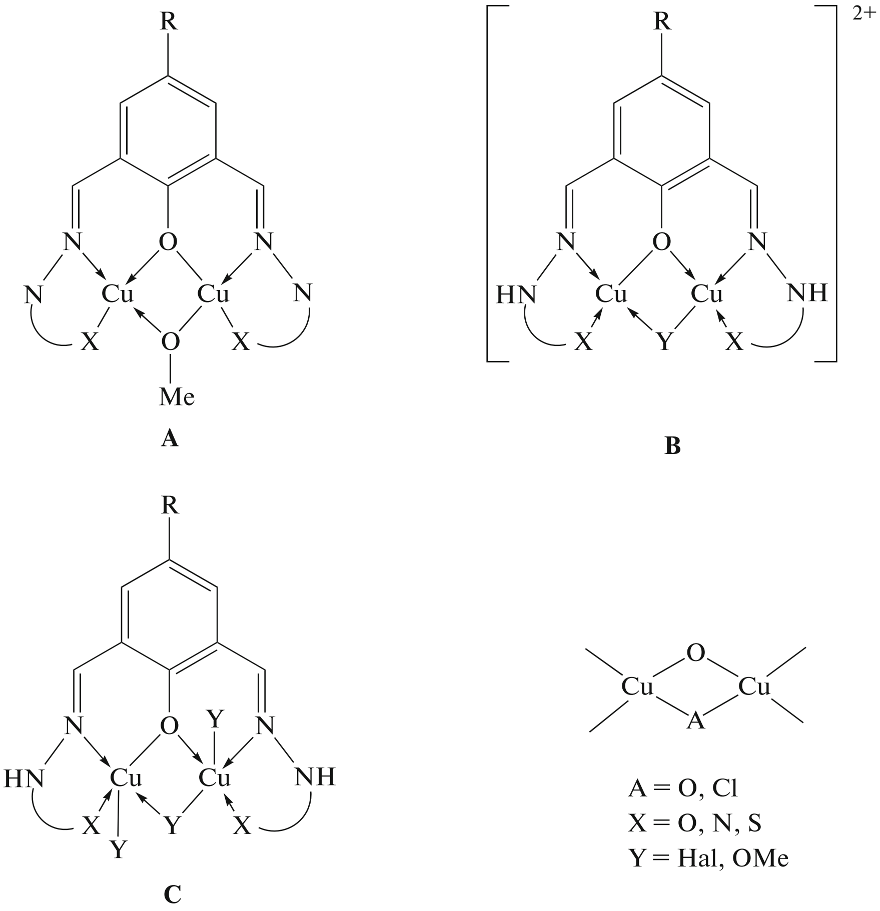
Fig. 28. Molecular structures of complexes **LVI**, **LVII**, and **LVIII** [124].

ions in compound **LXXII** are nonacoordinated and bonded to three oxygen atoms of the carbonyl groups, three nitrogen atoms of the azomethine groups, and three phenolate oxygen atoms.

A similar coordination mode is observed in Dy(III) complexes **LXXIII** and **LXXIV** with 2,6-diformyl-4-R-phenol bis(aroylhydrazones) (H_3L) of the composition $[Dy_2(H_2L)_3]\cdot 3NO_3$ (the following H_3L^1 was chosen for **LXXIII**: $R^1 = F$, $R^2 = H$; H_3L^2 for **LXXIV**: $R^1 = OMe$, $R^2 = Me$). These complexes represent a racemic mixture of right- and left-handed helicates (Fig. 36) and demonstrate the magnetic properties characteristic of molecular magnets [135].

The binuclear complexes of the first-row transition metals with the Robson-type ligands were well studied as convenient models to examine the factors affecting the character and strength of the magnetic exchange interaction between the paramagnetic centers [136].

The structure of bis(hydrazone) acting as a hexadentate bridging ligand assumes the presence of the "exogenic" bridged fragment in the complex molecule, and methoxyl (hydroxyl) or halide ions act as such bridges (Scheme 17) [137].



A = O, Cl
X = O, N, S
Y = Hal, OMe

Scheme 17.

At the same time, the structure of the copper(II) complex with 2,6-diformyl-4-*tert*-butylphenol bis(imidazolinylhydrazone) **(LXXV)** in which two metal ions are bound by the phenoxide bridge only (Fig. 37) was described [138].

