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Coordination Chemistry and Magnetic Properties of Bi- and Polynuclear Exchange-Coupled Cu(II) and Ni(II) Metal Oximates

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Abstract—This review is an attempt to describe the potential of magnetochemical approach for describing the structure and properties of bi- and polynuclear metal chelates based on coordination compounds with a limited number of ligand types, mainly oxime-containing azomethines and their analogues. The review systematically addresses the published data on bi- and polynuclear copper(II) and nickel(II) complexes in which the paramagnetic centers are coupled by both intra- and intermolecular exchange interactions. Within the limited analysis, the main types and mechanisms of exchange interactions are considered and some electronic and geometric factors that determine the magnetic properties of bi- and polynuclear copper(II) and nickel(II) complexes with oximate ligands are identified. The relationship between electronic and geometric features of the complexes and the nature of exchange effects are considered, and an attempt is made to systematize the magneto-structural correlations in the discussed compounds, which are important model objects for developing a strategy for targeted design of one-, two-, and three-dimensional magnetically ordered structures.

Keywords: oxime-containing azomethines, exchange-coupled complexes, magneto-structural correlations, exchange parameters

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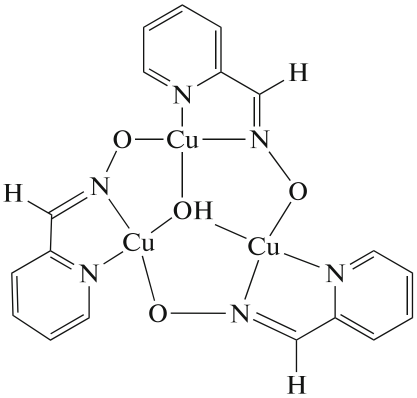
INTRODUCTION

Exchange-coupled complexes in which spin–spin interactions between paramagnetic metal ions are transmitted through structurally and compositionally diverse bridging moieties have been for decades highly popular investigation objects for scientists engaged in targeted search for new magnetically active materials that also exhibit unusual photochemical and biochemical properties, primarily with regard to their decisive role in the biosynthesis of protein molecules [1–11]. In this respect, oxime-containing ligands play a key role, starting with the pioneering works of Chugaev, who was the first to use dimethylglyoxime as an analytical reagent for nickel ions. The combination of high stability, on the one hand, and marked reactivity, on the other hand, accounts for the wide use of these compounds as biochemical models, objects of organometallic chemistry, and in chemical practice of preparation of materials valuable for technology [12–22]. As will be shown below, the presence of a free OH group in most metal oxime chelates potentially enables self-assembly of macromolecular architectures, which can play a crucial role in controlling their optical, electronic, and magnetic properties [8, 9, 23, 24]. In addition, the coordination chemistry of oxime-containing ligands has appeared in recent years to be quite attractive investigation area, as such systems are able to stabilize definite oxidation states of many metals and serve as selective reagents and catalysts for oxygen activation and as compounds with interesting optical properties [25–27]. From the medicinal standpoint, it is known that various oxime-containing ligands and their metal complexes showed clear-cut biological activity as chelating therapeutic drugs, inhibitors of pathological enzymatic catalysis, important intermediates in the biosynthesis of nitrogen oxides [28, 29], antibacterial and antitumor drugs [30, 31], fungicides [32], bactericides [33], and antioxidants [34].

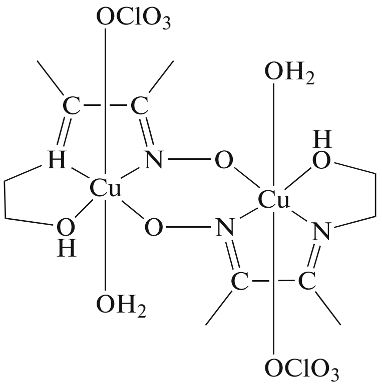
This review presents analysis of publications devoted to bi- and polynuclear complexes with oxime-containing ligands and is focused on the magnetic properties of these complexes. Detailed discussion is given for the systems in which either important magneto-structural correlations have already been implemented, or this presumptive work would be especially valuable.

EXCHANGE INTERACTION IN BI- AND POLYNUCLEAR Cu(II) COMPLEXES WITH OXIMATE BRIDGES

It is noteworthy that the oxime-containing ligands that form bi- and polynuclear copper(II) chelates promote, in most cases, clear-cut exchange interaction between paramagnetic centers. For a number of compounds, complete spin pairing occurs even at room temperature, which was noted for the first time for the trinuclear complex with pyridine-2-aldoxime: type **I** $[Cu_3(L)_3(OH)SO_4]$ [35].

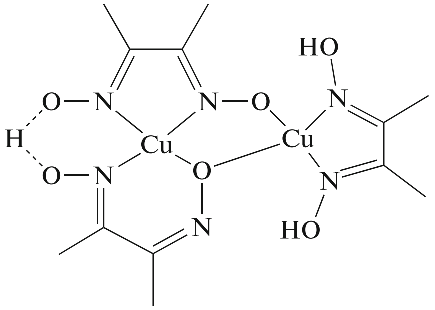


(I)



(II)

The first diamagnetic binuclear copper(II) complex, type **II** $[Cu_2(HL)_2(H_2O)_2(ClO_4)_2]$, with exchange via oximate bridges was reported in [36]. The unique ability of the oximate NO group to promote a significant antiferromagnetic coupling, regardless of whether paramagnetic centers are bound via the nitrogen and oxygen atoms or via only the oxygen atom, was also demonstrated for type **III** tetranuclear metal chelate containing binuclear moieties, for which the exchange parameter $J = -475$ cm^{-1} was found [37, 38].



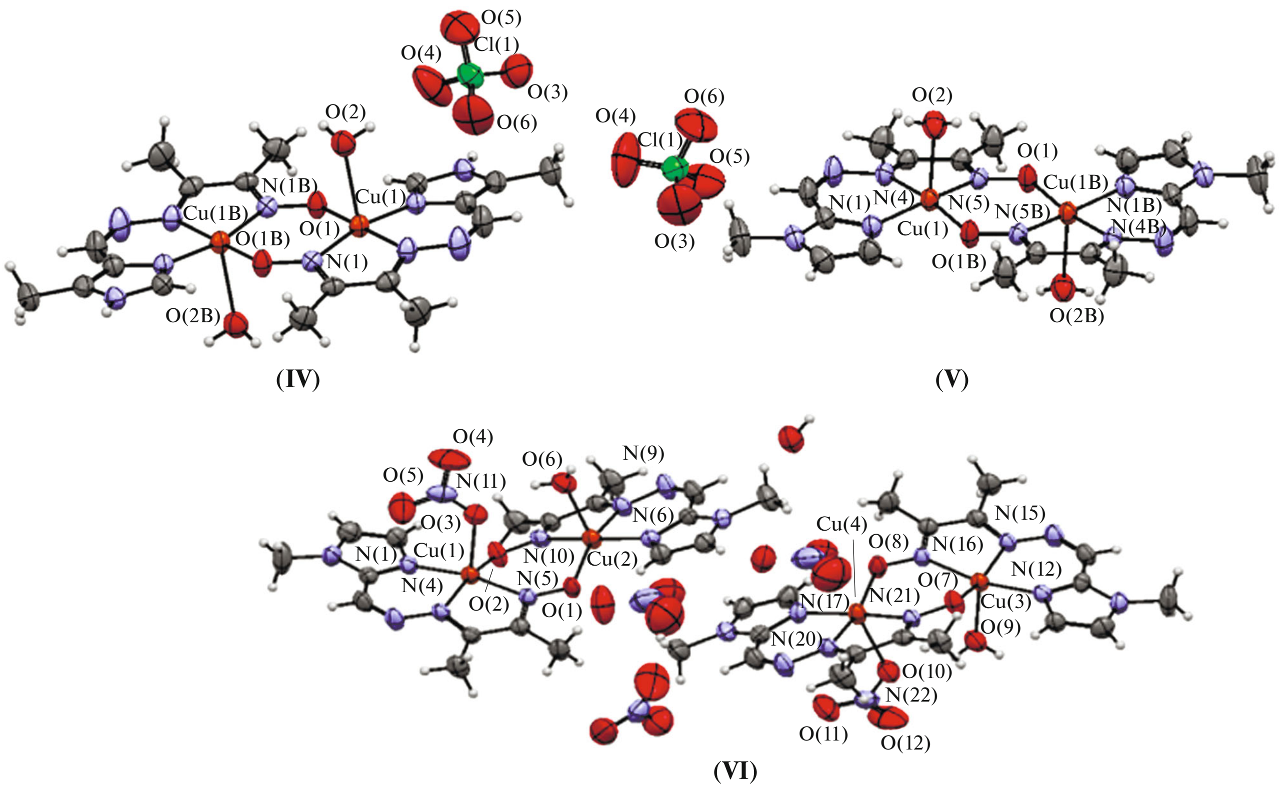
(III)

It is believed that the strength of the spin–spin coupling in metal complexes depends on the N–O and C=N bond lengths in the oxime moiety of the ligand; in the opinion of the authors, the latter fact provides a reliable evidence indicating that π-exchange is not the main mechanism of transmission of magnetic interactions. This statement is considered below in relation to the most recent data on copper(II) oximate complexes. In addition, binuclear copper(II) oximate complexes can be divided into two groups in accordance with the nature and strength of exchange effects:

(a) systems with pronounced antiferromagnetic exchange interactions, resulting in diamagnetism of these complexes even at room temperature, irrespective of whether or not the $Cu_2(NO)_2$ moiety is planar;

(b) systems with very weak ferro- or antiferromagnetic exchange characterized by a substantial distortion of the oximate bridging moiety; in this case, important magneto-structural correlations were identified on the basis of extended Hückel quantum chemical calculations [39].

