

# (Guanidine)copper complexes: structural variety and application in bioinorganic chemistry and catalysis

Olga Bienemann, Alexander Hoffmann and  
Sonja Herres-Pawlis\*

Anorganische Chemie II, Technische Universität  
Dortmund, Otto-Hahn-Straße 6, D-44227 Dortmund,  
Germany

\*Corresponding author  
e-mail: sonja.herres-pawlis@tu-dortmund.de

## Abstract

In this paper, guanidine copper compounds are reviewed with an emphasis on structural characteristics and their application in bioinorganic chemistry and catalysis. The literature survey includes the copper coordination chemistry of biological guanidine derivatives, peralkylated guanidines including bicyclic ones and of further nitrogen-rich guanidine-type systems such as azoimidazoles, triazolopyrimidines and triaminoguanidines. From a sporadic interest dating back to the 1960s, research on this ligand class and its use in copper coordination chemistry has gained new impetus since 2000. With the synthesis of examples with sophisticated substitution at the characteristic  $\text{CN}_3$  framework, complex problems can be addressed in several fields of chemistry. This paper analyses the different types of guanidines for their special donor properties and highlights the specific advantages of guanidines as neutral donor ligands in copper coordination chemistry where a great variety of coordination modes was found. These compounds offer the ability to distribute the formal positive charge of the metal throughout the guanidine unit and represent more than simple  $\sigma$ -donating ligands.

**Keywords:** azoimidazoles; copper; guanidines; imidazolin-2-imines; triazolopyrimidines.

## Introduction

The coordination chemistry of guanidines developed rather slowly in the past decades but benefited from a rapid expansion in the past 10 years. This may be due to the high basicity of the neutral guanidines and the facile formation of guanidinium species upon contact with proton sources. In contrast to this, the coordination chemistry of guanidines  $[(\text{RN})_2\text{CNR}_2]^+$  and  $[(\text{RN})_2\text{C}=\text{NR}]^{2+}$  is already known for a rich variety of coordination modes and excellent donor properties leading to compatibility with a wide range of metal ions from all parts of the periodic table since the 1960s (Scheme 1). For this reason, guanidine chemistry has already been thoroughly reviewed by Bailey and Pace (2001), Edelmann (2008), and Coles (2006). A special class of guanidines are

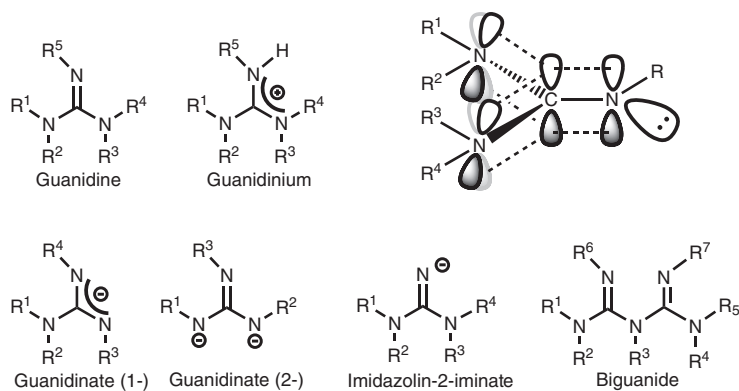
the imidazolin-2-iminato ligands which have been established as powerful ancillary ligands in catalysis (Kuhn et al. 1995, 1997, Tamm et al. 2004, 2006, Beer et al. 2007a,b, 2008, 2009, Stelzig et al. 2008, Haberlag et al. 2010, Sharma et al. 2010, Trambitas et al. 2010, 2011). As the use of neutral guanidines emerged in coordination chemistry, they have been considered in reviews, but always stood in the shadow of the more thoroughly investigated guanidines (Mehrota 1987, Kuhn et al. 1995, 1997, Mitewa 1995, Bailey and Pace 2001, Tamm et al. 2004, 2006, Coles 2006, Beer et al. 2007a,b, 2008, 2009, Edelmann 2008, Stelzig et al. 2008, Haberlag et al. 2010, Sharma et al. 2010, Trambitas et al. 2010, 2011).

Guanidines and guanidines contain at least one Y-shaped  $\text{CN}_3$  moiety which shows a special delocalisation behaviour of the six  $\pi$ -electrons which has been discussed as Y-aromaticity (Gobbi and Frenking 1993). This resonance stabilisation is a major reason for the high basicity of guanidines ( $\text{p}K_{\text{BH}^+}$  of  $[\text{H-NMe-C}(\text{NMe}_2)_2]$  in MeCN: 25.00) (Schwesinger 1990, Sundermeyer et al. 2009). In a special case, the  $\text{CN}_3$  group is part of a bigger  $\text{C}_2\text{N}_5$  unit in the so-called biguanides which have found prominent use as an antidiabetic drug (metformin) (Schäfer 1983). The chemistry of biguanides and their complexes has been reviewed elsewhere (Ray 1961, Ray and Kauffman 1999, Hubberstey and Suksangpanya 2004).

In nature, organic guanidines occur ubiquitous for several reasons: (i) their facile biosynthesis starting from the amino acid arginine makes this functional group relatively easily accessible; (ii) owing to their basicity, they are protonated in aqueous media and act as guanidinium cations in stabilising tertiary structures through multiple hydrogen bonds; and (iii) their donor strength enables them to coordinate to transition metals. The resulting flourishing wealth of isolated and chemically synthesised natural products containing guanidine groups is regularly reviewed (Berlinck et al. 2010).

Parallel to this biological guanidine chemistry, applications as ionic liquids (Gao et al. 2005, Sauer et al. 2008) and in organocatalysis have emerged (Ishikawa and Kumamoto 2006, Ishikawa 2009, Kiesewetter et al. 2009). In technical systems, guanidines are found as components or intermediates in the production of pharmaceuticals and pesticides such as chloronicotinyguanidine (Kagabu and Hirozumi Matsuno 1997). Some guanidinium salts have become important as impregnants or flameproofing agents as well as emulsifiers or antistatic agents in the textile industry (Güthner et al. 2006). Copper guanidinium nitrate is used in pyrotechnic formulations (Kosanke et al. 2004).

In academia, neutral guanidines have been the focus of considerable interest since 2000, owing to their ability to coordinate copper in a multitude of coordination motifs. The  $\text{N}_{\text{imine}}$  donor function resembles the  $\delta$ -imine donor function of histidine which makes them highly valuable for the synthesis



**Scheme 1** Generic representations for guanidine derivatives and resonance stabilisation in neutral guanidines.

of bioinorganic copper complexes mimicking type 2 and type 3 copper proteins (Sundermeyer et al. 2009).

The present review focuses on the copper coordination chemistry of neutral guanidines containing a substituted  $\text{RN}=\text{C}(\text{NR}_2)_2$  moiety because the coordination chemistry of this specific ligand class has been developed very successfully towards numerous applications in bioinorganic chemistry and catalysis. The wealth of guanidine stabilised copper complexes was classified into different groups depending on the subtype of guanidine functionality incorporated into a bigger framework. As larger sub-categories, biologically occurring guanidines, peralkylated guanidines and further nitrogen-rich guanidine-type ligands have been identified.

### Mono(guanidine) systems

The first acyclic guanidine adducts were reported in 1965 when Longhi and Drago presented a series of complexes of 1,1,3,3-tetramethylguanidine (TMG) at divalent transition metals (Longhi and Drago 1965). In the following decades, the coordination chemistry much preferred the anionic forms of guanidines (Kuhn et al. 1995, 1997, Bailey and Pace 2001, Tamm et al. 2004, 2006, Coles 2006, Beer et al. 2007a,b, 2008, Edelmann 2008, Stelzig et al. 2008, Haberlag et al. 2010, Sharma et al. 2010, Trambitas et al. 2010, 2011). In the 1990s, Schneider et al. used TMG as ancillary ligands for the stabilisation of gold complexes (Schneider et al. 1997), but the use for copper chemistry remained underdeveloped. Only in 2004, Coles et al. reported a binuclear copper iodido complex with two molecules of  $\text{Me}_2\text{NC}(\text{N}^i\text{Pr})(\text{NH}^i\text{Pr})$  and no hydrogen bonding was observed in the solid state (Oakley et al. 2004c). The substitution pattern of the  $\text{CN}_3$  unit can

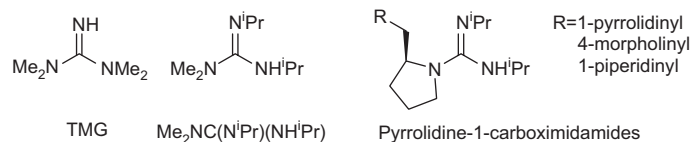
easily be changed by various methods and only a selection of ligands is depicted in Scheme 2 (Bailey and Pace 2001, Köhn et al. 2004, 2005, 2006, Oakley et al. 2004c, Edelmann 2008). Without having been used until now in copper chemistry, the chiral pyrrolidine-1-carboximidamides should be listed here for their good chelating properties explored in zinc and molybdenum chemistry (Köhn et al. 2004, 2005, 2006).

The TMG unit was also successfully used by Bunge and coworkers who reported copper compounds with interesting polynuclear motifs containing the anionic form of TMG as guanidinate (Bunge and Steele 2009, Bunge et al. 2009).

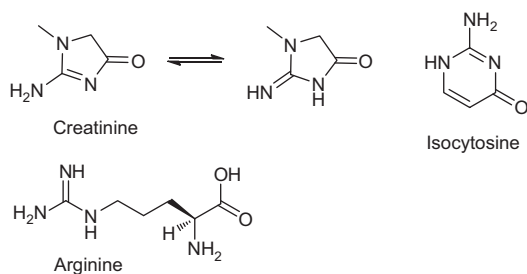
### Biologically occurring guanidines

The most prominent naturally occurring guanidines used for copper coordination chemistry are arginine, creatinine and isocytosine. In nature, arginine serves as a water solubility mediating functional group or as a carboxylate-specific hydrogen bond donor in proteins and other natural products.

The challenge in using these compounds for coordination chemistry lies in the potential choice of the binding site for the metal and multiple tautomeric forms (Scheme 3). For example, the search for tautomers and conformers of the small molecule arginine is still a vital field of recent research (Di Costanzo et al. 2006, Schlund et al. 2008). Understanding the role of copper in DNA binding is crucial as Cu(II) mediates polypeptide-polynucleotide interactions (Bean et al. 1977, Koren and Mildvan 1977, Bere and Helene 1979). Additionally, copper supports self-assembly processes but also radical processes involving hydroxyl radicals (Minisci 1996, Leininger et al. 2000, Swiegers and Malefetse 2000).



**Scheme 2** Examples of mono(guanidine) ligands used in coordination chemistry.



**Scheme 3** Biological guanidine ligands.

Therefore, the detailed knowledge about copper favoured binding sites in these ligands helps the understanding of several biologic processes. With this incentive, Parajon-Costa and coworkers synthesised the binary copper complex  $\text{Cu}(\text{creat})_2\text{Cl}_2$  (Parajon-Costa et al. 1997). García-Raso et al. (1995, 1998, 2002, 2003, 2006) and Castiñeiras et al. (2006) presented a series of ternary copper complexes comprising creatinine or isocytosine as an additional stabilising ligand. In all these complexes, copper is bound via the  $\text{N}_{\text{imine}}$  atom, whereas the free amino group stabilises a secondary interaction to other electronegative atoms (Cl, O). Previous crystallographic investigations of metal complexes of creatinine have demonstrated that creatinine normally binds to the metal ion through the ring  $\text{N}_{\text{imine}}$  atom (Mitewa et al. 1988, Gencheva et al. 1992), although chelation through the exocyclic and ring nitrogen atoms (Canty et al. 1978) and exocyclic oxygen atom (Panfil et al. 1993) binding have also been observed.

Arginine offers even more donor sites because it can bind metals at the amino acid side or the guanidine side. In arginine copper complexes, copper is mostly coordinated by the amino acid terminus (Ohata et al. 2000, Shields et al. 2000, Zabel et al. 2008, Patra et al. 2009). Ohata et al. reported a very interesting case where copper is coordinated by the amino acid terminus. The guanidine functions of the arginine stabilise via hydrogen bonds chiral double helical structures (Ohata et al. 1996).

In fact, N-alkylation hinders the formation of several tautomeric forms and leads to a more definitive coordination chemistry.

### Peralkylated guanidines

The biggest class of guanidine ligands are the peralkylated guanidines. Within this major class, subdivisions can be identified depending on the number of guanidine units combined in the ligand and the cyclicity of the ring system in which the guanidine is incorporated.

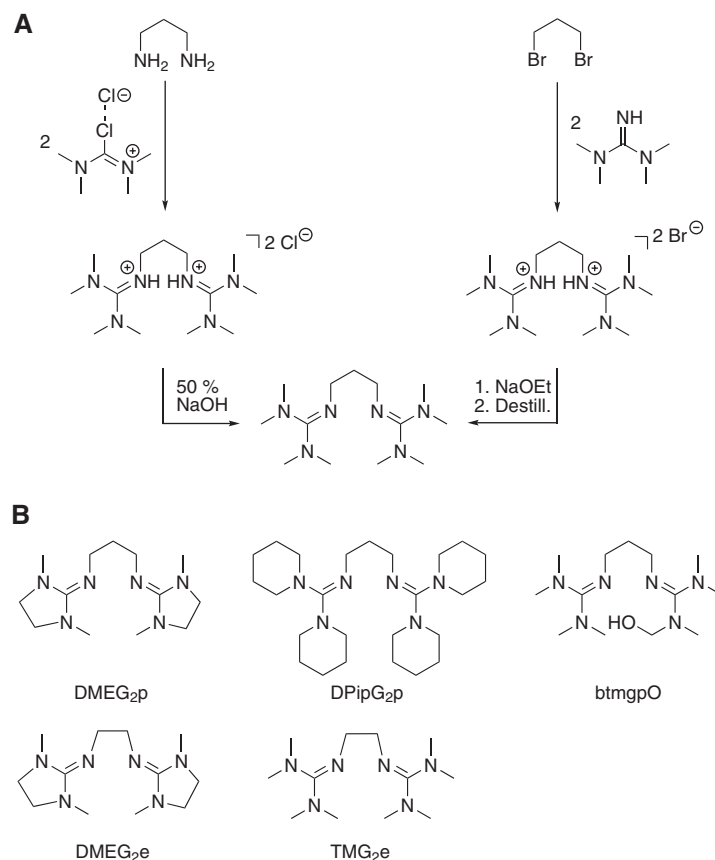
### Acyclic and monocyclic guanidine copper complexes

**Bis(guanidines)** The history of saturated bis(guanidines) and their use in metal complexation started in the Pohl group in the 1980s (Waden 1999). Only in 2001, the first bis(guanidine) 1,3-bis(*N,N,N',N'*-tetramethylguanidino)propane (btm<sub>2</sub>gp) was published simultaneously by the Henkel and Pohl groups (Pohl et al. 2000a,b) and the Sundermeyer group (Wittmann et al.

