Review

Structural diversity of copper(II) amino alcoholate complexes

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ABSTRACT

Amino alcohols which carry both amino and hydroxyl groups in the same molecule are good chelating and bridging ligands. They have been broadly used for the preparation of copper(II) amino alcoholate complexes through the self-assembly process, which generally leads to the formation of diverse structures from mononuclear to polynuclear copper(II) clusters. There are three main factors to control the nuclearity of these clusters: (i) the molar ratio of Cu(II) to amino alcohol, (ii) the choice of the counter anions and (iii) the nature of the amino alcohol. These structures can be used as model systems in magnetic studies, allowing a better understanding about the magnetic interactions between the metal centres, as well as simplified models of the active sites of many copper enzymes, which catalyse the hydroxylation of alkanes and other substrates. This review comprises the literature survey of copper (II) amino alcoholate complexes, presenting the structural diversity from mono- to nonanuclear clusters, from discrete molecules to coordination polymers or networks obtained using small bridging and chelating amino alcoholates with copper(II) ions. Several applications of these complexes have been presented.

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Contents

1. Introduction

The coordination chemistry of polynuclear copper(II) complexes has received considerable attention due to their intriguing architectures and potential applications in the fields of coordination polymers [1–4], magnetochemistry [5–8], bioinorganic chemistry [9–13] and catalysis [14–16]. These polynuclear copper(II) complexes can be obtained using cheap and commercially available multidentate amino alcohols, which having both amino and alcohol groups can act as a bridging and chelating N- and O-donor ligands. An early review on this chemistry is from the year 1995 [17].

Amino alcohols have been broadly used in the past six decades in the preparation of copper(II) complexes through the self-assembly process, since the hydroxyl groups of amino alcohols can be easily deprotonated in the presence of copper(II) salts and the resulting alcoholate ions can act as a bridge between copper atoms leading to the formation of diverse structures; from mononuclear to nonanuclear copper(II) clusters, coordination polymers and networks. In addition to the structural studies, the magnetic properties of copper(II) amino alcohol complexes have been extensively studied. These alkoxo-bridged complexes can act as model systems for Cu(II) based magnetic materials allowing a better understanding on the magnetic interactions between the metal centres, since the single unpaired electron on each copper (II) ion forms a relatively simple magnetic exchange system. So far, over 70 articles have been published presenting the magnetic properties along with the preparation and structural characterization of these complexes.

Having N,O-environments around the copper(II) atoms and containing polynuclear structures, the copper(II) amino alcoholate complexes can also be viewed as simplified models of active sites of many copper enzymes such as particulate methane monooxygenase (pMMO) that can catalyse the hydroxylation of alkanes and other substrates. During the past ten years, copper(II) amino alcoholate complexes have been successfully applied as homogenous catalysts for the oxygenation of alkanes to alkyl peroxides, alcohols and ketones, the oxidation of alcohols to ketones and the hydrocarboxylation of cyclic and linear alkanes to carboxylic acids [16]. Moreover, within the same timeframe as the catalytic studies, reports have been published where copper(II) amino alcoholate complexes have been used as precursors in chemical vapour deposition (CVD) of crystalline copper thin films [18–27].

This review focuses on illustrating the structural diversity of copper(II) amino alcoholate complexes and their use in several applications. The representative amino alcohols, which are utilized as proligands in the formation of these complexes, are presented in Scheme 1. The Schiff base derivatives of amino alcohols are not included.

The complexes presented here are divided into five categories by the number of the copper ions in a structural unit, i.e. to the mono-, di-, tri- and tetranuclear structures as well as complexes with higher nuclearity. Heterometallic amino alcoholate complexes are included when necessary although the topic has been reviewed recently [28].

2. Syntheses of copper(II) amino alcoholate complexes

The syntheses of copper(II) complexes with didentate N,N-dialkylaminoethanols, $[Cu_2(R_2NCH_2CH_2O)_2X_2]$ (where R = CH_3, C_2H_5, C_4H_9, X = Cl^-, Br^-) were first presented by Hein and Beerstecher 60 years ago [29]. These dinuclear complexes were made of copper(II) chloride or bromide and N,N-disubstituted amino alcohols with copper to amino alcohol ratios of 1:2. The use of the excess amino alcohol enhanced the deprotonation of coordinated amino alcohols leading to the complex formation in a 1:1 ratio. Hein and Beerstecher also predicted that the complexes were dinuclear alkoxo-bridged ones, which was later confirmed [30]. During the 1960s, the magnetic properties of these complexes were studied [31,32] and new complexes with mono- and dicarboxylic acids were reported [33]. The synthetic procedure presented by Hein and Beerstecher is still one of the main routes in the preparation of copper(II) amino alcoholate complexes.

As one molecule of amino alcohol in the reactions acts as a base it can be replaced by organic bases like triethylamine or inorganic bases as sodium hydride or hydroxide. Generally number of the metal atoms in the complex can be adjusted by the stoichiometry and choice of the ligands and anions. The pH control is important if the reaction is done in water. As copper(II) ion is a labile cation, also crystal packing energies are important in the formation of a given complex. In this respect the alkylation of N atom decreases a number of possible H-bonds and thus influences on the crystal packing. Mononuclear neutral copper(II) amino alcoholate complexes from simple amino alcohols, e.g. amino ethanol or amino propanol, are not common and their preparation demands special conditions. Especially strong basic anions like methoxide can be useful [19]. On the other hand, the mononuclear Cu(II) complex with a multidentate diamino alcohol (N,N-dibenzyl-N′,N′-bis(2-hydroxyethyl)ethylenediamine) is easy to prepare. The product is useful as a starting material for polynuclear homo and heteronuclear metal complexes [34].

3. Structures of copper(II) complexes with amino alcoholates

In the copper(II) complexes with amino alcohols, the alcohol group is usually deprotonated and it can bridge two to four copper(II) ions together to form polynuclear complexes. Consequently, quite a few mononuclear complexes are obtained so far. The coordination number of the metal ion varies between four and six. The copper(II) ion has a strong Jahn-Teller distortion due to the d^9 electron configuration leading typically to the formation of distorted
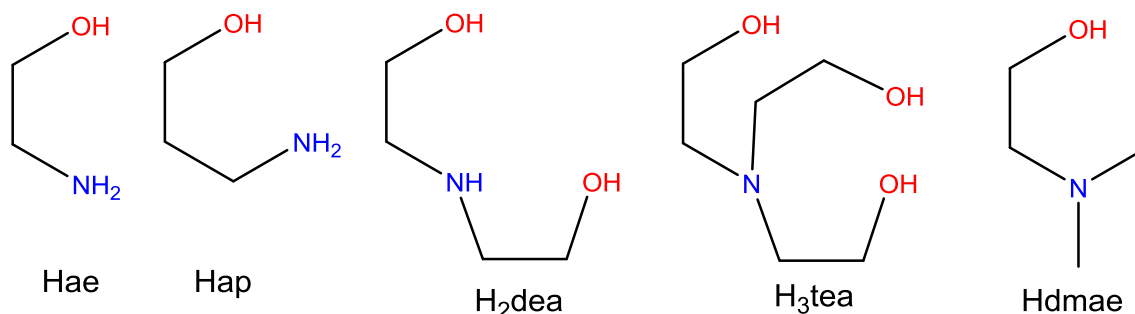
Scheme 1. Common amino alcohol proligands for the copper(II) complexes presented in this review. More intricate ligands have been obtained by alkyl substitution of NH and CH hydrogens as in N,N-dimethylaminoethanol, Hdmae.

forms of octahedron (tetragonal elongation or compression). Also different distorted forms of square pyramid and trigonal-bipyramid are common. The coordination number of four is quite rare (square planar or tetrahedral coordination) in copper(II) complexes with amino alcoholates.

3.1. Mononuclear Cu(II) amino alcoholate and amino alcohol complex units with their H-bonded dimers and ligand bridged complexes

3.1.1. Mononuclear Cu(II) units with amino alcoholates and di- or tridentately coordinated amino alcohols

The mononuclear copper(II) amino alcoholate and amino alcohol complexes presented below are generally obtained using didentately or tridentately coordinating vicinal amino alcohols which can form five-membered chelate rings. Within these mononuclear (typically in a 1:2 metal to ligand ratio) complexes, the amino alcohols are coordinated as neutral, anionic or both type ligands. The mononuclear units of copper(II) complexes with two didentately coordinating amino alcohols have a general formula of $[Cu(aa)_2]$ or $[Cu(aa)(Haa)]^+$, where Haa = amino alcohol and aa^- = amino alcoholate anion (Fig. 1i–ii).

The possible remaining coordination sites of copper(II) ions can be occupied by the donor atoms of solvent molecules or counter ions. The chelating amino alcoholate ligands adopt the *trans*-arrangement in the square planar, square pyramidal or elongated octahedral coordination environment of copper(II) ions depending on the neutral coordinating donors (D_n, $n = 0$–2) in the $[Cu(aa)_2D_n]$ [19–21,35–41]. Separated mononuclear units of type $[Cu(aa)(Haa)]^+$ and $[Cu(aa)(Haa)_2]^+$ are rare as these units generally form H-bonded dimers, however, $[Cu(ae)(Hae)I]$ [42] and $[Cu(ae)(Hae)_2]$triflate [43] can be mentioned.

Also a few complexes where a simple amino alcohol molecule acts as a neutral ligand are worth to include. Generally, in these $[Cu(Haa)_2]^{2+}$ mononuclear complexes (Fig. 1iii) [44–54], the hydroxyl oxygen atoms are positioned axially with respect to the square planar coordination plane while the equatorial sites are occupied by the nitrogen atoms of the amino alcohols in a *trans* position and the coordinating atoms of the anions (carboxylate anions pre-

vailing). The coordination number of copper(II) varies between four and six as seen in $[Cu(Haa)_2]^{2+}$, $[Cu(Haa)_2X]^+$ and $[Cu(Haa)_2X_2]$ (X = an anion).

3.1.2. H-bonded dimeric Cu(II) units with amino alcoholates and di- or tridentately coordinated amino alcohols

The H-bonded copper(II) amino alcohol dimers $[Cu(aa)(Haa)]_2^{2+}$ (coordinating anions or counter ions: Cl^-, Br^-, I^-, ClO_4^-, NCS^-, NO_3^-, SO_4^{2-}, CrO_4^{2-}, $CdBr_4^{2-}$, CdI_4^{2-}, triflate, *o*-chlorobenzoato) [43,55–64] are formed when the deprotonated and neutral chelating amino alcohol ligands adopt the *cis*-arrangement generally in the square planar or square pyramidal coordination environment of copper(II) atoms (Figs. 1iv and 2).