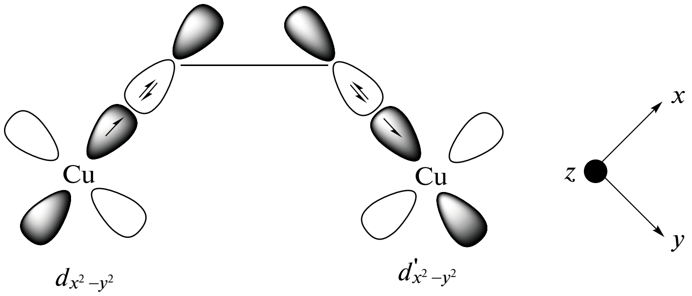
It should also be mentioned that the clear-cut antiferromagnetism of the complexes is virtually independent of the angles between the planes of the coordination units of copper(II) chelates, which is in line, in the authors' opinion [40], with the predominant exchange along the system of σ- rather than π-bonds, since in the latter case, this dependence would have been pronounced. It is believed that in this case, the ground state of the copper ion is $d_{x^2-y^2}$; in view of the σ-character of the exchange, this leads to effective overlap of the indicated magnetic orbitals with the MOs of the oximate bridge (sp^2-hybridization of nitrogen and oxygen atoms). Thus, in view of orientation of the magnetic orbitals of copper ions in a binuclear complex with an oximate bridge (Scheme 1), the symmetry-allowed exchange channel has the form $d_{x^2-y^2}\|\sigma^2_{\mathrm{SP}}\,(\mathrm{NO})\|d_{x^2-y^2}$ [41].



(**IV**) (**V**)

(**VI**)

Fig. 1. Structures of complexes $[Cu_2L_2(H_2O)_2](ClO_4)_2]$ (**IV**), $[Cu_2L'_2(H_2O)_2](ClO_4)_2]$ (**V**), and $[Cu_2L'_2(NO_3)(H_2O)]$-$(NO_3)\cdot0.5H_2O]$ (**VI**).



Scheme 1.

It was stated that participation of the oximate bridge in the *syn*- or *anti*-configuration and in the case of coordination only via the oxygen atom always leads to a pronounced antiferromagnetic exchange interaction. Meanwhile, even when the antiferromagnetic exchange parameters are relatively high, minor structural variations of structurally similar complexes with identical exchange transmission channels may lead to substantial changes in these values. As an example, consider the results of magnetochemical analysis of exchange-coupled copper chelates based on two ligand systems resulting from condensation of diacetyl monooxime monohydrazone with 4-methylimidazole-5-carboxyaldehyde (H_2L) or 1-methylimidazole-2-carboxyaldehyde (H_2L') [42]. The structures of the complexes $[Cu_2L_2(H_2O)_2](ClO_4)_2]$ (**IV**), $[Cu_2L'_2$-$(H_2O)_2](ClO_4)_2]$ (**V**), and $[Cu_2L'_2(NO_3)(H_2O)](NO_3)\cdot$ $0.5H_2O$ (**VI**) are depicted in Fig. 1.

The exchange parameters J are –718, –795, and –880 cm^{-1} for **IV**, **V**, and **VI**, respectively. According to the authors of that study, antiferromagnetic exchange interaction should be somewhat more pronounced for **IV** than for **V**. However, the presence of a hydrogen bond between the H_2O molecule and the ClO_4^- ion, which is absent in **V**, reduces the parameter J; this is in good agreement with the previously obtained results [43–46] and with X-ray diffraction data [47, 48].

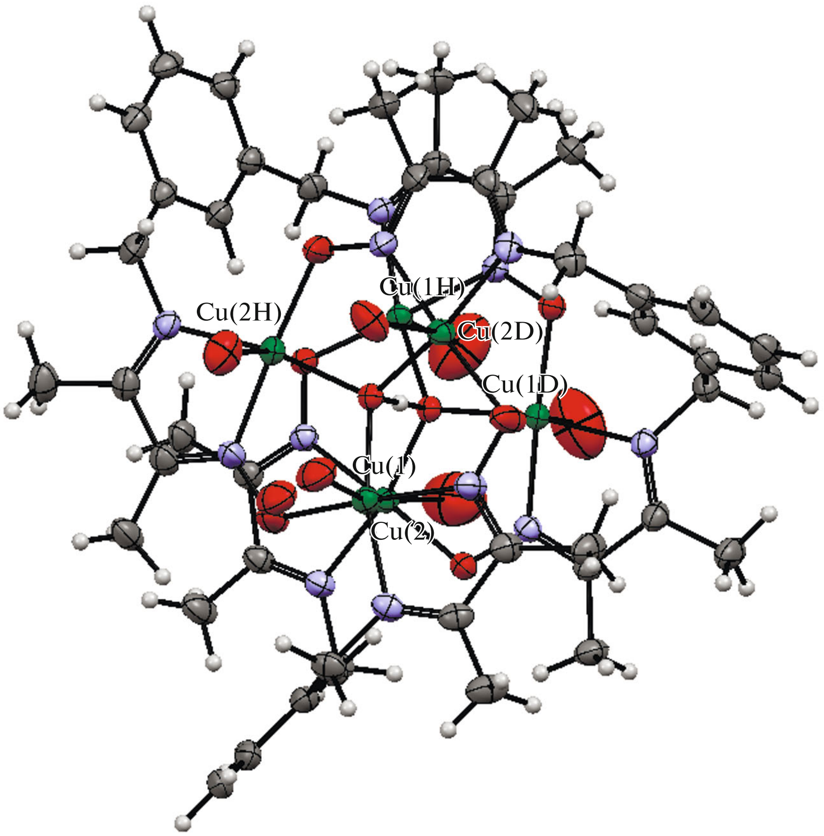
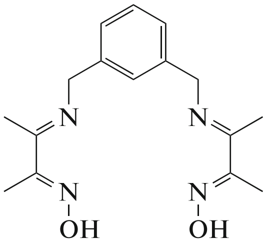


Fig. 2. Structure of complex $[Cu_6^{II}(\mu_3\text{-O...H...O-}\mu_3)L_3(H_2O)_6]X_3$ ($X = BF_4$) (**VIII**).

Regarding the value $J = -880$ cm^{-1}, the authors of [42] noted that this value is rough because of the presence of rather large amount of a paramagnetic impurity in this compound [49].

As we noted previously [50], the intermolecular non-covalent interactions that determine the molecular packing of functional nano-scale materials can be considered as the main driving force for generation or as a means for controlling the magnetic exchange interaction in supramolecular architectures. In particular, the formation of hydrogen bonds and cation–anion, π–π, and van der Waals contacts between single molecules can be deliberately used to form exchange interaction channels, with both the sign and magnitude of the interaction being specified [51, 52]. In the papers cited below, it is noted that these contacts can, in some cases, be equally or even more efficient for the formation of various types of exchange than the traditional covalent bonds determining the intramolecular nature of the magnetic interaction. The authors of [53–55] considered dioximate systems of type **VII** (H_2L) to be convenient ligands for the synthesis of supramolecular complexes.



H_2L (**VII**)

Using this ligand, copper(II) complexes $[Cu_6^{II}(\mu_3\text{-O...H...O-}\mu_3)L_3(H_2O)_6]X_3$ ($X = BF_4$; $X = ClO_4$) with identical structures of the hexanuclear unit were obtained; the structure of complex **VIII** ($X= BF_4$) is depicted in Fig. 2.

The doubly deprotonated ligand is coordinated to the Cu(1) and Cu(2) ions via the imine and oximate nitrogen atoms, while the oxygen atoms coordinate a copper ion of the neighboring moiety. The distance between Cu(1) and Cu(2) is 3.686(1) Å. In addition, two μ_3-oxygen atoms are located on a threefold axis, which gives rise to a hexanuclear copper cluster containing $[Cu_3O]$ moieties. The authors also noted the presence of a clearly defined H-bond between the

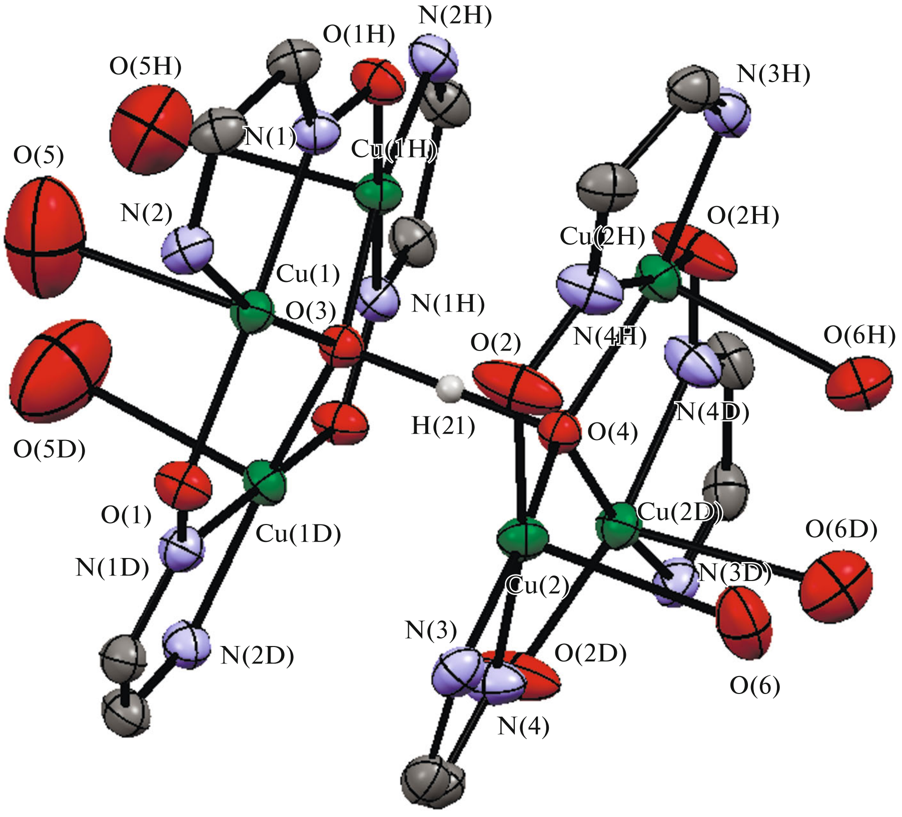


Fig. 3. Structure of the hexanuclear moiety of complex **VIII**.

indicated moieties involving the proton encapsulated within the hexanuclear structure (Fig. 3).

