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Copper and nickel chelate complexes with polydentate N,O-ligands: structure and magnetic properties of polynuclear complexes

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Copper and nickel chelate complexes with polydentate N,O-ligands: structure and magnetic properties of polynuclear complexes †

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A comparative analysis of the structures of copper(II) and nickel(II) chelate complexes with N-substituted 2-aminoethanols, 3-aminopropan-1-ols, glycines and β-alanines is performed. It is shown that tetradentate ligands based on 3-aminopropan-1-ol and β-alanine, sterically hindered 2-aminoethanol derivatives and tridentate enamino ketone derivatives tend to form oligonuclear copper(II) and nickel(II) complexes. Glycine derivatives do not provide the formation of oligonuclear copper(II) and nickel(II) complexes. The magnetic properties of a number of polynuclear complexes are compared.
The bibliography includes 182 references.

Contents

I. Introduction

One of the main aims of the chemistry of coordination compounds is to establish relationships between the chemical structure of the ligands and the structure and properties of the complexes with these ligands. A growing demand in modern materials, in which the cluster arrangement of metal centres provides specific electronic effects,[1, 2] means new tasks concerning targeted synthesis of coordination compounds, primarily, of polynuclear complexes and clusters. The solution of this difficult and versatile problem would allow researchers to approach the design of a broad range of chemical compounds required as enzyme biomimetics,[3 – 5] catalysts[6 – 8] and molecular electronics components.[9 – 12] It is evident that precise knowledge of relationships between the structure of the ligands, on the one hand, and the denticity > 2 and the structure of the resulting polynuclear complexes, on the other hand, is necessary for the synthesis of desired metal-containing complexes. It is such ligands that tend to form polychelates, thus providing the necessary spatial arrangement of atoms and, as a consequence, the appearance of unique properties of coordination compounds. Since such dependences are multifactor, a common system of relationships between the ligand and the structure of the complex is lacking. Scarce empirical data on the structures of complexes with rather simple (bidentate) ligands,[13] azomethines,[14] amidinate derivatives,[15] β-diketones,[16] imides[17] and aminomethylphosphines[18] are available in the literature. Attempts are made to perform certain comparisons. However, they do not allow researchers to develop the synthesis of ligands ensuring the required nuclearity (the number of metal atoms) for complexes with particular metals. In order to establish reliably structure – property relationships even for compounds of one series, it is necessary to synthesize ligands with regularly changing structures and to study their complexation properties.

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Current research interests: heterocyclic and coordination compounds.

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† Dedicated to Academician of the Russian Academy of Sciences O N Chupakhin on the occasion of his 80th birthday.

The amino group is one of the main structural units for the construction of chelating ligands having denticity of $\geqslant 3$, which can form oligonuclear complexes with transition metals. In this class of organic compounds, the basic (both Brønsted and Lewis) properties of the amino group can be changed by introducing hydrocarbon substituents directly at this nitrogen atom.[19] The known effect of the chemical structure of amines on their nucleophilic and basic properties is successfully used in synthetic organic chemistry.[20] Another, more efficient, way of varying the basicity of amines toward Lewis acids — transition metal ions — is based on the introduction of functional groups into a hydrocarbon moiety bonded to the nitrogen atom. Amines modified in such a way can tend to give chelates. This property has a substantial effect on their donor and complexation properties. Actually, functionalized amine derivatives can have substantially higher complexation constants with the same metal ions compared to the starting compounds.[21] Hydroxy- and carboxyalkyl-substituted amine derivatives, *viz*., amino alcohols and amino acids, as well as enamino ketones, which are prone to form five- and six-membered N,O-chelates, are of considerable interest in this respect. Advantages of this group of compounds are their relatively simple chemical structures, their commercial availability due to rather facile methods for their synthesis and the possibility of varying the structures of the ligands in order to construct more complex coordination structures.

This review is one of the first to systematically consider the published data on the structures and properties of complexes based on the simplest series of N,O-ligands. Information for this review was compiled by searching the Cambridge Structural Database, which contains reliable and comprehensive data on molecular structures. An analysis of the structures of copper(II) and nickel(II) complexes is based on the published results of X-ray diffraction analysis, the only direct method for the molecular structure determination. Data on the structures of complexes in solution are scarce and non-systematic. These data cannot be used for the comparative analysis not only of the structures but also of magnetic properties of complexes, *i.e*., for the establishment of structure–property relationships, because compounds as single-molecule magnets are intended to be employed in the crystalline state.

II. Amino alcohols

In this class of derivatives, 2-aminoethanol and 3-aminopropan-1-ol are parent compounds for a series of ligands having denticity $\geqslant 2$. These compounds can form five- and six-membered chelate rings, respectively, upon coordination to metal ions. An additional functionalization at the nitrogen atom of these amino alcohols has an effect on the electronic structure of the amino group, resulting in changes in the Lewis basic properties and, as a consequence, in the composition of the complexes and the lengths of characteristic bonds. The steric hindrance due to bulky substituents at the nitrogen atom also substantially influences the basic properties of the amino group as the metal coordination centre.

II.1. 2-Aminoethanol

2-Aminoethanol is a bidentate ligand.[22–24] When forming complexes with copper[25] and nickel,[26] the hydroxy group can be deprotonated. This leads to the enhancement of coordination properties, as evidenced by a decrease in the corresponding bond lengths (Tables 1 and 2). The presence of bulky substituents directly at the amino group (*N*,*N*-dialkyl-2-aminoethanol)[56] or in its vicinity (2-amino-2,2-dimethylethanol)[27] is responsible for substantial changes in both the coordination ability and the acid-base properties of amino and hydroxy groups. The latter can be deprotonated

Table 1. Characterization of copper(II) complexes with 2-aminoethanol derivatives.

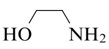
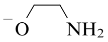
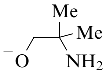
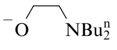
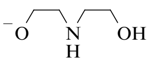
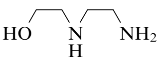
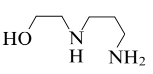
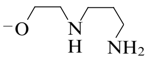
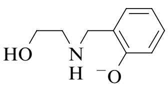
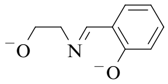
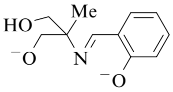
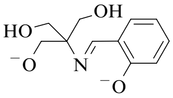
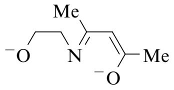
Ligand (L)	Composition of complex[a]	Bond length /Å		Distance Cu···Cu /Å[b]	Ref.
		Cu–OH	Cu–N		
	$[CuL_2(OH)_2]$	2.369	2.064		22
	$[CuLCl_2]$	2.025	2.025		23
	$[CuL(HL)]_2(NO_3)_2$	1.963[c]	1.986		25
	$[Cu_4L_4Cl_4]$	1.969[c]	1.983	3.302 3.306	27
	$[Cu_4L_4Br_4]$	1.949[c]	2.068	3.135 3.478	28
	$[Cu_2L_2](SCN)_2$	1.947[c]	1.999	2.865	29
	$[Cu_4L_4](NO_3)_4$	1.945[c]	2.027	3.213 3.340	30
	$[CuL_2](PhCO_2)_2$	2.443	2.044		31
	$[CuLCl]Cl$	1.996	1.952		32
	$[CuL_2](SCN)_2$	2.441	2.054		33
	$[Cu_2L_2]I_2$	1.969[c]	2.017	2.970	34
	$[Cu_4L_4](NO_3)_4$	1.942[c]	2.012	3.222 3.442	35

Table 1 (continued).

Ligand (L)	Composition of complex[a]	Bond length /Å		Distance Cu···Cu /Å[b]	Ref.
		Cu–OH	Cu–N		
	$[\mathrm{CuL}_2]$	2.710	1.994		36
	$[\mathrm{Cu}_4\mathrm{L}_4]$	1.966[c]	1.929	3.112 3.346	37
	$[\mathrm{Cu}_4\mathrm{L}_4]$	1.952[c]	1.921	3.144 3.522	38
	$[\mathrm{Cu}_4\mathrm{L}_4(\mathrm{H}_2\mathrm{O})]$	1.952[c]	1.927	3.090 3.470	37
	$[\mathrm{Cu}_4\mathrm{L}_4]$	1.953[c]	1.916	3.065 3.311	39

[a] Solvent molecules are omitted for the sake of simplicity; [b] here and in the following tables, the metal–metal distances within one polynuclear complex are given; two values refer to the minimum and maximum values; [c] the Cu–O$^-$ bond.

Table 2. Characterization of nickel(II) complexes with 2-aminoethanol derivatives.

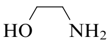
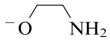
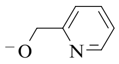
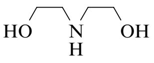
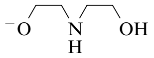
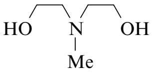
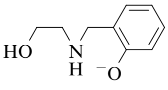
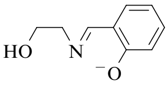
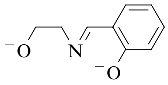
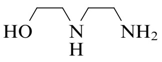
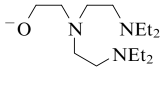
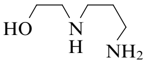
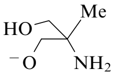
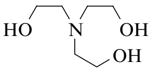
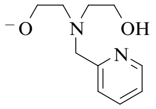
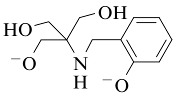
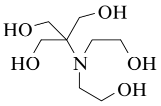
Ligand (L)	Composition of complex[a]	Bond length /Å		Distance Ni···Ni /Å	Ref.
		Ni–OH	Ni–N		
	$[\mathrm{NiL}_2](\mathrm{NCS})_2$	2.141	2.102		24
	$[\mathrm{NiL}(\mathrm{LH})_2]\mathrm{ClO}_4$	2.075	2.081		26
	$[\mathrm{Ni}_4\mathrm{L}_4\mathrm{Cl}_4(\mathrm{H}_2\mathrm{O})_4]$	2.033[b] 2.048[b]	2.060 2.078	3.106 3.199	40
	$[\mathrm{NiL}_2](\mathrm{SCN})_2$	2.076	2.096		41
	$[\mathrm{Ni}_4\mathrm{L}_4\mathrm{Cl}_4]$	2.039[b] 2.050[b]	2.100 2.123	3.100 3.208	42
	$[\mathrm{NiL}_2]\mathrm{Cl}_2$	2.068	2.081		43
	$[\mathrm{Ni}_2\mathrm{L}_2(\mathrm{MeOH})_2\mathrm{Cl}_2]$	2.108	2.055	3.112	44
	$[\mathrm{NiL}_2]$	2.183	1.955 2.008		45
	$[\mathrm{Ni}_2\mathrm{L}_2(\mathrm{H}_2\mathrm{O})_2\mathrm{Cl}_2]$	2.213	1.945 2.074	3.141	46
	$[\mathrm{Ni}_4\mathrm{L}_4(\mathrm{MeOH})]$	2.019[b] 2.033[b]	1.981 1.995	3.032 3.195	47
	$[\mathrm{NiL}_2](\mathrm{NO}_3)_2$	2.134 2.164	2.050 2.063		48
	$[\mathrm{Ni}_2\mathrm{L}_2](\mathrm{ClO}_4)_2$	1.975[b]	2.087	3.091	49

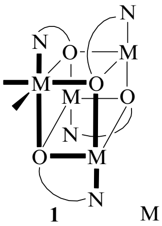
Table 2 (continued).