In the binuclear complexes of this type, the Robson-type ligand can exist in both the enol (α-oxazine) and ketone (hydrazone) form, which is primarily caused by the nature of the metal salt used in the synthesis. For example, the reactions of bis(hydrazones) with Cu(II) acetate form complexes containing the ligand in the triply deprotonated (α-oxazine) form, while the monodeprotonated (hydrazone) form is observed for the reactions with halides, nitrate, and perchlorate [137].

The use of Cu(II) acetate, nitrate, and perchlorate results in the formation of the complexes containing either hydroxyl, or alkoxyl exogenic bridge and a nearly planar exchange fragment leading to a strong antiferromagnetic interaction between the paramagnetic centers. In the case of halides, the formed complex contains, as a rule, the bridging halide ligand resulting in a substantial distortion of the structure of the complex and, as a consequence, in the weakening of the antiferromagnetic exchange interaction [136].

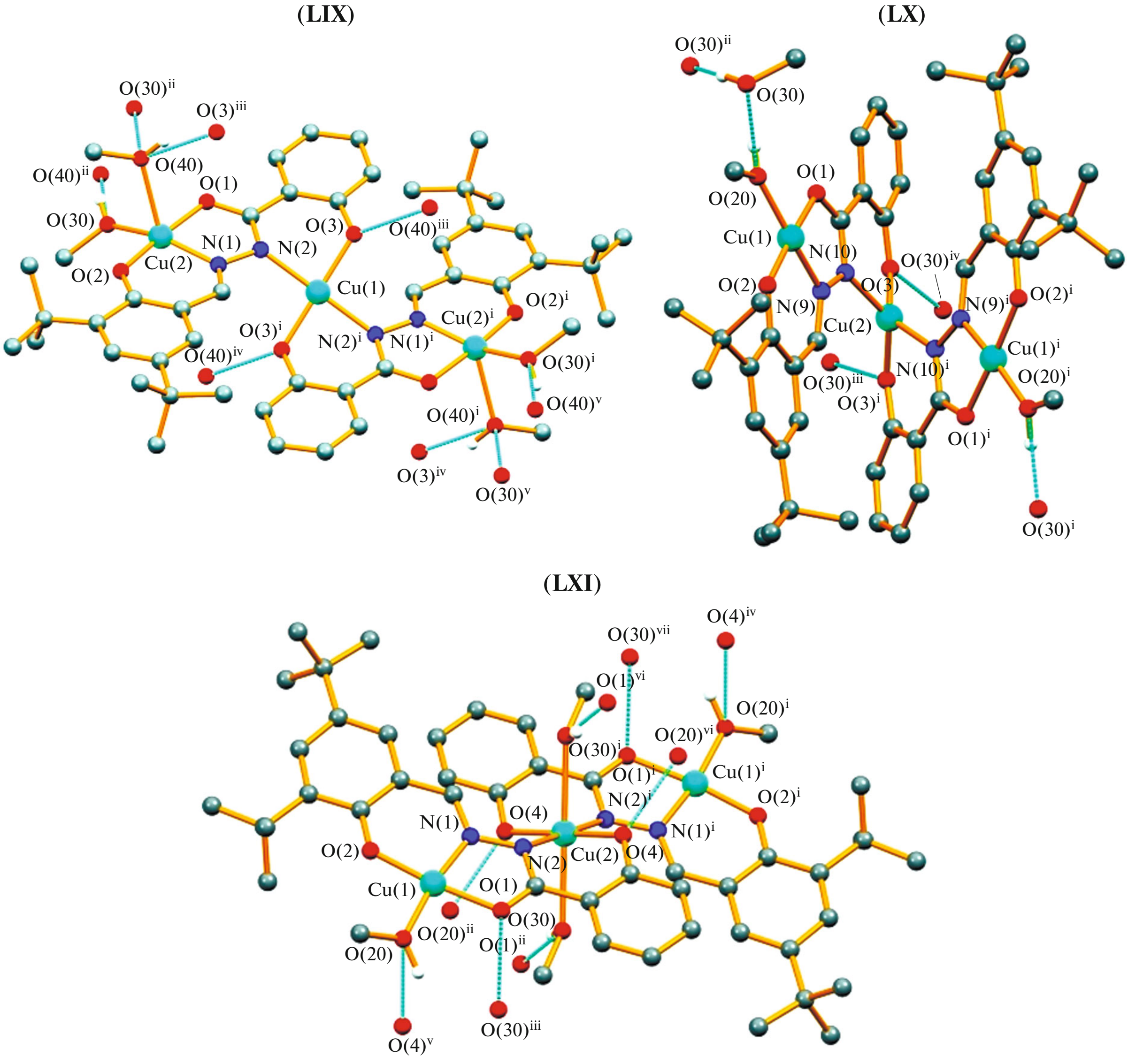


Fig. 29. Molecular structures of complexes **LIX**, **LX**, and **LXI** [125].