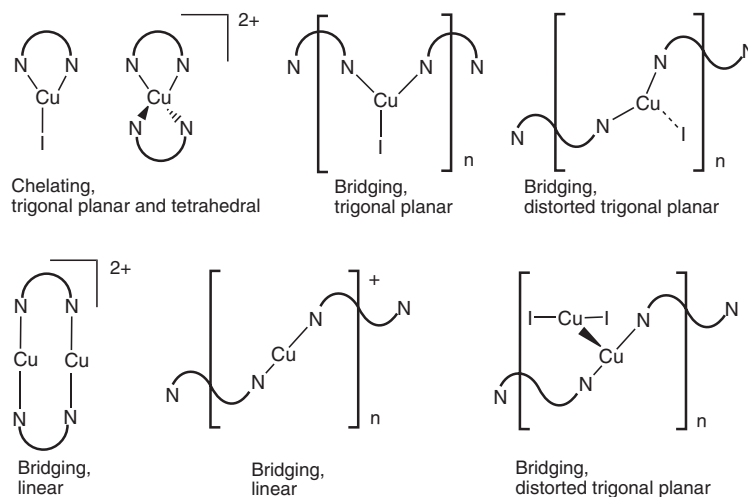
2000, 2001). Remarkably, the groups used totally different synthetic approaches: Henkel and Pohl combined in a large-scale experiment 1,3-dibromopropane and tetramethylguanidine [ $\text{HN}=\text{C}(\text{NMe}_2)_2$ , TMG] in excess for days at 150°C (Scheme 4, right-hand side). After subsequent distillation of excess TMG, a deprotonation step with sodium ethoxide and purification by distillation, they finished off with yields of 30–40%. The Sundermeyer group followed a more efficient rather medium-scale synthetic protocol originally developed by Kantlehner et al. (1984): they used the reaction of the electrophilic chloroformamidinium chlorides with bis(amines) (some hours at MeCN reflux) followed by deprotonation of the bis(hydrochloride) in the two-phase system 50% KOH(aq)/MeCN and obtained the pure, free ligand in 95% yield (Scheme 4, left-hand side).

These bis(guanidines) have been applied in very diverse chemistry: owing to their excellent N donor strength, the Henkel group used them for the stabilisation of biomimetic copper complexes (Pohl et al. 2000a, Herres et al. 2005). In this context, the class of bis(guanidines) has been extended into a library of bis(guanidines) (Herres-Pawlis et al. 2005b) following the Kantlehner protocol (Kantlehner et al. 1984). These ligands are able to stabilise copper(I) complexes in chelating and bridging motifs (Scheme 5).

Some examples of complexes with chelating or bridging motifs are shown in Figure 1. Bis(guanidines) are such strong donors that they can easily stabilise linear coordination under formation of binuclear compounds or coordination polymers. The whole guanidine unit takes part in the coordination owing to the delocalisation within the  $\text{CN}_3$  unit. Hence, the lengths of the formal double  $\text{C}=\text{N}$  bond and the formal  $\text{C}-\text{NR}_2$  single bonds are leveled. For the evaluation of the elongation of the  $\text{C}=\text{N}$  double bond and the shortening of the  $\text{C}-\text{NR}_2$  bonds within the guanidine unit, the  $\rho$ -value was introduced by the Sundermeyer group (Raab et al. 2003). It is calculated by the formula  $\rho=2a/(b+c)$ , where  $a$  is the  $\text{C}=\text{N}$  bond length and  $b$  and  $c$  are the  $\text{C}-\text{NR}_2$  bond lengths. In the case of a  $\text{C}_3$ -symmetrical  $\text{CN}_3$  unit, the  $\rho$ -value is equal to one. Key geometrical parameters of selected bis(guanidine) complexes are collected in Table 1. The length of the  $\text{Cu}-\text{N}_{\text{imine}}$  bond decreases with smaller coordination number (e.g., in the binuclear linear complexes  $[\text{Cu}_2(\text{btm}\text{gp})_2][\text{PF}_6]_2$ ,  $[\text{Cu}_2(\text{DMEG}_2\text{p})_2][\text{PF}_6]_2$ ,  $[\text{Cu}_2(\text{DPipG}_2\text{p})_2][\text{PF}_6]_2$ ) (Herres-Pawlis et al. 2005a) and higher oxidation state. This change in donation is accompanied by structural changes within the guanidine unit. Owing to the delocalisation, the whole guanidine unit answers to the stronger donation of the  $\text{N}_{\text{imine}}$  atom to a stronger Lewis acid under elongation of the  $\text{C}_{\text{imine}}-\text{N}_{\text{imine}}$  bond and concomitant shortening of the  $\text{C}_{\text{imine}}-\text{N}_{\text{amine}}$  bonds. Hence, for btm<sub>2</sub>gp complexes, the tendency can be derived that  $\rho$  increases with decreasing coordination number and higher oxidation state because the guanidine has to stabilise more positive charge transferred from the copper. This donor characteristic makes guanidines very efficient in transition metal coordination. The most useful ligand backbones are propylene and ethylene units due to the favourable coordination ‘bite’. It is evident that in ligands with ethylene backbone similar



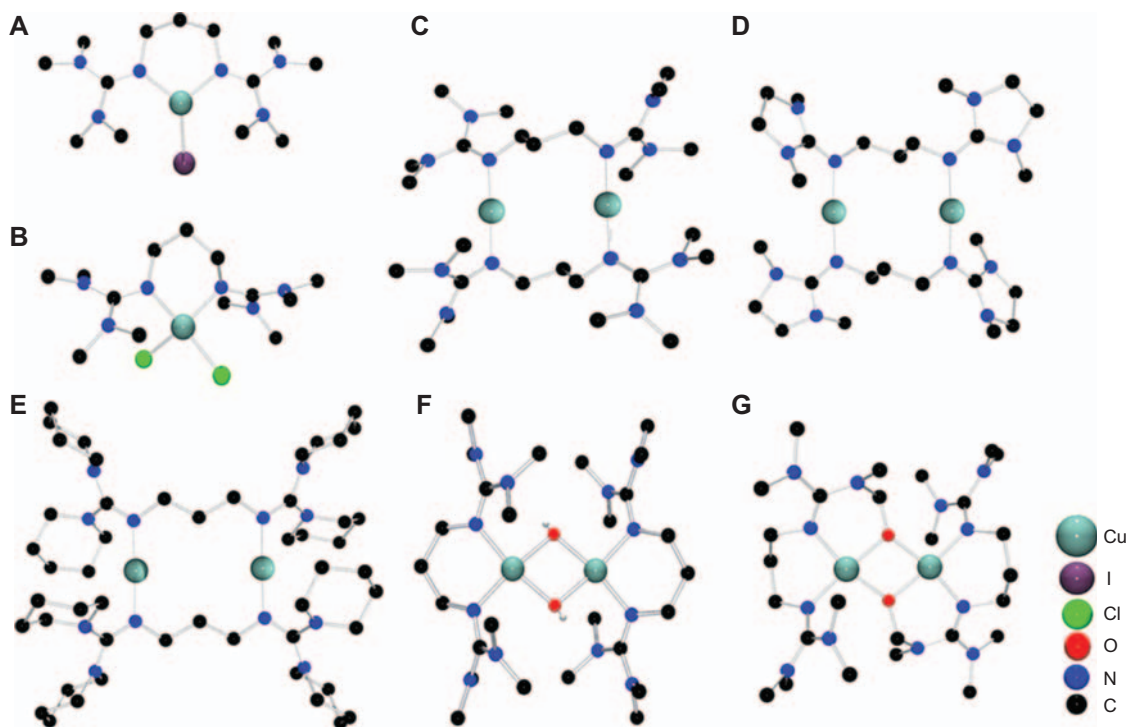
**Scheme 4** (A) Syntheses of bis(tetramethylguanidino)propane (btmgp or TMG<sub>2</sub>p) and (B) examples of further bis(guanidines).



**Scheme 5** Coordination topologies enabled by guanidine ligands.

trends appear for guanidine coordination: in copper(II) complexes the Cu-N<sub>imine</sub> bonds are shortened and the delocalisation parameter  $\rho$  indicates slightly stronger delocalisation within the guanidine unit than in copper(I) complexes (Figure 2 and Table 2) (Herres-Pawlis et al. 2008, Neuba et al. 2008, Bienemann et al. 2010).

In addition to the use in bioinorganic coordination chemistry, the bis(guanidine) ligands DMEG<sub>2</sub>e and TMG<sub>2</sub>e have recently been used for the stabilisation of copper complexes for atom transfer radical polymerisation of styrene (Bienemann et al. 2010). The coordinative performance of the bis(guanidine) ligands btmgp and DMEG<sub>2</sub>e is convincing



**Figure 1** Molecular structures of (A)  $[\text{Cu}(\text{btmgp})\text{I}]$ , (B)  $[\text{Cu}(\text{btmgp})\text{Cl}_2]$ , (C)  $[\text{Cu}_2(\text{btmgp})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{btmgp})_2][\text{PF}_6]_2$ , (D)  $[\text{Cu}_2(\text{DMEG}_2\text{p})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{DMEG}_2\text{p})_2][\text{PF}_6]_2$ , (E)  $[\text{Cu}_2(\text{DPipG}_2\text{p})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{DPipG}_2\text{p})_2][\text{PF}_6]_2$ , (F)  $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-OH})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{btmgp})_2(\mu\text{-OH})_2][\text{PF}_6]_2$  and (G)  $[\text{Cu}_2(\text{btmgp})_2\text{O}]^{2+}$  in crystals of  $[\text{Cu}_2(\text{btmgp})_2\text{O}][\text{PF}_6]_2$ .

with regard to coordinational motifs and scope of metals as summarised elsewhere (Neuba et al. 2008, 2010).

Several of the copper(I) bis(guanidine) complexes form upon reaction with dioxygen at low temperatures binuclear  $\text{Cu}_2\text{O}_2$  motifs, namely bis( $\mu$ -oxo)dicopper(III) complexes and  $\mu\text{-}\eta^2\text{:}\eta^2$ -peroxo-dicopper(II) complexes (Scheme 6) (Herres et al. 2005, Herres-Pawlis et al. 2005a). These bioinorganic model complexes for hemocyanine can be distinguished UV/Vis-spectroscopically by their characteristic ligand-to-metal charge transitions (LMCTs): the  $[\text{Cu}^{\text{III}}_2(\mu\text{-O})_2]^{2+}$  core shows oxo $\rightarrow$ Cu(III) LMCTs at 300 and 400 nm and the  $[\text{Cu}^{\text{II}}_2(\mu\text{-O}_2)]^{2+}$  core at 350 and 500 nm (Mirica et al. 2004). As a special feature of guanidine-type ligands, these bis( $\mu$ -oxo)dicopper(III) species exhibit a further absorption band in the visible range at 550 nm which is caused by  $\pi_{\text{gua}}\rightarrow\text{Cu}(\text{III})$  LMCTs (Herres-Pawlis et al. 2009c). An association between the torsion within the guanidine groups and the formation of bis( $\mu$ -oxo)dicopper(III) complexes and  $\mu\text{-}\eta^2\text{:}\eta^2$ -peroxo-dicopper(II) complexes was found for bis(guanidine) stabilised  $\text{Cu}_2\text{O}_2$  species (Herres-Pawlis et al. 2005a). Upon warming up of the solution of these  $\text{Cu}_2\text{O}_2$  complexes to room temperature, guanidine methyl groups are hydroxylated and the resulting products are isolated to be bis( $\mu$ -alkoxo)dicopper(II) complexes and – as a concomitantly formed coproduct – bis( $\mu$ -hydroxo)dicopper(II) complexes (Herres et al. 2004, 2005). When the substitution pattern at the guanidine is considerably expanded, the  $\text{Cu}_2\text{O}_2$  core unit is shielded which precludes reactions with substrates or solvent molecules. The resulting bis( $\mu$ -oxo)dicopper(III) complexes

with the ligand  $N^1,N^3$ -bis[bis(2,2,6,6-tetramethylpiperidin-1-yl)methylen]propan-1,3-diamine [B(TMPip)G<sub>2</sub>p] comprises so many sterically demanding groups which cannot easily be C-H activated that this species is stable in solution for several days (Herres-Pawlis et al. 2009a).

Chaudhuri et al. were successful to characterise the sulphur analogue of a  $\mu\text{-}\eta^2\text{:}\eta^2$ -peroxo-dicopper(II) complex (Chaudhuri et al. 2009). They used btmgp and  $N,N'$ -[2-methyl-2-(2-pyridyl)propan-1,3-diyl]bis(tetramethylguanidine) for copper complexation and obtained the  $\mu\text{-}\eta^2\text{:}\eta^2$ -disulfido-dicopper(II) complexes depicted in Scheme 7. In the UV/Vis spectrum, these complexes display characteristic charge transfer transitions at 376 and 477 nm. Additionally, they reported the cupric chloride complex and the bis( $\mu$ -hydroxo)dicopper complex with  $N,N'$ -[2-methyl-2-(2-pyridyl)propan-1,3-diyl]bis(tetramethylguanidine). Key geometrical parameters of the  $\mu\text{-}\eta^2\text{:}\eta^2$ -disulfido-dicopper(II) complexes are summarised in Table 3. The Cu–N<sub>imine</sub> bond lengths are shorter than in the comparable bis( $\mu$ -hydroxo) dicopper complexes.

In these ligands, the ligand backbone is aliphatic, but a multitude of further bis(guanidines) with aromatic backbones have been developed (Pruszyński et al. 1992).