The magnetic properties of the complex were interpreted under the assumption that two exchange channels are present in the hexanuclear moiety:

(a) antiferromagnetic exchange between the copper(II) ion in the [Cu_3O] moiety (exchange parameter J_1) via μ_3-oxo(hydroxo) group (the CuOCu bond angle is 113.98°) and the Cu–N–O–Cu oximate moiety.

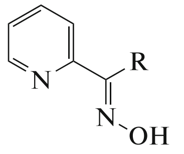
(b) antiferromagnetic exchange between the [Cu_3O] moieties (exchange parameter J_2) along the Cu–O...H...O–Cu channel.

The spin Hamiltonian of this system was calculated using equation (1); the structure of the exchange moiety is shown in Fig. 4.

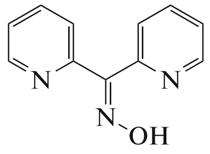
$$\begin{aligned}\hat{H} = &-2J_1\left(S_1S_{1A} + S_1S_{1B} + S_{1A}S_{1B} + S_2S_{2A} + S_2S_{2B} + S_{2A}S_{2B}\right)\\ &- 2J_2\left(S_1S_2 + S_1S_{2A} + S_1S_{2B} + S_{1A}S_2 + S_{1A}S_{2A} + S_{1A}S_{2B} + S_{1B}S_2 + S_{1B}S_{2A} + S_{1B}S_{2B}\right).\end{aligned} \quad (1)$$

The calculated exchange parameters were $J_1 = -201.5$ cm^{-1}, $J_2 = -4.5$ cm^{-1}; the authors pointed out that the latter value is well correlated with the known published data on the exchange through H-bonds [56–59].

The authors of [60] obtained trinuclear complexes using so-called "ligand blend" by the reaction of copper(II) carboxylates with di-2-pyridyl ketone oximes **IX**, **X**.



(Py)C(R)NOH (**IX**)



$(Py)_2CNOH$ (**X**)

The structure of the complex [$Cu_3^{II}(\mu_3\text{-}OH)(O_2CMe)_2(Py)_2(CNO)_3$] is shown in Fig. 5.

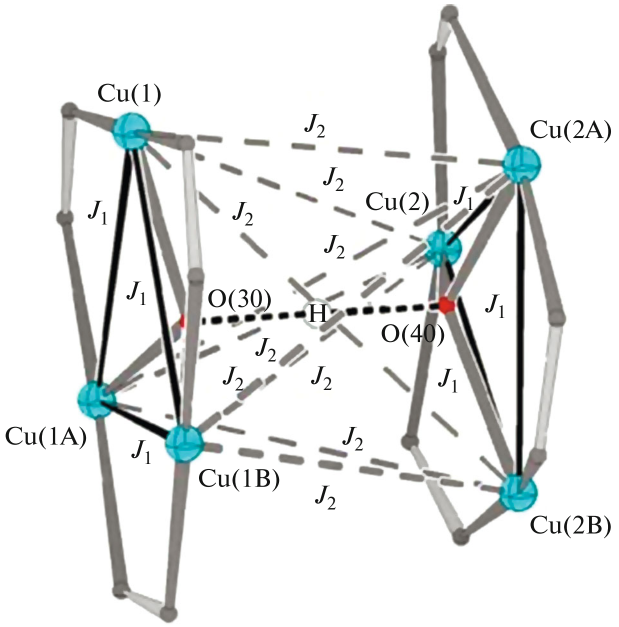


Fig. 4. Exchange interaction channels in the hexanuclear moiety of complex **VIII**.

A study of the temperature dependence of the magnetic susceptibility revealed a pronounced antiferromagnetic exchange interaction. Unfortunately, the authors did not report the exchange parameter J; however, an ESR study of this compound indicated that this interaction is an anisotropic antisymmetric exchange.

Figure 6 shows the ESR spectrum of this compound in the X-range recorded at 4.2 K. The spectrum exhibited a highly intense signal at ~3 kG with $g_{\rm eff} \approx 2.2$ and a shoulder in a lower field. According to the authors, of most interest is the broad signal with $g_{\rm eff} \approx 1.17$, which cannot be attributed to $g_\perp$ of the ground state with $S = 1/2$ [61].

Conversely, as stated by the authors, this feature of the ESR spectra was noted for a number of copper(II) complexes containing the $\{Cu_3(\mu_3\text{-OH})\}^{5+}$ three-ion core and characterized by antisymmetric exchange [62, 63].

The antisymmetric exchange interaction in trinuclear copper(II) complexes with oximate ligands was considered in more detail in [64]. The authors isolated two binuclear complexes, $[Cu_2L_2(H_2O)](ClO_4)_2$ (type **XI**) and $[Cu_2L_2(H_2O)](BF_4)_2$ (type **XII**), and hexanuclear derivative **XIII** with the general formula $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)](ClO_4)_7$, containing Cu_3O trinuclear moieties. The synthesis of these complexes is described in Scheme 2.

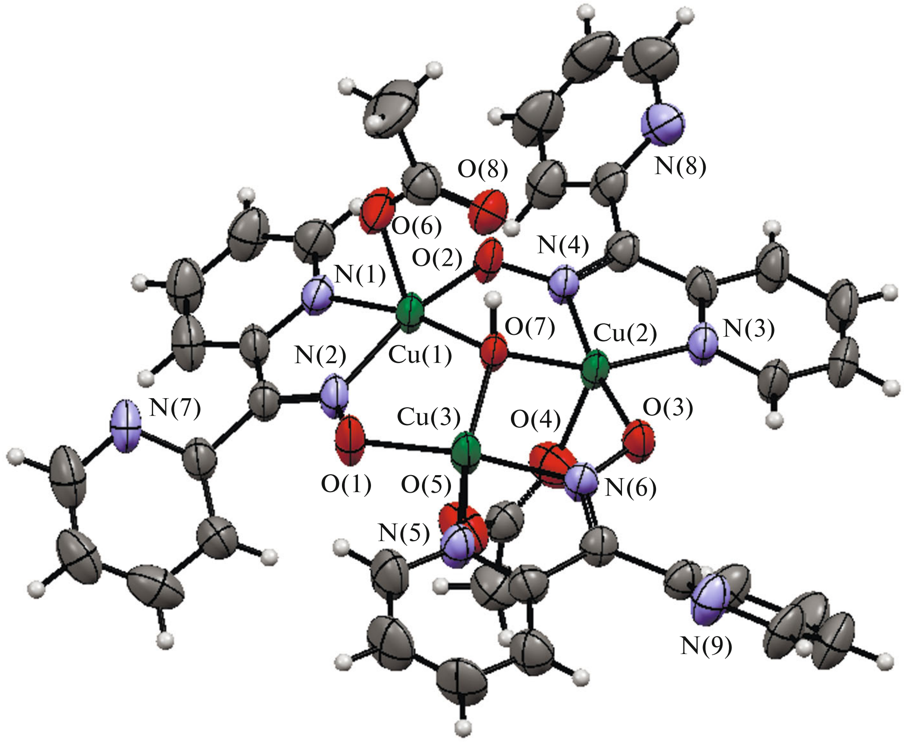
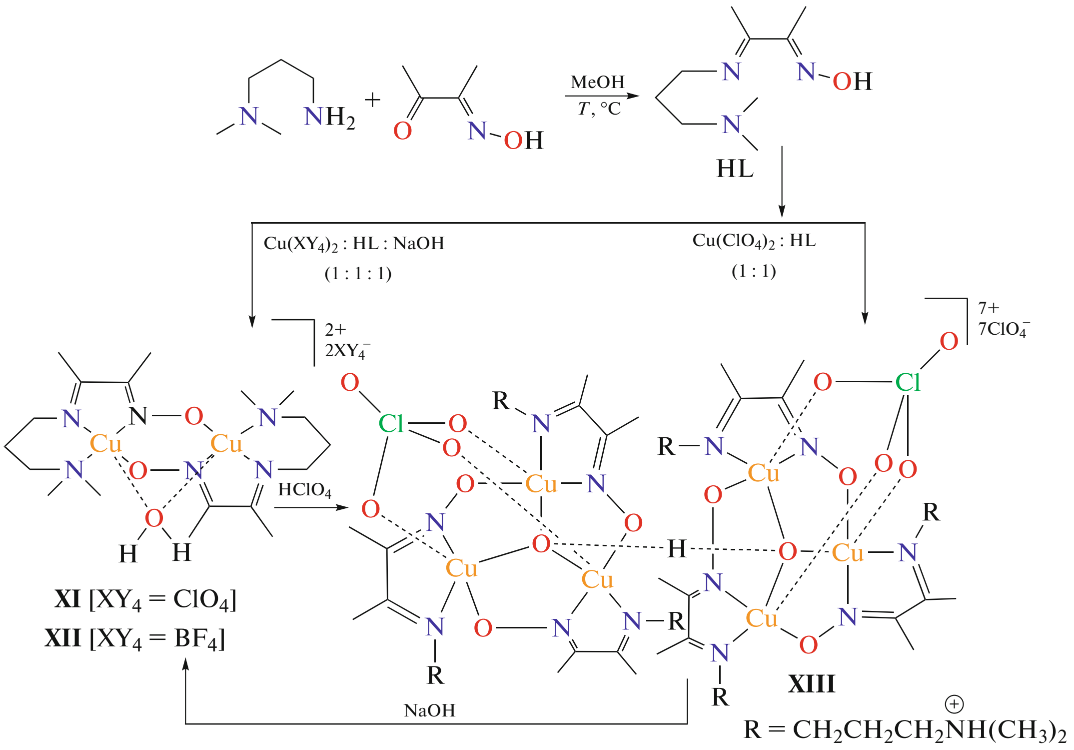


Fig. 5. Structure of complex $[Cu_3^{II}(\mu_3\text{-OH})(O_2CMe)_2(Py)_2(CNO)_3]$.



Scheme 2.

The authors noted that hexanuclear derivative **XIII** was synthesized under the same conditions as binuclear complexes **XI** and **XII**, but in the absence of NaOH. The structures of the trinuclear moiety and metal chelate **XIII** are shown in Figs. 7 and 8.