To conclude, the performed analysis of the scientific literature indicates a variety of coordination modes of the ligands to metals in the metal complexes of aroyl(acyl)hydrazones: 2-hydroxy- and 2-(*N*-tosylamino)benzaldehydes, ketones, 2,6-diformylphenols, and thiophenols. The coordination occurs in the keto (hydrazone) or enol forms and in both forms simultaneously, depending on the nature of ligands, type of metal atoms, and synthesis conditions. When metal acetates are used in the synthesis of the aroyl(acyl)hydrazone complexes, the compounds containing the ligands in the enol form are usually formed, whereas the ligands in the monodeprotonated (ketone) form coordinate in the complexes when metal halides, nitrates, or perchlorates are used. In the most part of cases, the hydroxy group of the salicyloylhydrazone fragment is not involved in coordination to the metal. The data on the practically significant properties of aroyl(acyl)hydrazones, such as biological activity, photo- and electroluminescence, catalytic activity, and magnetic characteristics, are presented.

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The study was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation, state task in the field of scientific activity,

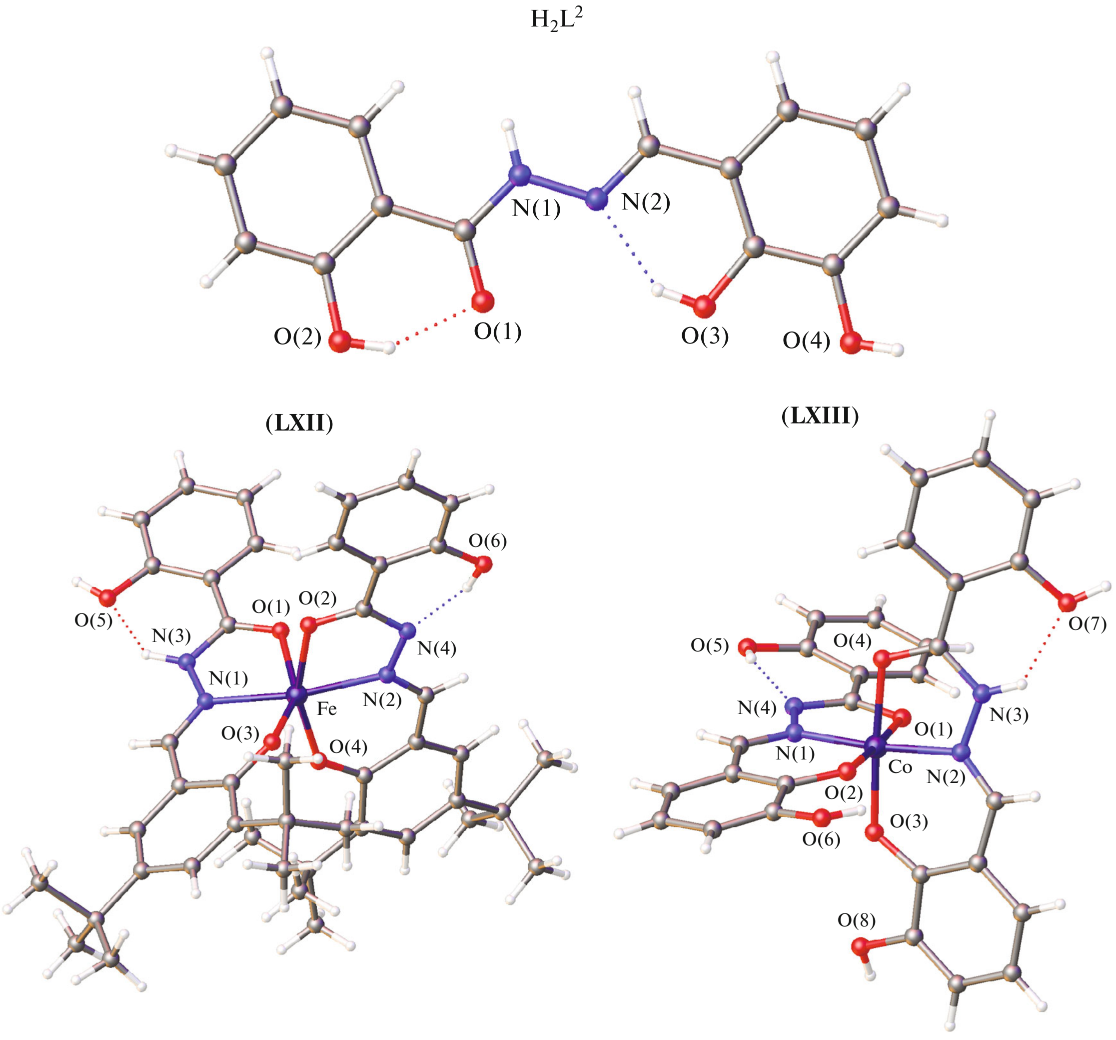


Fig. 30. Molecular structures of compounds H_2L^2, **LXII**, and **LXIII** [126].

(LXIV)

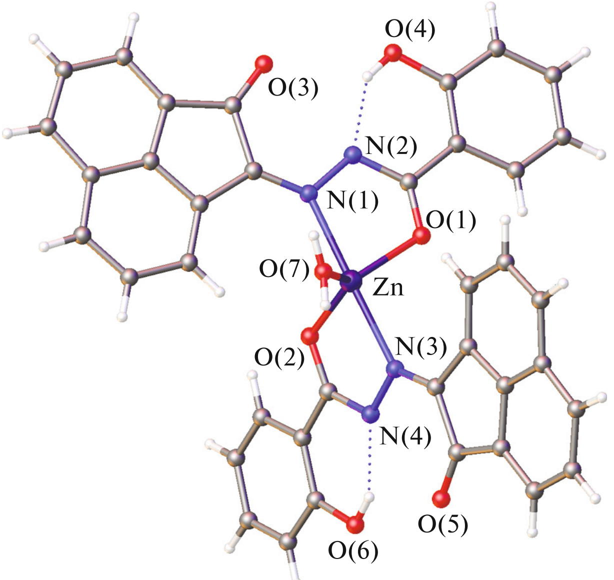


Fig. 31. Molecular structure of complex **LXIV** [127].

(**LXV**)

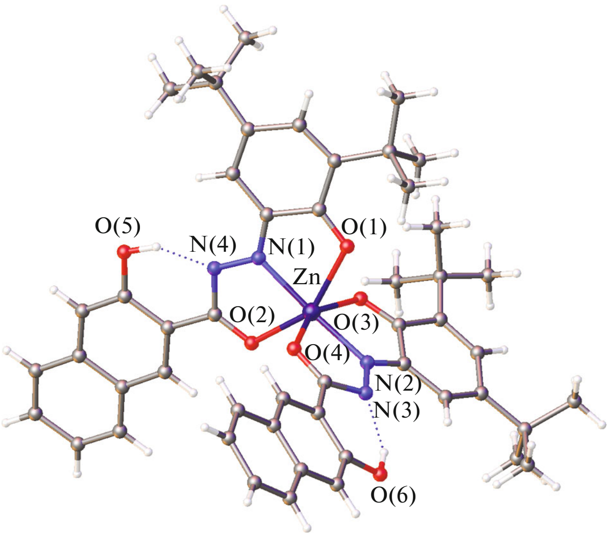
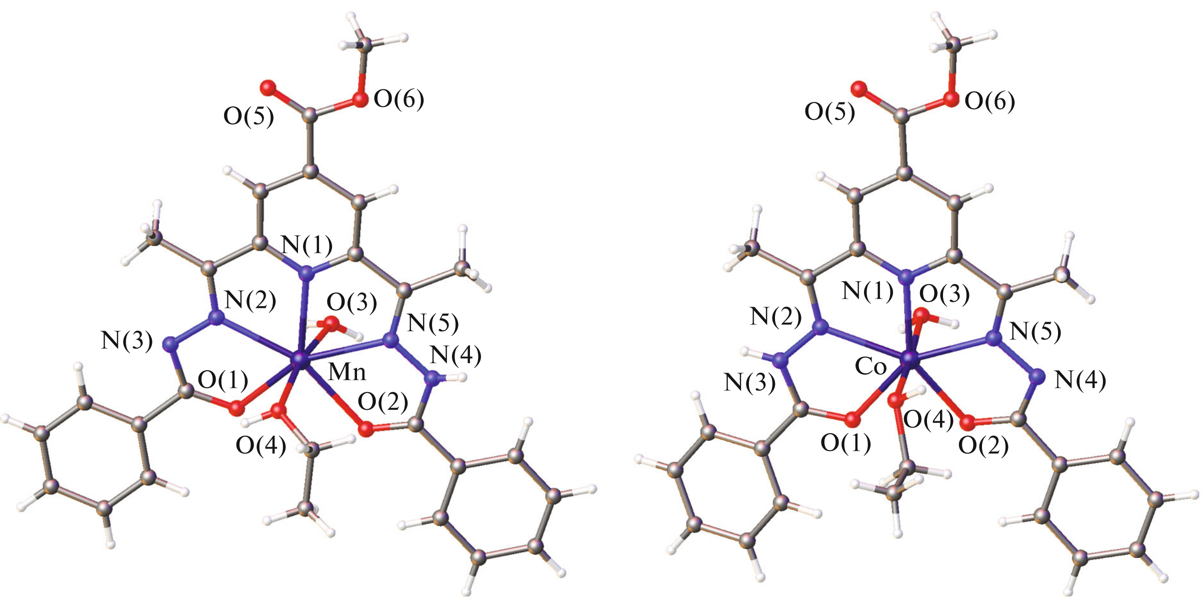