As an example of bis(guanidine) with aromatic amine function, 2,2'-bis[2N-(1,1',3,3'-tetramethylguanidino)]diphenylene-amine (TMG<sub>2</sub>PA) was used for the synthesis of copper complexes (Herres-Pawlis et al. 2009b). Remarkably, the reaction of this ligand with CuI in MeCN results in the formation of  $[\text{Cu}^{\text{II}}(\text{TMG}_2\text{PA}_{\text{amid}})\text{I}]$  indicating that Cu<sup>I</sup> is the target of an

**Table 1** Selected bond lengths (Å) and angles (°) of selected propylene-bridged bis(guanidine) complexes<sup>a</sup>.

	[Cu(btmgp)I]	[Cu(btmgp)Cl <sub>2</sub> ]	[Cu <sub>2</sub> (btmgp) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>	[Cu <sub>2</sub> (DMEGp) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>	[Cu <sub>2</sub> (DPipG <sub>2</sub> p) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>	[Cu <sub>2</sub> (btmgp) <sub>2</sub> (OH) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>	[Cu <sub>2</sub> (btmgpO) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>
Cu-N <sub>imine</sub>	2.010(5), 2.002(5)	1.988(5), 1.992(4)	1.876(2), 1.878(2)	1.878(2), 1.873(2)	1.856(3), 1.876(3)	1.962(2), 1.968(2)	1.937(2), 1.961(2)
N <sub>imine</sub> =C <sub>imine</sub>	1.287(8), 1.302(8)	1.315(7), 1.306(7)	1.323(3), 1.315(3)	1.310(3), 1.318(3)	1.320(5), 1.297(4)	1.321(3), 1.313(3)	1.314(3), 1.311(3)
C <sub>imine</sub> -N <sub>imine</sub>	1.363-1.387	1.351-1.354	1.356-1.363	1.345-1.370	1.356-1.374	1.356-1.364	1.348-1.374
N <sub>imine</sub> -Cu-N <sub>imine</sub>	103.3(2)	89.7(2)	176.7(1)	175.3(1)	176.8(2)	94.0(2)	93.3(1)
ρ	0.942	0.969	0.971	0.967	0.959	0.970	0.965
References	(Pohl et al. 2000a)	(Pohl et al. 2000a)	(Herres-Pawlis et al. 2005a)	(Herres-Pawlis et al. 2005a)	(Herres-Pawlis et al. 2005a)	(Herres et al. 2005)	(Herres et al. 2005)

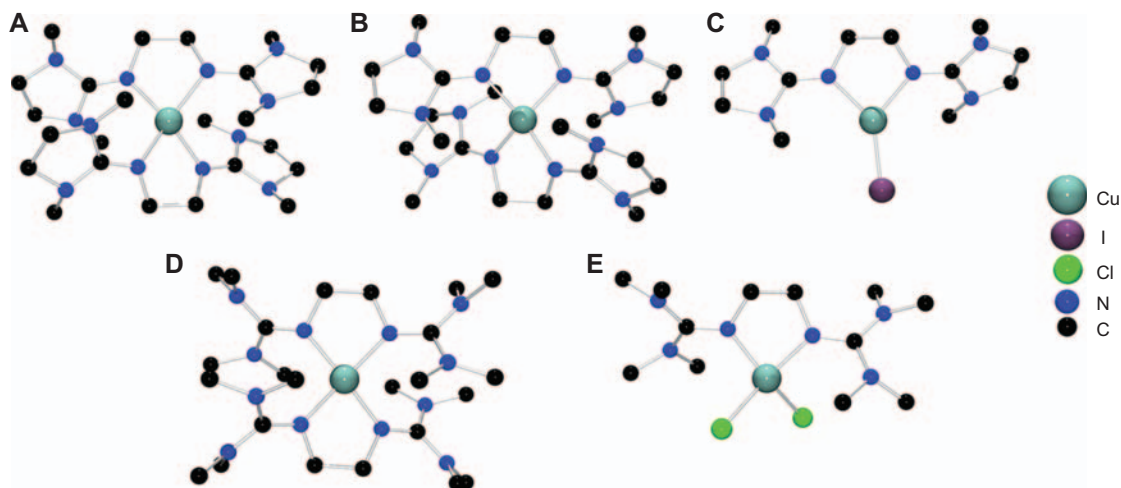
<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.

oxidative attack of the N-H proton of the ligand which itself is converted to molecular hydrogen. In [Cu<sup>II</sup>(TMG<sub>2</sub>PA<sub>amid</sub>)I], copper resides in a distorted tetrahedral coordination environment. When [Cu(MeCN)<sub>4</sub>][PF<sub>6</sub>]<sub>2</sub> is used as the copper(I) source, [Cu<sup>I</sup><sub>2</sub>(TMGbenz)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> with linear copper coordination is obtained instead (Figure 3). The use of the non-coordinating counter ion [PF<sub>6</sub>]<sup>-</sup> apparently prevents Cu<sup>I</sup> from oxidation but induces itself a cyclisation reaction within the ligand which results in the formation of the benzimidazole-guanidine ligand 2-[2-(2-(dimethylamino)-1H-benzo[d]imidazol-1-yl)phenyl]-1,1,3,3-tetramethylguanidine (TMGbenz).

Complementary to these coordination chemistry studies, the Sundermeyer group used the high basicity and developed the ‘proton sponges’ tetramethylguanidinonaphthalene (TMGN) (Raab et al. 2002) and dimethylethyleneguanidinonaphthalene (DMEGN) (Scheme 8) (Raab et al. 2003). In experimental and theoretical studies, the special basic activity was investigated and directly related to the ability to delocalise the positive charge within the guanidine framework (Kovacevic and Maksic 2002, Przybylski et al. 2007, Coles et al. 2009). In the case of these proton sponges, the effect of ‘chelating’ a proton between the two adjacent guanidine N<sub>imine</sub> atoms makes the sponge so strong (Raab et al. 2003, Sundermeyer et al. 2009). As a matter of course, these ligands are able to coordinate copper, as exemplified in the complex [(TMGN)CuI] with Cu-N<sub>imine</sub> bond lengths of 1.977(8) and 1.971(2) Å and C=N<sub>imine</sub> bond lengths of 1.335(4) and 1.331(2) Å (Sundermeyer et al. 2009). Wild et al. (2008) were also successful to report further metal complexes with the proton sponge TMGN.

Parallel to the development of saturated bis(guanidines), the class of imidazolin-2-imines (also called 2-iminoimidazoline) has been introduced into coordination chemistry by Kuhn and coworkers (1998, 2002, 2003). In general, imidazolin-2-imines can be synthesised by the reaction of bis(tosylates) with substituted guanidines (Scheme 9) but also by the Staudinger reaction via the combination of organic azides with carbenes (Petrovic et al. 2008). This intriguing ligand family is typically regarded to be a slightly stronger donor compared to guanidines owing to the strong contribution of the ylide-type mesomeric form (Petrovic et al. 2007, Tamm et al. 2007).

The Tamm group used the bis(imidazolin-2-imine) copper complex of 1,2-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-imino)ethane (BL<sup>IPr</sup>) in the bioinorganic application of stabilising a bis(μ-hydroxo)dicopper complex which exhibits shifted charge transfer bands at 400 and 585 nm instead of the ‘classical’ oxo→Cu(III) LMCTs of a [Cu<sub>2</sub>(μ-O)<sub>2</sub>]<sup>2+</sup> core at 300 and 400 nm. Additionally, the copper complex of BL<sup>IPr</sup> is active in the atom transfer radical polymerisation of styrene (Petrovic et al. 2008). In further studies, this group synthesised pincer type ligands with two imidazolin-2-imine groups (e.g., 2,6-bis[1,3-di-tert-butylimidazolin-2-imino)methyl]pyridine) (Petrovic et al. 2007, Tamm et al. 2007). As already found for bis(guanidines), these bis(imidazolin-2-imines) are able to form complexes with a great variety of metals throughout the periodic system (Filimon 2009, Börner et al. 2010, Filimon et al. 2010, Glöge et al. 2010).



**Figure 2** Molecular structures of (A)  $[\text{Cu}^{\text{I}}(\text{DMEG}_2\text{e})_2]^+$  in crystals of  $[\text{Cu}^{\text{I}}(\text{DMEG}_2\text{e})_2][\text{CuCl}_2]$ , (B)  $[\text{Cu}^{\text{II}}(\text{DMEG}_2\text{e})_2]^{2+}$  in crystals of  $[\text{Cu}^{\text{II}}(\text{DMEG}_2\text{e})_2][\text{Cu}_2\text{I}_4]$ , (C)  $[\text{Cu}(\text{DMEG}_2\text{e})\text{I}]$ , (D)  $[\text{Cu}(\text{TMG}_2\text{e})_2]^{2+}$  in crystals of  $[\text{Cu}(\text{TMG}_2\text{e})_2][\text{Cu}_2\text{I}_4]$  and (E)  $[\text{Cu}(\text{TMG}_2\text{e})\text{Cl}_2]$ .

**Table 2** Selected bond lengths (Å) and angles (°) of ethylene-bridged bis(guanidine) complexes<sup>a</sup>.

	$[\text{Cu}^{\text{I}}(\text{DMEG}_2\text{e})_2][\text{CuCl}_2]$	$[\text{Cu}^{\text{II}}(\text{DMEG}_2\text{e})_2][\text{Cu}_2\text{I}_4]$	$[\text{Cu}(\text{DMEG}_2\text{e})\text{I}]$	$[\text{Cu}(\text{TMG}_2\text{e})_2][\text{Cu}_2\text{I}_4]$	$[\text{Cu}(\text{TMG}_2\text{e})\text{Cl}_2]$
Cu-N <sub>imine</sub>	2.078(2), 2.062(2)	1.960(2), 1.979(2)	2.046(1), 2.029(1)	1.994–2.000	1.975(1)
N <sub>imine</sub> =C <sub>imine</sub>	1.294–1.296	1.305(4), 1.298(4)	1.293(2), 1.291(2)	1.310–1.327	1.310
C <sub>imine</sub> -N <sub>amine</sub>	1.377–1.397	1.362–1.372	1.384(2), 1.381(3)	1.351–1.379	1.361–1.368
Cu-X			2.450(1)		2.258(1)
N <sub>imine</sub> -Cu-N <sub>imine</sub>	84.0(1)	84.4(1)	85.48(6)	83.8(1)	83.9(1)
N <sub>imine</sub> -Cu-X	–	–	133.31(4), 141.15(4)	–	96.4(1), 146.7(1)
$\rho$	0.930	0.950	0.946	0.970	0.960
References	(Bienemann et al. 2010)	(Herres-Pawlis et al. 2008)	(Neuba et al. 2008)	(Bienemann et al. 2010)	(Bienemann et al. 2010)

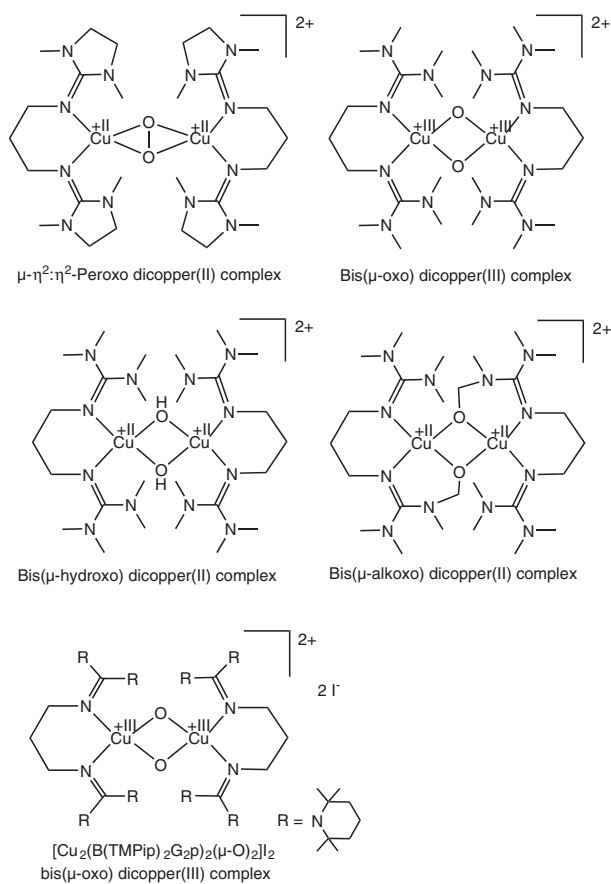
<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.

As prominent examples, some copper complexes of BL<sup>Pr</sup> are shown in Figure 4 and selected bond lengths and angles are collected in Table 4. Interestingly, the stronger coordination of copper(II) by BL<sup>Pr</sup> can be directly observed by the expansion of the N<sub>imine</sub>=C<sub>imine</sub> bond. The calculation of the parameter  $\rho$  (which is normally insightful for guanidines) gives an unclear picture here: there is no direct association between oxidation state, coordination number and degree of delocalisation. This shows that the mesomeric imidazolium form contributes considerably to the binding characteristics of imidazolin-2-imines and that the imine nitrogen atom offers additional  $\pi$ -donor density in the coordination.

**Tris(guanidines)** The most prominent tris(guanidine) TMG<sub>3</sub>tren has been the focus of much attention as a ‘superligand’ for transition metal chemistry. The synthesis was performed after Kantlehner’s protocol in 2001 by the Sundermeyer group (Wittmann et al. 2000, 2001). After the first coordination chemistry experiments with various metals (Wittmann et al. 2000, 2001) and emphasis on copper (Raab et al. 2001a), this special ligand exhibited the ability to stabilise an extraordinary copper-superoxo complex in a series of studies by Sundermeyer, Schindler and Holthausen (Schatz et al. 2004a,b, Würtele et al. 2006, Maiti et al. 2008a,b).

The copper(I) precursor complexes already allow interesting insights into the guanidine binding situation: the three guanidine units form a cavity around the copper atom with a tetrapodal coordination of the copper. In several copper(I) complexes (examples given in Scheme 10), the copper ion is exclusively coordinated by the TMG<sub>3</sub>tren ligand. In copper(II) complexes, this tetrapodal coordination is not sufficient and ancillary ligands as chloride or acetonitrile complement the coordination sphere. In the copper(II) complexes, the parameter  $\rho$  is larger than in the copper(I) complexes (Table 5).