Binuclear complexes **XI** and **XII** (Scheme 2) are characterized by a pronounced antiferromagnetism ($J = -562.6$ cm^{-1} for **XI** and $J = -633.1$ cm^{-1} for **XII**), which is usual for this type of systems. The exchange interaction in the trinuclear moiety predominates for compound **XIII**. As noted by the authors of the cited study, an attempt to interpret the magnetic properties using isotropic Hamiltonian (2) did not meet with success.

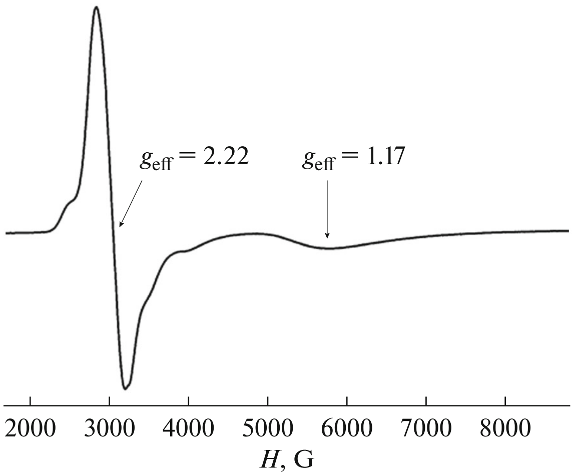


Fig. 6. ESR spectrum of complex $[\text{Cu}_3^{\text{II}}(\mu_3\text{-OH})(\text{O}_2\text{CMe})_2(\text{Py})_2(\text{CNO})_3]$.

$$\hat{H} = -J_{12}S_1S_2 - J_{23}S_2S_3 - J_{13}S_1S_3. \tag{2}$$

According to the authors, if so-called "spin frustration" is taken into account [61, 65–67], an adequate interpretation of the magnetic properties of **XIII** requires inclusion of the antisymmetric component of the exchange interaction, which leads to Hamiltonian (3).

$$\begin{aligned}\hat{H} &= -J\left(S_1S_2 + S_2S_3\right) - j\left(S_1S_3\right)\\ &+ G_Z\left[\left(S_1S_2\right) + \left(S_2S_3\right) + \left(S_1S_3\right)\right],\end{aligned} \tag{3}$$

where $J = J_{1,2} = J_{2,3}$, $j = J_{1,3}$, G_Z is the antisymmetric exchange parameter.

Taking account of Hamiltonian (3) in [67] and $J_{\text{av}} = (2J + j)/3$, the anisotropic magnetic susceptibility values were found from the expressions

$$\chi_M^{\|} = \frac{N\beta^2 g_{\|}^2}{4kT}\left[\frac{\cosh(x) + 5\exp(3J_{\text{av}}/2kT)}{\cosh(x) + \exp(3J_{\text{av}}/2kT)}\right], \tag{4}$$

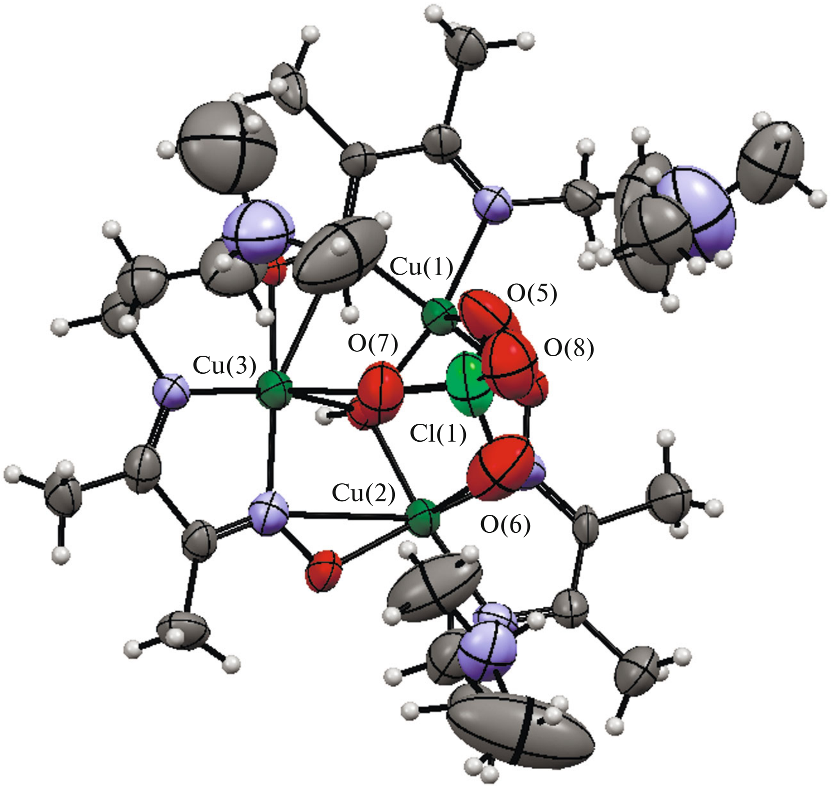


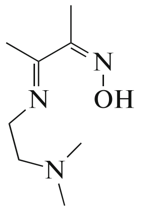
Fig. 7. Structure of the trinuclear moiety $[Cu_3(HL)_3(ClO_4)(\mu_3\text{-}O)]^{3+}$.

$$\chi_M^{\perp} = \frac{N\beta^2 g_{\perp}^2}{4kT}\left[\frac{\rho^2\cosh(x) + 5\exp(3J_{av}/2kT) + \left(1 - \rho^2\cosh(x)/(x)\right)}{\cosh(x) + \exp(3J_{av}/2kT)}\right]; \quad \chi_M^{av} = \frac{\chi_M^{\parallel} + 2\chi_M^{\perp}}{3}, \tag{5}$$

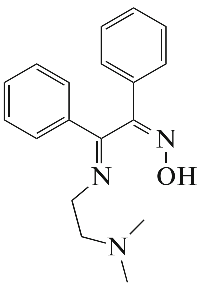
where $x = \Delta/2kT$ and $\rho = \delta/\Delta$.

These expressions and taking account of parameter θ, reflecting the exchange between the trinuclear moieties via H-bonds (Fig. 4), gave the following values: $J_{av} = -636$ cm^{-1}, $g_{\parallel} = 2.05$, $g_{\perp} = 2.11$, $\Delta = 87.3$ cm^{-1}, $\delta = 36.8$ cm^{-1}, $\theta = -0.18$, while recalling the expression $G_z = ((\Delta^2 - \delta^2)/3)^{1/2}$ gives $G_z = 45.5$ cm^{-1}. Since $J_{av} = (2J + j)/3$ and $\delta = J - j$, the authors found $J = -623.7$ cm^{-1} and $j = -660.7$ cm^{-1}; in the opinion of the authors, these results were in an excellent agreement with the results of magnetochemical interpretation of similar trinuclear systems with antisymmetrical exchange [61, 68, 69].

Cluster complexes based on oximate ligands containing more than three copper atoms in the exchange moiety and possessing interesting physicochemical properties were reported in [70]. The structures of ligand systems **XIV** and **XV**, which were used to obtain polynuclear copper(II) complexes, are shown below.



HL^1 **(XIV)**



HL^2 **(XV)**

The reaction of $Cu(ClO_4)_2$ with HL^1 gave the binuclear complex $[Cu_2(L^1)_2(H_2O)_2](ClO_4)_2$ **(XVI)**; a similar reaction in the presence of SCN$^-$ ions resulted in a partial $Cu^{II} \rightarrow Cu^{I}$ reduction and gave mixed-valence 3D structure $\{[Cu_2^{II}(L^1)_2][Cu_4^{I}(\mu_{1,3}\text{-}SCN)_4(\mu_{1,1,3}\text{-}SCN)_2]\}_n$ **(XVII)** in the case of HL^1 and pentanuclear mixed-valence cluster $\{[Cu_2^{II}(L^2)_2(NCS)]_2[Cu^{I}(SCN)(\mu_{1,1}\text{-}SCN)(\mu_{1,3}\text{-}SCN)]\}$ **(XVIII)** in the case of HL^2. The structures of complexes **XVI**–**XVIII** are shown in Fig. 9.

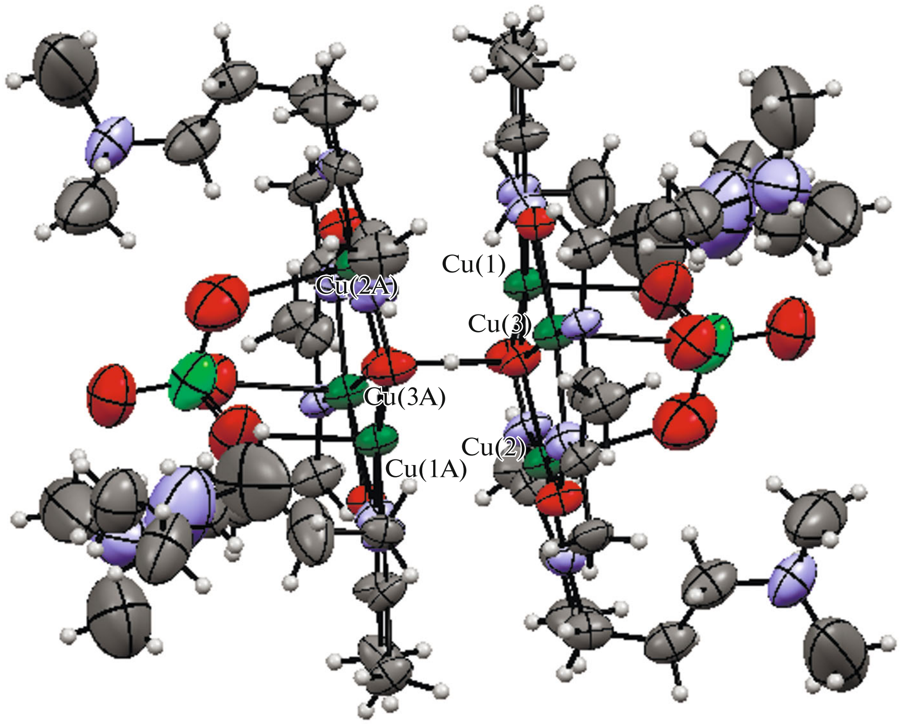
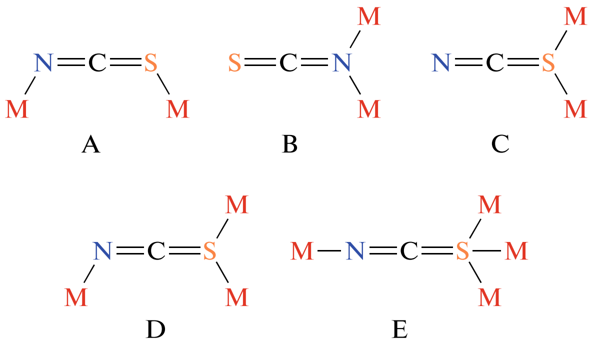


Fig. 8. Structure of the hexanuclear cation $[\{Cu_3(HL)_3(O_3ClO)(\mu_3\text{-}O)\}_2(\mu\text{-}H)]^{7+}$.