Fig. 32. Molecular structure of complex **LXV** [128].


(**LXVIII**)

(**LXVIX**)

Fig. 33. Molecular structures of complexes **LXVIII** and **LXIX** [129].

(LXX)

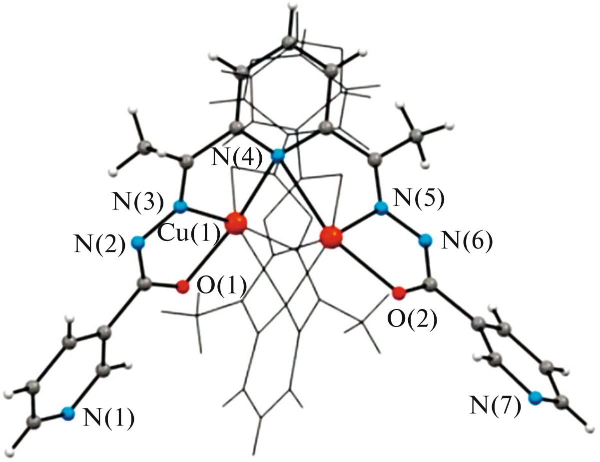


Fig. 34. Molecular structure of complex **LXX** [132].

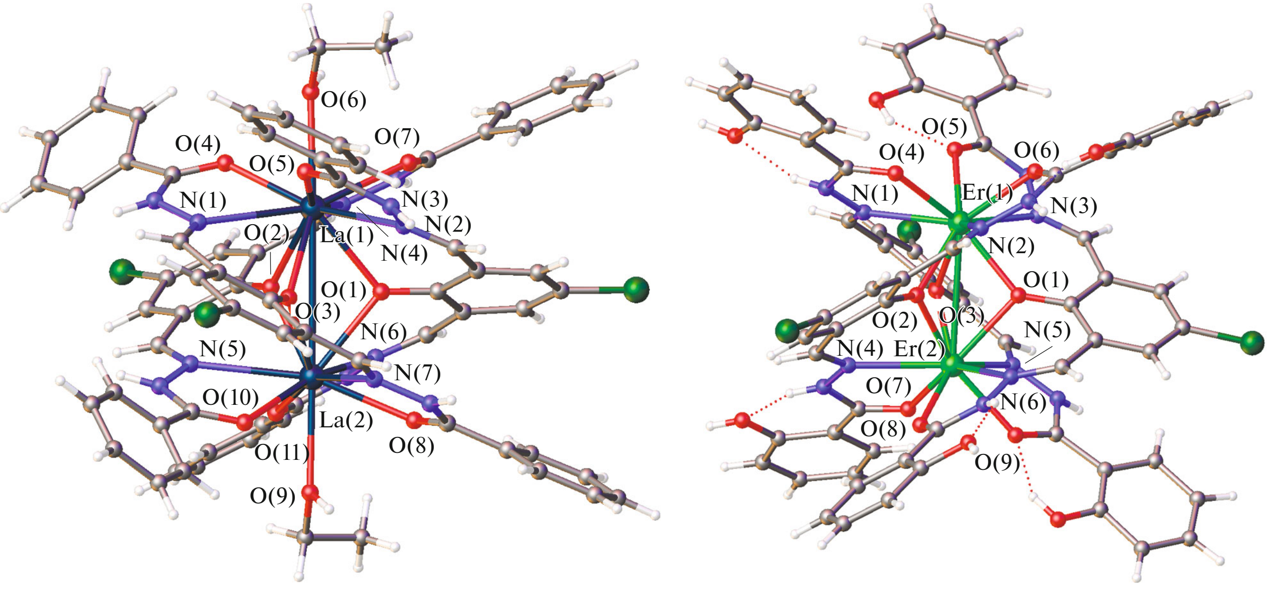

(LXXI) **(LXXII)**