Anions and solvents can occupy the remaining coordination sites whereas the coordination number varies between four and six. The two mononuclear copper(II) amino alcohol $[Cu(aa)(Haa)]^+$ units are connected by short and thus strong hydrogen bonds ($O\cdots O$ distances between 2.4 and 2.5 Å) with the alcohol groups serving as hydrogen-bond donors and the alcoholate oxygen atoms serving as a hydrogen-bond acceptors forming $[Cu(aa)(Haa)]_2^{2+}$ dimers. In Fig. 2 the dimeric structure of $[Cu(Mep)(HMep)H_2O]_2(NO_3)_2$ (HMep = 2-methyl-2-aminopropanol) with H bonds is shown.

An H-bonded linear trimer structure from an amino alcohol, (*R*, *S*)-2-aminopropanol (*RS*-Hpa) with Cu(II) ion has been reported [64]. The complex having a general formula of $[Cu_3(RS$-pa$)_2(RS$-Hpa$)_6][CF_3SO_3]_4$ is actually $\{[Cu(RS$-Hpa$)_3]_2[Cu(RS$-pa$)_2(CF_3SO_3)_2]\}$ $[CF_3SO_3]_2$, in which the two terminal copper(II) ions have a similar coordination sphere whereas the metal ion in the middle is differently coordinated.

3.1.3. Mononuclear Cu(II) units in binuclear and polymeric structures from triethanolamine and related amino alcohols and amino alcoholates

Mononuclear copper(II) complexes with a single amino alcohol ligand have been prepared using tetradentate amino alcohols like triethanolamine (H_3tea). In these $[Cu(H_3tea)D_2]^{2+}$ [65] or $[Cu(H_3tea)X_n]^{(2-n)+}$ [66–69] mononuclear units the neutral amino
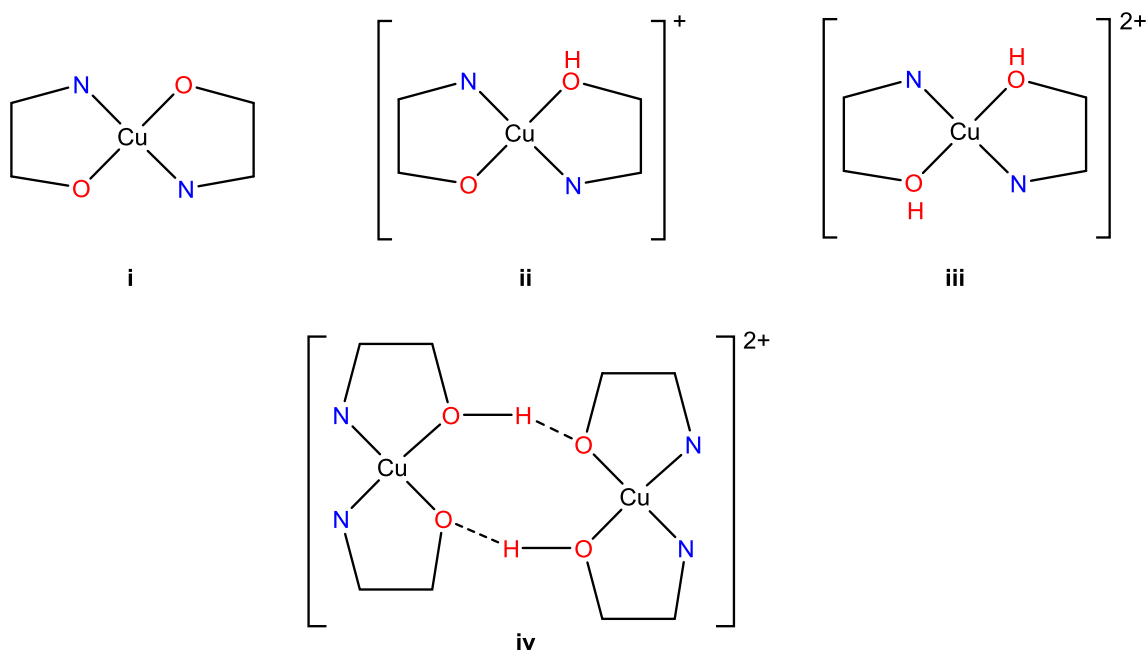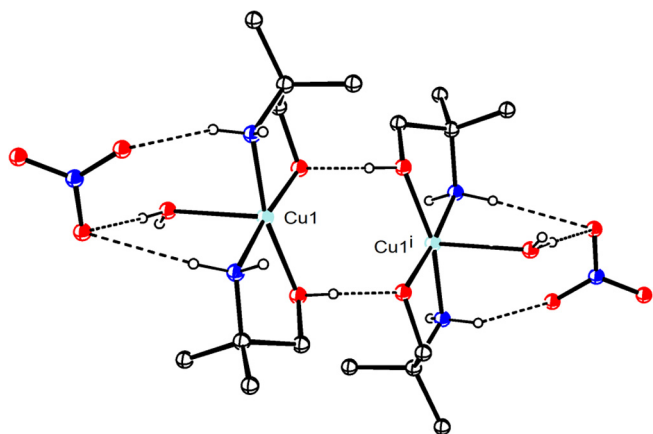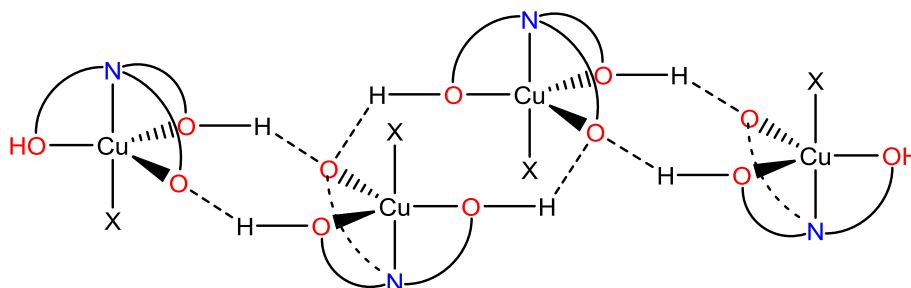

Fig. 1. Simplified structural types of mononuclear copper(II) complexes with 1,2-amino alcohols and amino alcoholates. The N and C substituents (alkyl groups and hydrogen atoms) and additional coordinating donor atoms are not presented.
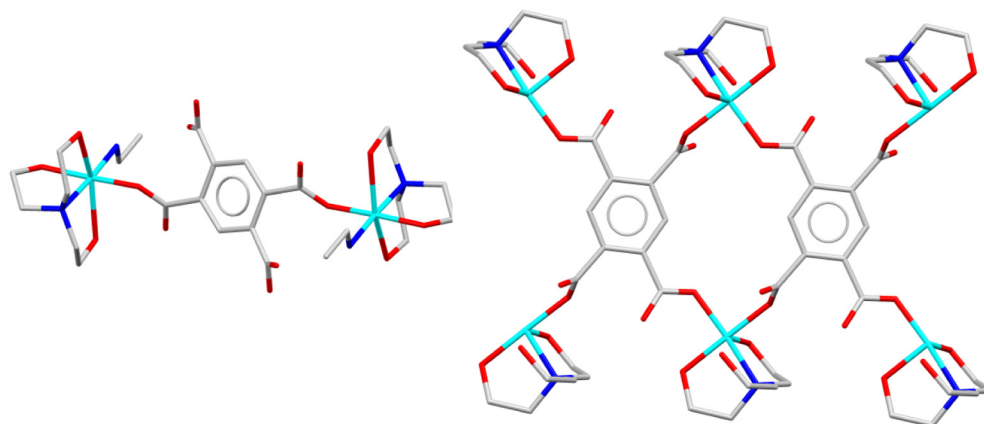
Fig. 2. The H-bonded dimer of [Cu(Mep)(HMep)H$_2$O]$_2$(NO$_3$)$_2$ [55]. CH hydrogen atoms are omitted for clarity. Colour code throughout in this paper: turquoise = copper, grey = carbon, blue = nitrogen, red = oxygen.

Supramolecular binuclear ligand-bridged complexes with one and two dimensional (1D, 2D) coordination polymers have been crystallised using [Cu(Htea)], [Cu(H$_2$tea)]$^+$ and [Cu(H$_3$tea)]$^{2+}$ (H$_3$tea = triethanolamine) mononuclear units with 4,4'-bipyridine (4,4'-bipy) [75] and pyromellitic acid (H$_4$pma, 1,2,4,5-benzenetetracarboxylic acid) [76,77]. The 4,4'-bipy acts as a bis-monodentate bridging ligand connecting two mononuclear [Cu(H$_2$tea)]$^+$ units, in which there are two open coordination sites. The adjacent [Cu$_2$(H$_2$tea)$_2$(4,4'-bipy)]$^{2+}$ dimers are further connected through short hydrogen bonds between [Cu(H$_2$tea)]$^+$ units forming a polymer. If one coordination site of copper(II) is occupied by ethylamine (EtNH$_2$) in the [Cu(H$_3$tea)]$^{2+}$ mononuclear unit and the pma^{4-} anion acts as a bis-monodentate bridging ligand, a discrete dimer [Cu$_2$(μ_2-pma)(H$_3$tea)$_2$(EtNH$_2$)$_2$] is formed (Fig. 4, left) [76]. Then again, if both coordination sites are free, the pma^{4-} anion acts as a bis-didentate bridging ligand and a 1D coordination polymer [Cu$_2$(H$_3$tea)$_2$(μ_4-pma)]$_n$ is formed (Fig. 4, right) [77]. In the 2D heterometallic coordination polymer [78] [Cu$_2$Mg$_2$(μ-Htea)$_2$(μ_6-pma)(H$_2$O)$_6$]$_n$·6H$_2$O the [Cu(Htea)] units are connected by a Mg atom through alkoxo oxygen bridges forming a Cu$_2$Mg cluster. The clusters are connected by pma^{4-} anion coordinating to two cluster Mg and Cu atoms and to two separate Mg atoms surrounded by water ligands forming the 2D network.

3.2. Dinuclear complexes

Over one third of the copper(II) complexes with amino alcohols are dinuclear ones having a general formula of [Cu$_2$(aa)$_2$D$_2$], where the square planar coordination environment of copper(II) ion is occupied by two alkoxo oxygen atoms forming μ_2-alkoxo-bridged Cu$_2$O$_2$-core, one amine nitrogen atom and the remaining equatorial and axial coordination sites (D, Fig. 5) have been occupied by hydroxo and amine groups of tri- or multidentate amino alcohols,

alcohol ligands occupy four or five coordination sites of copper(II) and the remaining coordination sites are occupied by solvent molecules (H$_2$O) or carboxylate anions forming the neutral complex.