Ligand (L)	Composition of complex [a]	Bond length /Å		Distance Ni···Ni /Å	Ref.
		Ni–OH	Ni–N		
	$[NiL_2]Cl_2$	2.170	2.078		50
	$[Ni_4L_4(OAc)_4]$	2.047 [b] 2.089 [b]	2.061 2.092	3.061 3.131	51
	$[NiL_2](NO_3)_2$	2.053	2.114		52
	$[Ni_3L_2(OAc)_2(HCO_2)_2]$	2.022 [b]	2.094	3.074	53
	$[Ni_4L_4]$	2.037 [b]	2.049	3.021	54
	$[NiL(H_2O)]SO_4$	2.073 2.080	2.053 2.053		55

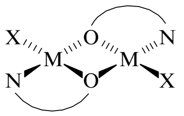
[a] Solvent molecules are omitted for the sake of simplicity; [b] the Ni–O$^-$ bond.

and act as bridges in heteronuclear cuboid structures (Structures **1**).

Structures 1, 2



1 M = Cu, Ni



2 M = Cu, Ni

N-Functionalization of the amino group of 2-aminoethanol generally leads to an increase in the denticity of the ligand. As can be seen from Table 1, the nature of the introduced functional group and the size of the resulting conjugated chelate ring have a substantial effect on the coordination properties of both the amino and hydroxy groups compared to starting 2-aminoethanol. Actually, in copper complexes with diethanolamine,[29,30] the presence of the second aminoethanol chelate ring results in an increase in the coordination ability of the amino group. Thus, the Cu–N bond length decreases, and the deprotonation of the hydroxy group leads to the enhancement of its electron-donating properties. This is manifested in shortening of the Cu–O bond, as well as in the appearance of the ability of the hydroxy group to be involved in bridging bonds. This gives rise to binuclear (**2**) and cuboid (**1**) structures containing counterions in the outer sphere (Figs 1 and 2).[29,30] The opposite effect is not observed. Thus, an increase in the acidity of the hydroxy group in the additional chelate ring does not promote the enhancement of the coordination ability of the amino group.[36]

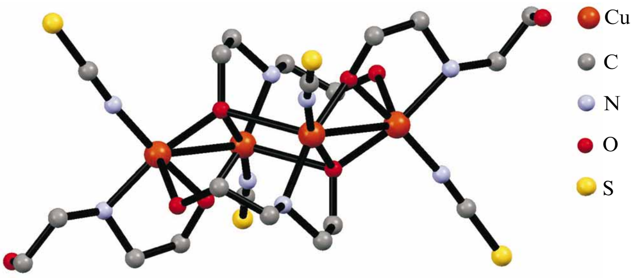


Figure 1. Molecular structure of bis(μ-diethanolaminato-*N*,*O*)diisocyanatodicopper(II).[29]
Dimeric molecules are linked together to form tetramers, which form a three-dimensional framework *via* hydrogen bonds in the crystal.

In the case of introduction of the second alkylamino group into the 2-aminoethanol molecule, the electron-donating properties of the starting amino group depend on the size of the chelate ring. Thus, the presence of the additional ethylenediamine chelate ring has virtually no effect on the basicity of the amino group and leads to a decrease in the electron-donating ability of the hydroxy group.[31] An increase in the chelate ring size to six-membered, *i.e.*, the formation of the propane-1,3-diamine chelate ring, results in the strengthening of the Cu–N coordination bond and the enhancement of the coordination ability of the hydroxy group due to its deprotonation.[34,35] Depending on the type of the second ligand, mono-, bi- and tetranuclear structures containing counterions in the outer sphere can be produced (Figs 3 and 4).[33–36]

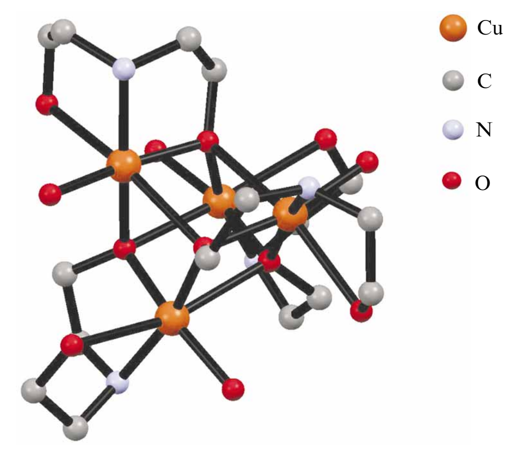


Figure 2. Structure of the cation in the crystal hydrate of tetrakis{μ-2-(2-hydroxyethylamino)ethanolato}tetraaquatetracopper(II) tetranitrate.[30]

Figure 3. Fragment of the polymeric cation in *catena*-μ-iodobis[μ-{2-(3-aminopropylamino)ethanolato-*N*,*N′*,*O*}copper(II)] iodide dihydrate.[34]
The dimeric copper(II) complexes are linked together to form a chain *via* bridging I^- ligands.

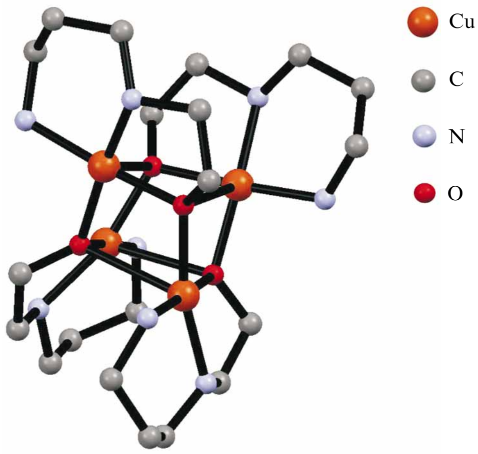


Figure 4. Structure of the cation in tetrakis-μ_3-{2-(3-aminopropylamino)ethanolato}tetracopper(II) tetranitrate dihydrate.[35]

In reactions with copper(II) nitrate, chloride, bromide, sulfate or malonate, *N*-(3-aminopropyl)-2-aminoethanol forms tetranuclear copper complexes. A tetranuclear complex is also produced in the presence of perchlorate anions, but the latter complex has different geometry.[57] The application of Schiff bases based on 2-aminoethanol and salicylaldehyde or other aldehydes containing an enol group [37–39, 56, 57] for the complexation gives rise to tetranuclear structures. Evidently, the introduction of the phenol or enol moiety having stronger acidic properties compared to the hydroxy group of 2-aminoethanol results in an increase in the coordination ability of the OH group. In all cases, this group is deprotonated and acts as a bridge.[37–39]

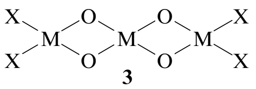
The Cu···Cu distance is to a large extent determined by the presence of additional anions and their sizes (see Table 1) rather than by the structure of the ligand.[30, 35]

Therefore, the increase in the ligand denticity to three in copper complexes with 2-aminoethanol by introducing an electron-donating functional group (a weak Brønsted acid) leads to the enhancement the coordination ability of both functional groups of amino alcohol, thus providing the formation of binuclear or cuboid tetranuclear structures.

In nickel(II) complexes, the hydroxy group of 2-aminoethanol can also undergo deprotonation (see Table 2).[24, 26] The presence of bulky substituents in amino alcohols (2-amino-2-methylpropane-1,3-diol) [51] promotes a substantial increase in the coordination ability of amino and hydroxy groups; the latter group is able to undergo deprotonation even in the presence of a stronger acid, acting as a bridge in a tetranuclear complex. A substantial change in the electronic structure of the nitrogen atom, for example in 2-pyridylmethanol, results in the same effect.[40]

Another character of the influence of additional denticity on the coordination ability of functional groups of amino alcohols was found by structural analysis of nickel(II) complexes with N-substituted 2-aminoethanols (see Table 2). The presence of the second aminoethanol [41] or ethylenediamine [48] chelate ring does not change the coordination ability of the amino group. The tendency of the hydroxy group to be coordinated to metals remains unchanged in the former case and decreases in the latter case. The composition of the complex is independent of the size of the conjugated alkyldiamine ring, but the latter parameter influences the coordination ability of functional groups.[52] Only in the presence of two ethylenediamine chelate rings, the hydroxy group is deprotonated and acts as a bridge, thus facilitating the formation of a binuclear structure.[49] A greater steric crowding of the nitrogen atom [43, 52] or the aminoethanol moiety [55] in related conjugated chelate rings is not accompanied by such changes even despite an increase in the potential denticity of the ligand and regardless of the nature of the acidic residue used (nitrate, chloride or acetate).[52] An increase in the steric hindrance at the nitrogen atom by introducing the 2-pyridylmethyl moiety combined with a stronger base results in the formation of a trinuclear structure with a linear arrangement of metal centres (Structures **3**, Fig. 5).[53]

Structures 3



3

M = Cu, Ni

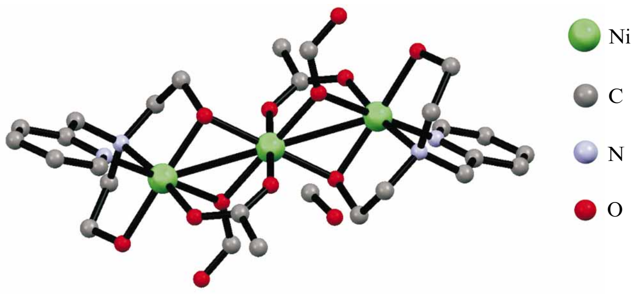


Figure 5. Molecular structure of bis[(μ-acetato-*O*,*O*′-μ-formato-*O*,*O*′){*N*-(2-pyridyl)iminodiethanol-*N*,*N*′,*O*,*O*′}]trinickel(II) (MeOH solvent molecules are omitted for the sake of simplicity).[53]