Fig. 35. Molecular structures of complexes **LXXI** and **LXXII** [134].

(LXXIII)

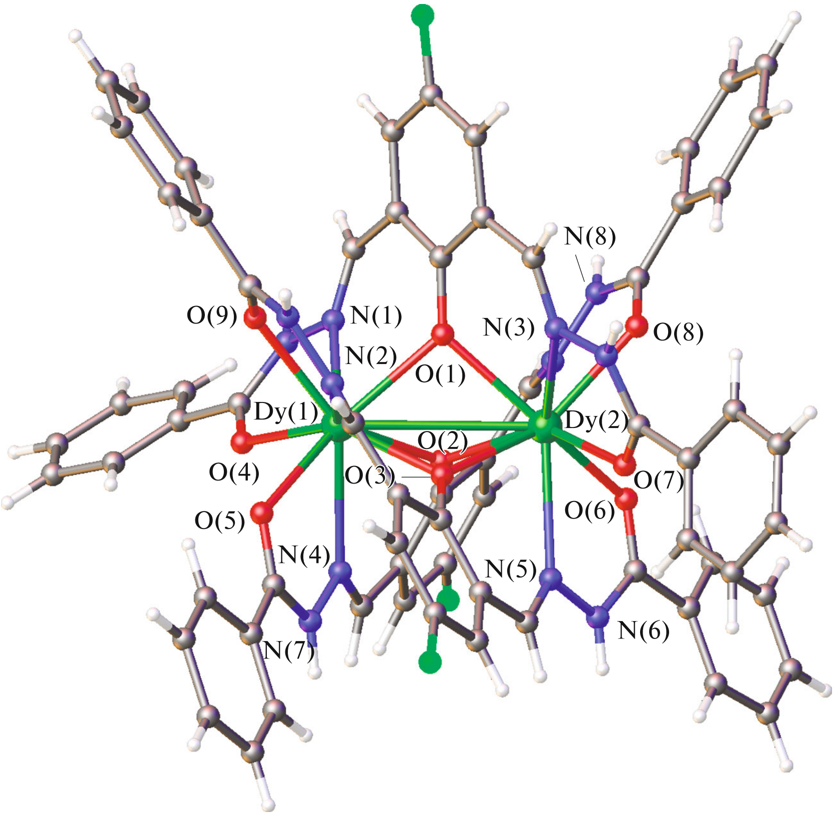


Fig. 36. Molecular structure of complex **LXXIII** [135].

(LXXV)

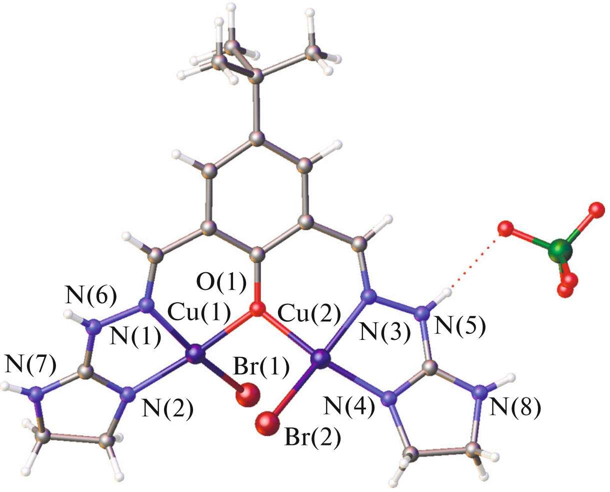


Fig. 37. Molecular structure of complex **LXXV** [138].

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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