Hydrogen bonded dimers and polymers with tetra- and pentadentate singly deprotonated amino alcohols from mononuclear [Cu(H$_2$aa)X] units (X = Cl$^-$, NCS$^-$, N$_3^-$, hfacac$^-$ or counter ion ClO$_4^-$) [18,70–74] have also been reported. For example, the mononuclear [Cu(H$_2$tea)X] (X = Cl$^-$, SCN$^-$ and N$_3^-$) [71,73] units are connected by short hydrogen bonds, similar to dimeric complexes above, forming dimers or polynuclear hydrogen bonded networks (Fig. 3).

Fig. 3. Hydrogen bonded network formed from mononuclear [Cu(H$_2$tea)X] units.

Fig. 4. The [Cu$_2$(μ_2-pma)(H$_3$tea)$_2$(EtNH$_2$)$_2$] dimer [76] (left) and the [Cu$_2$(H$_3$tea)$_2$(μ_4-pma)]$_n$ 1D coordination polymer [77] (right). Hydrogen atoms are omitted for clarity.

counter ions, bridging ligands and/or solvent molecules. In general, the two Cu(II) centres are strongly antiferromagnetically coupled via the bridging O-atoms, but the topological analyses indicate the lack of direct Cu···Cu interaction [79].
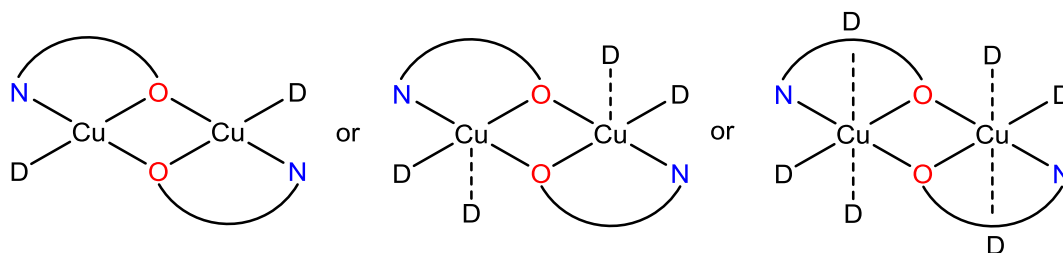
Dinuclear copper(II) amino alcohol complexes have been crystallised with Cl$^-$, Br$^-$, I$^-$, NO$_2^-$, NO$_3^-$ anions [30,79–89], NCO$^-$, NCS$^-$, N$_3^-$ pseudo-halides [24,41,71,84,91–99], organic ligands (monocarboxylate anions prevailing) [18,26,41,85,89,90,100–114] or using tetra- and pentadentate polyamino alcohols with several counter ions (ClO$_4^-$, Cl$^-$, I$^-$, NO$_3^-$ and PF$_6^-$) [115–119]. Depending on the amino alcohol and/or a counter ion in the use, discrete molecules or coordination polymers or networks are obtained (Fig. 6). Also, many tetranuclear complexes are made of the dinuclear units, as described in Chapter 3.4 (see below). The formation of the discrete dinuclear molecules depends on the substituents at the nitrogen or carbons atoms. Especially, the bulky substituents at the N atoms prevent effectively the polymerization (Fig. 6).

Discrete dinuclear molecules are found for example in [Cu$_2$(deap)$_2$Br$_2$] [30] [Cu$_2$(deap)$_2$I$_2$] [88], [Cu$_2$(deap)$_2$(NCO)$_2$] [91] and [Cu$_2$(H$_2$tea)X$_2$] [109,110]. The majority of dinuclear copper (II) amino alcoholates are coordination polymers for example [Cu$_2$(dmap)$_2$X$_2$]$_n$ (X = Cl$^-$ or Br$^-$) [91] [Cu$_2$(ap)$_2$ (NO$_3$)$_2$]$_n$ [79] [Cu$_2$(dmap)$_2$(NCO)$_2$]$_n$ [92], [Cu$_2$(dpap)$_2$(NCS)$_2$]$_n$ [92] and [Cu$_2$(ap)$_2$ (HCOO)$_2$] [111] or H-bond networks as in [Cu$_2$(ap)$_2$(PhCOO)$_2$] [85]. In these polymeric structures, the bridging anions occupy the axial coordination site of the copper atom of the adjacent dinuclear unit. The formation of coordination polymer depends on the

substituents at N-atoms (partly also at C atoms) and of the size and shape of the anion.

Coordination polymers with a general formula of [Cu(Haa)$_2$X$_2$] [Cu$_2$(aa)$_2$X$_2$] (Haa = 2-aminoethanol (Hae) or (*R*)-2-amino-butan-1-ol (*R*-Hab), X = Cl$^-$ or Br$^-$) [63,120] consist of neutral mononuclear and dinuclear units assembled in chains. In these coordination polymers the halides act as μ$_3$- or μ$_4$-bridging ligands connecting copper atoms from one mononuclear and two adjacent dinuclear units forming chain type structures. In addition to the alkoxo-bridges formed between two copper(II) ions within the dinuclear unit, amino alcohols can act as bridging ligands between adjacent dinuclear units forming linear coordination polymers or networks [89,119,121]. In these structures as in [Cu(ap)$_2$(Hap)$_2$ (H$_2$O)$_2$]I$_2$ [121], the neutral amino alcohol (Hap) bonds via N-atoms equatorially to Cu(II) ions and its neutral oxygen atom binds to a copper atom of the adjacent dinuclear unit (the axial coordination site). Iodide ion forms H-bonds to hydrogens of water molecules, alcohol molecules and with NH hydrogens.

In the past decade, a widely used strategy in designing coordination polymers has been the so-called "node-and-spacer" approach [122–125], where coordination polymers are built of metal ions (and metal clusters) functioning as nodes and bridging symmetrical or unsymmetrical organic ligands functioning as spacers. Using this approach, several studies have been published where coordination polymers and networks have been obtained from the alkoxo-bridged dinuclear [Cu$_2$(aa)$_2$]$^{2+}$ units, which contain labile ligands in their coordination sites, functioning as nodes

Fig. 5. A simplified scheme of the dinuclear units (four, five or six coordination) of copper(II) amino alcoholate complexes. D is a donor atom from an anion, polyamino alcohol, a solvent molecule or an additional ligand.
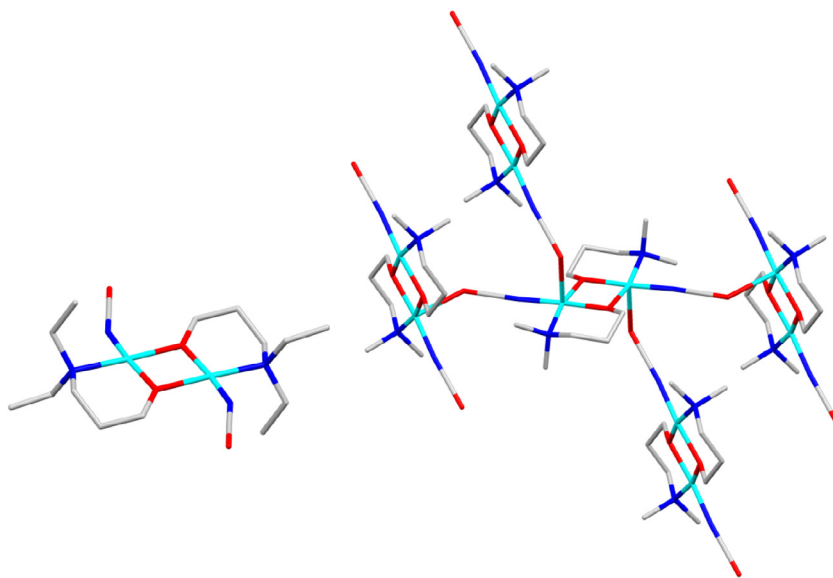
Fig. 6. The [Cu$_2$(deap)$_2$(NCO)$_2$] molecule [91] (left) and part of [Cu$_2$(dmap)$_2$(NCO)$_2$]$_n$ 2D coordination network [92] (right) obtained using *N,N*-diethylaminopropanol (Hdeap) or *N,N*-dimethylaminopropanol (Hdmap). These structures demonstrate the role of the *N,N*-substituents (Me or Et) of the amino alcohol in the formation of different structures. Hydrogen atoms are omitted for clarity.

and neutral or anionic organic N or O donor ligands as spacers [41,73,126–137]. The structures obtained from these studies show that the dimensionality of the coordination polymer can be varied with the choice of the denticity of the amino alcohol. Using tri- and tetradentate amino alcohols, the 1D polymeric chains are formed (Fig. 7), whereas with didentate amino alcohols 1D polymeric chains, 2D grid-like sheets (Fig. 7) and interlocked 3D structures (resulting from the inclined interpenetration of 2D grid-like sheets) have been reported. Thus, the lower the denticity of the amino alcohol the higher dimensionality of the coordination polymer can be expected.

Furthermore, coordination polymers from 1D to 3D with [Cu$_2$(aa)$_2$]$^{2+}$ nodes have been synthesised using polycyanometallates as spacers [138–142]. The reaction between copper tetrafluoroborate and 3-aminopropanol (Hap), followed by the addition of K[Au(CN)$_2$] lead to the formation of 2D layers [{Cu$_2$(ap)$_2$}{Au(CN)$_2$}$_2$], whereas 3D network [{Cu$_2$(ap)$_2$}{Ni(CN)$_4$}] was formed by the addition of K$_2$[Ni(CN)$_4$] [128]. By increasing the number of cyano groups in the spacer, the dimensionality of the polymers based on the equivalent type of dinuclear node could be increased.

A few exceptions to the above-mentioned general type of dinuclear copper(II) amino alcoholate complexes consist of structures with dinuclear [Cu$_2$(aa)]$^{3+}$ units, in which the type of amino alcoholate leads to different structure. Such dinuclear units with one bridging diamino alcoholate ligand have been prepared using 1,3-diamino-2-propanol (Hdap), *N*-methyl-1,3-diamino-2-

propanol (Hmdap) or 1,3-bis(dimethylamino)-2-propanol (Hbdmap) as tridentate ligands [143–146]. Additional bridge between copper atoms in the dinuclear [Cu$_2$(aa)]$^{3+}$ unit is formed by nitrite, azide or bidentate carboxylate anions (Fig. 8). Depending on the anion, discrete dinuclear complexes and coordination polymers are formed.

Moreover, some structures where the dinuclear [Cu$_2$(aa)]$^{3+}$ units act as nodes with a tricyanometallate spacer have also been published [146].