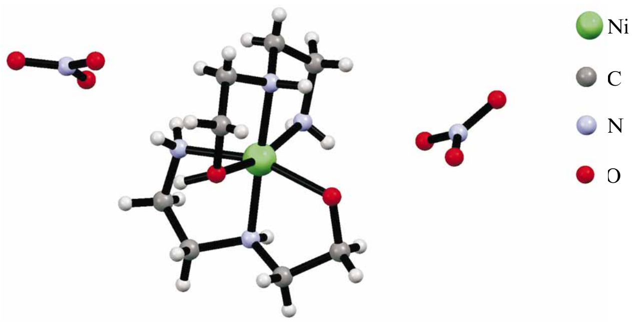


Figure 7. Molecular structure of bis{*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*O*}nickel(II) dinitrate.[48]

As opposed to copper complexes, an increase in the acidity of the introduced hydroxy group favours an increase in the coordination ability of the amino group in nickel(II) complexes.[44–47,54] The Ni–N bond is shorter than that in the nickel complex with 2-aminoethanol, but the coordination ability of the hydroxy group diminishes because of the longer Ni–OH bond. As a result, the hydroxy group is involved in the coordination without losing a proton, due to which bi- and tetranuclear nickel structures can be prepared if a phenol derivative is present as the ligand.[44,46,47] In these cases, the hydroxy group in the aromatic ring is deprotonated and acts as a bridge with the involvement of both chloride and acetate ions.[44,46] The deprotonation of the hydroxy group ensures the formation of cuboid tetranuclear complexes.[47,54] The Ni···Ni distance between the metal centres is determined primarily by the denticity of the ligand (see Table 2): the higher the denticity, the shorter the Ni···Ni distance.[40,42,49,53,54] For bi- and tridentate ligands, the distance between the metal centres does not depend on the structure of the ligand.[40,42,44,46,47,51]

Therefore, in nickel(II) complexes, an increase in the denticity of 2-aminoethanol to three or more by introducing an electron-donating functional group (a weak Brønsted acid) has almost no effect on the coordination ability of both functional groups of amino alcohols. Bi- or tetranuclear structures can be prepared by introducing a functional group with higher Brønsted acidity.

A comparison of the regularities found for copper(II) and nickel(II) complexes shows that the coordination ability of functional groups of 2-aminoethanol is influenced not only by its further functionalization but also by the nature of the metal centre. This is manifested both in the M–OH and M–N bond lengths (in most of the copper complexes, these bonds are shorter) and in the conformation of the tridentate ligand. In copper complexes, the ligand adopts mainly a facial conformation, whereas the same ligand in nickel complexes has a meridional conformation (Figs 6 and 7).

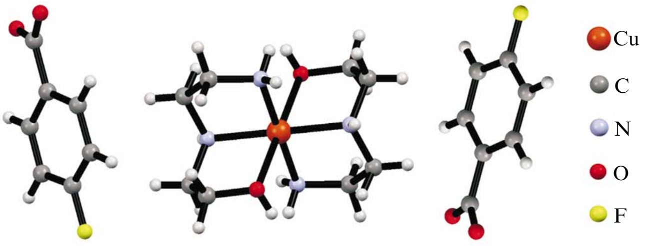


Figure 6. Molecular structure of bis{*N*-(2-hydroxyethyl)ethylenediamine-*N*,*N*′,*O*}copper(II) bis(4-fluorobenzoate).[31]

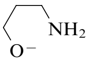
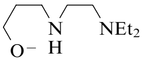
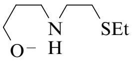
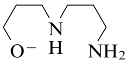
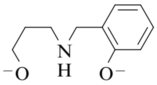
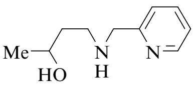
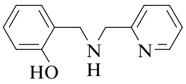
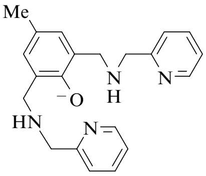
II.2. 3-Aminopropan-1-ol

Unmodified 3-aminopropan-1-ol also acts as a bidentate ligand.[55,58,59] However, unlike 2-aminoethanol, 3-aminopropan-1-ol exists in copper(II) complexes only in the deprotonated state. Due to this fact, mono-, bi- and trinuclear structures is possible can form depending on the reaction conditions (Table 3). In complexes of the latter two types, the hydroxy group is deprotonated and acts as a bridge (Figs 8 and 9), the metal centres in the trinuclear complex being arranged in a linear mode (see Structures **3**).

The functionalization of the amino group of 3-aminopropan-1-ol leads to an increase in the denticity of the ligand, while the coordination properties of the amino and hydroxy groups of amino alcohol remain virtually unchanged. The latter group is deprotonated regardless of the structure of the additional function.[61–66] Even the introduction of the phenol OH group (a much stronger Brønsted acid) does not hinder the deprotonation of the hydroxy group of 3-aminopropan-1-ol.[66] This is the only example of cuboid tetranuclear structures, in which both oxygen atoms are bridging, in the series of N-substituted 3-aminopropan-1-ols. The metal centres in the trinuclear complex are arranged in a linear mode (see Structures **3**).[63] As can be seen from Table 3, the Cu···Cu distance is also almost independent of the nature of the introduced additional group. However, in the case of 2-pyridylmethyl derivatives of 3-aminopropan-1-ol, both an increase in the steric hindrance[67] and a simultaneous change in the electronic structure of the hydroxy group with an increase in the steric hindrance[68] reduce the coordination ability of amino and hydroxy groups and diminish the Brønsted acidity of the latter. As a consequence, mononuclear complexes are formed regardless of the structure of the acidic residue.[68,69] Only the use of 2,6-disubstituted phenol as the ligand results in the formation of a binuclear complex with the 2-pyridylmethylamine chelate ring conjugated with the aminopropanol ring (see, for example, Structures **4**).[70]

Therefore, the functionalization of N-substituents of 3-aminopropan-1-ol in copper(II) complexes does not

Table 3. Characterization of copper(II) complexes with 3-aminopropan-1-ol derivatives.

Ligand (L)	Composition of complex	Bond length /Å		Distance Cu···Cu /Å	Ref.
		Cu–O	Cu–N		
	$[\mathrm{CuL(HL)}]\mathrm{I}$	1.928	1.975	3.034	58
	$[\mathrm{Cu_2L_2(NO_3)_2}]$	1.922	1.970	2.939	59
	$[\mathrm{Cu_3L_4}](\mathrm{NO_3})_2$	1.915	1.981	2.952	60
		1.952	2.018	3.011	
	$[\mathrm{Cu_2L_2}](\mathrm{ClO_4})_2$	1.953	1.972	2.953	61
	$[\mathrm{Cu_2L_2Ni(CN)_4}]$	1.924	1.992	2.981	62
	$[\mathrm{Cu_3L_2(OH)_2}](\mathrm{ClO_4})_2$	1.909	1.976	2.903	63
	$[\mathrm{Cu_2L_2Cl_2}]$	1.952	1.991	2.946	64
	$[\mathrm{Cu_2L_2(EtOH)_2}](\mathrm{BF_4})_2$	1.910	2.007	3.045	65
	$[\mathrm{Cu_4L_4}]$	1.962	1.982	3.147	66
	$[\mathrm{CuL(NO_3)_2}]$	1.990[a]	1.986		67
	$[\mathrm{CuL_2}](\mathrm{OAc})_2$	2.449[a]	2.002		68
		2.494[a]	2.004		
	$[\mathrm{CuL_2}](\mathrm{ClO_4})_2$	2.540[a]	2.042		69
	$[\mathrm{Cu_2(OH)L}](\mathrm{ClO_4})_2$	1.925	1.975	2.924	70
		1.935	1.978		

[a] Cu–OH bonds.

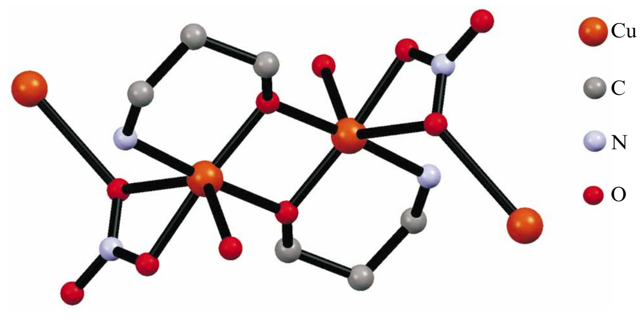


Figure 8. Molecular structure of *catena*[bis(μ-3-aminopropan-1-ol-*N*,*O*)(dinitrato-*O*,*O*′)dicopper(II)].[59]

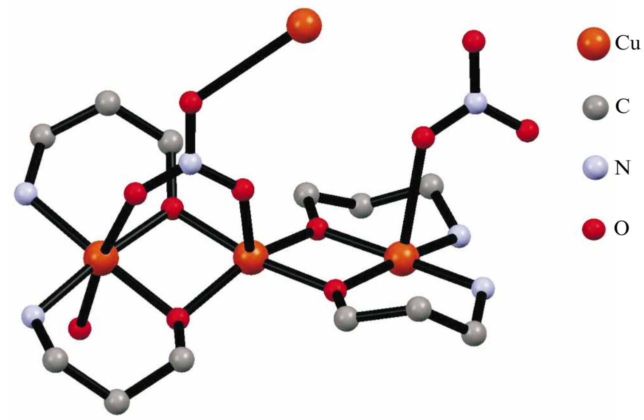


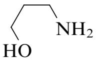
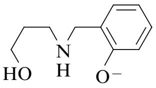
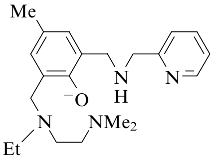
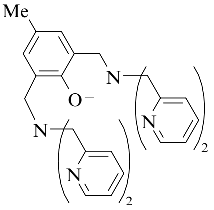
Figure 9. Molecular structure of tetrakis(μ-3-aminopropan-1-olato-*O*,*O*,*N*)tricopper(II) dinitrate.[60]
The CuONOCu interaction through which the complexes are linked together to form layers is shown.

change the coordination ability of the ligand molecule, but controls the degree of coordinative saturation of the metal centres in the resulting complexes. Tridentate ligands based on 3-aminopropan-1-ol provide the formation of bi-, tri- or tetranuclear structures.