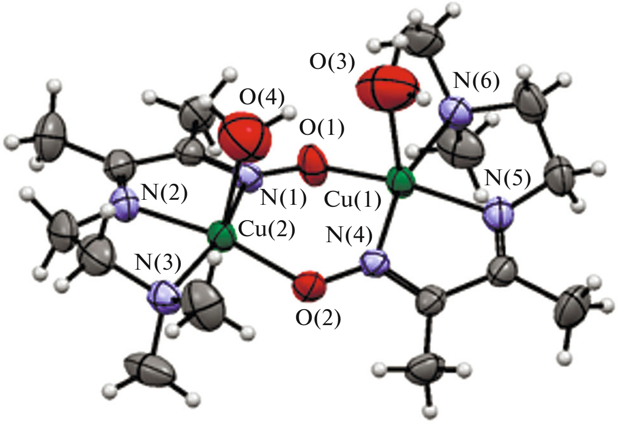
In the case of compound **XVIII**, A and A' represent binuclear moieties linked to the central anionic moiety B. Complexes **XVI**–**XVIII** exhibit clear-cut antiferromagnetic exchange, which is adequately interpreted in terms of the isotropic HDVV model [71]; the exchange parameters are $J = -721$ and -744 cm^{-1} for **XVI** and **XVII**, respectively. The identical structural parameters of the two binuclear moieties in pentanuclear cluster **XVIII** allowed the authors [70] to suggest that they were magnetochemically equivalent and finally to obtain the exchange parameter $J = -988$ cm^{-1}.

It was noted [72] that thiocyanate ion is a brilliant example of an ambident ligand with two donor atoms N and S that can be coordinated in a number of fashions (A–E), which are shown in Scheme 3 [73–78].

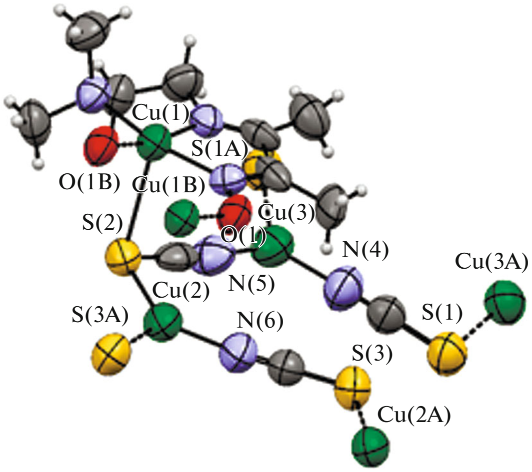


Scheme 3.

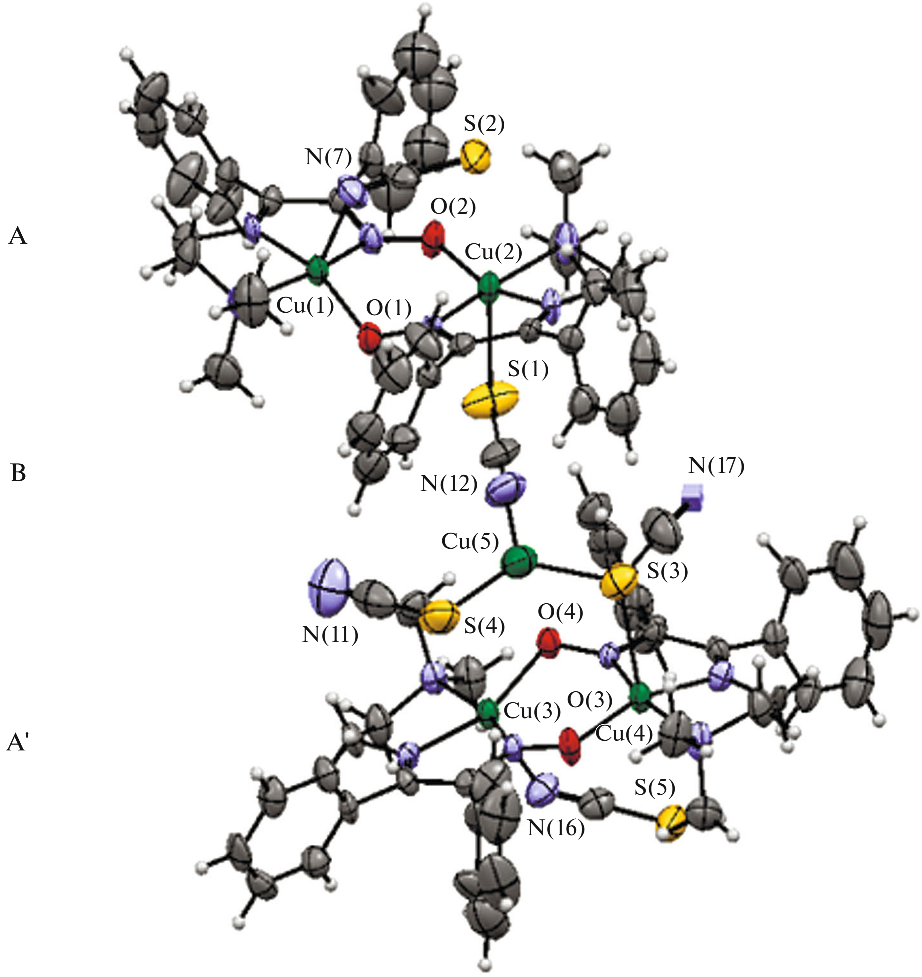
Four new copper oximate complexes with the ligand systems HL^1 (3-[2-(dimethylamino)ethylimino]butan-2-one) and HL^2 (3-[2-(diethylamino)ethylimino]butan-2-one) were prepared [72]; the compositions of the complexes are given by $[Cu_2L^2_2(EtOH)_{0.5}(ClO_4)](ClO_4)$ (**XIX**), ${}^{2}_{\infty}[\{(Cu^{II}_2L^1_2)\}$-$\{Cu^{I}_4(\mu_{1,3}\text{-}SCN)_2(\mu_{1,1,3}\text{-}SCN)_4\}]_n$ (**XX**), and ${}^{2}_{\infty}[\{(Cu^{II}_2L^2_2)\}$-$\{Cu^{I}_2(\mu_{1,3}\text{-}SCN)_2(\mu_{1,1,3}\text{-}SCN)_2\}]_n$ (**XXI**), respectively. The synthesis of metal chelates **XIX**–**XXI** is depicted in Scheme 4.



XVI

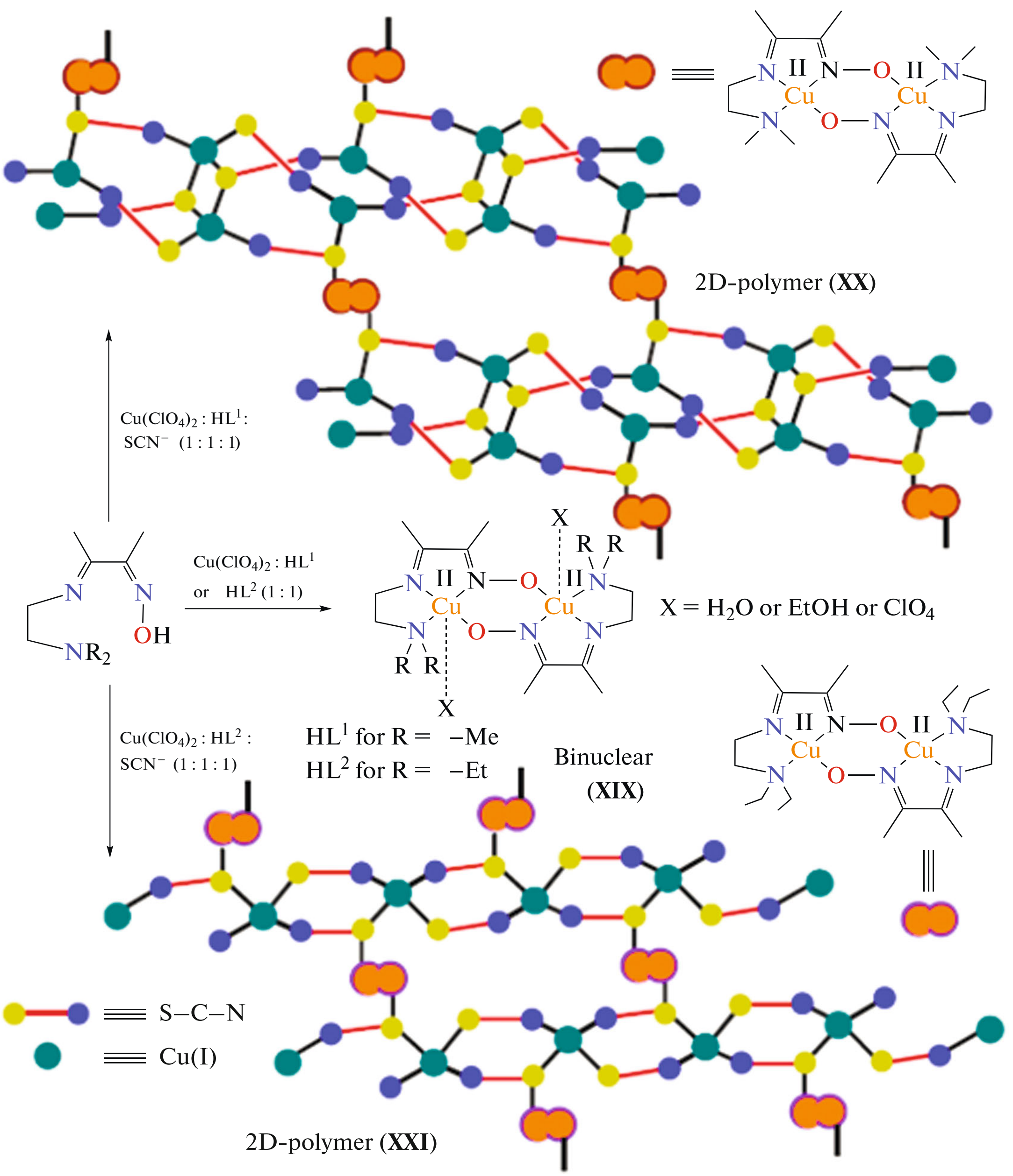


XVII



XVIII

Fig. 9. Structure of complexes **XVI** and **XVII**, incorporating asymmetrical anionic moiety, and **XVIII** with identification of moieties A, A', and B [70].



