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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

Abbreviations: Hae, 2-aminoethanol; Hdmae, *N*,*N*-dimethylaminoethanol; Hdeae, *N*,*N*-diethylaminoethanol; Hap, 3-aminopropanol; Hdmap, *N*,*N*-dimethylaminopropanol; Hdeap, *N*,*N*-diethylaminopropanol; Hdpap, Hab, 4-aminobutanol; *R*-Hab, (*R*)-2-amino-butan-1-ol; Hape, 5-aminopentanol; Hah, 6-aminohexanol; Hdap, 1,3-diamino-2-propanol; Hmdap, *N*-methyl-1,3-diamino-2-propanol; Hbdmap, 1,3-bis(dimethylamino)-2-propanol; hfacac, hexafluoroacetylacetonate; H_2dea, diethanolamine; H_3tea, triethanolamine; H_3tris, 2-amino-2-hydroxymethyl-1,3-propanediol.

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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].

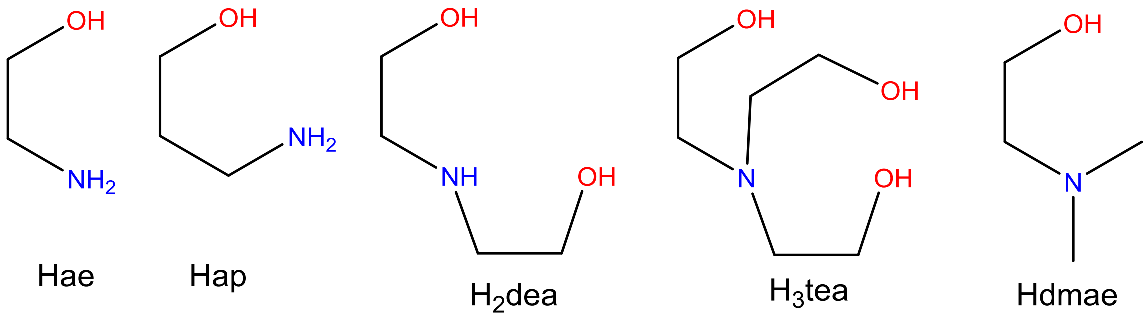
2. Syntheses of copper(II) amino alcoholate complexes

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.

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