Unfortunately, nickel(II) complexes with 3-aminopropan-1-ol and its N-derivatives are much less characterized (Table 4). Because of the shortage of these data, it is impossible to establish relationships between the composition and structure of the complexes and the chemical structure of the ligand used.

Nevertheless, a comparison of the data presented in Tables 3 and 4 shows that 3-aminopropan-1-ol does not

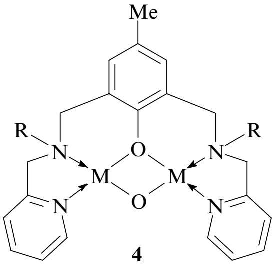
Table 4. Characterization of nickel(II) complexes with 3-aminopropan-1-ol derivatives.

Ligand (L)	Composition of complex	Bond length /Å		Distance Ni···Ni /Å	Ref.
		Ni – OH	Ni – N		
	$[NiL_2](NCS)_2$	2.096	2.085		71
	$[Ni_3L_2(MeOH)_2(OAc)_4]$	2.064	2.065	3.069	44
	$[Ni_2L(OAc)_2(MeOH)(H_2O)]PF_6$	1.948 [a] 2.001 [a]	2.083	3.541	72
	$[Ni_2L(OAc)_2]BF_4$	2.022 [a]	2.118 2.122	3.400	73

[a] The Ni – O⁻ bond.

behave as a Brønsted OH-acid toward nickel(II) ions.[71] As in the case of nickel(II) complexes based on N-substituted 2-aminoethanols (see Table 2), the introduction of the phenol OH group promotes the formation of an oligonuclear complex containing metal centres in a linear arrangement,[44] but the hydroxy group of the 3-aminopropanol chelate ring is not prone to deprotonation. Further transformations of the tridentate ligand to penta- and heptadentate ligands (*i.e.*, the formation of the structure of 2,6-disubstituted phenol, see Table 4) give rise to dimeric nickel(II) complexes (see Structures **4**).[72, 73]

Structures 4



4

M = Cu, Ni; R is alkyl or substituted alkyl

A comparison of the data on the structures of copper(II) and nickel(II) complexes based on 3-aminopropan-1-ol and its N-derivatives shows that the coordination ability of the functional groups of this amino alcohol is influenced mainly by the nature of the metal centre rather than by the functionalization of the ligand. This is manifested in the M – OH and M – N bond lengths. Thus, these bonds are shorter in most of the copper complexes.

A comparison of the coordination ability of the functional groups in unmodified 2-aminoethanol and 3-aminopropan-1-ol and the character of changes in this ability of their N-derivatives shows that the latter amino alcohol is a stronger complex-forming agent. Actually, the Cu – O and Cu – N bonds in complexes with 3-aminopropan-1-ol are substantially shorter than the corresponding bonds in complexes with 2-aminoethanol and its N-derivatives. This gives rise to oligonuclear structures, in which the hydroxy group is deprotonated and acts as a bridge. Due to this fact, the tridentate ligand adopts a meridional conformation in complexes with N-substituted 3-aminopropan-1-ols as opposed to the preferential facial conformation in complexes with N-substituted 2-aminoethanols. An analogue of the propanolamine chelate ring can be formed in a series of phenol derivatives. As can be seen from Tables 1 – 4, the 2-hydroxybenzyl (or 2-hydroxybenzylidene) moiety is favourable for the formation of a binuclear complex due to stronger acidic properties of the phenol OH group and its ability to act as a bridge. The introduction of N-substituted aminomethyl or azomethine moieties in positions 2 and 6 of phenol is used for the construction of ligands that form exclusively binuclear structures (see Structures **4**).[3, 74]

Therefore, the functionalization of 2-aminoethanol and 3-aminopropan-1-ol giving rise to tri- and tetradentate ligands is a promising direction of modifications, because such modifications can be used for the synthesis of rather simple and, consequently, accessible organic molecules, which are prone to form oligonuclear complexes.

III. Amino acids

As it follows from the regularities considered in the previous section, an increase in the Brønsted acidic properties of functional groups, in particular of the hydroxy group, is favourable for the formation of oligonuclear structures due to the enhancement of its coordination ability and, as a consequence, the ability to act as a bridge between metal centres. One of approaches to increasing the acidity of the hydroxy group is based on the transformation of the hydroxymethyl carbon atom into the carboxyl carbon atom. This gives rise to a carboxy group having much stronger Brønsted acidic properties.

Carboxylic acids can form binuclear structures[75] and are used for the design of desired ligands facilitating the construction of oligonuclear structures.[10] The distinguishing feature of these complexes is that the metal centres form a core having an irregular shape, the geometry of which being unpredictable.[76]

By analogy with a comparison of the complexation ability of 2-aminoethanol and 3-aminopropan-1-ol, which form five- and six-membered chelate rings, respectively, let us consider the complexation properties of glycine, β-alanine and their N-derivatives. Actually, the introduction of the amino group into acetic and propionic acids results in a substantial increase in the complexation constants.[21] As a consequence, stable mononuclear complexes with copper(II)[77,78] and nickel(II) ions[79,80] are produced regardless of the size of the closed chelate ring. However, it was shown that under particular conditions, amino acids are not involved as chelating ligands in the coordination of copper or nickel ions;[81,82] instead they act only as bidentate bridging O,O-ligands or even as monodentate O-ligands.[83–85] Thus, β-alanine forms a dimeric tetracarboxylate complex with copper(II) nitrate (Fig. 10), which is structurally similar to the tetraacetate $Cu_2(OAc)_4 \cdot 2\,H_2O$.[86]

A comparison of the characteristics of copper(II) and nickel(II) complexes with unmodified 2-aminoethanol, 3-aminopropan-1-ol, glycine and β-alanine shows that an increase in the acidity of the hydroxy group in amino acids compared to amino alcohols leads to a decrease in its coordination ability in the case of copper(II) complexes (Cu–O bonds are longer) and an increase in the denticity of the amino group as the ligand in nickel(II) complexes (Ni–N bonds are shorter). Therefore, as it was found for 3-aminopropan-1-ol, the coordination ability of functional groups substantially depends on the nature of the central coordinating ion.

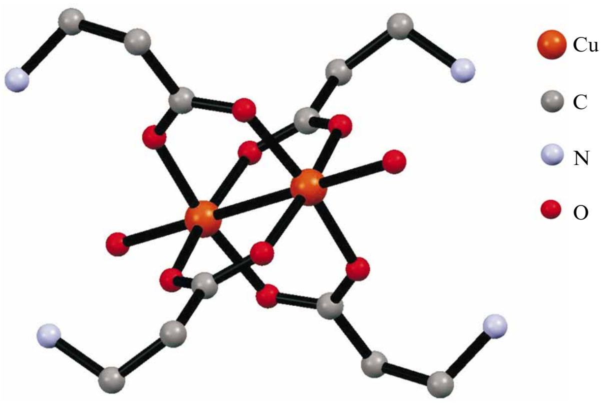


Figure 10. Structure of the cation in tetrakis(μ-β-alanine-*O*,*O*′)diaquadicopper(II) tetranitrate tetrahydrate.[82]

III.1. Glycine

The functionalization of the amino group of glycine increases the denticity of the ligand. However, as can be seen from Tables 5 and 6, neither the nature of functional groups nor their number have an effect on the composition of copper(II) and nickel(II) complexes. In some cases, even variations in the nature of a monodentate co-ligand has only a slight effect on the composition of the resulting complex.[94]

Actually, in copper(II) complexes with glycine and its derivatives (see Table 5), the presence of the second conjugated aminoethanol,[87,88,90,91] ethylenediamine[96,97] or glycinate[99,100] chelate ring or the presence of the second and third related rings[93,94,98,101,102,104–111] or an increase in the denticity of the ligand to five[95] and six[124] provides the formation of 1 : 1 and 1 : 2 mononuclear complexes. A comparison of the bond lengths in copper(II) complexes shows that the N-functionalization reduces the coordination ability of the amino group (in all cases, the Cu–N bond length increases) and does not change or also reduces the coordination ability of the carboxyl oxygen atom. It should be noted that the carboxy group is coordinated in a bidentate fashion almost in all complexes, giving rise to coordination polymers in the crystalline state. Two binuclear[92,103] and one trinuclear[89] complexes based on N-substituted glycines were synthesized under particular conditions only by changing the electronic structure of the conjugated aminoethanol chelate ring or in the case of considerable steric hindrance. Under other conditions, the same ligands can give rise to mononuclear complexes.[90,91] The ability of 2,6-disubstituted phenols[103] to form binuclear complexes (see Structures **4**) does not depend on the nature of electron-donating groups in substituents. It should also be noted that the introduction of a strong electron-donating group as the fourth donor moiety into the iminodiacetic acid leads to the *trans* arrangement of the carboxy groups in the complex as opposed to their *cis* positions in the complexes of the starting acid and its N-derivatives with weak electron-donating groups.

A situation observed for nickel(II) complexes with N-substituted glycines (see Table 6) is, on the whole, similar to that observed for copper(II) complexes. Even the presence of the second conjugated aminoethanol chelate ring with the steric hindrance similar to that observed in copper(II) complexes[112,113] does not give rise to binuclear complexes. A comparison of the bond lengths in nickel(II) complexes shows that in this case the N-functionalization reduces the coordination ability of the amino group (the Ni–N bond length increases) and does not change or also reduces the electron-donating ability of the carboxyl oxygen atom. The only binuclear structure with the Ni···Ni distance of 3.178 Å was synthesized with the use of *N*-carboxymethyl-*N*-methyl-β-alanine.[114]

Therefore, the N-functionalization of glycine leads to an increase in the denticity of the ligand but reduces the coordination ability of both groups. As a result, ligands based on glycine are not prone to form oligonuclear structures in the case of copper(II) complexes, all the more in the case of nickel(II) complexes. Compared to 2-aminoethanol, glycine acquires stronger acidic properties as a result of N-functionalization and is no longer able to increase the coordination ability of both functional groups, which is manifested in the mitigation of the differences

Table 5. Characterization of copper(II) complexes with glycine and its N-derivatives.