3.3. Trinuclear complexes

The structures of trinuclear copper(II) amino alcoholate complexes can be classified into three different types, *i.e.* (1) open triangular (V-type), (2) closed triangular and (3) linear, according to the spatial arrangements of the metal centres [147].

Open triangular structures have been made using 1,3-diamino-2-propanolate (dap$^-$) [148,149], or 1,3-bis(dimethylamino)-2-propanolate (bdmap$^-$) as ligands [150,151]. In the trinuclear cation, a central copper atom is linked to two terminal copper atoms by two alcoholate bridges. The nitrogen atoms of each bridging dap$^-$ or bdmap$^-$ ligands are coordinated to different copper atoms. The coordination of the terminal copper(II) ions in the equatorial plane in dap$^-$ complexes is completed by the nitrogen atoms of the chelating neutral Hdap ligand (Fig. 9i) [149]. In the bdmap$^-$ complex the terminal copper atoms are chelated by the nitrogen and oxygen atoms of the deprotonated bdmap$^-$ ligand forming a
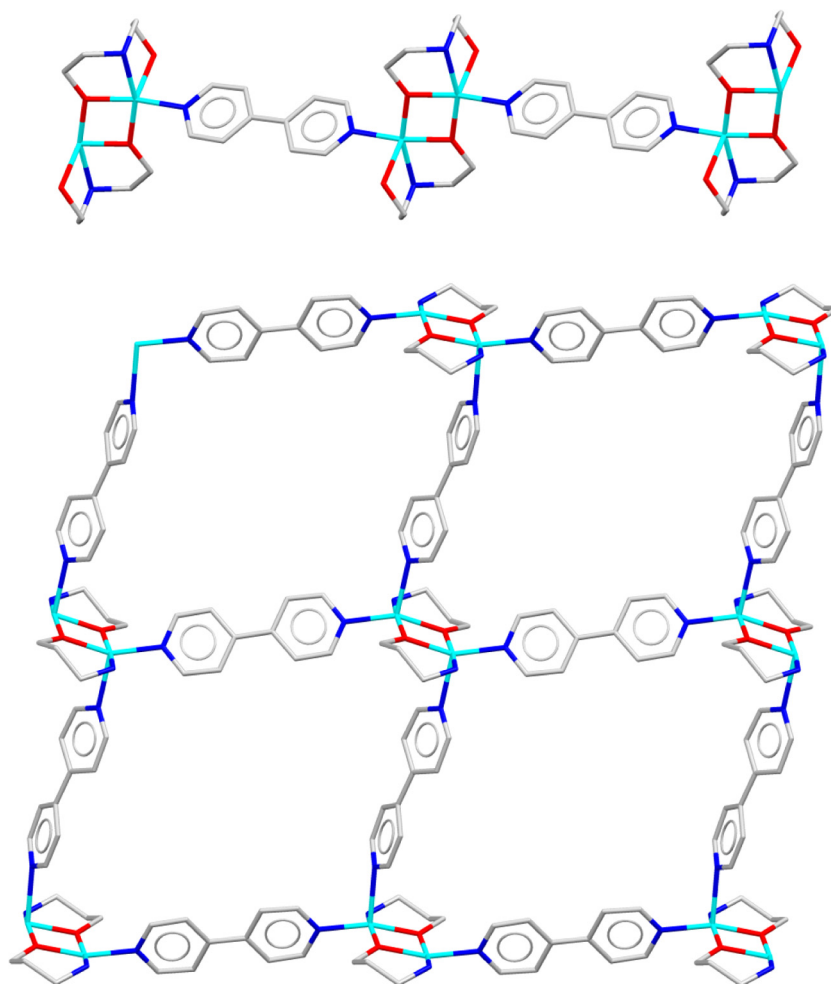
Fig. 7. The [Cu$_2$(Hdea)$_2$(4,4′-bipy)](ClO$_4$)$_2$ 1D coordination polymer [127] (above) and the 2D grid-like sheets [127] of [Cu$_2$(ap)$_2$(4,4′-bipy)$_2$](ClO$_4$)$_3$·(4,4′-bipy)·(H$_2$ap) (below, H$_2$dea = diethanolamine, Hap = 3-aminopropanol, 4,4′-bipy = 4,4′-bipyridine). Counter ions, uncoordinated 4,4′-bipy, Hap and water molecules, which are located in the channels of the crystal, as well as hydrogen atoms are omitted for clarity.
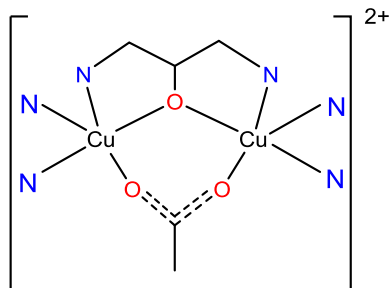
Fig. 8. Simplified unit of the dinuclear $[Cu_2(aa)(\mu_2\text{-acetato})]^{2+}$ unit containing carboxylate bridge [144].

V-shaped molecule with two dangling noncoordinating amino groups (Fig. 9ii) [150].

In the 1,3-bis(dimethylamino)-2-propanolate (bdmap$^-$) complex four of the six nitrogen atoms of the ligands occupy the equatorial sites of copper(II) ions while the remaining two occupy the axial coordination sites, the equatorial sites of two copper atoms are occupied by anions [152]. Coordination polymer with a potassium cations sandwiched between two triangular tricopper(II) dap$^-$ units has been reported [153].

The closed triangular orientation of copper(II) ions for trinuclear complexes obtained using Hdap [154–156] or Hbdmap [157] consist of three copper atoms bridged by three alkoxo oxygen atoms of the dap$^-$ or bdmap$^-$ ligands forming a six-membered ring. In the dap$^-$ complexes the nitrogen atoms of each of the ligands are coordinated to two different copper(II) ions in the equatorial plane (Figs. 10i and 11), the axial sites of two copper atoms are occupied by anion and/or a solvent molecule.

Closed triangular structures have been also obtained using 2-diethylaminoethanol (Hdeae) and carboxylates as ligands [158]. The adjacent copper centres in the mixed-bridged complexes are connected by the oxygen atoms of deae$^-$ and bidentate carboxylate ligand. In addition, the carboxylate anion coordinates to both terminal copper atoms as monodentate ligand. The bending from linearity and the ring closure in these complexes is caused by one μ_3-O atom of the coordinating water molecule (Figs. 10ii and 12).

Two other examples of closed triangular copper(II) amino alcoholate complexes, $[Cu_3(dmae)_3(acac)_2Cl]$, include a structure having a triangular plane of copper atoms: one copper ion is bridged with μ_2- and other two with μ_3-alkoxo oxygen atoms [26] and another example is a structure with diamondoid-like $[Cu_3B(\mu\text{-O})_6]$ core [159].

The linear trinuclear copper(II) amino alcoholate complexes can be divided into structures containing bidentate amino alcohols [160–164] (Fig. 13i) and mixed-bridged structures containing both amino alcoholate and carboxylate ligands [130,165–170] (Fig. 13ii).

The linear trinuclear bridged cation from bidentate amino alcoholates (Fig. 13i) can be either centrosymmetric or non-centrosymmetric and has a general formula of $[Cu_3(aa)_4]^{2+}$, where the adjacent copper atoms are connected by two μ-alkoxo-oxygen bridges (Fig. 14). Four bridging oxygen atoms occupy the equatorial coordination sites of the central copper atom and two terminal copper atoms are equatorially coordinated to two bridging oxygen atoms and two amine nitrogen atoms. The axial coordination sites of the copper atoms can be occupied by anions and/or solvents. Coordination polymers have been obtained with Br$^-$ and NO$_3^-$ anions [163]. These structures also include a linear trinuclear structure, where the adjacent copper atoms are connected by only
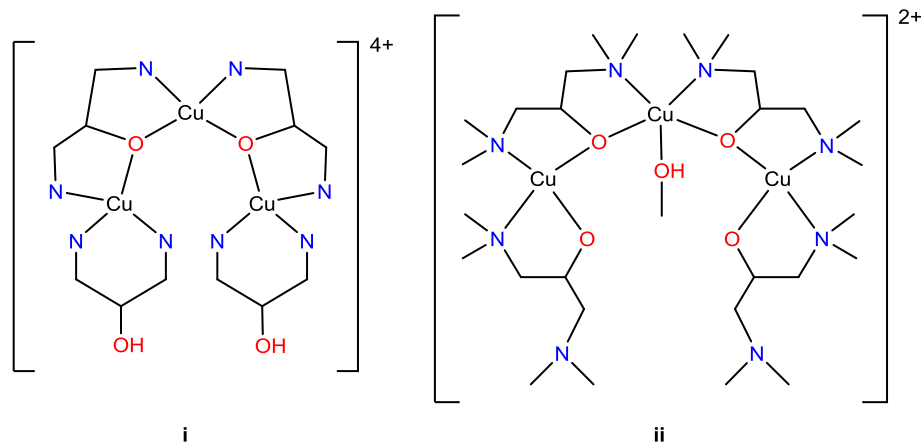

Fig. 9. Simplified figures of the open triangular structures of two copper(II) amino alcoholates. In (i) the ligand is dap$^-$ [149] and in (ii) bdmap$^-$ [150].
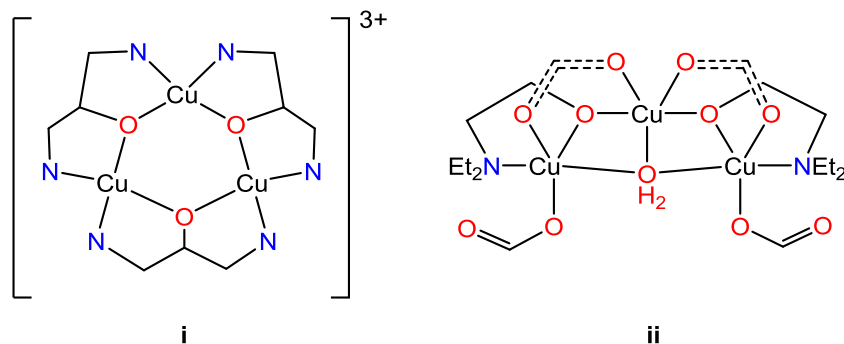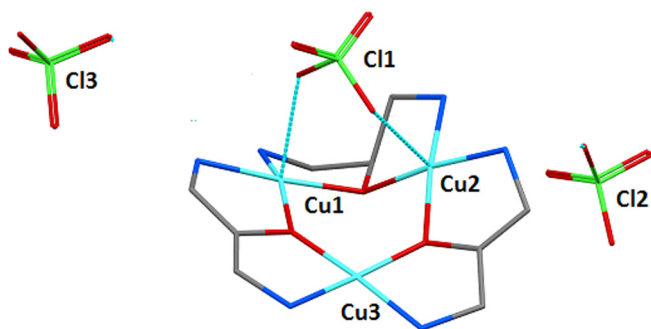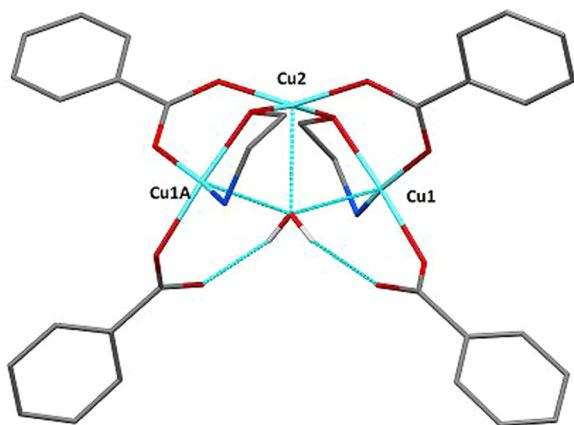

Fig. 10. Simplified figures of the closed triangular structures of two copper(II) amino alcoholates. In (i) the ligand is dap$^-$ [154–156] and in (ii) it is deae$^-$ [158].