After the first spectroscopic and theoretical studies on the existence of a persistent end-on copper superoxo complex in 2004 (Schatz et al. 2004a,b), the structural characterisation of the end-on superoxo  $[\text{Cu}^{\text{II}}(\eta^1\text{-O}_2^-)(\text{TMG}_3\text{tren})][\text{SbF}_6]$  complex shed light on a new 1:1 CuO<sub>2</sub> species which is formed reversibly from the corresponding cuprous analogue at low temperatures (Figure 5 and Scheme 11) (Würtele et al. 2006a,b). This fascinating superoxo complex loses the bound oxygen upon warming to room temperature during seconds which proves the stability of the tetramethylguanidine groups against C-H activation. The O-O bond length measures 1.280(3) Å with an O-O-Cu angle of 123.53(18)°. This geometry is in accordance with crystallographic results on the dioxygen complex of the peptidylglycine  $\alpha$ -hydroxylating monooxygenase (PHM),



**Scheme 6** Bis(guanidine) stabilised  $\text{Cu}_2\text{O}_2$  motifs.

an enzyme which hydroxylates and amidates selected aliphatic C-H positions (Prigge et al. 2004). Furthermore, such an end-on superoxo copper(II) species is likely to be a crucial intermediate in the dopamine  $\beta$ -monooxygenase (D $\beta$ M) (Klinman 1996). PHM and D $\beta$ M catalyse the stereospecific hydroxylation of substrate C-H bonds being important in neuropeptide and neurotransmitter biosynthesis. PHM catalyses the hydroxylation of the glycine  $\alpha$ -carbon of glycine-extended peptides and D $\beta$ M catalyses the conversion of dopamine to norepinephrine (Klinman 1996).

In an isotopic probing investigation, Lanci et al. reported that  $[\text{Cu}(\eta^1\text{-O}_2)(\text{TMG}_3\text{tren})]^+$  is paramagnetic due to a triplet

**Table 3** Selected bond lengths (Å) and angles (°) of bis(guanidine)  $\mu\text{-}\eta^2\text{:}\eta^2\text{-disulphido-dicopper(II)}$  complexes (Chaudhuri et al. 2009)<sup>a</sup>.

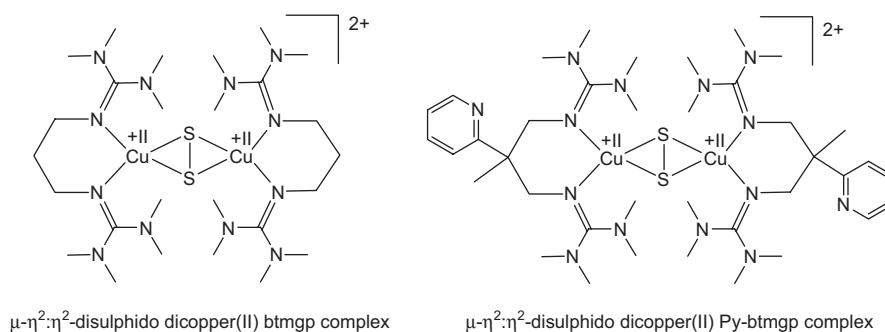
	$[\text{Cu}_2(\text{btmgp})_2(\text{S}_2)]$ $[\text{PF}_6]_2$	$[\text{Cu}_2(\text{Py-btmgp})_2(\text{S}_2)]$ $[\text{PF}_6]_2$
Cu-N <sub>imine</sub>	1.932(2), 1.936(2)	1.919(4), 1.926(3)
N <sub>imine</sub> =C <sub>imine</sub>	1.314	1.323
C <sub>imine</sub> -N <sub>amine</sub>	1.361	1.352
Cu-S	2.1533(9)	2.1264(15)
S-S	2.1993(14)	2.204(2)
N <sub>imine</sub> -Cu-N <sub>imine</sub>	99.77(9)	98.95(16)
S-Cu-S	61.44(3)	62.44(5)
$\rho$	0.965	0.978

<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.

electronic structure (in contrast to other copper compounds with side-on bound  $\text{O}_2$ ) and that the compound possesses within the valence bond description a greater ionic ( $\text{Cu}^{\text{II}}\text{-O}_2^{\cdot-}$ ) character than other  $\text{M-O}_2$  compounds (Lanci et al. 2007). The  $^{18}\text{O}$  equilibrium isotope effect (EIE) determined for  $[\text{Cu}(\eta^1\text{-O}_2)(\text{TMG}_3\text{tren})]^+$  (EIE=1.0148) is consistent with the proposal of the pre-equilibrium formation of the copper(II) end-on superoxide intermediate in D $\beta$ M and PHM (Gherman and Cramer 2004). In a very recent spectroscopic (absorption, MCD, VTVH-MCD and rR excitation profiles) and theoretical study, the reason for the triplet ground states was elucidated (Woertink et al. 2010).  $[\text{Cu}(\eta^1\text{-O}_2)(\text{TMG}_3\text{tren})]^+$  possesses two perpendicular magnetic orbitals separated by an energy splitting of less than  $9500\text{ cm}^{-1}$  being smaller than the estimated spin pairing energy of  $\sim 18,600\text{ cm}^{-1}$ .

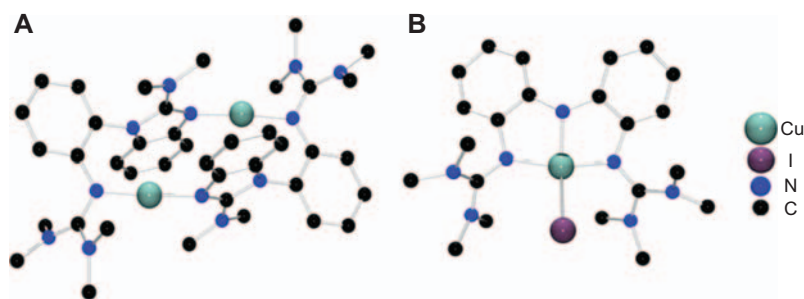
Addition of phenolic substrates results in substrate oxidation to orthoquinones or radically coupled bisphenols (Maiti et al. 2008a,b). As byproduct, the complex  $[\text{Cu}^{\text{II}}(\text{TMG}_3\text{trenO})][\text{B}(\text{C}_6\text{F}_5)_4]$  has been isolated revealing that a methyl position of one of the guanidine groups was hydroxylated similar to the observed reactivity in bis(guanidine) copper complexes (*vide supra*) (Herres et al. 2005).

This hydroxylation reaction could also be evoked by a hydrogen atom source such as TEMPO under subsequent O-O bond cleavage (Maiti et al. 2008a,b) or by applying PhIO to  $\text{TMG}_3\text{tren}$  copper(I) complexes (Gaoutchenova 2006, Sundermeyer et al. 2009). This reactivity shows that the end-on superoxo copper species is an excellent model

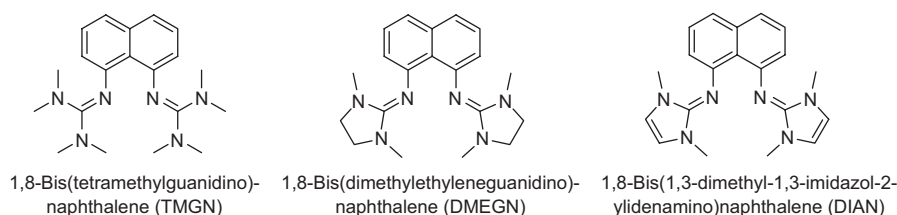


**Scheme 7** Bis(guanidine)  $\mu\text{-}\eta^2\text{:}\eta^2\text{-disulphido-dicopper(II)}$  complexes.

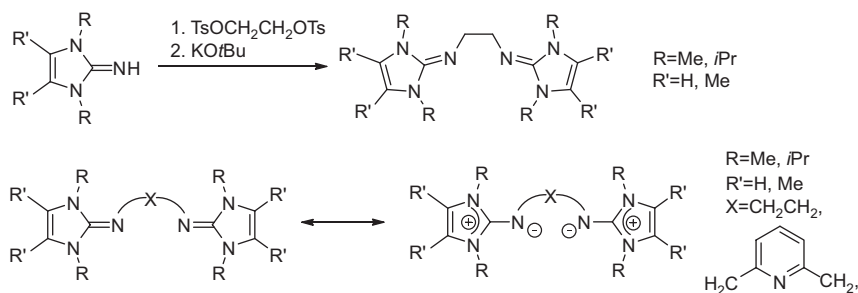




**Figure 3** Molecular structures of (A) the  $[\text{Cu}_2(\text{TMGBenz})_2]^{2+}$  cation in crystals of  $[\text{Cu}_2(\text{TMGBenz})_2][\text{PF}_6]_2$  [ $\text{Cu}-\text{N}_{\text{imine,benz}}$  1.879(5),  $\text{Cu}-\text{N}_{\text{imine,gua}}$  1.895(6),  $\text{N}_{\text{imine,benz}}-\text{C}_{\text{imine}}$  1.307(8),  $\text{N}_{\text{imine,gua}}-\text{C}_{\text{imine}}$  1.324(9) Å] and of (B)  $[\text{Cu}(\text{TMGA}_2\text{PA}_{\text{amid}})\text{I}]$  [ $\text{Cu}-\text{N}_{\text{amide}}$  1.903(5),  $\text{Cu}-\text{N}_{\text{imine}}$  1.961(5),  $\text{N}_{\text{imine}}-\text{C}_{\text{imine}}$  1.348 Å] (Herres-Pawlis et al. 2009b).



**Scheme 8** Guanidine based proton sponges.



**Scheme 9** Synthesis of imidazolin-2-imine ligands and limiting mesomeric structures thereof.

for  $\text{D}\beta\text{M}$  and  $\text{PHM}$ . Analogue to the reaction with  $\text{PhIO}$ ,  $\text{TMG}_3\text{tren}$  copper(I) complexes reacted with tosyl azide ( $\text{TosN}_3$ ) to a copper complex which is aminated at a methyl group of one of the guanidine groups (Gaoutchenova 2006, Sundermeyer et al. 2009). This represents an analogue reaction to the described hydroxylation reaction which follows the  $\text{PhIO}$  addition. A nitrene species is discussed as intermediate.

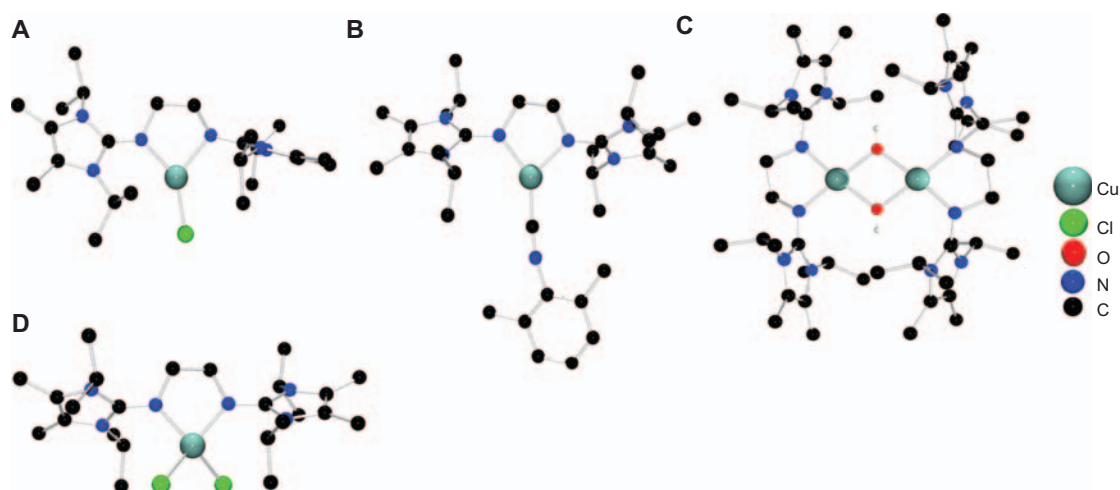
In further studies, Maiti et al. investigated the reactivity of the end-on superoxo copper species towards nitrogen monoxide (Maiti et al. 2008). At low temperature, a peroxynitrite copper(II) complex is formed which decays into a copper(II) nitrito complex (Maiti et al. 2008, Sundermeyer et al. 2009).

Parallel to the exploration of the bioinorganic performance of  $[\text{Cu}(\text{TMG}_3\text{tren})]\text{Cl}$ , the Sundermeyer group discovered that this complex is active in the oxidative carbonylation of methanol to dimethylcarbonate and water (Raab et al. 2001b, Sundermeyer et al. 2009), which is highly useful

as an alternative to the traditional phosgene-based route to dimethylcarbonate, a precursor in many industrial processes. In the mechanism of this reaction, the copper(I) complex reacts with  $\text{O}_2$  in the presence of methanol under formation of a copper(II) methoxy species. The masked coordinated methoxy radicals are transferred to  $\text{CO}$  to give dimethylcarbonate and the initial copper(I) complex which allows starting the next cycle.

The common change in substitution pattern of the used chloroformamidinium salts enabled the synthesis of the related ligands  $\text{DMPG}_3\text{tren}$  (Wittmann et al. 2000, 2001) and  $\text{DMEG}_3\text{tren}$  (Gaoutchenova 2006), which display similar chemistry as  $\text{TMG}_3\text{tren}$  including hydroxylation and nitrito chemistry.