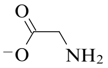
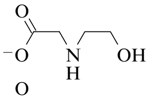
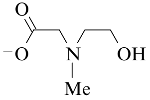
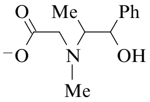
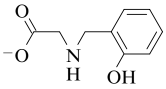
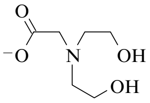
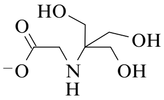
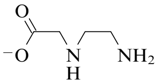
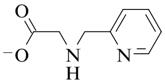
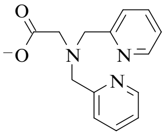
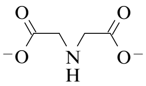
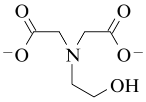
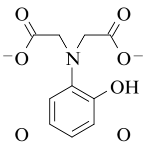
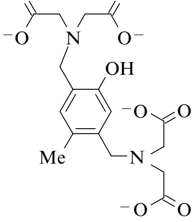
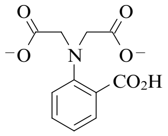
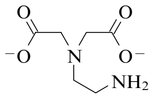
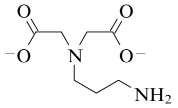
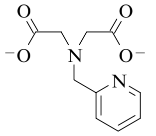
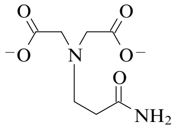
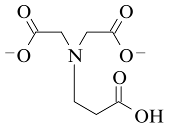
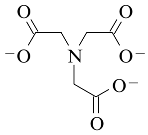
Ligand (L)	Composition of complex	Bond length /Å		Ref.
		$Cu-O(CO_2)$ [a]	$Cu-N$	
	$[CuL_2(H_2O)]$	1.955	1.996	77
	$[CuL_2]$	1.966	2.000	87
	$[CuL_2]$	1.953	2.034	88
	$[Cu_3(L-H)_3(H_2O)_3]$ [b]	1.995	2.017	89
	$[CuL_2]$	1.944	2.050	90
	[CuL(bipy)]Cl (bipy is 2,2′-bipyridine)	1.956	2.005	91
	$[Cu_2(L-H)_2(H_2O)]$ [c]	1.939	1.996	92
	$[CuL_2]$	1.949	2.062	93
	$[CuL]ClO_4$	1.995	2.003	94
	$[CuL_2]$	1.976	2.039	95
	$[CuL]ClO_4$	2.357	2.078	96
	$[CuL_2]$	2.251	2.032	97
	$[CuL]ClO_4$	2.246	2.059	98
	$[CuL(H_2O)_2]$	1.945 (eq) 2.501 (ax)	2.015	99
	$K_2[CuL_2]$	1.960 (eq) 2.441 (ax)	1.973	100
	[CuL]	1.942	2.004	101
	$[CuL(H_2O)_2]$	1.974 (eq)	2.035	102
		1.987 (eq)		
	$[Cu_2L(H_2O)_3]$ [d]	1.983 (eq) 2.693 (ax)	2.043	103

Table 5 (continued).

Ligand (L)	Composition of complex	Bond length /Å		Ref.
		Cu – O(CO$_2$)[a]	Cu – N	
	[CuL(H$_2$O)]	1.926 (eq) 2.295 (ax)	2.058	104
	[CuL(phen)] (phen is 1,10-phenanthroline)	2.264 (ax) 2.426 (ax)	2.150	105
	[CuL(phen)]	2.010 (eq) 2.381 (ax)	2.040	106
	[CuL(pca)] (pca is 2-picolylamine)	1.961 (eq) 2.359 (ax)	2.054	107
	[CuL(H$_2$O)]$_4$	1.950 (eq) 1.977 (eq)	1.998	108
	[CuL(H$_2$O)]	1.963 (eq) 1.972 (eq)	1.997	109
	[Cu(H$_2$L)$_2$]	1.954 (eq) 2.321 (ax)	2.062	110
	Li[CuL]	1.453	2.092	111

[a] ax is axial, eq is equatorial; [b] the Cu···Cu distance is 3.553 Å; [c] the Cu···Cu distance is 2.973 Å; [d] the Cu···Cu distance is 3.403 Å.

Table 6. Characterization of nickel(II) complexes with N-substituted glycines.

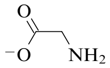
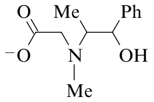
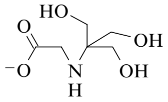
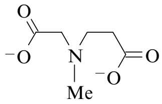
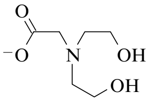
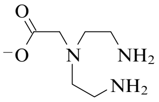
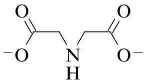
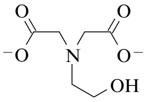
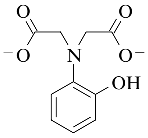
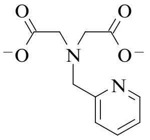
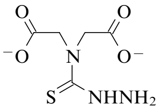
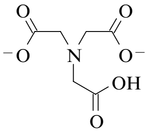
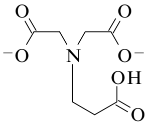
Ligand (L)	Composition of complex	Bond length /Å		Ref.
		Ni – O(CO$_2$)	Ni – N	
	[NiL$_2$(H$_2$O)$_2$] [Ni(HL)(H$_2$O)$_4$](NO$_3$)$_2$	2.067 2.052	2.077	79 81
	[NiL$_2$]	2.032	2.120	112
	[NiL$_2$]	2.037	2.126	113
	[Ni$_2$L$_2$(H$_2$O)$_4$]	2.065	2.086	114

Table 6 (continued).

Ligand (L)	Composition of complex	Bond length /Å		Ref.
		Ni – O(CO$_2$)	Ni – N	
	[NiL$_2$]	2.025	2.107	115
	[Ni(Im)L]ClO$_4$ (Im is imidazole)	2.080	2.113	116
	[NiL]	2.027 (eq) 2.123 (ax)	2.055	117
	[NiL(H$_2$O)$_2$]	2.026 (eq) 2.085 (ax)	2.062	118
	[NiL(H$_2$O)$_2$]	2.033 (eq) 2.047 (eq)	2.065	119
	[NiL(H$_2$)]	2.032 (eq) 2.054 (eq)	2.090	120
	[NiL]	2.015 (eq) 2.094 (ax)	2.082	121
	[NiL(H$_2$)$_3$]	2.021 (eq) 2.025 (eq)	2.146	122
	[NiL(H$_2$)$_2$]	2.054 (eq) 2.074 (ax)	2.070	123

between the copper(II) and nickel(II) complexes, which are clearly observed for N-substituted 2-aminoethanols.

III.2. β-Alanine

The functionalization of the amino group of β-alanine, unlike that of glycine, causes the opposite effect, although both unsubstituted ligands form complexes of the same composition and structure. As can be seen from Table 7, any N-modification of β-alanine leads to the strengthening of the Cu – O coordination bond, *i.e.*, to an increase in the electron-donating ability of the hydroxy group. The tendency of the amino group to be coordinated to metal atoms is retained or slightly decreases. The introduction of an additional functional Brønsted acidic group containing an electron-donating atom gives rise to the conjugated aminoalkanol chelate ring and promotes the formation of bi- (see Refs 130 – 132, 135, 137, 139 and 142), tri- (see Ref. 134) or cuboid tetranuclear [127, 129] coordination compounds of copper(II) (Figs 11 – 13).

A comparison of the bond lengths in copper complexes with β-alanine and its derivatives confirms the stated patterns of relationships. In oligonuclear complexes, both Cu – N and Cu – O coordination bonds are shorter, which attests to the enhancement of the coordination ability of amino and hydroxy groups compared to unmodified β-alanine. It should be noted that the composition of the complex containing Brønsted acid as a co-ligand is independent of the conditions of the synthesis.[131, 132, 142] The composition of complexes containing a Brønsted base as a co-ligand depends on the conditions of their preparation.[98, 136 – 139] The replacement of the carboxyl carbon atom by a sulfur atom (or the S=O group) leads to a considerable increase in the Brønsted acidity of the hydroxy group with the chelate ring size remaining unchanged. As a

Table 7. Characterization of copper(II) complexes with N-substituted β-alanines.

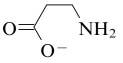
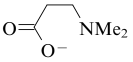
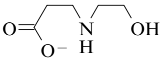
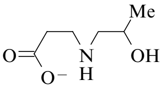
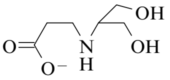
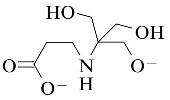
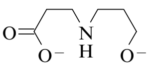
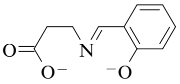
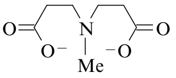
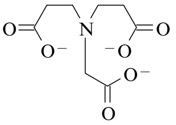
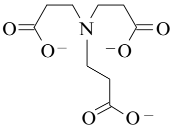
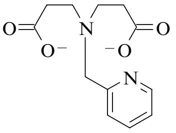
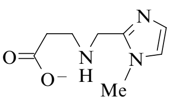
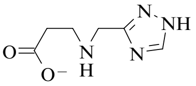
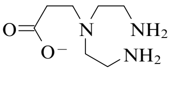
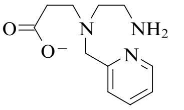
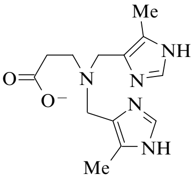
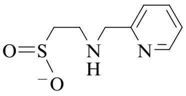
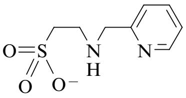
Ligand (L)	Composition of complex	Bond length /Å		Distance Cu···Cu /Å	Ref.
		Cu – O(CO_2)	Cu – N		
	$[CuL_2]$	2.009	1.982		78
	$[Cu_2(HL)_4(H_2O)_2](NO_3)_4$	1.961 1.981		2.639	82
	$[CuL_2]$	1.940 1.943	2.056		125
	$[CuL_2]$	1.968	2.017		126
	$[Cu_4L_4(NO_3)_4]$	1.943	1.979	4.486	127
	$[CuL_2]$	1.966 (eq) 2.319 (ax)	2.024		128
	$[Cu_4L_4]$	1.939 1.960	1.987 1.997	3.193 3.458	129
	$[Cu_2L_2]$	1.919	1.991	3.037	130
	$[Cu_2L_2(H_2O)]$	1.917	1.920	3.028	131
	$[Cu_2L_2(H_2O)_2]$	1.941	1.942	3.384	132
	$[CuL(H_2O)]$	1.994	2.018		133
	$[Cu_4L_2(H_2O)_{10}]SO_4$	1.953	2.013	4.560	127
	$[Cu_3L_2(H_2O)_3]$	1.929 1.964		5.447	134
	$[Cu_2L_2]$	1.944 (eq) 2.226 (ax)	2.033	3.275	135
	$[CuL]ClO_4$	1.935	1.991		136
	$[CuL(py)]ClO_4$ (py is pyridine)	1.916	1.991		137
	$[CuL(SCN)]$	2.032	2.067		138
	$[Cu_2L_2](ClO_4)_2$	1.958	2.020	3.18	139

Table 7 (continued).