Fig. 11. The closed triangular trinuclear [$Cu_3(dap)_3$](ClO_4)$_3$ complex [156]. The CH-hydrogen atoms are omitted for clarity reasons.

Fig. 12. The closed triangular trinuclear [$Cu_3(deae)_2(PhCOO)_4(H_2O)$] complex [158]. The CH-hydrogen atoms and ethyl groups at N atoms are omitted for clarity reasons.

a single μ-alkoxo-oxygen bridge of the bidentate amino alcohol [171].

The linear trinuclear mixed-bridged complexes (Fig. 13ii) have a general formula of [$Cu_3(aa)_2(RCOO)_4(solvent)_n$] ($n = 0–2$), where the adjacent copper centres are connected by the oxygen atoms of deprotonated amino alcohol and bidentate carboxylate ligand. The charge in the molecule is balanced with two monodentate carboxylate anions coordinating to the terminal copper atoms. Two solvent molecules are coordinated (Fig. 14) to the central copper atom when bidentate amino alcohols have been used, whereas additional bridges between copper atoms can be formed with a tetradentate amino alcohol, such as triethanol amine (H$_3$tea) [73,130,170,172–174].
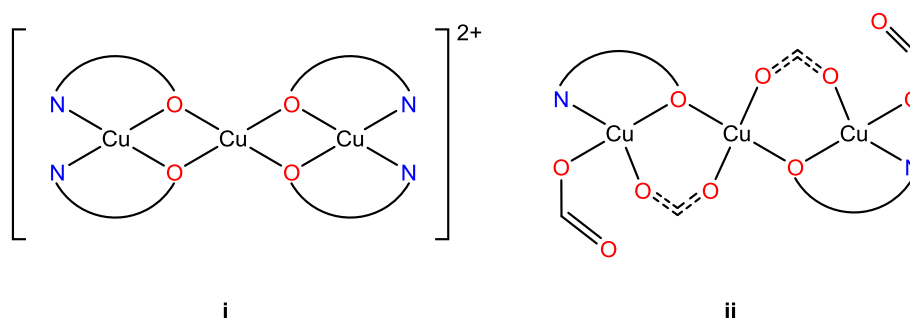
3.4. Tetranuclear complexes

The majority of tetranuclear copper(II) amino alcohol complexes reported have the cubane Cu_4O_4 core (Fig. 15i). The dinuclear complexes have a tendency to form tetranuclear structures with additional bridges between two alkoxo oxygen atoms (μ$_3$-O) and two copper atoms of an adjacent dinuclear unit. The Cu_4O_4-cubane core can be classified into two different types based on the distribution of long Cu–O distances in the cube (Fig. 15ii) proposed by Mergehenn and Haase [175]. Later, Alvarez et al. [176] made a scheme by dividing the known structures into three groups: 2+4, 4+2 and 6+0 classes. In the last one all Cu–O distance are similar. These two systems are compared in Fig. 15. So far the structures with 6+0 notation are very rare.

The type I structure consists of four long Cu–O distances between the two pseudo-dinuclear units, whereas type II is an open- or pseudo-cubane structure with long Cu–O distances within each of the pseudo-dimeric units. Both cubane structure types and various intermediates between these two extremes, type I and II, have been obtained for copper(II) amino alcoholate complexes. Discrete tetranuclear copper(II) amino alcohol molecules have been reported to carry Cl$^-$, Br$^-$, NO$_3^-$, ClO$_4^-$, SO$_4^{2-}$, Htea^{2-} anions, [23,83,177–187] NCO$^-$, NCS$^-$ pseudo-halides [88,175,188–192] or carboxylate ligands [22,26,27,189–201]. Copper atoms have five or six coordination in these complexes, both or only one coordination site D (Fig. 15i) can be occupied. Both free coordination sites can be occupied with amine and/or alcohol groups of tri- and tetradentate amino alcohols [182,185,187] or with carboxylate groups diagonally bridging to two copper atoms [22,27,196–201]. Examples from type I and II structures are shown in Fig. 16 with selected distances (Å).

In contrast to the several examples of coordination polymer structures existing for dinuclear complexes, tetranuclear copper (II) amino alcohol 3D coordination networks have been obtained only by using [Au(CN)$_2$]$^-$ and [M(IV)(CN)$_8$]$^{4-}$ (M = Mo or W) polycyanometallates as bridging ligands [140,202]. As for mononuclear and dimeric (H-bonded) structures, the cubane type structures have been reported only for amino alcohols forming five-membered chelate rings with copper(II) ions.

Although the cubane Cu_4O_4 structure type is the most common for tetranuclear copper(II) amino alcoholate complexes, other different structure types have also been reported (Fig. 17). Copper(II) amino alcoholate complexes containing the $Cu_4(μ_4$-O) distorted tetrahedron (Fig. 17i) have been reported using 2-dimethylaminoethanol (Hdmae) [25,203] and H$_3$tea [130] as bridging ligands.

In the hexanuclear heterometallic complexes with tetrahedral $Cu_4(μ_4$-O) unit [$M_2Cu_4(μ_4$-O)(CH$_3$COO)$_6$(dmae)$_4$]·nH_2O (where M = Cd [25,203] or Zn [25], $n = 1–3$) two triangular MCu$_2$ units are connected by four dmae$^-$ μ$_3$-alkoxo and one μ$_4$-oxo bridges.

Fig. 13. Simplified figures of the linear trinuclear complex units of copper(II) amino alcoholates: a dialkoxo bridged complex (i) and an alkoxo and carboxylate bridged complex (ii).
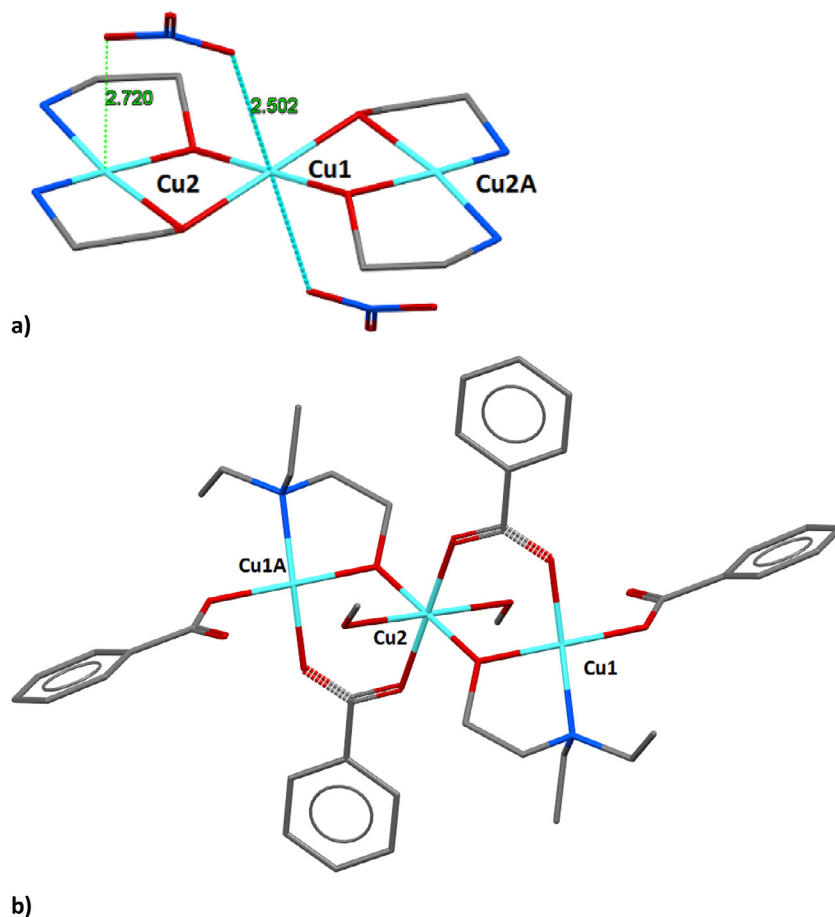
Fig. 14. (a) The linear trinuclear [Cu$_3$(ae)$_4$(NO$_3$)$_2$] complex unit [163]. (b) The linear trinuclear [Cu$_3$(deae)$_2$(PhCOO)$_4$(MeOH)$_2$] complex [166]. Hydrogen atoms are omitted for clarity reasons.
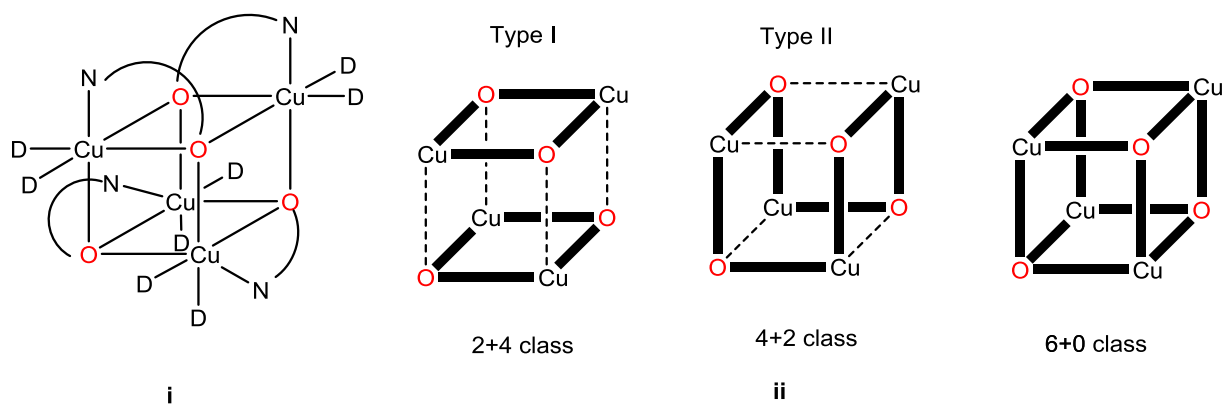
Fig. 15. The simplified structures of the tetranuclear Cu(II) amino alcoholates: (i) the general cubane type, where D is an anion or a donor atom of an extra ligand, (ii) the three different types of Cu$_4$O$_4$-cubane core based on the distribution of long Cu–O distances.