Although the ligands  $\text{ToI}_6\text{H}_6\text{GuaTren}$  and  $i\text{Pr}_6\text{H}_6\text{GuaTren}$  (synthesised from carbodiimides and the corresponding primary amines) are not peralkylated their copper complexes are depicted here (Scheme 12) because they directly belong to the tris(guanidine)-tren family (Gaoutchenova 2006). Reaction

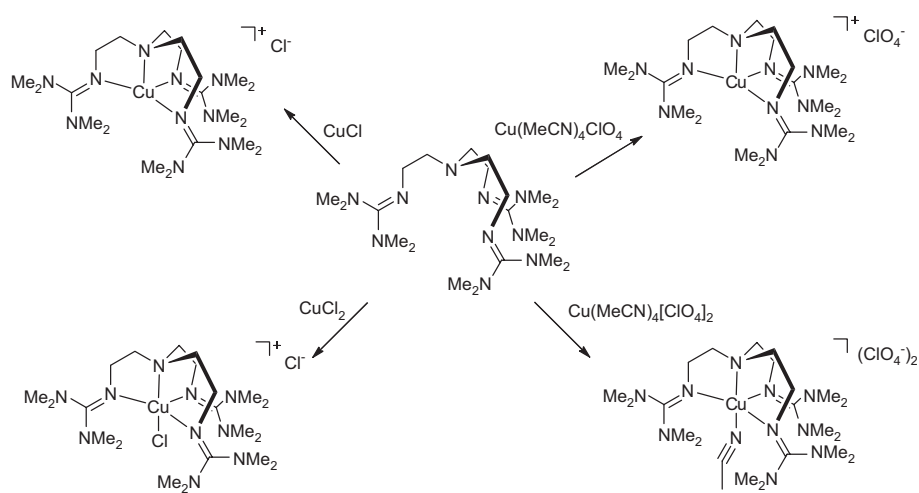


**Figure 4** Molecular structures of (A)  $[\text{Cu}(\text{BL}^{\text{Pr}})\text{Cl}]$ , (B)  $[\text{Cu}(\text{BL}^{\text{Pr}})(\text{CNXy})]^+$  in crystals of  $[\text{Cu}(\text{BL}^{\text{Pr}})(\text{CNXy})][\text{PF}_6]$ , (C)  $[\text{Cu}_2(\text{BL}^{\text{Pr}})_2(\text{OH})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{BL}^{\text{Pr}})_2(\text{OH})_2][\text{PF}_6]_2$  and (D)  $[\text{Cu}(\text{BL}^{\text{Pr}})\text{Cl}_2]$ .

**Table 4** Selected bond lengths (Å) and angles ( $^\circ$ ) of imidazolin-2-imine copper complexes<sup>a</sup>.

	$[\text{Cu}(\text{BL}^{\text{Pr}})\text{Cl}]$	$[\text{Cu}(\text{BL}^{\text{Pr}})(\text{CNXy})][\text{PF}_6]$	$[\text{Cu}_2(\text{BL}^{\text{Pr}})_2(\text{OH})_2][\text{PF}_6]_2$	$[\text{Cu}(\text{BL}^{\text{Pr}})\text{Cl}_2]$
Cu-N <sub>imine</sub>	2.058(1), 2.002(1)	1.977(3), 1.957(3)	1.916(2), 1.950(2)	1.971(1)
N <sub>imine</sub> =C <sub>imine</sub>	1.324(2), 1.313(2)	1.319(4), 1.328(4)	1.342(3), 1.340(3)	1.329(1)
C <sub>imine</sub> -N <sub>amine</sub>	1.367–1.384	1.363–1.378	1.350–1.361	1.359(1), 1.364(1)
Cu-X	2.159(1)	1.814(4)	1.932(2), 1.930(2)	2.246(1)
N <sub>imine</sub> -Cu-N <sub>imine</sub>	85.22(5)	86.0(1)	84.52(8)	83.39(7)
N <sub>imine</sub> -Cu-X	128.98(3), 145.24(3)	130.6(1), 143.3(1)	100.78(8), 99.32(8)	140.14(4), 98.52(4)
$\rho$	0.963	0.966	0.988	0.976
References	(Petrovic et al. 2008)	(Petrovic et al. 2008)	(Petrovic et al. 2008)	(Glöge et al. 2010)

<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.



**Scheme 10** Synthesis of copper  $\text{TMG}_3\text{tren}$  complexes.

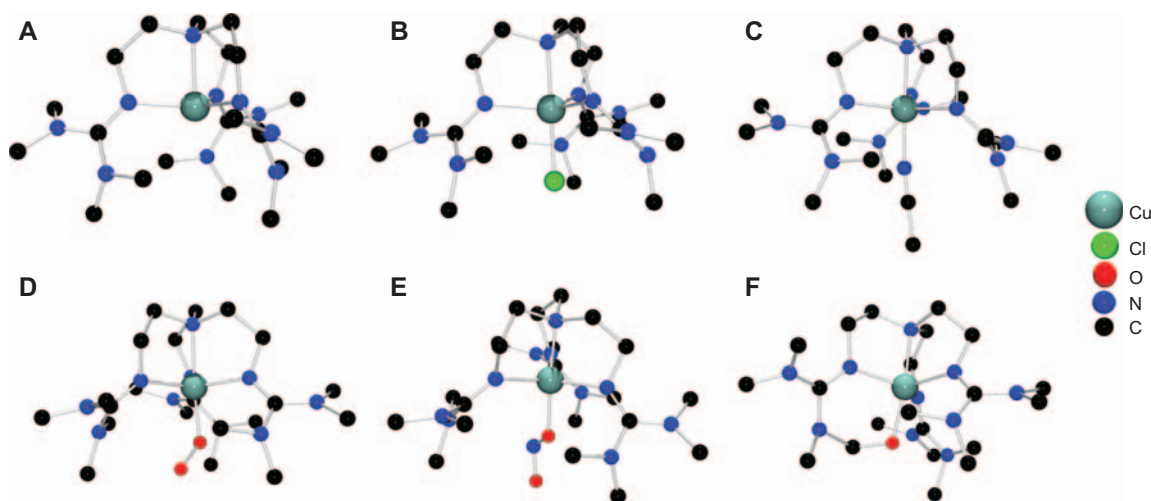
with halogenated solvents such as  $\text{CH}_2\text{Cl}_2$  affords radical dehalogenation for both types of  $\text{Gua}_3\text{tren}$  copper complexes as depicted in Scheme 11. In contrast to their peralkylated counterpart  $\text{TMG}_3\text{tren}$ , their dioxygen chemistry remains to be explored in more detail.

The attractive copper-dioxygen chemistry of  $\text{TMG}_3\text{tren}$  inspired several further studies with this ligand focusing on iron-oxygen (England et al. 2009a,b, 2010, Janardanan et al. 2010) and cobalt-oxygen reactivity (Pfaff et al. 2011). In a series of studies by the Que group, the special role of the

**Table 5** Selected bond lengths (Å) and angles (°) in TMG<sub>3</sub>tren copper complexes<sup>a</sup>.

	[Cu <sup>I</sup> (TMG <sub>3</sub> tren)]Cl	[Cu <sup>II</sup> (TMG <sub>3</sub> tren)Cl]Cl	[Cu <sup>II</sup> (TMG <sub>3</sub> tren)(NCMe)][ClO <sub>4</sub> ] <sub>2</sub>	[Cu(O <sub>2</sub> )(TMG <sub>3</sub> tren)][SbF <sub>6</sub> ]	[Cu <sup>II</sup> (NO <sub>2</sub> )(TMG <sub>3</sub> tren)][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]	[Cu <sup>II</sup> (TMG <sub>3</sub> trenO)][B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> ]
Cu-N <sub>imine</sub>	2.052(2)	2.091–2.109	2.054–2.082	2.080–2.095	2.084–2.090	2.053–2.117
Cu-N <sub>amine</sub>	2.190(3)	2.111(3)	2.078(5)	2.128	2.068	2.091(2)
N <sub>imine</sub> =C <sub>imine</sub>	1.295	1.309–1.316	1.299–1.313	1.307–1.320	1.306	1.302–1.303
C <sub>imine</sub> -N <sub>amine</sub>	1.370, 1.381	1.357–1.374	1.350–1.374	1.359–1.375	1.361–1.370	1.365–1.380; 1.415
Cu-L <sub>ax</sub>		2.285(1)	2.002(5)	1.927(2)	1.940	1.972(5)
N <sub>amine</sub> -Cu-L <sub>ax</sub>		178.40(9)	177.62(2)	173.8	174.2	170.01(2)
ρ <sub>amine</sub>	0.942	0.963	0.960	0.961	0.957	0.950, 0.937
Reference	(Raab et al. 2001a)	(Raab et al. 2001a)	(Raab et al. 2001a)	(Würtele et al. 2006a,b)	(Maiti et al. 2008a)	(Maiti et al. 2008b,c)

<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.



**Figure 5** Molecular structures of (A) [Cu(TMG<sub>3</sub>tren)]<sup>+</sup> in crystals of [Cu(TMG<sub>3</sub>tren)]Cl, (B) [Cu(TMG<sub>3</sub>tren)Cl]<sup>+</sup> in crystals of [Cu(TMG<sub>3</sub>tren)Cl]Cl, (C) [Cu(TMG<sub>3</sub>tren)(MeCN)]<sup>2+</sup> in crystals of [Cu(TMG<sub>3</sub>tren)(MeCN)][ClO<sub>4</sub>]<sub>2</sub>, (D) [Cu(O<sub>2</sub>)(TMG<sub>3</sub>tren)]<sup>+</sup> in crystals of [Cu(O<sub>2</sub>)(TMG<sub>3</sub>tren)][SbF<sub>6</sub>], (E) [Cu(NO<sub>2</sub>)(TMG<sub>3</sub>tren)]<sup>+</sup> in crystals of [Cu(NO<sub>2</sub>)(TMG<sub>3</sub>tren)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and (F) [Cu(TMG<sub>3</sub>trenO)]<sup>+</sup> in crystals of [Cu(TMG<sub>3</sub>trenO)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

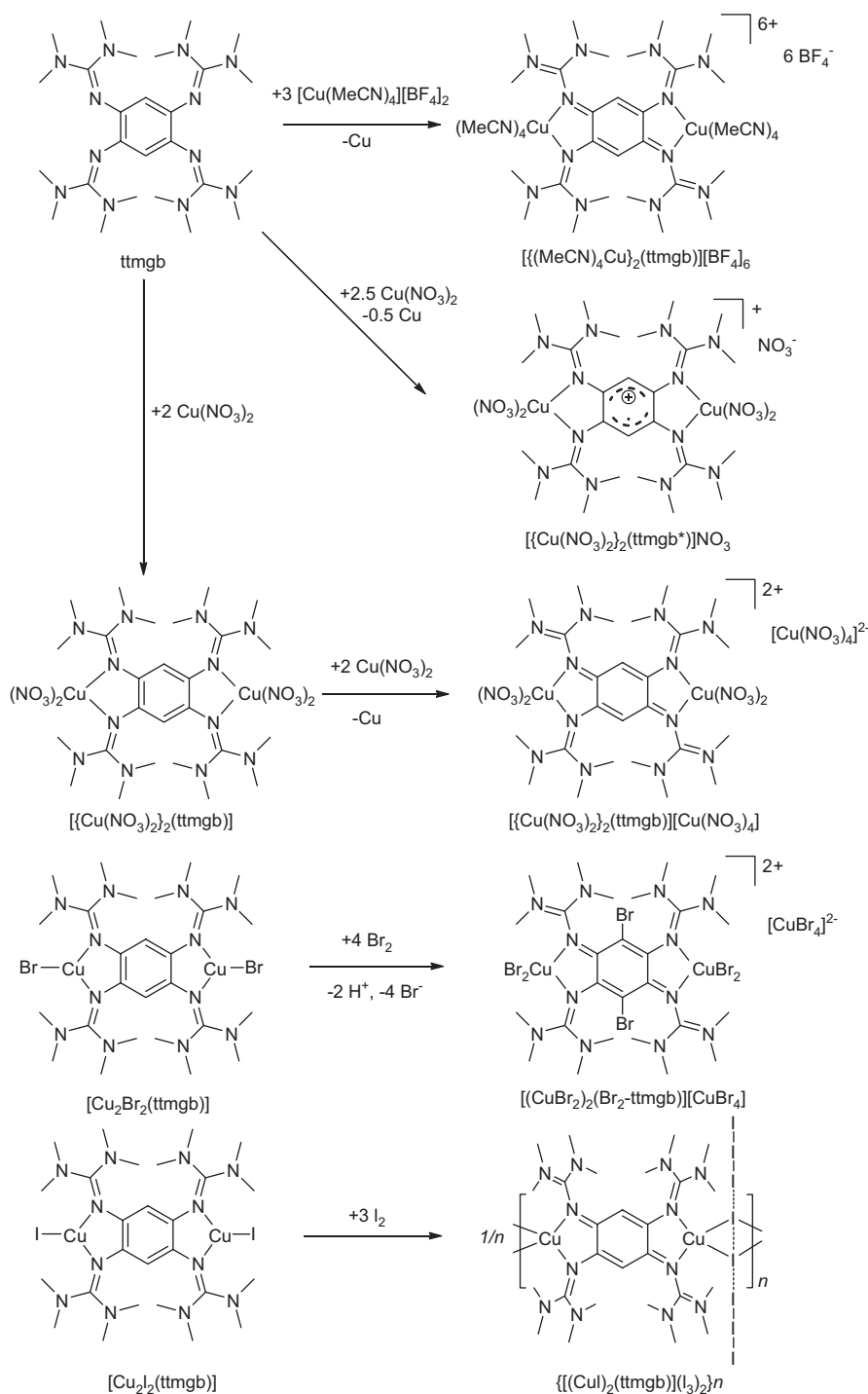
TMG<sub>3</sub>tren ligand for the stabilisation of an iron(IV) species and its oxidative capability was investigated by numerous spectroscopic and theoretical methods (England et al. 2009a,b, 2010, Janardanan et al. 2010). A similar hydroxylation activity is directed towards the guanidine methyl substituents as observed for their copper analogues (England et al. 2010).