Ligand (L)	Composition of complex	Bond length /Å		Distance Cu···Cu /Å	Ref.
		Cu–O(CO$_2$)	Cu–N		
	[CuL]ClO$_4$	2.393	2.024		98
	[Cu$_2$L$_2$](ClO$_4$)$_2$	2.259 2.263	2.081	3.256	137
	[Cu$_2$L$_2$(H$_2$)$_2$]Cl$_2$	1.967[a]	2.000	3.445	140
	[Cu$_2$L$_2$Cl$_2$]	1.978[a]	2.005	3.461	141

[a] The Cu–O(SO$_n$) bond length.

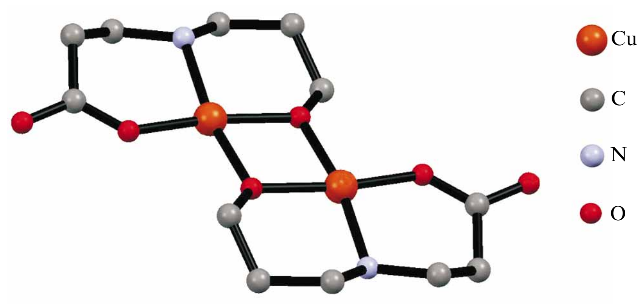


Figure 11. Molecular structure of bis{*N*-(3-hydroxypropyl)-β-alaninato}dicopper(II).[130]

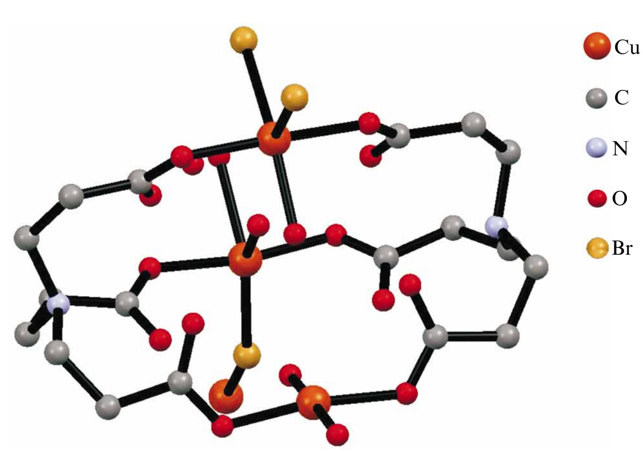


Figure 12. Structure of a fragment of the chain formed by the complexes in the crystals of *catena*[bis(μ$_3$-nitrilotripropionato)(μ-bromo)bromopentaaquatricopper(II)] trihydrate.[134]

result, the electron-donating ability of the hydroxy group increases due to mitigation of the mesomeric effect, and binuclear structures are formed regardless of the co-ligand used.[140, 141, 143]

Therefore, the functionalization of the amino group of glycine diminishes the overall electron-donating ability of the ligand in copper(II) complexes. On the contrary, the N-modification of β-alanine enhances this ability. As in the case of amino alcohols, the formation of a six-membered chelate ring in the case of amino acids is more favourable and promotes the formation of oligonuclear coordination compounds of copper(II). Glycine is a stronger Brønsted acid than β-alanine, which is responsible for the formation of a stable mononuclear compound with a complete coor-

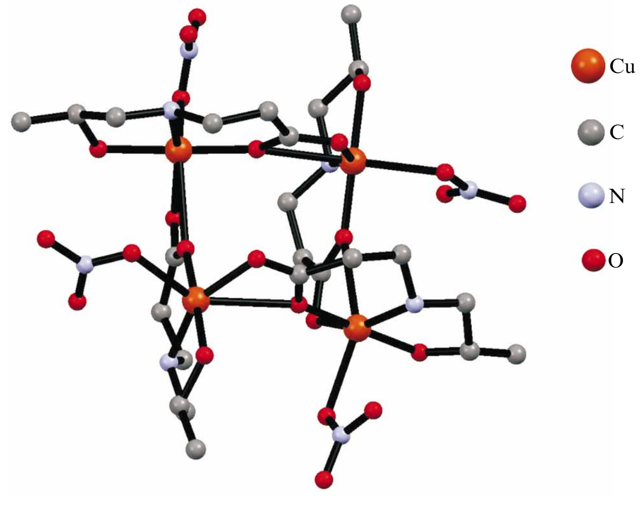
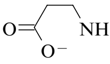
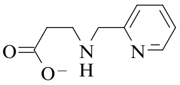
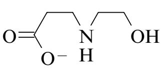
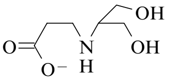
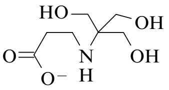
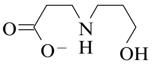
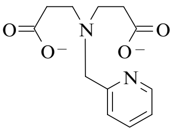
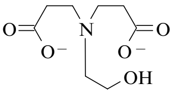
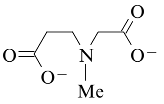
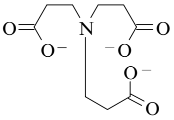
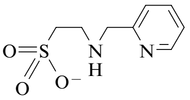
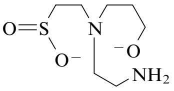


Figure 13. Molecular structure of tetrakis{μ-*N*-(2-hydroxypropyl)-3-aminopropionato}tetra(nitrato-*O*)tetracopper(II).[127]

dination sphere. Actually, the competitive closure of the glycinate and β-alaninate chelate rings gives rise to a stable mononuclear complex containing deprotonated acetate groups.[123]

Although data on nickel(II) complexes with N-substituted β-alanines (Table 8) are not so numerous, the general features found for copper(II) complexes are observed also for the Ni metal centre. As opposed to N-substituted glycines, any N-modification of β-alanine leads to the strengthening of the Ni–O bond, *i.e.*, to the enhancement of the electron-donating ability of the hydroxy group. The coordination ability of the amino group in mononuclear nickel(II) complexes remains unchanged,[135, 144, 145] whereas it increases in oligonuclear structures.[146–149] Consequently, as opposed to copper(II) complexes, the influence of the nature of the metal centre on the coordination ability of functional groups is the same as in the case of amino alcohols. The distinguishing features of oligonuclear nickel(II) complexes based on β-alanine derivatives containing ⩾ 4 metal centres is that the metal atoms are in one plane (Figs 14 and 15).[146, 147, 149]

Table 8. Characterization of nickel(II) complexes with N-substituted β-alanines.

Ligand (L)	Composition of complex [a]	Bond length /Å		Distance Ni···Ni /Å	Ref.
		Ni–O(CO_2)	Ni–N		
	[$NiL_2(H_2O)_2$]	2.085	2.075		80
	[NiL_2]	2.043	2.107		135
	[NiL_2]	2.026 (eq) 2.069 (ax)	2.041		144
	[NiL_2]	2.043 (eq) 2.044 (ax)	2.077		145
	[$NiL(H_2O)(py)$]Cl	2.042	2.074		145
	[NiL_2]	2.062	2.080		145
	[$(NiL)_6Ni_7(OH)_{12}$]$(OH)_2$	2.051 (eq) 2.132 (ax)	2.065	3.012 3.032	146
	[$(NiL)_6Ni_{12}(OH)_{22}$]Cl_2	2.096 (eq) 2.125 (ax)	2.057	1.988 3.188	147
	[$Ni_2L_2(H_2O)_2$]	2.039	2.031	3.216	148
	[$Ni_2L_2(H_2O)_4$]	2.065	2.086	3.178	114
	[$Ni_4L_2(OH)_2(H_2O)_6$]	2.007 2.094	2.065	3.058 3.153	149
	[$Ni_4L_4(OH)_4$]	2.125 [a] 2.129 [a]	2.094 2.106	3.096 3.138	150
	[NiL_2]	2.088 [a]	2.112		151
	[Ni_2L_2]	2.128 [a] 2.232 [a]	2.153	3.012	152

[a] The Ni–O(SO_n) bond length.

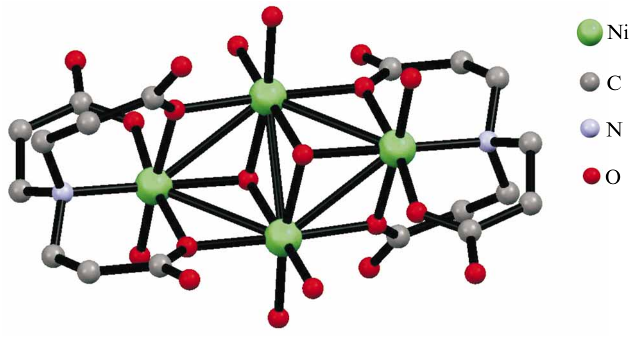


Figure 14. Molecular structure of bis(μ_3-hydroxo)bis(μ_3-nitrilotripropionato)hexaaquatetranickel(II) dihydrate.[149]

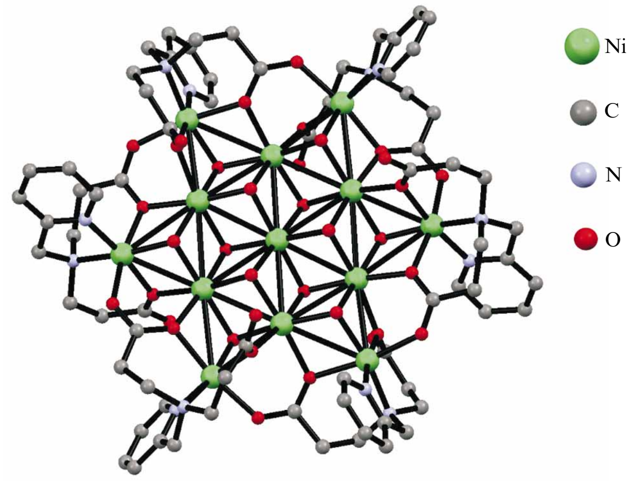


Figure 15. Molecular structure of hexakis{*N*-(2-pyridylmethyl)iminodipropionatonickel(II)}dodecahydroxoheptanickel(II) hydroxide dihydrate.[146]

As in the copper(II) complexes, the replacement of the carboxyl carbon atom by a sulfur atom (or the S=O group) leads to a considerable increase in the Brønsted acidity of the hydroxy group with the chelate ring size remaining unchanged. This gives rise to binuclear nickel(II) complexes.[150, 152]

Therefore, the functionalization of the amino group of β-alanine in nickel(II) complexes increases the total coordination ability of the ligand as opposed to the N-modification of glycine. As a result, the closure of the six-membered amino acid chelate ring, as in the case of amino alcohols, is more favourable and facilitates the formation of oligonuclear coordination compounds of copper(II) and nickel(II).