The acetate ligands in these hexanuclear heterometallic complexes have a variety of coordination modes. In the tetranuclear [Cu$_4$(µ$_4$-O)(tea)$_4$(BOH)$_4$][BF$_4$]$_2$ complex [130] the pentacoordinated copper atoms consists of one nitrogen and three oxygen atoms of the deprotonated tea^{3-} molecule and the µ$_4$-O centre. The copper atoms are clustered through bridges between tea^{3-} ligands and µ$_3$-B–OH groups (converted from [BF$_4$]$^-$ in an alkaline medium).

Tetranuclear copper(II) amino alcoholate complexes with ring structures have been obtained when Hbdmap has been used as a bridging ligand (Fig. 17ii) [144,204,205]. These tetranuclear struc-

tures form 12- or 16-membered rings which consist of two carboxylate ligands or two dicyanamide anions, two oxygen atoms of bdmap$^-$ ligands and four copper atoms. Four copper atoms in these rings are arranged in rectangular fashion and therefore additional bridges between the axial coordination sites of two copper(II) ions are formed with Cl$^-$, OH$^-$, CH$_3$COO$^-$ and H$_2$O ligands. The µ$_4$-hydroxo- and alkoxo-bridged tetranuclear copper (II) complexes, [Cu$_4$(µ$_4$-OH)(dmae)$_4$][M(NO$_3$)$_4$] (M = Ag, Na, K) consist of almost planar tetranuclear [Cu$_4$(µ$_4$-OH)(dmae)$_4$]$^{3+}$ units, in which Cu(II) ions are also weakly bonded to nitrate anions. The
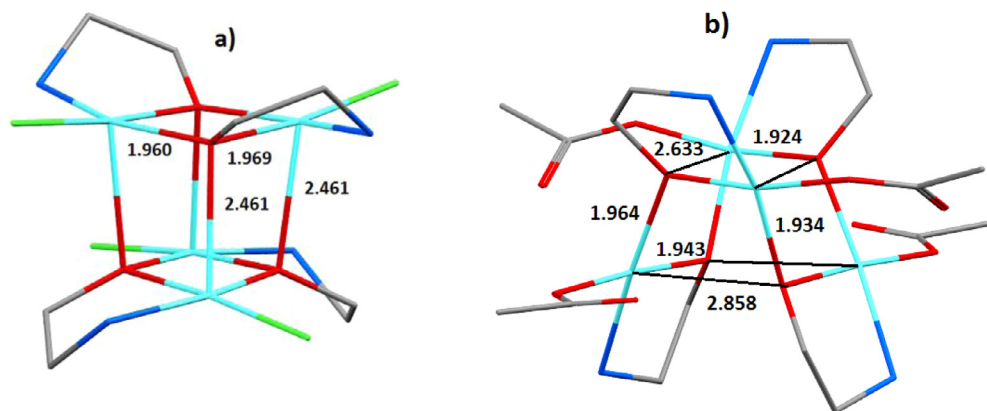
Fig. 16. (a) The cubane structure (I) of tetranuclear [Cu$_4$(2-amino-2-methyl-propanolato)$_4$Cl$_4$] complex [178]. (b) The open cubane structure (II) of tetranuclear [Cu$_4$(dmae)$_4$(Cl$_2$CHCOO)$_4$] complex [197]. Distances are given in Å. Hydrogen and chlorine atoms plus N-methyl groups are omitted for clarity reasons.
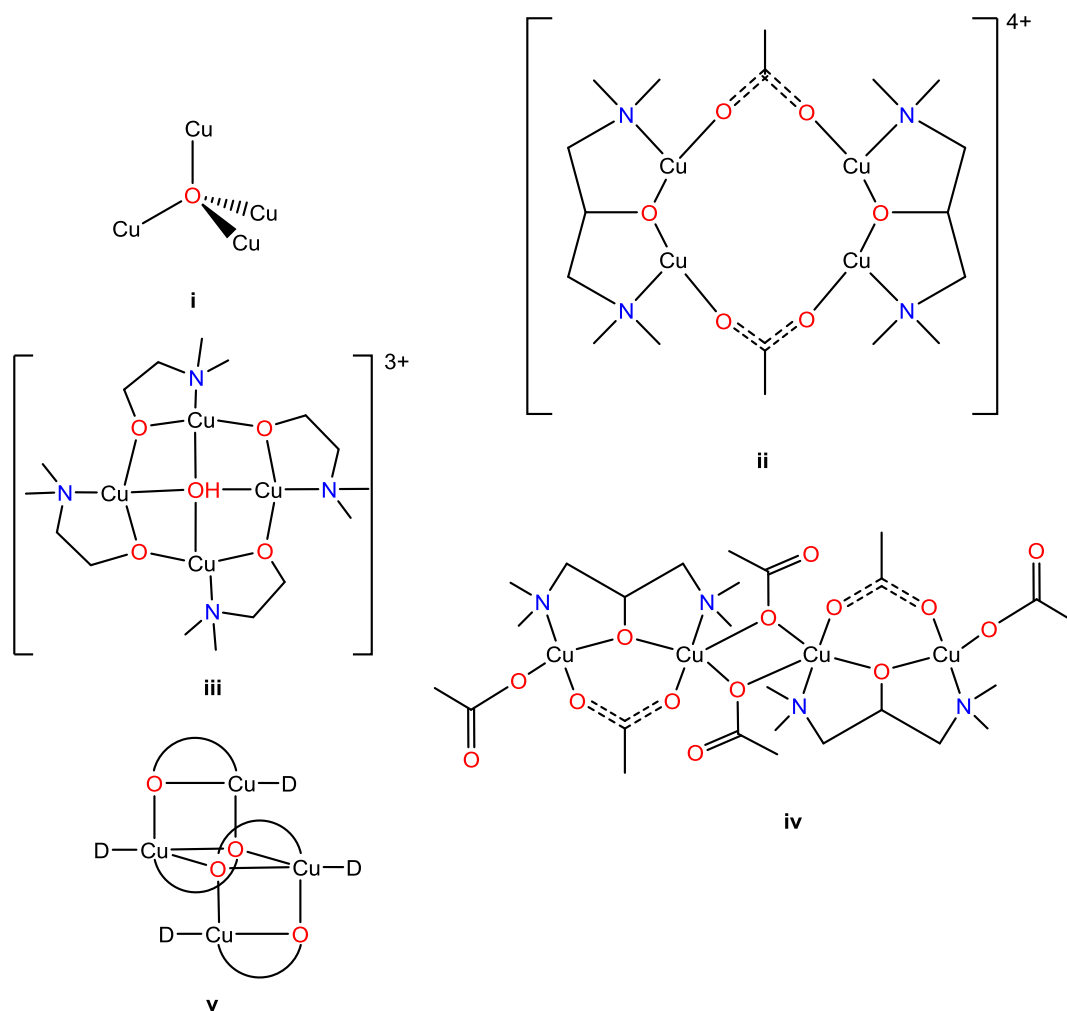
Fig. 17. Other tetranuclear structure types (i–v) obtained for copper(II) amino alcoholates.

adjacent tetranuclear units are connected by ionic interactions between nitrate anions and heterometallic cations resulting in the formation of 1D polymers (Fig. 17iii) [206].

The tetranuclear chain structures [27,144,157,207] reported consist of two dinuclear [Cu$_2$(RCOO)$_2$(bdmap)]$^+$ units (R = CH$_3$ or C$_6$H$_5$) where two copper atoms are bridged by an oxygen atom of the tridentate bdmap$^-$ ligand and a bridging bidentate carboxylato group. Two dinuclear units are linked together through the

μ$_2$-oxygen atoms of two monodentate acetate ligands (Fig. 17iv) [27,157], di-μ$_{1,1}$-thiocyanate bridges [144] or di-μ$_{1,3}$-azide bridges forming the tetranuclear complexes [207].

Other examples of tetranuclear structures include, a stepped cubane structure [208] which consists of two dinuclear units connected by two μ$_3$-oxygen atoms, one from both dinuclear units, forming an additional bridge between the sides of two dinuclear units (Figs. 17v and 18) and a structure with four copper atoms

in trigonal pyramid orientation [209], where the alkoxo oxygen atoms form bridges between the copper atom at the apex and the copper atoms at the trigonal base. The copper atoms at the corners of the base are bridged by μ_3-OH oxygen atom.

3.5. Hexa-, octa- and nonanuclear complexes

For the hexa-, octa- and nonanuclear copper(II) amino alcoholate complexes no general structural trend is observed. These clusters complexes form unique structures and are limited in number. In addition to the bridging amino alcohol molecules in these cluster structures, additional bridges between copper atoms are formed with hydroxo groups, carboxylate ligands, anions and/or solvents.

Within the hexanuclear complexes there are three examples where the copper atoms are connected strictly by the bridging alkoxo oxygen atoms of amino alcohols. The "bicapped-cubane" complex [206,210] has a cation with Cu_6O_8 core formed by alternating copper and alkoxo oxygen atoms. The top and bottom faces of the cubane Cu_4O_4 subcore are capped by copper atoms. Two capping copper atoms are joined via alkoxo oxygen bridges to two copper atoms in the top and bottom faces of the cubane Cu_4ae_4 subcore (Fig. 19).

Octanuclear heterometallic Cu(II)/Cd complex with a hexanuclear Cu_6O_6 core consist of zigzag chain of metal atoms bridged by alkoxide arms of tetradentate $Htea^{2-}$ [211]. Two CdI_2 entities act as terminal ligands in both ends of the hexanuclear copper chain.

In three instances a hexanuclear structure with Cu_6O_6 core built from two distorted cubes with one common Cu–O–Cu–O face have been obtained using *N,N*-dialkylaminoethanol [212–214]. In these structures the Cu_6O_6 core consists of six copper atoms, two μ_3-bridging hydroxo groups, two μ_3-bridging and two μ_2-bridging alcoholate oxygen atoms, additional bridges between copper atoms are formed with bidentate carboxylate ligands and a bridging water molecule with population parameter 0.5 (Fig. 20).