#### Further peralkylated poly(guanidine) compounds

Assembling more guanidine units within one molecule is possible in tetra(guanidines) as was recently shown by the Himmel group (Wild et al. 2008, Peters et al. 2009, Emeljanenko et al. 2010a,b, Roquette et al. 2010, Trumm et al. 2010, Vitske et al. 2010). The distinct electrochemistry of these compounds makes them very valuable for the synthesis of (semi)conductive coordination polymers. In recent structural investigations, the Himmel group isolated binuclear copper complexes with 1,2,4,5-tetrakis(tetramethylguanidino)benzene (ttmgb) (Peters et al. 2009, Emeljanenko et al. 2010b). The ligand ttmgb reacts with excess copper(II) tetrafluoroborate to

a binuclear copper(II) complex with a simultaneously oxidised ligand and under precipitation of elemental copper (Scheme 13) (Peters et al. 2009). When ttmgb reacts with stoichiometric amounts of copper(II) nitrate, the complex [{Cu(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(ttmgb)] is formed which readily decomposes under ligand oxidation and copper reduction to give the complex [{Cu(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(ttmgb)][Cu(NO<sub>3</sub>)<sub>4</sub>]. At an ingenious choice of reaction conditions the complex [{Cu(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(ttmgb)][NO<sub>3</sub>] comprising a monocationic unit with a radical ttmgb\* ligand was isolated (Trumm et al. 2010). The halogenido complex [Cu<sub>2</sub>Br<sub>2</sub>(ttmgb)] can be oxidised and brominated in one step by reaction with bromine in MeCN at room temperature (Emeljanenko et al. 2010b). The reaction of the complex [Cu<sub>2</sub>I<sub>2</sub>(ttmgb)] with iodine leads only to ligand oxidation and formation of {[(CuI)<sub>2</sub>(ttmgb)](I<sub>3</sub>)<sub>2</sub>]<sub>n</sub> as coordination polymer with incorporated guanidine-functionalised aromatic compounds. The black polymer is an electrical semiconductor with a band gap of around 1 eV and is metastable towards oxidation of copper and reduction of iodine. Tetra(guanidines) such





**Scheme 13** Copper complexes with tetra(guanidines).

measure 2.064(4) Å and are thus larger than those in  $[\text{Cu}_2\text{I}_2(\text{ttmgb})]$  [2.0159(18)/2.0165(17) Å] (Emeljanenko et al. 2010b).

When the ttmgb ligand is coordinating in its unoxidised form (in  $[\text{Cu}_2\text{Br}_2(\text{ttmgb})]$ ,  $[\text{Cu}_2\text{I}_2(\text{ttmgb})]$  and  $[\text{Cu}_2(\text{NO}_3)_2]_2(\text{ttmgb})$ ), especially short  $\text{C}_{\text{imine}}=\text{N}_{\text{imine}}$  bonds can be found [1.311(5)–1.346(3) Å]. Upon oxidation, the

formal  $\text{C}=\text{N}$  bond loses its character under expansion to larger bond lengths [1.383(7)–1.412(5) Å]. In the series of nitrate complexes, the stepwise oxidation of ttmgb to the radical ion  $\text{ttmgb}^{\bullet+}$  to the dicationic  $\text{ttmgb}^{2+}$  is reflected in the formal  $\text{C}_{\text{imine}}=\text{N}_{\text{imine}}$  bonds going from 1.340 (av) over 1.372 to 1.399 Å for the dicationic ligand. Simultaneously, the  $\text{N}_{\text{imine}}-\text{C}_{\text{arom}}$  bond to the benzene backbone shortens in the same

Table 6 Selected bond lengths (Å) and angles (°) of ttmgb copper complexes.

	$[(\text{MeCN})_4\text{Cu}]_2$ (ttmgb)[BF <sub>4</sub> ] <sub>6</sub>	$[\text{Cu}_2\text{Br}_2]$ (ttmgb)	$[\text{Cu}_2\text{I}_2]$ (ttmgb)	$[(\text{CuBr}_2)_2(\text{Br}_2\text{-ttmgb})]$ [CuBr <sub>4</sub> ]	$[(\text{CuI})_2(\text{ttmgb})]$ (I <sub>3</sub> ) <sub>n</sub>	$[(\text{Cu}(\text{NO}_3)_2)_2]$ (ttmgb)	$[(\text{Cu}(\text{NO}_3)_2)_2(\text{ttmgb})]$ [Cu(NO <sub>3</sub> ) <sub>4</sub> ]	$[(\text{Cu}(\text{NO}_3)_2)_2]$ (ttmgb*)][NO <sub>3</sub> ]
Cu-N <sub>imine</sub>	1.9985(14)	1.992(3)	2.0159(18)	1.998(3)	2.064(4)	1.963(2)	1.971(3)	1.9533(16)
	1.9984(16)	2.059(3)	2.0165(17)	2.013(3)		1.969(2)	1.963(2)	1.9535(16)
N <sub>imine</sub> -C <sub>imine</sub>	1.4085(19)	1.311(5)	1.324(2)	1.391(5)	1.383(7)	1.333(3)	1.412(5)	1.371(2)
	1.4050(18)	1.327(5)	1.322(2)	1.405(5)		1.346(3)	1.386(4)	1.373(2)
C <sub>imine</sub> -N <sub>imine</sub>	1.3232(19)	1.363(5)	1.358(3)	1.331(5)	1.328(6)	1.358(4)	1.328(4)	1.328(3)
	1.325(2)	1.352(5)	1.364(3)	1.319(5)	1.344(7)	1.344(3)	1.333(5)	1.339(3)
N <sub>imine</sub> -Cu-	80.20(6)	82.89(12)	83.45(8)	78.63(13)	77.5(2)	84.63(9)	80.45(11)	82.23(7)
N <sub>imine</sub>								
N <sub>imine</sub> -C <sub>arom</sub>	1.3370(18)	1.409(5)	1.415(2)	1.343(5)	1.334(6)	1.414(3)	1.313(4)	1.366(2)
	1.3337(18)	1.413(4)	1.405(2)	1.327(4)			1.340(4)	
Reference	(Peters et al. 2009)	(Emeljanenko et al. 2010b)	(Emeljanenko et al. 2010b)	(Emeljanenko et al. 2010b)	(Emeljanenko et al. 2010b)	(Trumm et al. 2010)	(Trumm et al. 2010)	(Trumm et al. 2010)

series, as this formal single bond gains more double bond character upon oxidation [1.414(3)→1.366(2)→1.322 Å]. For  $[(\text{MeCN})_4\text{Cu}]_2(\text{ttmgb})[\text{BF}_4]_6$ ,  $[(\text{CuBr}_2)_2(\text{Br}_2\text{-ttmgb})][\text{CuBr}_4]$  and  $\{[(\text{CuI})_2(\text{ttmgb})](\text{I}_3)_2\}_n$  – complexes with oxidised ttmgb – the same proposition is valid.

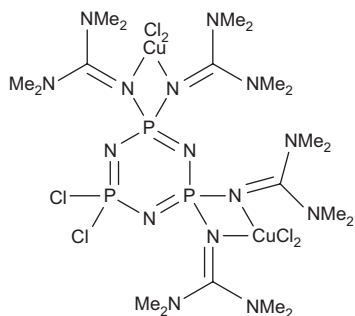
The TMG group can be attached not only to organic frameworks but also to phosphorus via the reaction of hexachlorocyclotriphosphazene with tetramethylguanidine for three days under reflux. The obtained 2,2-dichloro-4,4,6,6-tetra-(*N,N,N',N'*-tetramethylguanidin)-2λ<sup>5</sup>,4λ<sup>5</sup>,6λ<sup>5</sup>-cyclotriphosphaza-1,3,5-triene reacts with CuCl<sub>2</sub> to a binuclear complex with Cu-N<sub>imine</sub> bond lengths lying between 1.985(9) and 2.02(1) Å with N-Cu-N bite angles of only 71° (Scheme 14) (Bloy and Diefenbach 2000).

### Bicyclic systems

A totally different building principle underlies the class of bicyclic aliphatic guanidines incorporating the hpp unit. Hpp represents the 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2- $\alpha$ ]pyrimidine unit. Coles and coworkers used this strong donor unit in copper chemistry (Coles and Hitchcock 2001, Oakley et al. 2003). The complex  $[\text{CuCl}(\text{hppH})_2]$  was structurally investigated and used as catalyst for the atom transfer radical polymerisation of methyl methacrylate. In addition to the study with the parent compound hppH, they accomplished the synthesis of *N*-substituted hpp systems, e.g., hppMe and hppSiMe<sub>3</sub> and their copper complexes (Oakley et al. 2004b). Here, the influence of the prohibition of hydrogen bonding on solid-state structures was highlighted in detail. As advancement, they combined two hpp units within one ligand in further studies and obtained copper chelate complexes such as  $[(\text{Me}_2\text{Si}\{\text{hpp}\})_2\text{CuCl}]$  and  $[(\text{H}_2\text{C}\{\text{hpp}\})_2\text{CuCl}]$  (Oakley et al. 2004a,b).

Bicyclic guanidines are strong donors which suit copper easily in complexes with small coordination numbers (Scheme 15, Figure 6 and Table 7). The complex  $[(\text{H}_2\text{C}\{\text{hpp}\})_2\text{CuCl}]$  serves as an example for a bis(guanidine) which is linked via the N<sub>amine</sub> atoms and not via the N<sub>imine</sub> atoms (as described above) (Oakley et al. 2004a). The coordination environment in this complex is trigonal-planar and the guanidine binding features are very similar to other bis(guanidine) copper(I) complexes. The use of the delocalisation parameter  $\rho$  seems to be reasonable because the trend already observed for N<sub>imine</sub> linked bis(guanidines) appears here as well: with decreasing coordination number and increasing oxidation state,  $\rho$  increases indicating a greater degree of delocalisation within the guanidine unit.

In recent studies, Coles varied the bicyclic guanidine framework beyond the restriction of six-membered rings and used the resulting guanidines, guanidates and guanidinium cations for multiple applications (Coles 2009). Simultaneously, Chiarella et al. reported copper cluster compounds which are stabilised by bicyclic guanidines with five-membered rings (Scheme 15) (Chiarella et al. 2009, 2010). As anticipated, copper is coordinated by the N<sub>imine</sub> atom. By deprotonation, the guanidate anion of 1,4,6-triazabicyclo[3.3.0]oct-4-ene coordinates in a bidentate manner (Chiarella et al. 2010).



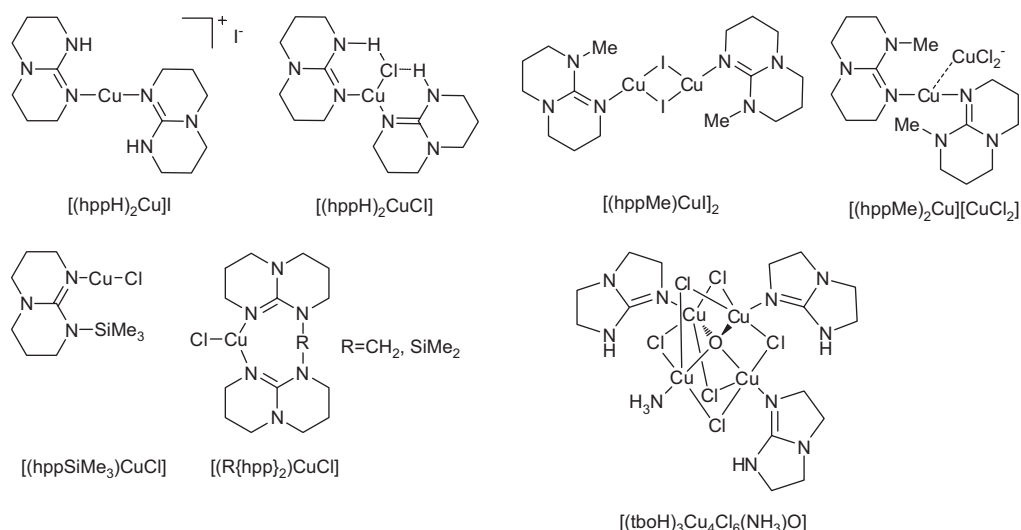
**Scheme 14** Tetra(guanidine) phosphazene copper complex.

### Further developments in the chemistry of peralkylated guanidines

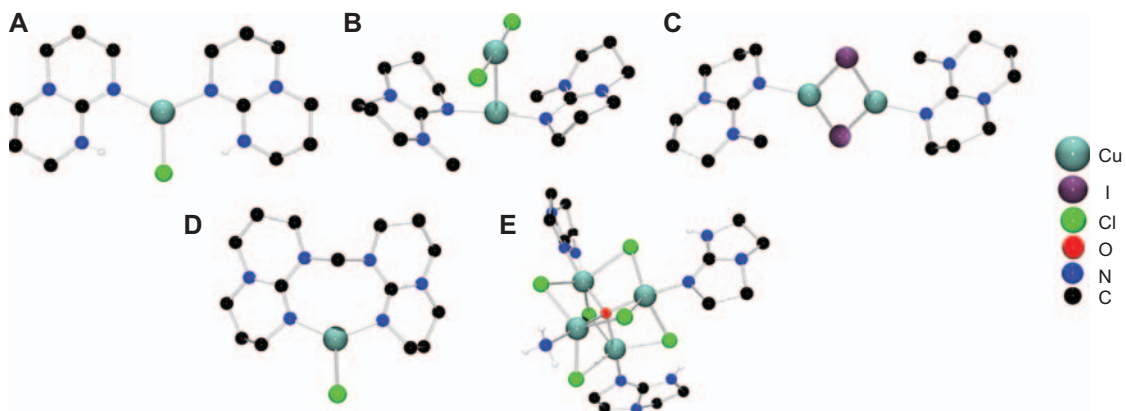
In addition to the combination of different numbers of guanidine groups at a variety of ligand backbone structures, recent

studies highlight the combination of only one or two guanidine groups with other N, O or S donor functions. Adding further donors via a flexible linker of sufficient length will enable further interaction between the ligand and the metal to which it is coordinated, enhancing stabilisation of such compounds through chelation. Moreover, the inclusion of different heteroatom functionalities offers the potential for new bonding modes involving the guanidine as ligand.

In this context, it was shown that amine-guanidine hybrid ligands enable in their copper-dioxygen complexes better substrate accessibility. In the case of (tetramethylguanidino)(dimethylamino)-propane (TMGdmap), biomimetic phenolate hydroxylation was observed via the bis( $\mu$ -oxo) dicopper(III) complex  $[(\text{TMGdmap})_2\text{Cu}_2(\mu\text{-O})_2]^{2+}$  (Herres-Pawlis et al. 2009c). This reactivity proves that  $[(\text{TMGdmap})_2\text{Cu}_2(\mu\text{-O})_2]^{2+}$  can be regarded as a good model system for the binuclear copper protein tyrosinase which mediates the orthohydroxylation of phenols (Decker et al. 2006, Matoba et al. 2006). Interestingly, in nature, this



**Scheme 15** Selected copper complexes with bicyclic guanidines.



**Figure 6** Molecular structures of (A)  $[(\text{hppH})_2\text{CuCl}]$ , (B)  $[(\text{hppMe})_2\text{Cu}][\text{CuCl}_2]$ , (C)  $[(\text{hppMe})\text{Cu}]_2$ , (D)  $[(\text{H}_2\text{C}\{\text{hpp}\}_2)\text{CuCl}]$  and (E)  $[(\text{tboH})_3\text{Cu}_4\text{Cl}_6(\text{NH}_3)\text{O}]$ .