IV. Enamino ketones

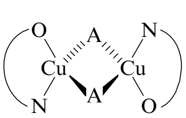
Enamino ketones are structurally similar to β-alanine and comprise an important class of N,O-ligands that form a six-membered chelate ring. As opposed to amino acid derivatives, enamino ketones are only NH-acids, *i.e.*, the electron-donating ability of oxygen and nitrogen atoms in these compounds radically differs from that in β-alanine.

Figure 16. Molecular structure of bis(3-amino-1-phenylbut-2-enoato)copper(II).[153]

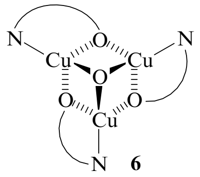
In copper(II) and nickel(II) complexes (Tables 9 and 10), unmodified bidentate enamino ketones act as monoprotic NH-acids [153, 154, 162, 168] and form mononuclear 1 : 2 chelates (Fig. 16). The M–O and M–N bonds are shorter than the corresponding bonds in chelates with amino alcohols and amino acids, which attests to higher coordination ability of oxygen and nitrogen atoms in enamino ketones. Due to the enhancement of the complexation ability of enamino ketones, the latter are prone to give stable mononuclear compounds with a complete coordination sphere.

In complexes with tridentate N-substituted enamino ketones, the Cu–O bond length decreases, whereas the Cu–N bond length slightly increases (see Table 9). As mentioned above, a similar situation is observed for β-alanine derivatives, due to which the formation of oligonuclear complexes becomes possible. Thus, almost all known tridentate N-substituted enamino ketones are prone to form oligonuclear complexes, including bi- (Structures **5**),[156, 158, 161, 163] tri- (Structures **6**) [159, 160] and tetranuclear (see Structures **1**) [163] complexes. A further increase in the denticity of the ligand to four,[165, 167] five [164] or six [162] gives rise exclusively to mononuclear copper(II) complexes (see Table 9). The lengths of Cu–O and Cu–N coordination bonds remain virtually unchanged and, consequently, the strong steric crowding substantially limits the close arrangement of several metal centres.

Structures 5, 6



5



6

A is the donor atom of the acid anion

An increase in the denticity of the ligand in nickel(II) complexes (see Table 10) has almost no effect on the number of metal centres in the complexes; in all cases mononuclear structures are formed.[154, 155, 167 – 173] Only the use of a heptadentate co-ligand based on 2,6-disubstituted phenol [174] enables researchers to prepare a binuclear nickel(II) complexes containing enamino ketone derivatives. A comparative analysis of the lengths of Ni–O and Ni–N coordination bonds shows that these values decrease as the denticity increases. This is indicative of the enhancement of coordination ability of ligands, giving rise to mononuclear

Table 9. Characterization of copper(II) complexes with enamino ketone derivatives.

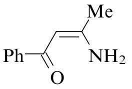
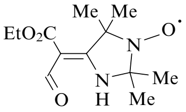
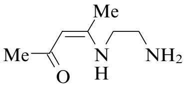
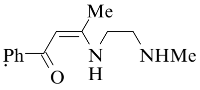
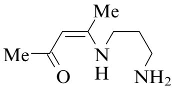
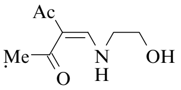
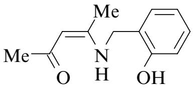
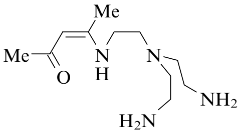
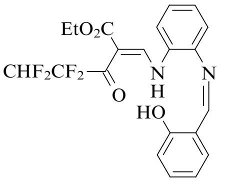
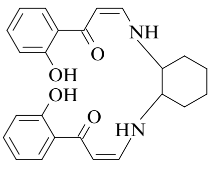
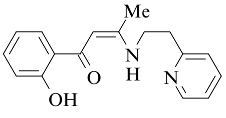
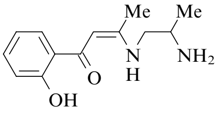
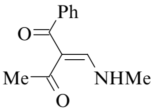
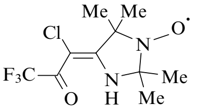
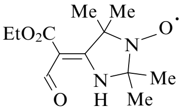
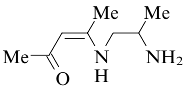
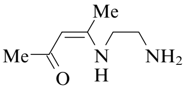
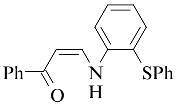
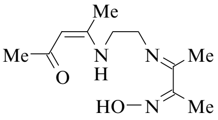
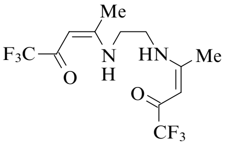
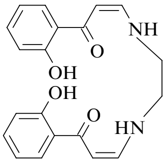
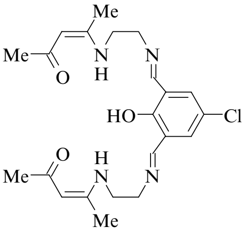
Ligand (L)	Composition of complex	Bond length /Å		Distance Cu···Cu /Å	Ref.
		Cu–O	Cu–N		
	$[Cu(L-H)_2]$	1.954	1.919		153
	$[Cu(L-H)_2]$	1.871 1.901	1.941 1.992		154
	$[Cu(L-H)(4\text{-}Im)]ClO_4$ (4-Im is 4-methylimidazole)	1.906	1.933		155
	$[Cu_2(L-H)_2Cl_2]$	1.918	1.959	3.445	156
	$[Cu_2(L-H)_2Br_2]$	1.912	1.951	3.545	157
	$[Cu_2(L-H)_2(OAc)_2]$	1.924	1.938	3.305	158
	$[Cu_3(L-H)_3(OH)](ClO_4)_2$	1.917	1.968	3.252 3.317	159
	$[Cu_3(L-H)_3(OH)](ClO_4)_2$	1.893 1.915	1.946	3.172 3.202	160
	$[Cu_2(L-H)_2Cl_2]$	1.926	1.965	3.418	161
	$[Cu_4(L-2\,H)_4]$	1.915	1.901 1.910	3.100 3.344	162
	$[Cu_2(L-2\,H)_2]$	1.881 1.900	1.974 2.004	2.987	163
	$[Cu(L-H)]BPh_4$	1.894	1.930		164
	$[Cu(L-2\,H)]$	1.943	1.925		165
	$[Cu(L-2\,H)]$	1.890 1.904	1.900 1.952		166
	$[Cu(L-H)(OAc)]$	1.897	1.960		167
	$[Cu_2(L-H)_2(OAc)_2]$	1.926 1.934	1.913 1.967	3.507	167

Table 10. Characterization of nickel(II) complexes with enamino ketone derivatives.

Ligand (L)	Composition of complex	Bond length /Å		Ref.
		Ni–O	Ni–N	
	$[Ni(L-H)_2]$	1.833	1.901	162
	$[Ni(L-H)_2(MeOH)_2]$	1.981	2.136	168
	$[Ni_2(L-H)_4]$[a]	1.942	1.986	154
	$[Ni(L-H)(N_3)]$	1.831	1.843	169
	$[Ni_2(4\text{-}Im-H)(L-H)_2]ClO_4$ (see [b])	1.841	1.857	155
	$[Ni(L-H)_2]$	2.024	2.008	170
	$[Ni(L-2H)]$	1.828	1.842	171
	$[Ni(L-2H)]$	1.851	1.861	172
	$[Ni(L-2H)]$	1.850	1.854	173
	$[Ni_2(L-3H)]Br$ (see [c])	1.836	1.837	174

[a] The Ni··· Ni distance is 3.262 Å; [b] the Ni··· Ni distance is 5.840 Å; [c] the Ni··· Ni distance is 3.130 Å.

compounds with a complete coordination sphere. Apparently, as in copper(II) complexes, this is due to strong steric hindrance created by the ligand.

To conclude this section, it should be noted that the functionalization of the amino group of enamino ketones enhances the total coordination ability of the ligand, as in the case of β-alanine, despite the different nature of N,O-donor groups. However, the closure of the six-membered chelate ring facilitates the formation of oligonuclear coordination structures only in the case of copper(II) complexes with tridentate N-substituted enamino ketones. An increase in the denticity of the ligand in nickel(II) complexes results in the formation of mononuclear chelates due to strong steric hindrance created by the ligand and the enhancement of its electron-donating ability.

V. Single-molecule magnets

A comparative analysis of the magnetic properties of oligonuclear complexes depending on the ligand structure shows that these properties of copper complexes with N-substituted amino alcohols, amino acids and enamino ketones (Table 11) substantially depend on the distance between metal centres regardless of their arrangement. At Cu···Cu distances < 3.045 Å observed in dimeric complexes,[29, 59, 62, 64, 65] there is a strong exchange interaction between metal centres responsible for antiferromagnetic properties. At Cu···Cu distances in the range of 3.144 – 3.553 Å, the exchange interaction between metal centres becomes substantially weaker, resulting in weak antiferromagnetic properties[66, 89, 103, 156 – 160] or their absence.[38] At longer Cu···Cu distances (> 4.486 Å), metal centres interact with each other through bridging atoms and, consequently, complexes exhibit ferromagnetic properties.[127, 134, 161]

Table 11. Characterization of the magnetic properties of polynuclear copper(II) complexes with N-substituted 2-aminoethanols, 3-aminopropan-1-ols, glycines, β-alanines and enamino ketones.