Scheme 4.

Binuclear complexes **XIX** were synthesized by the reaction of copper(II) perchlorate with HL^1 and HL^2 in ethanol solution; compounds **XX** and **XXI** were prepared in a similar way, but in the presence of sodium thiocyanate; this reagent caused partial reduction of Cu(II) to Cu(I) during the complex formation reaction at room temperature. All complexes have clear-cut antiferromagnetic exchange interactions, with the exchange parameters being $J = -549.6$ (R = Et), -578.7, and -663.8 cm^{-1} for **XIX**, **XX**, and **XXI**, respectively.

It was noted [72] that the distances between two cooper ions in 2D polymers **XX** and **XXI** exceed 8 Å; hence, the potential exchange interaction involving the Cu^ISCN moiety should be negligible; therefore, the above exchange parameters for **XX** are **XXI** are almost entirely attributable to the interaction in binuclear moieties with oximate bridges.

EXCHANGE-COUPLED OXIMATE Ni(II) COMPLEXES

It is known [79, 80] that transfer from exchange-coupled copper(II) complexes to similar complexes formed by high-spin nickel(II) ions characterized by the total spin $S = 1$ and half-filled $d_{x^2-y^2}$ and d_{z^2}, magnetic orbitals results in the following potential exchange channels:

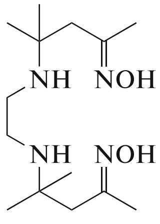
$$d_{x^2-y^2}\left\|\sigma_{sp^2}(\mathrm{NO})\right\|d'_{x^2-y^2} \quad \text{antiferromagnetic}$$

$$d_{z^2}\left\|\sigma_{sp^2}(\mathrm{NO})\right\|d'_{z^2} \quad \text{weakly antiferromagnetic}$$

$$d_{x^2-y^2}\left\|\sigma_{sp^2}(\mathrm{NO})\right\| \perp d'_{z^2} \quad \text{ferromagnetic.}$$

According to the exchange channel theory [79], this situation results most often, with all other factors being the same, in a considerable decrease of the absolute magnitudes of exchange parameters. Indeed, as shown below, virtually all exchange-coupled nickel oximate complexes synthesized to date have relatively weak antiferromagnetic interactions. One of the examples is the complex $[Ni_2(L)_2](ClO_4)_2$, synthesized in [81], which is depicted in Fig. 10. The distance between the two nickel(II) ions connected by oximate bridges is 3.706 (1) Å; according to the authors, this rules out direct exchange; the exchange parameter $J = -79$ cm^{-1} is consistent with the assumption that the exchange interaction is transmitted through the system of σ-bonds.

The reaction of the oximate ligand of system **XX** (H_2L^1) with nickel(II) perchlorate [82] furnished binuclear complex of type **XXIII**, which is depicted in Fig. 11.

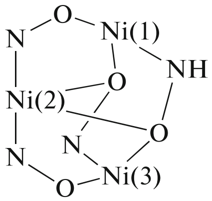


H_2L^1 (**XX**)

It can be seen from Fig. 11 that the two nickel ions are linked by two imine and two amine nitrogen atoms and also by the oxygen atom of the oximate moiety of the second ligand.

Binuclear Ni(II) complex **XXIII** is characterized by a rather weak antiferromagnetic exchange ($J = -12$ cm^{-1}). In the opinion of the authors, this is due to both the orbital factors noted above and the structural features of the $Ni_2(NO)_2$ exchange moiety.

In most cases, an increase in the number of nickel(II) atoms in the exchange moiety does not induce a crucial change in the magnetic properties. For example, the trinuclear $[Ni_3(L)(HL)_2](ClO_4)_2$ complex in which the octahedrally coordinated nickel ions are located at the vertices of an isosceles triangle incorporating oximate bridges (type **XXIV**) was reported [83].



(**XXIV**)

The magnetic analysis performed under the assumption of exchange interaction through two oximate bridges and an oxygen atom gave the following exchange parameters: $J_{XII} = J_{XXIII} = -14.4$ cm^{-1}, $J_{XIII} = -7.6$ cm^{-1}.

Bi-, tri-, and tetranuclear nickel(II) complexes were obtained [84] using Schiff bases, 3-[2-(diethylamino)ethylimino]butan-2-one oxime (HL^1) and 3-[3-(dimethylamino)propylimino]butan-2-one oxime (HL^2), as the ligands. The reactions of these ligands with nickel perchlorate yielded the binuclear complex $[Ni_2L^1_2](ClO_4)_2$ (**XXV**) and trinuclear complex $[Ni_3(HL^2)_3(\mu_3\text{-}O)](ClO_4)_4 \cdot CH_3CN$ (**XXVI**), while the addition of NaOH led to deprotonation of the oximate

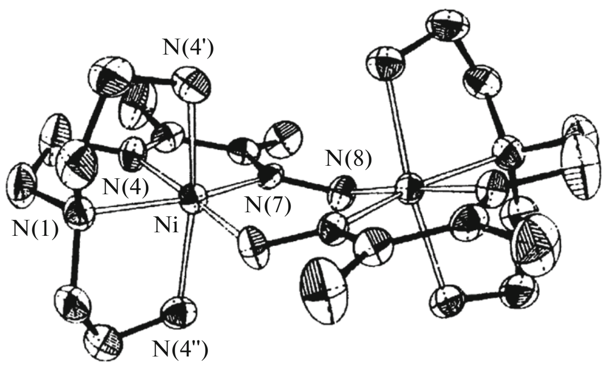
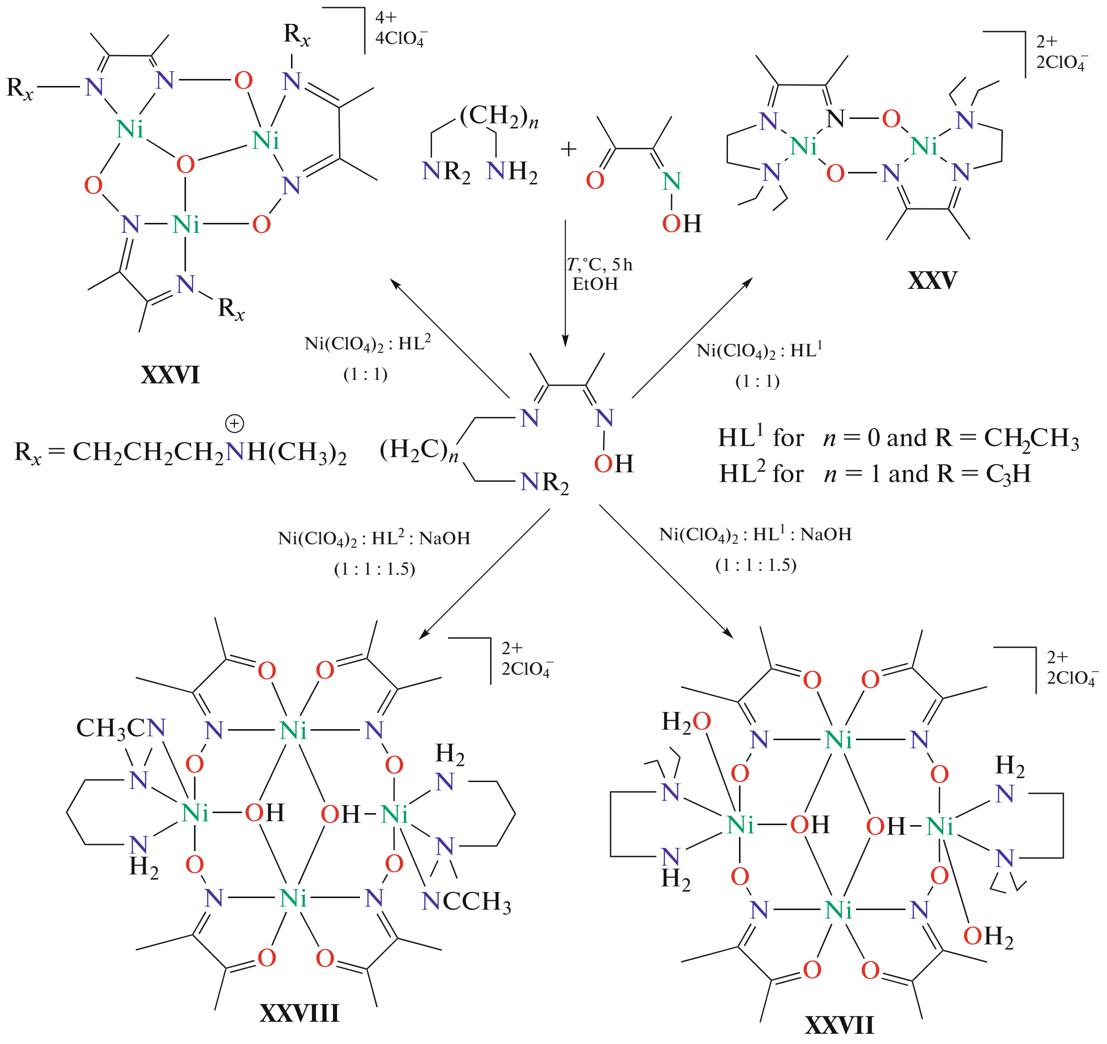


Fig. 10. Structure of complex $[Ni_2(L)_2](ClO_4)_2$.

hydroxy group and formation of the tetranuclear complexes $[\{Ni(Deen)(H_2O)\}_2(\mu_3\text{-}OH)_2\{Ni_2(Moda)_4\}](ClO_4)_2 \cdot 2CH_3CN$ (**XXVII**) and $[\{Ni(Dmpn)(CH_3CN)\}_2(\mu_3\text{-}OH)_2\{Ni_2(Moda)_4\}](ClO_4)_2 \cdot CH_3CN$ (**XXVIII**) (Deen = 2-(diethylamino)ethylamine, Dmpn = 3-(dimethylamino)methylamino)-1-propylamine, ModaH = butane-2,3-dione monooxime) (Scheme 5). In complexes **XXV** and **XXVI**, the oximate oxygen atom is deprotonated and linked to the nickel ion, while in the case of **XXVII** and **XXVIII**, the Schiff base is hydrolyzed to give diamine and oxime molecules, which form the $\{Ni(Diamine)\}^{2+}$ and $\{Ni(Moda)_2\}^{2+}$ moieties, which are then converted to tetranuclear complexes.