**Table 7** Selected bond lengths (Å) and angles (°) of copper complexes with bicyclic guanidines<sup>a</sup>.

	[(hppH) <sub>2</sub> CuCl]	[(hppMe) <sub>2</sub> Cu] [CuCl <sub>2</sub> ]	[(hppMe)CuI] <sub>2</sub>	[(H <sub>2</sub> C{hpp}) <sub>2</sub> CuCl]	[(tboH) <sub>3</sub> Cu <sub>4</sub> Cl <sub>6</sub> (NH <sub>3</sub> )O]
Cu-N <sub>imine</sub>	1.962, 1.966	1.894(2)	2.008(5)	1.956(4), 1.943(4)	1.930(4), 1.943(7)
N <sub>imine</sub> =C <sub>imine</sub>	1.316(3), 1.311(3)	1.327(3)	1.290	1.298(6), 1.304(6)	1.286(6)
C <sub>imine</sub> -N <sub>amine</sub>	1.345(3)–1.369(3)	1.358, 1.345	1.373	1.370(5)–1.382(5)	1.377(6), 1.336(6)
Cu-X	2.398	–	2.558(1), 2.552(1)	2.261(1)	2.366–2.542
N <sub>imine</sub> -Cu-N <sub>imine</sub>	130.37(9)	176.20(1)	–	126.45(2)	–
N <sub>imine</sub> -Cu-X	115.43(6), 113.86(7)	–	118.09(2), 121.87(2)	113.03(1), 120.38(1)	111.56–126.57
ρ	0.974, 0.963	0.982	0.940	0.942, 0.948	0.948
Reference	(Oakley et al. 2003)	(Oakley et al. 2004b)	(Oakley et al. 2004b)	(Oakley et al. 2004a)	(Chiarella et al. 2010)

<sup>a</sup>When no standard deviation is given, the table entries represent averaged values.

hydroxylation reactivity was carried out by the  $\mu$ - $\eta^2$ : $\eta^2$ -peroxy-dicopper(II) complex as active species for tyrosinase. For many years, the nature of the active species is under debate because both Cu<sub>2</sub>O<sub>2</sub> isomers are able to hydroxylate phenolic substrates. In a recent study (Herres-Pawlis et al. 2009c), the ligand attributes were highlighted that lead to biomimetic phenolate hydroxylation with a bis( $\mu$ -oxo) dicopper(III) complex in the ligand series of amines and guanidines: the congested complex with bis(guanidine) ligation reacts neither with phenols nor phenolates highlighting the importance of core accessibility in such oxidations. The least congested complex with bis(amine) ligation exclusively yields the C-C radical coupled bis-phenol product with both phenols and phenolates, a reactivity observed from most bis( $\mu$ -oxo) dicopper(III) complex species. This reaction occurs through a facile proton coupled electron transfer from the phenol yielding a phenoxyl radical, which subsequently dimerises, and a ( $\mu$ -hydroxo)( $\mu$ -oxo)dicopper(II,III) intermediate, which is inferred to be a more powerful oxidant than the initial bis( $\mu$ -oxo) dicopper(III) complex species (i.e., reductive oxidation enhancement). The more donating guanidine groups significantly attenuate the one-electron outer-sphere oxidising strength of the guanidine-amine species relative to the bis(amine) species that reduces the viability of a proton coupled electron transfer oxidation of phenols and outer-sphere oxidation of phenolates. This attenuation and the increased phenolate accessibility to the Cu<sub>2</sub>O<sub>2</sub> core are attributes that correlate with biomimetic phenolate hydroxylation observed in the guanidine-amine system [(TMGdmap)<sub>2</sub>Cu<sub>2</sub>( $\mu$ -O)<sub>2</sub>]<sup>2+</sup>. In comparison to the parent bis(amine) and bis(guanidine) systems, it has to be remarked that a distinct sideband in UV/Vis absorption could be identified for [(TMGdmap)<sub>2</sub>Cu<sub>2</sub>( $\mu$ -O)<sub>2</sub>]<sup>2+</sup> which was related to  $\pi_{\text{gua}} \rightarrow \text{Cu}_2\text{O}_2$  LMCTs. In the course of these studies, copper(I) complexes and a bis( $\mu$ -hydroxo) dicopper(II) complex could be structurally characterised. The different donor strengths of the two N donor functions appear very distinct here with Cu-N<sub>imine</sub> bond lengths of 1.961(2) and 2.037(2) Å in the copper(I) iodido complexes and 1.981(3) Å in the hydroxo complex compared to Cu-N<sub>amine</sub> bond lengths of 2.119(2), 2.160(2) and 2.046(3) Å, respectively (Figure 7).

In further studies on combined guanidine-amine ligands, a new library of aliphatic guanidine-amine systems has been

developed (Haase 2010; Haase et al. 2011) and some of their copper complexes were found to be efficient catalysts in the atom transfer radical polymerisation (Bienemann et al. 2011).

The combination of pyridine and guanidine donors in one ligand was enabled in the hybrid ligand 1,1,3,3-tetramethyl-2-[2-(pyridin-2-yl)ethyl]guanidine which stabilised a copper(I) iodido complex with bond lengths of 1.971(2) (Cu-N<sub>imine</sub>) and 2.050(2) Å (Cu-N<sub>amine</sub>) (Wortmann et al. 2009).

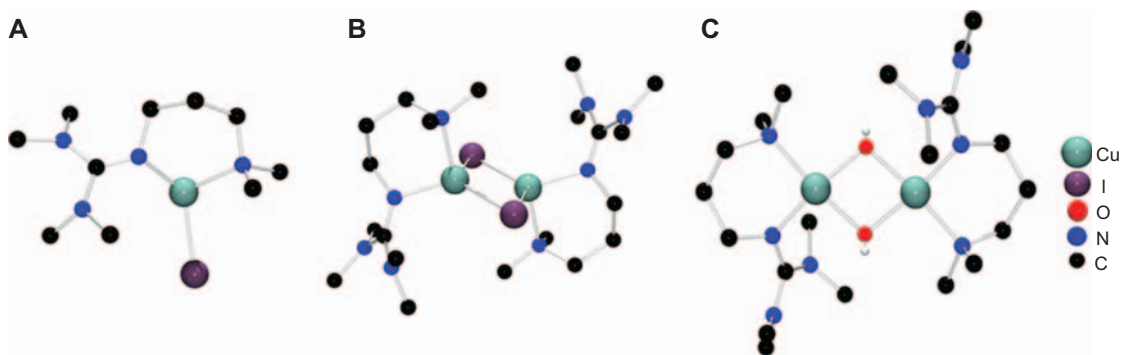
In the Henkel research group, thiolate-guanidine and thioester-guanidine hybrid ligands have been developed for bioinorganic copper chemistry (Scheme 16) (Neuba et al. 2007a,b,c, Neuba 2009). Carboxy guanidines combine carboxylate and ester functions with guanidine groups for use in iron chemistry (Akin 2010).

### Further nitrogen-rich guanidine-type ligands

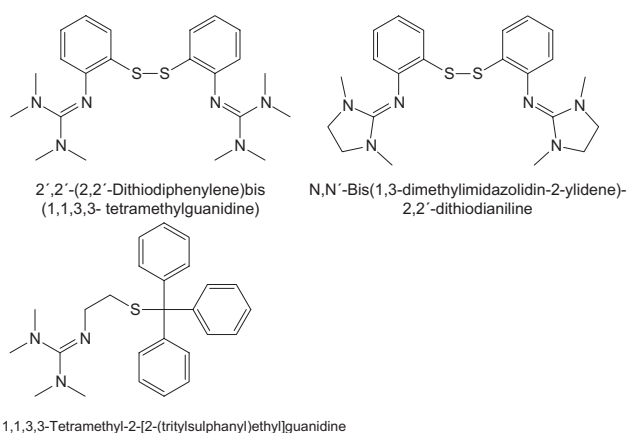
As guanidine compounds belong to the nitrogen-rich donor systems, the synthetic step to nitrogen-rich heterocycles as imidazoles, triazoles and tetrazoles in combination with amine and azo groups is close. In this regard, a great variety of nitrogen donor ligands have been developed and employed in copper coordination chemistry.

The combination of imidazoles with azo groups yielded the azoimidazoles (Scheme 17). They are synthesised by coupling of substituted phenyldiazonium ions with imidazole in aqueous sodium carbonate and subsequent alkylation of the imidazole unit (Ray et al. 2006). Ray et al. investigated the copper chemistry of several ligands (Ray et al. 2004). In the complex bis-[1-methyl-2-(phenylazo)imidazole]copper(I) perchlorate, the azoimidazole ligands form a bis-chelate using the imidazole nitrogen atoms and one N<sub>azo</sub> atom under formation of five-membered heterocycles (Cu-N<sub>imine</sub> 2.004 Å, Cu-N<sub>azo</sub> 2.021 Å). In the quinoline derivative bis-[1-ethyl-2-(naphthyl-azo)imidazole]copper(I) perchlorate, copper is coordinated preferentially by the N<sub>imine</sub> atoms (Cu-N<sub>imine</sub> 1.851 Å) with loose contacts to the N<sub>azo</sub> atoms (Cu...N<sub>azo</sub> 2.655 Å) resulting in a nearly linear coordination. In combination with a thioether function, Banerjee et al. synthesised a mononuclear Cu(II) complex with N<sub>imine</sub>, N<sub>azo</sub>, S donor set [Cu-N<sub>imine</sub> 2.014(2), Cu-N<sub>azo</sub> 2.022(2), Cu-S 2.3788(8) Å] (Banerjee et al. 2006). In further studies, they combined these ligands with





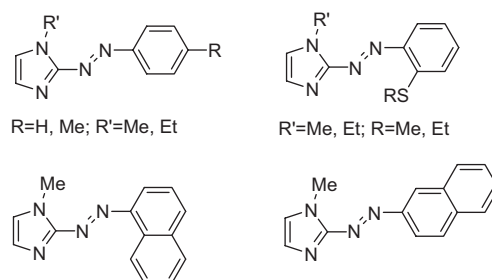
**Figure 7** Molecular structures of (A)  $[\text{Cu}(\text{TMgdmap})\text{I}]$ , (B)  $[\text{Cu}(\text{TMgdmap})\text{I}]_2$  and (C):  $[\text{Cu}_2(\text{TMgdmap})_2(\mu\text{-OH})_2]^{2+}$  in crystals of  $[\text{Cu}_2(\text{TMgdmap})_2(\mu\text{-OH})_2][\text{CuI}_3]$ .



**Scheme 16** Novel thioguanidine ligands (Neuba et al. 2007a,b,c, Neuba 2009).

azide as coligands for the synthesis of polynuclear copper complexes (Ray et al. 2006).

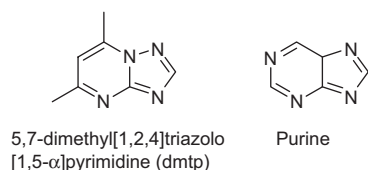
In addition to the previously described aliphatic bicyclics, several studies have been performed on aromatic nitrogen bicyclics incorporating the  $\text{CN}_3$  core. They are often not referred to as 'guanidines' but rather as triazolopyrimidine ligands (Biagini Cingi et al. 1983,1986, Haasnoot et al. 1984,1988, Favre et al. 1986, Dirks et al. 1987, Cornelissen et al. 1989, van Albada et al. 1991). Haasnoot and coworkers synthesised a multitude of copper complexes with this ligand family because they represent purine analogues and are used as models for purines (Scheme 18). For the coordination chemist, they offer several advantages over purine: by differing from the purine skeleton mainly in having a pyrimidine nitrogen atom in a bridge-head position instead, one coordination possibility is ruled out. Furthermore, none of the nitrogen atoms in these triazolopyrimidines are protonated in neutral or even weakly acidic solvents, which is in contrast with the purines. The coordination properties of [1,2,4]triazolo[1,5- $\alpha$ ]pyrimidines can be further modified by steric or electronic effects due to the presence of substituents, as the two methyl groups in 5,7-dimethyl[1,2,4]triazolo[1,5- $\alpha$ ]pyrimidine (dmtp). These triazolopyrimidine ligands disclose



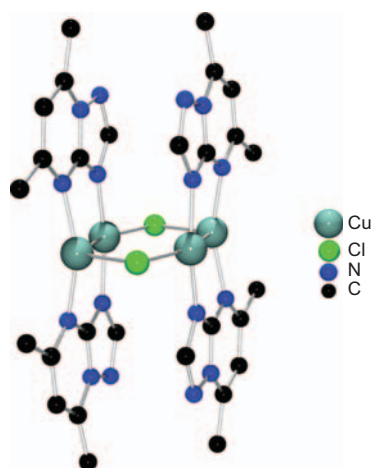
**Scheme 17** Azoimidazole ligands (Ray et al. 2004,2006, Banerjee et al. 2006).

a multifaceted coordination chemistry because they can coordinate with more than one donor function. However, generally, dmtp coordinates via the sterically least hindered  $\text{N}_{\text{imine}}$  atom (Biagini Cingi et al. 1983,1986, Haasnoot et al. 1984,1988, Favre et al. 1986, Dirks et al. 1987, Cornelissen et al. 1989, van Albada et al. 1991). Only in the complex  $[\text{Cu}_4(\text{dmtp})_4\text{Cl}_2]$   $[\text{Cu}_2\text{Cl}_4]$  (Figure 8) (Haasnoot et al. 1988), both single  $\text{N}_{\text{imine}}$  atoms are active in copper coordination and stabilise a very interesting complex motif: in the cation, two  $\text{Cu}_2(\text{dmtp})_2$  units are bridged by two chlorido ligands with a distance between the N-C-N-bridged Cu atoms in the  $\text{Cu}_2(\text{dmtp})_2$  units of 2.909 Å. The dmtp ligands are arranged parallel to each other (3.20 Å) and also to the dmtp ligands of the next cations in the crystal. The stacking effects of the rings seem to contribute to the stability of the structure. The Cu-N bond lengths for the N atom of the five-membered ring are 1.918 and 1.965 Å for the N donor of the six-membered ring.