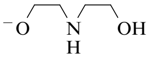
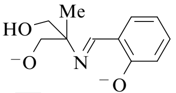
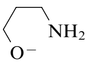
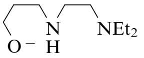
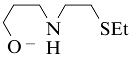
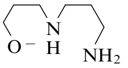
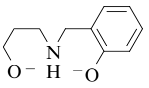
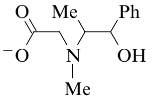
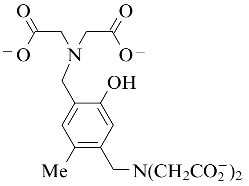
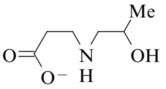
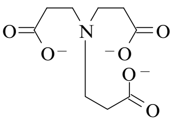
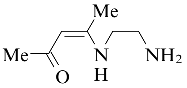
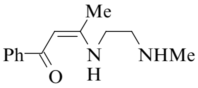
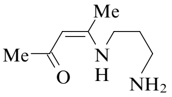
Ligand (L)	Composition of complex	Distance Cu···Cu /Å	Magnetic susceptibility χ_mT/cm^3 mol^{-1} K (T/K)	Magnetic moment μ_{eff} (T/K)[a] and exchange integral J/cm^{-1}	Type of interaction between metal centres	Ref.
	$[Cu_2L_2](SCN)_2$	2.865	–	μ_{eff} = 2.11μB (295)	exchange	29
	$[Cu_4L_4]$	3.144 3.522	1.65 (300)	–	non-interacting metal centres	38
	$[Cu_2L_2(NO_3)_2]$	2.939	0.0012 (300) < 0.0002 (< 50 K)	$2J$ = −387 cm^{-1}	strong antiferromagnetic	59
	$[Cu_2L_2Ni(CN)_4]$	2.981	0.0005 (300) < 0.0001 (75)	$2J$ = −622 cm^{-1}	strong antiferromagnetic	62
	$[Cu_2L_2Cl_2]$	2.946	0.0006 (300) 0.00012 (80)	μ_{eff} = 1.14 μB (295)	strong antiferromagnetic	64
	$[Cu_2L_2(EtOH)_2](BF_4)_2$	3.045	–	μ_{eff} = 0.50 μB (295) $2J$ = −860 cm^{-1}	strong antiferromagnetic	65
	$[Cu_4L_4]$	3.147	0.85 (300) 0.001 (50)	–	antiferromagnetic	66
	$[Cu_3L_3(H_2O)_3]$	3.553	0.65 (295) 0.4 (50)	–	antiferromagnetic	89
	$[Cu_2L(H_2O)_3]$	3.403	0.867 (100 – 300) 0.942 (15)	–	weak antiferromagnetic	103
	$[Cu_4L_4(NO_3)_4]$	4.486	1.77 (100 – 300) 3.22 (1.8)	–	magnetic	127
	$[Cu_3L_2(H_2O)_3]$	5.447	1.37 (100 – 300) 0.98 (1.8)	–	ferromagnetic (transition to antiferromagnetic with lowering temperature)	134

Table 11 (continued).

Ligand (L)	Composition of complex	Distance Cu···Cu / Å	Magnetic susceptibility χ_mT / cm^3 mol^{-1} K (T/K)	Magnetic moment μ_{eff} (T/K)[a] and exchange integral J / cm^{-1}	Type of interaction between metal centres	Ref.
	$[Cu_2(L-H)_2Cl_2]$	3.445	0.0012 (300) 0.005 (50)	$\mu_{eff} = 1.77\ \mu_B$ (300) $\mu_{eff} = 1.30\ \mu_B$ (4.6)	antiferromagnetic	156
	$[Cu_2(L-H)_2Br_2]$	3.545	–	–	antiferromagnetic	157
	$[Cu_2(L-H)_2(OAc)_2]$	3.305	–	–	weak antiferromagnetic	158
	$[Cu_3(L-H)_3(OH)](ClO_4)_2$	3.252 3.317	0.0014 (270) 0.005 (50)	$\mu_{eff} = 3.12\ \mu_B$ (270) $\mu_{eff} = 1.94\ \mu_B$ (10)	antiferromagnetic	159
	$[Cu_3(L-H)_3(OH)](ClO_4)_2$	3.172 3.202	1.27 (295) 1.78 (5)	–	antiferromagnetic	160
	$[Cu_2(L-H)_2Cl_2]$	3.418	0.0014 (290) 0.005 (50)	$\mu_{eff} = 1.83\ \mu_B$ (270) $\mu_{eff} = 1.90\ \mu_B$ (50)	ferromagnetic	161

[a] Here and in Table 12, the value is given per g-atom of metal; the temperature in K is given in parentheses.

Therefore, the structure of the ligand exerts a considerable effect not only on the number of metal centres in the oligonuclear complex but, as a consequence, also on its magnetic properties as a single-molecule magnet. Small ligand molecules are inefficient for the construction of oligonuclear complexes, because the closely spaced metal centres are involved in a strong interaction. Relatively large ligands having denticity ⩾ 4 and containing bulky substituents are responsible for considerable steric hindrance to interactions between metal centres. As a result, the latter behave as individual centres despite the oligonuclear structure of the complex as a whole.

A systematic analysis of the influence of the structure of chelating ligands differing from the ligands considered in the present review in the structures and the character of denticity (O,O-, N,N-, N,O-, *etc.*) on the magnetic properties of copper complexes is absent in the literature. However, based on publications on particular classes of organic compounds, it can be stated that in the case of, for instance, N,N-ligands having denticity ⩾ 2, intramolecular exchange interactions are determined primarily by the overall geometry of the complex rather than by the distance between metal centres.[22, 175, 176] This is attributed to the fact that the complex necessarily includes anions of inorganic acids, which are directly involved in exchange interactions even if metal centres are far from each other.[175–177] In the presence of an O-donor group in the chelating ligand, the type and strength of exchange interactions in polynuclear copper complexes substantially depend on the distance between the metal centres.[178–180] This is apparently associated with a smaller number of possible types of mutual arrangement of metal centres in complexes with N,O-ligands compared, for example, to complexes with N,N-ligands.

A comparative analysis of the magnetic properties of oligonuclear nickel(II) complexes depending on the structure of the ligands (Table 12) shows that the number of metal centres and their mutual arrangement have a consid-

Table 12. Characterization of the magnetic properties of polynuclear nickel(II) complexes with N-substituted 2-aminoethanols, 3-aminopropan-1-ols, glycines, β-alanines and enamino ketones.

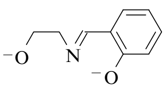
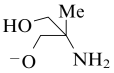
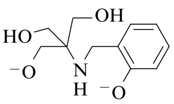
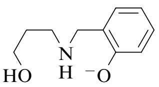
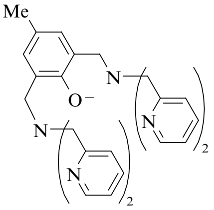
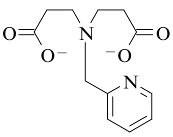
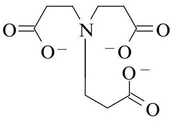
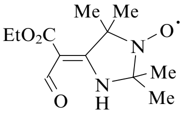
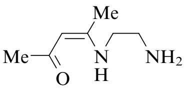
Ligand (L)	Composition of complex	Distance Ni···Ni / Å	Magnetic susceptibility χ_mT / cm^3 mol^{-1} K (T/K)	Magnetic moment μ_{eff} (T/K)	Type of interaction between metal centres	Ref.
	$[Ni_4L_4(MeOH)]$	3.032 3.195	5.6 (300) 11.4 (7.5)	–	ferromagnetic	47
	$[Ni_4L_4(OAc)_4]$	3.061 3.131	4.8 (300) 10.4 (8)	–	ferromagnetic	51

Table 12 (continued).

Ligand (L)	Composition of complex	Distance Ni···Ni /Å	Magnetic susceptibility $\chi_m T$/cm^3 mol^{-1} K (T/K)	Magnetic moment μ_{eff} (T/K)	Type of interaction between metal centres	Ref.
	$[Ni_4L_4]$	3.021	5.3 (300) 11.8 (11)	–	ferromagnetic	54
	$[Ni_3L_2(MeOH)_2(OAc)_4]$	3.069	3.76 (300) 4.01 (8)	–	weak ferromagnetic	44
	$[Ni_2L(OAc)_2]BF_4$	3.400	–	$\mu_{eff} = 3.07\mu_B$ (300)	weak ferromagnetic	73
	$[(NiL)_6Ni_{12}(OH)_{22}]Cl_2$	1.988 3.188	20.4 (12.6)	–	antiferromagnetic	181
	$[Ni_4(OH)_2L_2(H_2O)_6]$	3.058 3.153	5 (100 – 300) 7 (3.4)	–	ferromagnetic (transition to weak antiferromagnetic with lowering temperature)	149
	$[Ni_2(L-H)_4]$	3.262	–	$\mu_{eff} = 5.35\ \mu_B$ (300) $\mu_{eff} = 1.50\ \mu_B$ (2)	antiferromagnetic	154
	$[Ni_2(4\text{-Im}-H)(L-H)_2]ClO_4$	5.840	0	–	diamagnetic	155

erable effect on these properties. Due to exchange interactions, tetranuclear complexes acquire properties of ferromagnets.[47, 51, 54] Not only two closely spaced metal centres[73, 154] but also the planar arrangement of four metal centres[149] are conditions for the appearance of weak antiferromagnetic properties. An increase in the number of metal centres promotes the enhancement of this type of interactions.[181]

Therefore, the structure of ligands greatly influences the number of metal centres in oligonuclear nickel(II) complexes and their magnetic properties, as in copper complexes. However, definitive conclusions about the effect of the structure of the ligand on the magnetic properties cannot be drawn because of the shortage of information.

Data on the influence of the structure of chelating ligands on the magnetic properties of nickel(II) complexes are limited to one class of N,S-ligands, for which intramolecular exchange interactions also substantially depend on the number of metal centres and their mutual arrangement.[182]

* * *

The deliberate design of ligands providing the cluster arrangement of metal centres requires an extensive database of experimental data in order to establish relationships between the structure of the ligand and the structure of the resulting oligonuclear complex. For this approach to be employed, it is necessary not only to systematically arrange the available data but also to perform the synthesis of a series of ligands with successively changing structures, as well as to estimate their complexation ability. The present review is one of the first attempts to systematically consider data available in the literature on the influence of the structure of the ligand on the structure of copper(II) and nickel(II) complexes in series of N-substituted 2-aminoethanols, 3-aminopropan-1-ols, glycines and β-alanines and is a continuation of the field of research founded by the Corresponding Member of the Russian Academy of Sciences M A Porai-Koshits, the author of classic works on crystal chemistry in the USSR. The solution of this difficult problem seems to be realistic because modern methods of organic and coordination chemistry allow researchers to synthesize required series of organic molecules and complexes based on these molecules. Certain relationships have been already established. Thus, a ligand belonging to a series of derivatives considered above will facilitate the formation of oligonuclear copper(II) and nickel(II) complexes if the ligand is tetradentate and tends to form six-membered chelate rings based on 3-aminopropan-1-ol or β-alanine or five-membered chelate rings based on sterically hindered 2-aminoethanol derivatives. There is no doubt that further investigations of complexes with N,O-ligands will reveal new regularities and provide theoretical grounds for the practical application of materials based on these complexes.

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