Scheme 5.

The molecule of complex **XXVII** includes the centrosymmetric tetranuclear $[\{Ni(Deen)(H_2O)\}_2(\mu_3\text{-}OH)_2\{Ni_2(Moda)_4\}]^{2+}$ unit (Fig. 12a), with the coordination environment of each nickel ion being a distorted octahedron.

The structure of complex **XXVIII** is also composed of tetranuclear $[\{Ni(Dmpn)(CH_3CN)\}_2(\mu_3\text{-}OH)_2\text{-}\{Ni_2(Moda)_4\}]^{2+}$ units (Fig. 12b). The structures of both complexes are almost identical, except for the amine component and coordinated solvent or water molecules.

As found by the authors, the tetranuclear $Ni_4N_4O_6$ exchange moiety in both complexes has a chair conformation (Fig. 13).

This structure allowed the authors to assume that four nickel atoms are located at the vertices of a rhombus, and exchange interaction can be interpreted in terms of isotropic spin Hamiltonian (6) including three exchange parameters. The exchange interaction channels in complexes **XXVII** and **XXVIII** are depicted in Scheme 6.

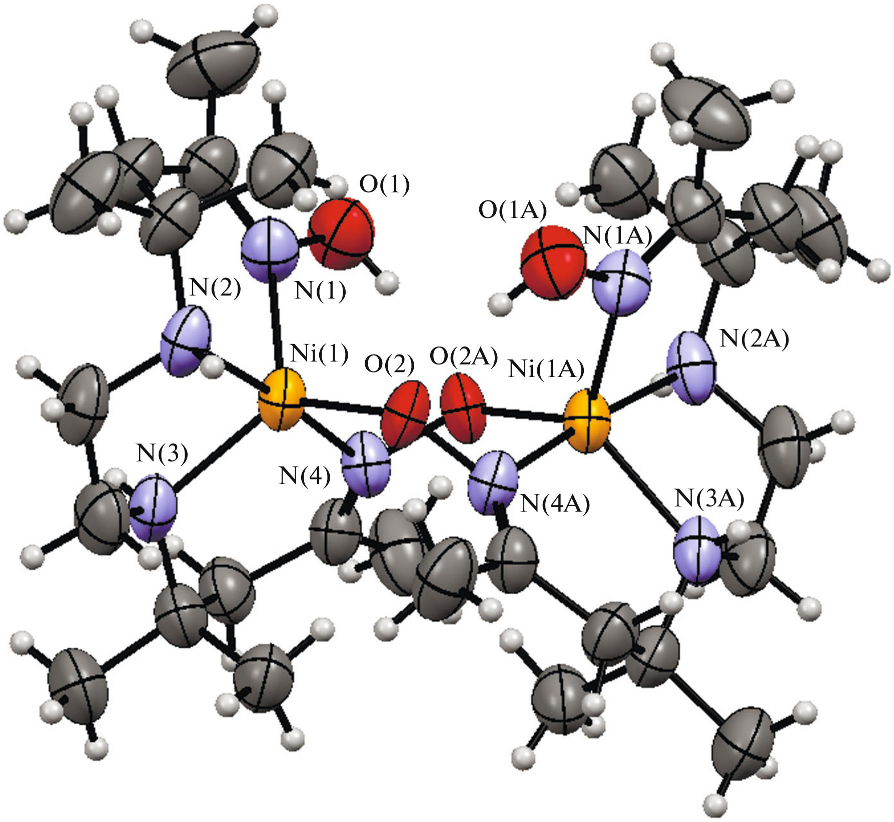
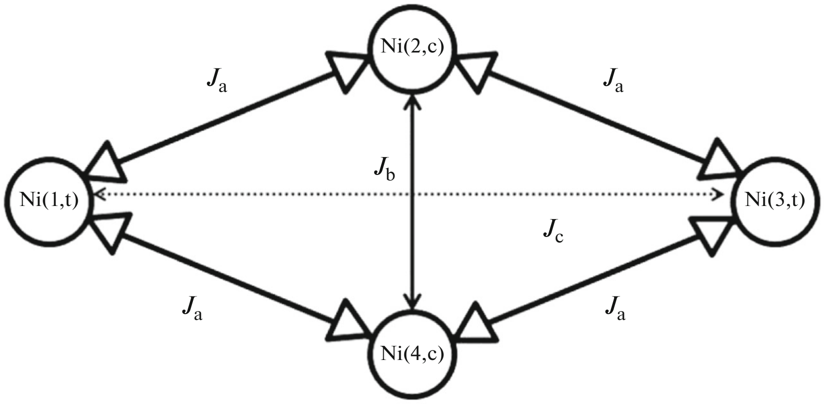


Fig. 11. Structure of binuclear nickel(II) complex (**XXIII**).

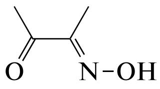


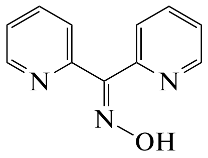
Scheme 6.

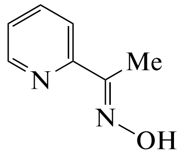
$$\hat{H} = -2J_a(S_1S_2 + S_1S_4 + S_2S_3 + S_3S_4) - 2J_b(S_2S_4) - 2J_c(S_1S_3). \quad (6)$$

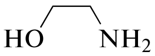
The calculated values were J_a = –43.5(1) cm^{-1}, J_b = 19(1) cm^{-1}, J_c = 0 for **XXVII** and J_a = –48.4(1) cm^{-1}, J_b = 15(1) cm^{-1}, J_c = 0 for **XXVIII**; the authors stated that this was in good agreement with published data [85–91].

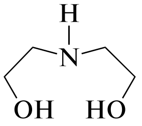
The ability of oximate ligands in combination with amino alcohols to generate metallacycles of different compositions and structures was reported in [92]. The authors implemented this task by choosing the ligand systems shown below: diacetyl monooxime (HDamo), di-2-pyridyl ketone oxime (HDpko), and methyl-2-pyridyl ketone oxime (HMpko), and amino alcohols (HEa, H_2Dea, HMea) as linkers.

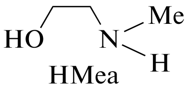

HDamo

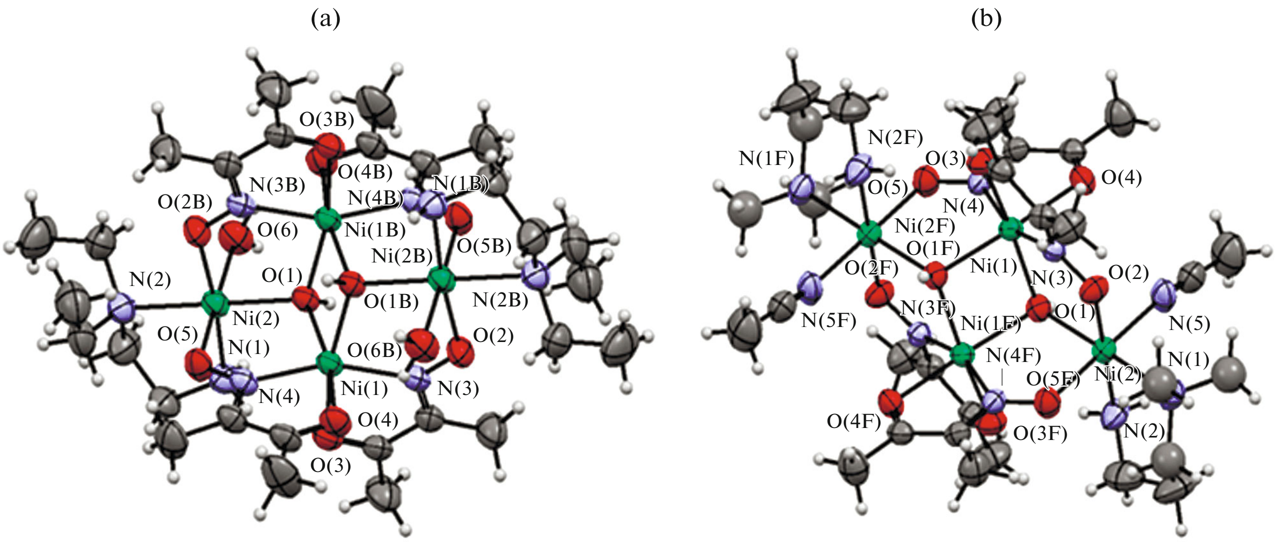

HDpko


HMpko


HEa


H_2Dea


HMea



XXVII **XXVIII**

Fig. 12. Structure of complexes **XXVII** and **XXVIII**.