Although the reported dinuclear copper(II) amino alcoholate complexes are typically discrete molecules or coordination polymers, a structure consisting of three dinuclear $[Cu_2(dmae)_2]^{2+}$ units bridged into a hexanuclear unit by carboxylato oxygen atoms has been reported [214]. The copper atoms in the central dinuclear unit have distorted square-pyramidal coordination environment, while the copper atoms in two terminal dinuclear units have distorted square-pyramidal or distorted octahedral coordinat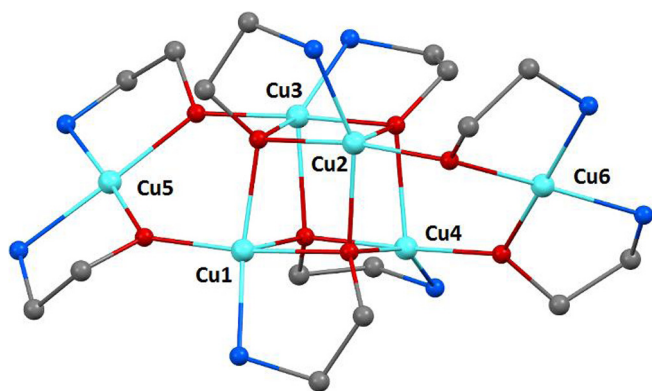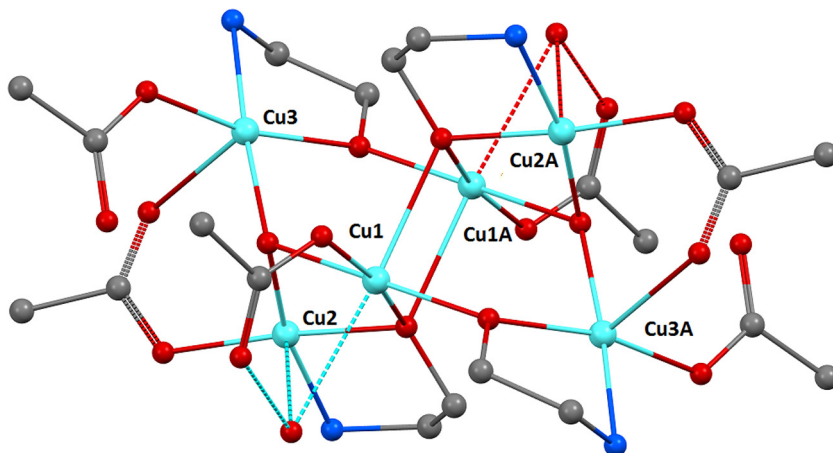ion. The water molecules coordinated to one copper atom in both terminal dinuclear units act as terminal ligands blocking the formation of polymer structure (Fig. 21).

Hexanuclear propeller and cage type structures have been obtained using Hbdmap as a bridging ligand [215,216]. These structures can be considered as being built from three $[Cu_2(bdmap)]^{3+}$ dinuclear units. In each dinuclear unit, two copper atoms are bridged by the oxygen atom of the bdmap⁻ ligand. The dinuclear units are bridged by a μ_3-oxygen atom and μ_3-OH group forming the hexacopper clusters. Two examples of both octa- and

Fig. 18. The stepped cubane structure of tetranuclear $[Cu_4(dea)_4(CH_3COO)_4]$ complex [208]. Hydrogen atoms are omitted for clarity reasons.

Fig. 19. The bicapped cubane structure of hexanuclear $[Cu_6(ae)_8(ClO_4)_2](ClO_4)_2\cdot$ MeOH complex [206]. Hydrogen atoms, perchlorate ions and methanol molecule are omitted for clarity reasons.

Fig. 20. The hexanuclear $[Cu_6(deae)_4(CH_3COO)_6(OH)_2]\cdot H_2O$ complex [212] with Cu_6O_6 core (Hdeae = *N,N*-diethylaminoethanol). Hydrogen atoms and N-ethyl groups are omitted for clarity.

Fig. 21. The hexanuclear [Cu$_6$(4-BrC$_6$H$_5$COO)$_6$(dmae)$_6$(H$_2$O)$_2$] complex [214] containing three dinuclear [Cu$_2$(dmae)$_2$]$^{2+}$ units. Hydrogen atoms are omitted for clarity

nonanuclear copper(II) amino alcohol complexes occur. The octanuclear complexes include a structure [143] which consists of four neutral dinuclear units containing one deprotonated bdmap$^-$ ligand, three nitrite anions and one water molecule. The adjacent dinuclear units are connected by nitrito bridges giving an octanuclear arrangement. The second octanuclear example [205] consists of two folded rectangular units of copper atoms connected by one μ$_2$-OH and two μ$_3$-OH oxygen bridges forming the octanuclear complex. In the rectangular unit, the copper atoms are bridged alternately by two bdmap$^-$ ligands, two cyanate ligands and two hydroxo groups (Fig. 22).

Recently, also two octanuclear Cu(II) complexes using *N-tert*-butyldiethanolamine (H$_2$tbDea) as a ligand precursor have been prepared and their magnetic properties studied [217,218]. The shape of these complexes is spherical.

The arrangement of copper atoms in the nonanuclear complex [205] can be described as a distorted cube with the ninth copper atom in the centre. Eight copper atoms are bridged alternately by bdmap$^-$ ligand through oxygen and two nitrogen atoms and by two cyanate ligands and one μ$_3$-OH group, which bridges to the central copper atom. The structure of the second nonanuclear

example [219] consists of one central copper atom in between two trigonal pyramids formed from four copper atoms. The central copper atom and two trigonal pyramids are joined together by four carboxylate and two μ$_3$-OH oxygen bridges. The copper atoms in the trigonal pyramid are connected by μ$_3$-oxygen bridges of three dmae$^-$ ligands and by two bridging carboxylate ligands (Fig. 23).

4. Magnetic properties

The copper amino alcoholate complexes have given an important contribution to developing Molecular Magnets, especially to understand the factors governing the magnetic coupling in polynuclear complexes with multiatom bridges.

Hydrogen bridged dimer complexes with amino alcoholate ligands are, probably, the clearest examples of how a hydrogen bond can transmit moderate to strong antiferromagnetic interactions [55,57]. Recently, DFT calculations have been carried out on these complexes to explain the value and magnitude of the magnetic coupling [220,221]. It was found that the magnetic coupling of these dimeric complexes is highly dependent on the structural
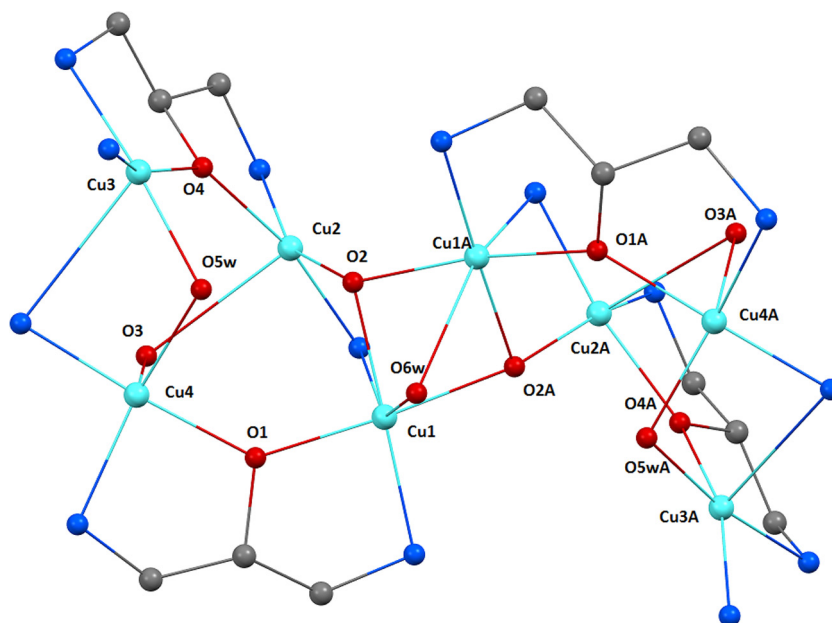
Fig. 22. The centrosymmetric octanuclear [Cu$_8$(NCO)$_2$(η^1:μ-NCO)$_4$(μ-OH)$_2$(μ$_3$-OH)$_2$(μ-OH$_2$)$_3$(μ-bdmap)$_4$](ClO$_4$)$_2$·2H$_2$O complex [205] with two folded rectangular copper units. Counter ions, hydrogen atoms, C atoms of N methyl groups, C and O atoms of NCO$^-$ ions and non-coordinated water molecules are omitted for clarity.
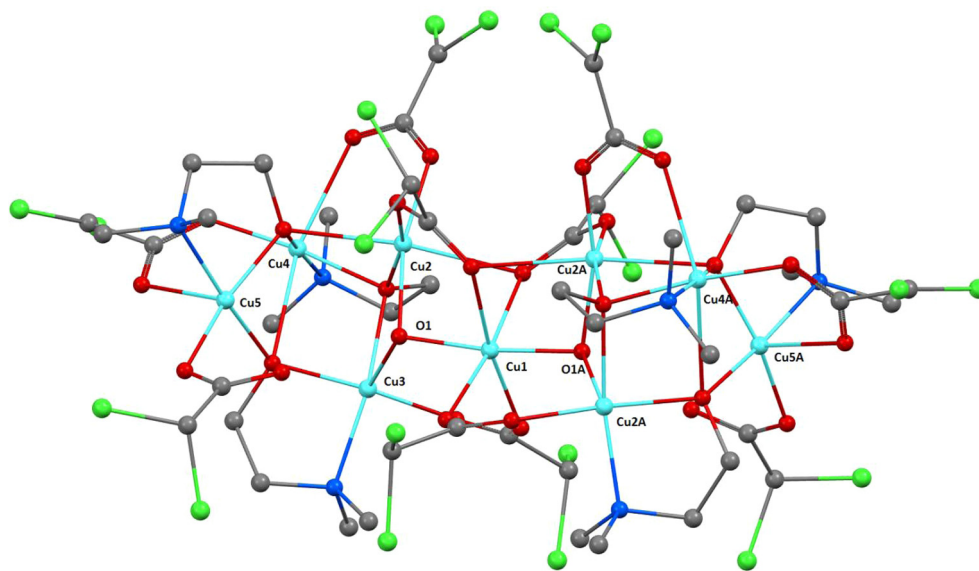
Fig. 23. The nonanuclear $[Cu_9(CHCl_2COO)_{10}(dmae)_6(OH)_2]$ complex [217] (dmae = *N,N*-dimethylaminoethanolate). Hydrogen atoms are omitted for clarity.

parameters of the bridging hydrogen. Especially the Cu···Cu distance between mononuclear units along H-bonds is an important factor for magnetic interaction.