Simultaneous to the studies of the Haasnoot group, Grodzicki et al. used 5,7-dimethyl-1,2,4-triazolo-[1,5- $\alpha$ ]pyrimidine and 5,7-diphenyl-1,2,4-triazolo-[1,5- $\alpha$ ]pyrimidine for the synthesis of copper(II) chloroacetate complexes (Grodzicki et al. 1999) and Salas et al. isolated a copper(II) perchlorate complex of 5,7-dimethyl[1,2,4]triazolo[1,5- $\alpha$ ]pyrimidine (Salas et al. 1993). These copper complexes are still under investigation as potential anti-parasitic agents as shown by recent work in this field by the Quirós group (Abdul Haj et al. 2002, Abul-Haj et al. 2003, Maldonado et al. 2008,



**Scheme 18** Analogy between purine and [1,2,4]triazolo[1,5- $\alpha$ ]pyrimidines.



**Figure 8** Molecular structure of the cation  $[\text{Cu}_4(\text{dmtp})_4\text{Cl}_2]^{2+}$  in crystals of  $[\text{Cu}_4(\text{dmtp})_4\text{Cl}_2][\text{Cu}_2\text{Cl}_4]$  (Haasnoot et al. 1988).

Boutaleb-Charki et al. 2009). As already mentioned above, the triazolopyrimidine ligands use the sterically free  $\text{N}_{\text{imine}}$  atom of the five-membered ring for copper coordination. As further aromatic bicyclic guanidine, 2,3-dihydroimidazo[1,2- $\alpha$ ]pyrimidine was recently isolated in a copper coordination polymer. The ligand is formed during the complexation reaction out of 2-aminopyrimidine and ethanol (Bi et al. 2008).

Another exciting macrocyclic ligand was reported by Ferrer et al. (2007). The reaction of a mixture of 3-acetylamino-5-amino-1,2,4-triazole and 3,5-diacetylamino-1,2,4-triazole

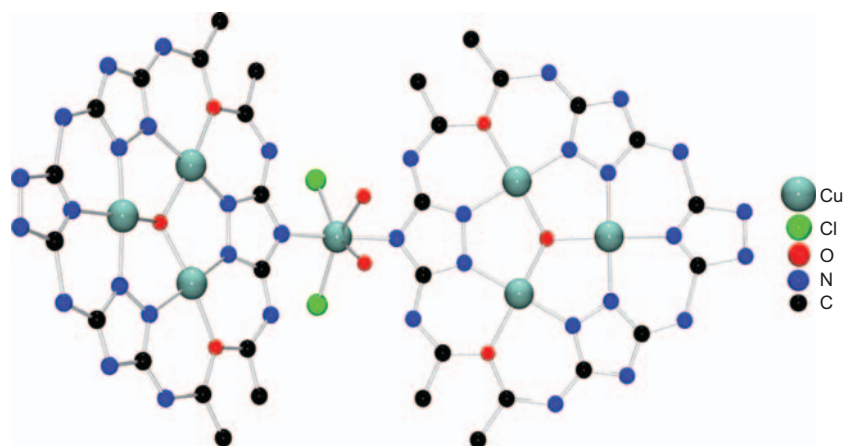
with a mixture of copper(II) chloride and copper(II) sulphate in aqueous media afforded a heptanuclear complex (Figure 9) with two trinuclear copper(II) cores both being coordinated by a macrocycle which contains by chance guanidine moieties. In fact, the donor characteristics of the triazole units are more important here for the stabilisation of this polynuclear compound than the guanidine donor advantages. However, nitrogen donor atoms which are part of a triazole and a formal guanidine unit show shorter Cu-N bonds [ $\text{Cu-N}_{\text{azo}}$ , 2.034(6) Å;  $\text{Cu-N}_{\text{azo, gua}}$  1.930 (av) Å].

The same conclusion is valid for the copper complex of an amino-triazole derivative reported by Stadler et al. who stabilise a trinuclear bimetallic framework for the investigation of electron transfer in mixed-valence sites (Stadler et al. 2001).

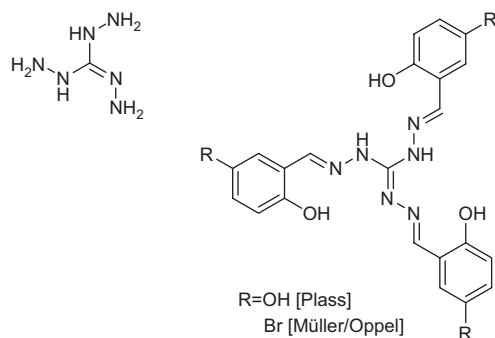
By adding further N donor sites in the guanidine substitution pattern, ligands for supramolecular applications can be obtained as reported by the groups of Müller (Müller and Robson 2000a,b, Müller et al. 2001, 2004, Müller and Möller 2005a,b, Müller et al. 2005a,b) and Plass (Zharkouskaya et al. 2005) (Scheme 19). The ligands are synthesised by reaction of guanidinium chloride with hydrazine to triaminoguanidine chloride followed by the condensation with salicylaldehyde derivatives (Müller and Möller 2005c).

Using the unsubstituted parent compound triaminoguanidine (TAG), Savel'eva et al. synthesised under acidic conditions a chelate copper(II) complex with twofold protonated TAG with Cu-N bond lengths of 1.987(2) Å to the formal guanidine N atom and of 2.043(2) Å to the additional N atom and a N-Cu-N angle of 79.16(8)° (Savel'eva et al. 2000).

Müller et al. synthesised via the reaction of the substituted TAG ligand  $\text{Br}_3\text{L}$  with  $\text{CuCl}_2$ , auxiliary barbiturate ( $\text{NaHbar}$ ) and triethylamine the trinuclear copper complex  $(\text{Et}_4\text{N})_2\{[\text{Cu}(\text{Hbar})\}_3\text{Br}_3\text{L}\}$  (Figure 10B, Müller and Möller 2005c). The molecular structure shows that the ligand is fully deprotonated and coordinated to three Cu(II) centres in a square-planar manner with Cu-N bond lengths of 1.98(1) and 1.959(6) Å. The N-N bonds amount to 1.390(6) Å, and the sum of the angles at the central C atom of the guanidine core is 360° indicating a planar guanidine moiety. Moreover, the whole  $\text{CN}_6$  unit is almost planar [average deviation  $\pm 0.04(1)$



**Figure 9** Heptanuclear copper complex with a novel macrocyclic triazole-guanidine ligand (Ferrer et al. 2007).

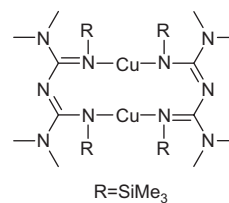


**Scheme 19** Triaminoguanidine-based ligand systems.

Å] with only small torsion angles to the phenyl groups of 9.9–31.3°. This structure demonstrates that it is possible to bind three co-ligands with high steric demand to a  $\text{Cu}_3\text{Br}_3\text{L}$  unit which is an important requirement when employing the  $\text{C}_3$  symmetric  $[\text{Cu}_3\text{Br}_3\text{L}]^{3n-5}$  units for the construction of coordination polymers and cages.

Zharkouskaya et al. characterised a trinuclear copper complex with the related TAG ligand  $\text{L}^{\text{OH}}$  which reveals in the solid state a three-dimensional porous framework that is composed of trigonal  $\{\text{Cu}_3\text{L}^{\text{OH}}\}^+$  units (Figure 10A) (Zharkouskaya et al. 2005). The copper nitrogen bond lengths do not differ considerably for the coordination of the two different donor types [ $\text{Cu}-\text{N}_{\text{aza}}$  1.929(6) Å,  $\text{Cu}-\text{N}_{\text{gua}}$  1.948(6) Å]. Here, the  $\{\text{Cu}_3\text{L}\}$  framework is not planar (in contrast to the copper complex reported by Müller et al.), but forms two subunits in propeller- and in bowl-conformation. Together, the  $\{\text{Cu}_6(\text{L}^{\text{OH}})_2\}$  building units form a three-dimensional coordination polymer.

By extending the family of  $\beta$ -ketiminate ligands to their aza analogues, Zhou et al. synthesised monoanionic 2,4- $N,N'$ -disubstituted 1,3,5-triazapentadienyl ligands incorporating one guanidine and one guanidinato moiety (Zhou et al. 2008). The synthesis was accomplished by the reactions of  $\text{LiN}(\text{SiMe}_3)_2$  with 2 equivalents of the  $\alpha$ -hydrogen free carbonitrile dimethylcyanamide or 1-piperidinecarbonitrile. Reaction with  $\text{CuCl}$  in diethylether yielded binuclear complexes with linear copper coordination [ $\text{N}-\text{Cu}-\text{N}$  174.1(2)°] and  $\text{Cu}-\text{N}$  bond lengths of 1.896(4) and 1.883(4) Å (Scheme 20). This coordination



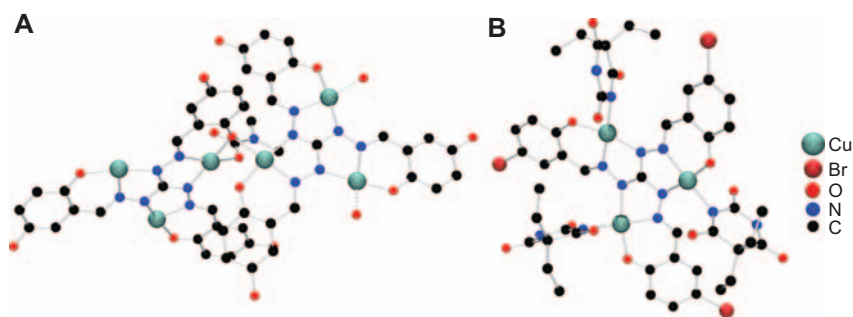
**Scheme 20** Copper complex with a monoanionic 2,4- $N,N'$ -disubstituted 1,3,5-triazapentadienyl ligand (Zhou et al. 2008).

environment strongly resembles that found for binuclear bis(guanidine) copper complexes discussed above. For the W-shaped ligand NCNCN backbone, a short-long-short-long pattern of C-N bond lengths was found with 1.321(5) and 1.315(5) Å as short C=N bonds and 1.371(5) and 1.360(6) Å as long C-N bonds, respectively. This pattern indicates characteristics of a conjugated system, but the  $\text{N}_3\text{C}_2$  framework is not coplanar.

## Conclusion and perspective

During the past 10 years, the copper coordination chemistry of neutral guanidines has made a remarkable progress – considerably more than in the preceding decades in which this chemistry was lying in a deep sleep.

It was highlighted that the central  $\text{CN}_3$  unit which defines a guanidine does not always guarantee similar coordination behaviour. In the case of aliphatic frameworks incorporating the  $\text{CN}_3$  unit, the guanidine unit acts as a very strong and versatile donor. This high nucleophilicity (and accompanying basicity) is caused by the distribution of the formal positive charge of the metal throughout the guanidine unit. The degree of charge distribution can be quantified by use of the parameter  $\rho$  which is valid in most guanidines with aliphatic frameworks with exception of the imidazolin-2-imines having more distinct imidazolium character. When the guanidine unit is part of an aromatic framework, the resulting N donor is also a good ligand but the typical guanidine properties are not pronounced, because the  $\text{N}_{\text{imine}}$  atom merely behaves like a classical N donor atom of a heteroaromatic ligand.



**Figure 10** Molecular structures of (A) a subunit of the three-dimensional network formed by  $\{\text{Cu}_6(\text{L}^{\text{OH}})_2\}$ , (B)  $[\{\text{Cu}(\text{Hbar})\}_3\text{Br}_3\text{L}]^{2-}$  in crystals of  $(\text{Et}_4\text{N})_2[\{\text{Cu}(\text{Hbar})\}_3\text{Br}_3\text{L}]$ .

Owing to the excellent donor properties of guanidines, this ligand class has conquered several fields in bioinorganic chemistry and has proven its superior viability for the synthesis of model complexes for type 2 and type 3 copper proteins. Moreover, copper guanidine complexes have shown activity in modern catalytic fields such as atom transfer radical polymerisation and oxidation catalysis as well as in the field of semiconducting materials. Hence, for the forthcoming years, transition metal complexes of guanidines have the potential to find widespread applications in further research fields and exciting developments have to be expected.

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Olga Bienemann studied chemistry at the Universität Paderborn, Germany, and did her bachelor thesis at the University of Qingdao, China, in 2007. She obtained her MSc degree in chemistry in 2009 performing research in the laboratories of Prof. Gerald Henkel (Universität Paderborn). She then started her graduate studies under the supervision of Dr. Herres-

Pawlis at the Technische Universität Dortmund supported by a fellowship of the Fonds der Chemischen Industrie. She is currently working on atom transfer radical polymerisation with (guanidine)copper complexes.



Alexander Hoffmann studied chemistry from 2002 to 2007 and did his master thesis at the Universität Paderborn in the laboratories of Prof. Gerald Henkel on (cobalt) guanidine complexes in fluorescence applications. He then joined Dr. Herres-Pawlis' group and moved with her in 2009 to the Technische Universität Dortmund where he recently finished his PhD

thesis. His thesis investigations were focused on poly(pyrazolyl)methane complexes with iron, cobalt, copper and zinc for the activation of small molecules and catalysis.



Sonja Herres-Pawlis studied chemistry from 1998 to 2002 at the Universität Paderborn, Germany, and the Ecole Nationale Supérieure de Montpellier, France. After her diploma thesis in 2002, she did her PhD thesis as a Fonds fellow on dioxygen activation with (guanidine)copper complexes under the supervision of Prof. Gerald Henkel at the Universität Paderborn (university thesis award 2006).

After a DAAD supported postdoctoral stay with Prof. T. Daniel P. Stack at Stanford University, California, she returned to Paderborn to start her own research. In 2009, she was awarded a Liebig junior research group, and moved to the Technische Universität Dortmund to work at her Habilitation under mentorship of Prof. Klaus Jurkschat. Her research interests focus on the activation of small molecules for oxidation and polymerisation with N donor transition metal complexes. Recently, she has been elected to the Junge Kolleg of the Northrhine-Westfalian Academy of Sciences and Arts.