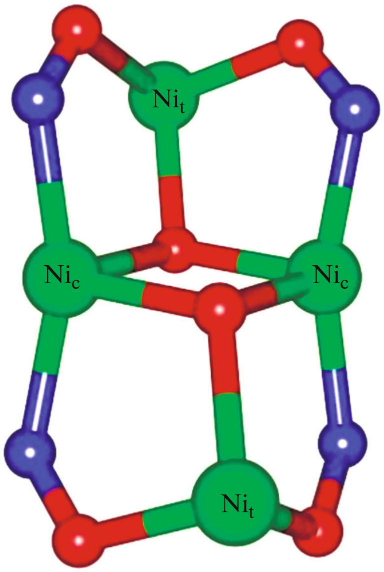
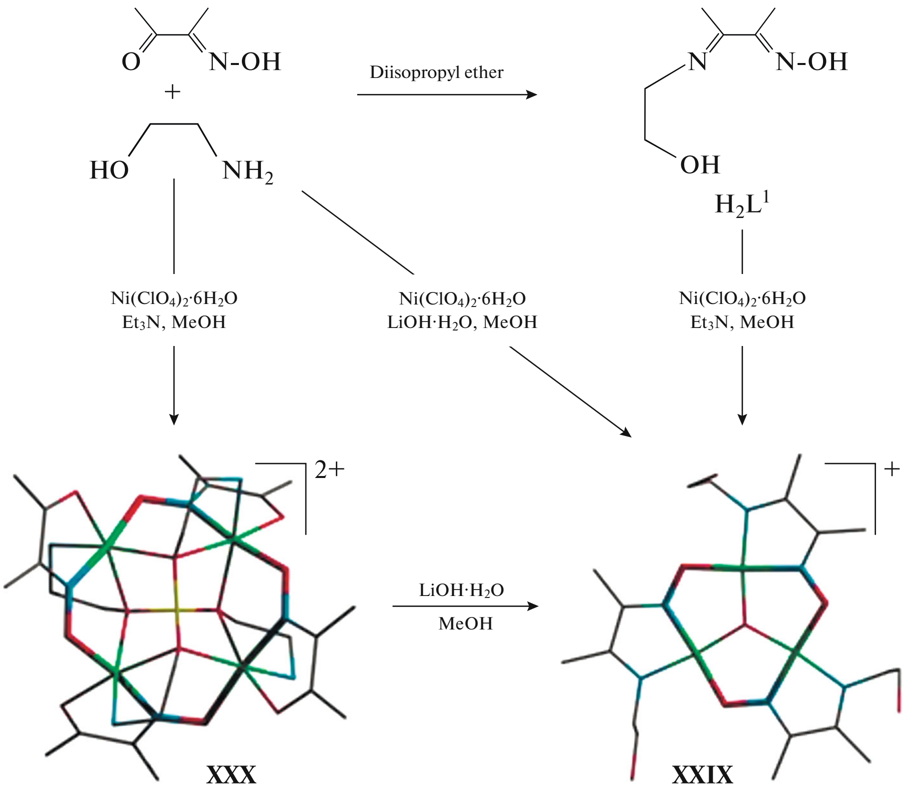


Fig. 13. Structure of the exchange moiety in **XXVII** and **XXVIII**.

The reaction of HDamo with $Ni(ClO_4)_2{\cdot}6H_2O$ in the presence of triethylamine resulted in the synthesis of trinuclear complex $[(NiHL^1)_3(\mu_3\text{-}O)]ClO_4$ (**XXIX**), while the addition of HEa led to the synthesis of tetranuclear complex $(Et_3NH)[Ni_4(Damo)_4(HEa)_2(Ea)_2](ClO_4)_3$ under similar conditions (**XXX**, Scheme 7).



Scheme 7.

According to the authors, complex **XXX** is a new type of metallacrown derivatives designated by 12-MC-4 with the inner cavity enclosing H-bonded anion pairs $(OH...O)^-$. The 12-MC-4 moiety was also present in structurally similar tetranuclear complexes, also obtained by the authors: $[Ni_4(Damo)_4(H_2Dea)_2(HDea)_2](ClO_4)_2{\cdot}2H_2O$, $[Ni_4(Dpko)_4(HEa)_2(Ea)_2](ClO_4)_2{\cdot}4H_2O$ (**XXXII**), and $[Ni_4(Mpko)_4(HMea)_2(Mea)_2](ClO_4)_2$ (**XXXIII**). The structure of complex **XXXI** is shown in Fig. 14.

The authors noted that nickel atoms in complexes **XXXI**–**XXXIII** form a square geometry and are located in octahedral coordination because of axial binding of, for example, imino oxime (Damo-) and amino alcohol (HDea-, in the case of **XXXI**) molecules.

The magnetic measurements showed that complexes **XXIX** and **XXX** were diamagnetic, while for complexes **XXXI**–**XXXIII**, antiferromagnetic type exchange interaction was noted. The dependence of χT on T is shown in Fig. 15.

The temperature dependence of the magnetic susceptibility was interpreted in terms of the model simplest for this situation, using only one exchange parameter J and isotropic spin Hamiltonian (7):

$$\hat{H} = -2J\left(S_{\mathrm{Ni1}}S_{\mathrm{Ni2}} + S_{\mathrm{Ni2}}S_{\mathrm{Ni3}} + S_{\mathrm{Ni3}}S_{\mathrm{Ni4}} + S_{\mathrm{Ni1}}S_{\mathrm{Ni4}}\right). \qquad (7)$$

The corresponding theoretical values of J were −23(1) K for **XXXI**, −26.4(4) K for **XXXII**, and −20.4(8) K for **XXXIII**. In the opinion of the authors, this was in good agreement with the known results for tetranuclear nickel complexes with a similar topology [9, 93, 94].

The above examples provide clear evidence of the scattered nature of analysis of the magnetic properties of exchange-coupled nickel(II) complexes with oximate ligands and the absence of significant magneto-structural correlations for these systems, which implies the need for further systematic experimental and theoretical studies along this line.

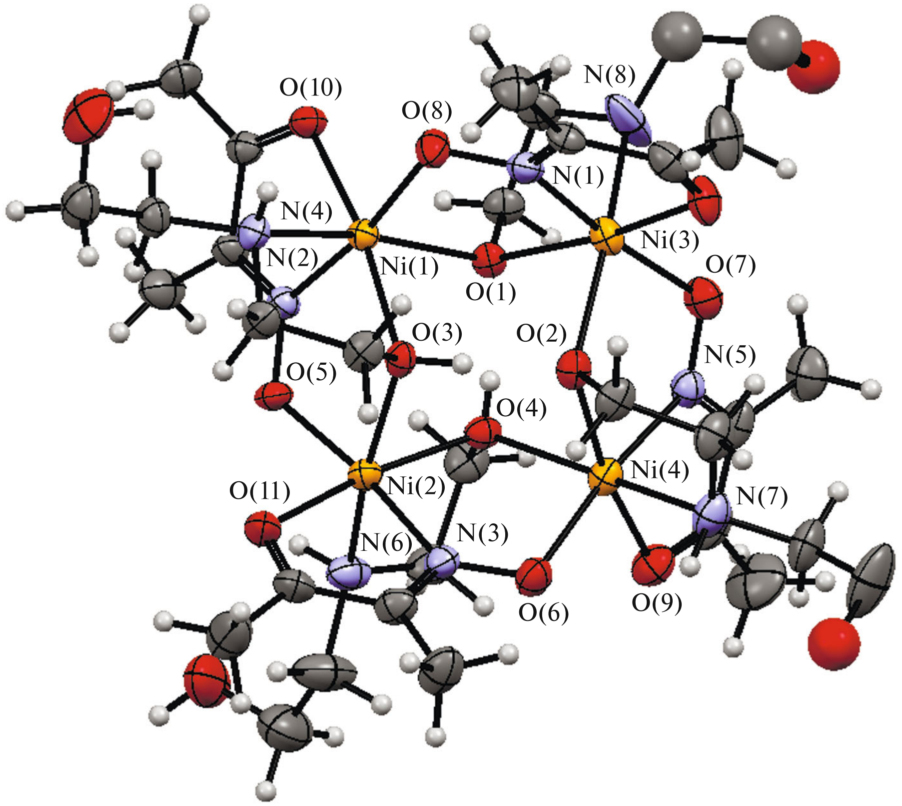


Fig. 14. Structure of tetranuclear complex **XXXI**.

In conclusion, it should be noted that, within the framework of limited analysis, this review addresses the key types and mechanisms of exchange interactions, identifies some electronic and geometric factors that have a decisive effect on the magnetic properties of bi- and tetranuclear copper(II) and nickel(II) complexes with oximate ligand. We deliberately restricted ourselves to the magnetic properties of exchange-coupled complexes in which the paramagnetic centers are in orbitally non-degenerate states. Meanwhile, it is quite obvious that further theoretical and experimental development of the magnetochemical method as regards adequate interpretation of the properties of such systems, which include 2nd and 3rd row transition elements and lanthanides, is highly relevant, especially for targeted design of supramolecular structures with specified or controlled physicochemical characteristics and for identification of the fundamental structure–property relationships in order to obtain new materials such as single-molecule magnets and for innovative technologies in the near future.

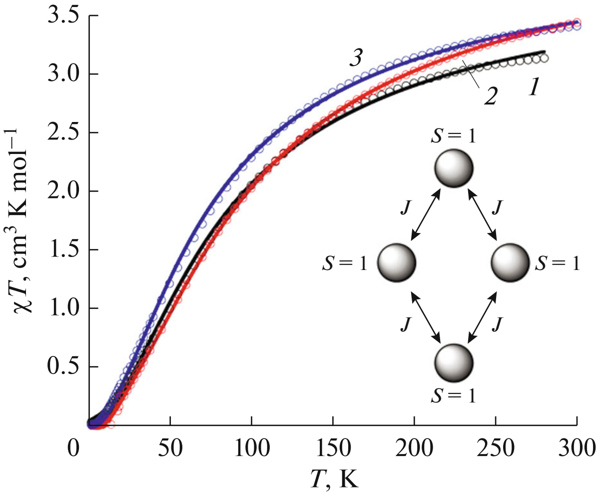


Fig. 15. Temperature dependence of χT for **XXXI–XXXIII**. The continuous lines for (*1*) **XXXI**, (*2*) **XXXII**, and (*3*) **XXXIII** correspond to theoretical exchange parameters.

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