The magnetic behaviour of hydroxo- and alkoxo-bridged polynuclear copper(II) complexes is well known from the experimental [63,84,98,112,113,135,140,170,190,222,223] and theoretical studies [224–233] indicating that the major factor controlling the magnetic exchange interaction in these copper(II) complexes is the value of the Cu–O–Cu angle (θ). A linear correlation between the experimentally determined exchange coupling constant (J) and the θ angle for dihydroxo-bridged complexes was established by Hatfield et al. [223] showing that the antiferromagnetic (AF) coupling between the copper(II) ions decreased with a decrease in the θ angle with a crossover point at 97.6° followed by a change from AF to ferromagnetic (F) coupling. A similar linear relationship for the di- and tetranuclear alkoxo-bridged copper(II) complexes was established by Merz and Haase [190] with a crossover point at 95.7°. Antiferromagnetic coupling is the most common for such complexes.

Although the θ angle is the single most important parameter, other geometric factors also play a significant role in determining the sign and magnitude of the exchange coupling. Theoretical calculations carried out on a dialkoxo-bridged model structure, containing a planar $Cu_2(\mu$-O$)_2$ skeleton and a methyl group bonded to each oxygen atom of the double bridge, predicted antiferromagnetic interactions for the whole range of the Cu–O–Cu angle (θ) when τ values (out-of-plane displacement of the methyl carbon atom from the Cu_2O_2 plane) were smaller than 40° [226,227]. Moreover, a correlation was established between θ and τ, showing that small values of θ are associated with the largest values of τ. Therefore, the AF coupling is favoured when θ increases and τ diminishes. Besides these two angles, other structural factors such as the dihedral angle of the O–Cu–O bridging planes (γ), the deviation of the copper(II) coordination geometry from square-pyramid or square-planar (δ), and the dihedral angle between the coordination planes of the Cu(II) atoms (ω), *etc*, can also affect the magnitude of the magnetic exchange interaction [229]. The increase of γ, δ and ω is expected to reduce the value of the anti-ferromagnetic exchange interaction. DFT calculations on planar bis(μ-dihydroxo-bridged trinuclear complexes showed very similar trends to those found for dinuclear dihydroxo- and dialkoxo-bridged complexes [232].

The recent analysis on the experimental data concerning dinuclear dialkoxo bridged Cu(II) complexes supports the results obtained from the theoretical calculations [113]. The main factors, which control the magnetic interactions are the Cu–O–Cu angle and out-of-plane displacement of the alcoholate group.

The copper(II) dinuclear species with two identical bridges are the most common, but also there are many dinuclear species where two bridges are not identical. Such a compound is shown in Fig. 8, which has an alkoxobridge and a carboxylate bridge. The magnetic properties of such type of complexes have been be explained using orbital complementarity and counter-complementarity [Ref. [5] pp. 164–167 and 144–145]. Also for a dinuclear complexes with quite similar Cu–O–Cu angles, but different τ values the magnetic properties can be rationalized with orbital complementarity and counter-complementarity [163].

In trinuclear Cu(II) amino alcoholate complexes, the linear tetra-alkoxo bridged and alkoxo and carboxylate bridged structures are the most common. The magnetic properties of tetra-alkoxo bridged complexes (Fig. 13i) follow similar rules as dinuclear ones and have generally an antiferromagnetic interaction between the nearest neighbours [102,163]. On the other hand the structures with two alkoxo and two carboxylate bridges (Fig. 13ii) display ferromagnetic behaviour due to the mismatch of the magnetic orbitals [170,174].

The tetranuclear Cu_4O_4 cubane cores with 2+4 class structure (type I) correspond to a couple of dinuclear units with long Cu–O bond distances between them. These systems usually present magnetic properties similar to those of the isolated dinuclear units [233]. Recently, Escuer et al. have shown that for Cu_4O_4 cubane cores (4+2 class, type II) the set of four α–δ Cu–O–Cu bond angles with selected criteria gives a reasonable estimation of the magnetic properties of this type of the complexes [234]. However, most of them are Cu complexes made of Schiff bases with alkoxo or phenoxo bridges.

For the other types of tetranuclear, hexanuclear and higher nuclearity Cu complexes it is difficult to find any simple structural parameter, which could give direct information on the magnetic properties of the complexes. However, the structure can be divided into smaller units using symmetry. Around the Cu(II) ions, there are normally four short bonds and 1 or 2 longer ones. This gives an idea of the location of the unpaired electrons and magnetic orbitals. With the help of the Cu–O–Cu values one can find magnetic

exchange pathways in the substructures and then finally estimate the total magnetic interaction [143,205].

5. Catalytic studies

5.1. Alkane oxidations and hydrocarbonylation

Pompeiro et al. have reviewed the catalytic alkane oxidation (Eq. 1) and hydrocarbonylation (Eq. 2) reactions with Cu(II) amino alcoholate complexes in 2012 [16]. It was shown that the catalytic oxidation of alkanes with hydrogen peroxide depends on many factors, in which the nuclearity of the copper catalyst, coordination sphere around the Cu(II) ion, lability of the extra ligands bonded to Cu(II) ion and acid co-catalyst are the most important ones.

$$R\text{-}H \xrightarrow[\substack{CH_3CN/H_2O,\ 50\ ^oC \\ \text{Acid promoter}}]{\substack{\text{Cu-aminoalcoholate} \\ H_2O_2\ (50\%)}} ROH + R\text{=}O$$
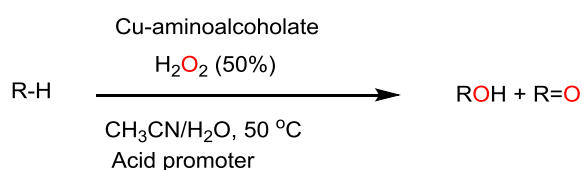
In the catalytic hydrocarbonylation reactions of alkanes with CO and water the oxidation is done using $K_2S_2O_8$.

$$R\text{-}H \xrightarrow[\substack{CH_3CN,\ 50\text{-}60\ ^oC}]{\substack{\text{Cu-aminoalcoholate} \\ CO,\ H_2O,\ K_2S_2O_8}} RCOOH$$
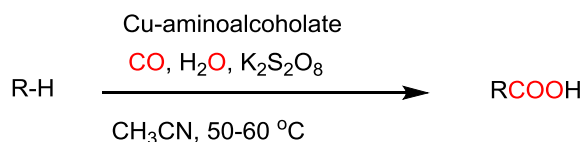
Since the review by Kirillov et al. [16] several papers on the topic have been published [137,172,235–239]. There are several advantages in the use of the copper amino alcoholates as catalysts in these reactions, e.g. simple catalyst systems, cheap reagents, low reaction temperatures and in many cases high yields.

5.2. Henry reaction

The catalytic asymmetric Henry nitroaldol reaction is an ideal, atom economical and powerful method for stereoselective carbon–carbon bond formation [240]. Many copper(II) complexes of the chiral 1,2-amino alcohols can catalyse the reaction with high enantioselectivity [241–244]. An example reaction is described in Eq. (3) [241].
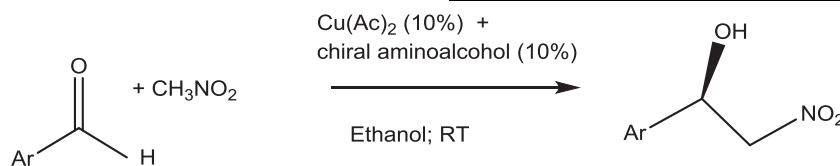
However, the nature and nuclearity of the active Cu(II) complex is unknown.

6. Other applications

Many amino alcoholate complexes have been used as precursors in chemical vapour deposition (CVD) of crystalline copper thin films [18–27]. Generally, the use of N,N-disubstituted amino alcohols makes it possible to prepare mononuclear complexes with relatively high volatility. Typically, the used copper(II) alkoxides decompose at relatively low temperatures by various reductive elimination reactions, so they are convenient precursors for the deposition of copper without a reducing agent. In some cases, the precursor synthesis leads to the formation of mixed ligand complexes, which carry β-diketonates or carboxylates as co-ligands. It is also possible to prepare volatile, heterometallic amino alcoholate clusters, which are useful in the preparation of mixed oxide films [245,246]. Also as described in Sections 3.1 and 3.2, many mono and dinuclear copper amino alcoholate complexes are used as nodes to form the coordination polymers of different dimensionality. The denticity of the amino alcohol and the ligand-to-metal (in the dinuclear unit) ratio determines the dimensionality.

Dinuclear and trinuclear mixed ligand Cu(II) complexes with triethanolamine and thiophen-2-yl saturated carboxylic acids have been used as anti-inflammatory/antioxidant activity as well as their antitumor activity [102].

7. Summary and outlook

Amino alcohols can be used to prepare a number of different copper(II) complexes through the self-assembly process. The hydroxyl groups of the amino alcohol molecules can be easily deprotonated in the presence of copper(II) salts and the resulting alkoxide ions can act as a bridge between copper atoms. Similarly, other anionic groups, e.g. oxide, hydroxide or carboxylates can bridge adjacent copper atoms. These bridges lead in the formation of diverse structures; from mononuclear to nonanuclear copper(II) clusters, coordination polymers and networks, whereas the nuclearity of the metal complex can be adjusted by the stoichiometry and choice of the ligands and anions. The substituents at N-atoms (partly also at C atoms) and of the size and shape of the anion control the formation of coordination polymers from the clusters. Large substituents at the N atoms favour of dinuclear clusters. In such copper(II) amino alcoholate complexes, the coordination number of the metal ion varies between four and six. The d^9 electron configuration of copper(II) ion with a strong Jahn-Teller distortion causes that the coordination sphere around the Cu(II) ion is flexible. The studies reported in the literature demonstrate the vast structural diversity of copper(II) amino alcohol complexes obtained using different amino alcohols and counter ions. These complexes can be used as building blocks for coordination polymers, as model systems in magnetic studies or as simplified models of active sites of enzymes, potential new catalysts and as starting materials for copper oxides or mixed metal oxides by CVD. The magnetic studies of complexes reveal that the two key structural factors determining the magnetic behaviour of the alkoxo-bridged copper(II) complexes are the Cu–O–Cu and O···O–C angles. The magnetic properties of dialkoxo and tetra-alkoxo bridged complexes follow similar rules and they have generally an antiferromagnetic interaction between the nearest neighbours. On the other hand, the trinuclear complexes with two alkoxo and two carboxylate bridges display ferromagnetic behaviour due to the disparity of the magnetic orbitals (orbital complementarity and counter-complementarity).

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