Coordination Chemistry of Unsymmetrical Tripodal Ligands with an NNO_2 Donor Set

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The synthesis of two new tripodal ligands $N(CH_2CH_2NH_2)(CH_2CH_2CH_2OH)_2$ (H_4-**1**) and N[2,3,5-C_6H_2-(OH)(SCH_3)(CH_3)]($CH_2CH_2CH_2NH_2$)($CH_2CH_2CH_2OH$) (H_4-**2**) is reported. Both tetradentate ligands contain a central tertiary nitrogen atom, as well as two OH and one NH_2 functionalized ligand arm. The tripods do not only exhibit an unsymmetrical N_2O_2 donor set, but also possess two C_3 and one C_2 chains between the central nitrogen atom and the terminal donors. On coordination of the central tertiary nitrogen atom, the ligands are capable of forming both six- and five-membered chelate rings in their metal complexes. Both ligands react with $[Cu(OAc)_2{\cdot}H_2O]_2$ to give the dinuclear copper(II) complexes $[Cu(\eta^4\text{-}\mu\text{-}O\text{-}H_3\text{-}\mathbf{1})_2Cu](PF_6)_2$ (**3**) and $[(\eta^3\text{-}H_3\text{-}\mathbf{2})Cu(\mu\text{-}OAc)_2Cu(\eta^3\text{-}H_3\text{-}\mathbf{2})]{\cdot}2CH_3CN$ (**4**·$2CH_3CN$). The molecular structures of **3** and **4**·$2CH_3CN$ have been determined by X-ray diffraction. Complex **3** contains two slightly distorted square-pyramidal ($\tau = 0.181$) copper atoms, with O-donors in the apical positions. The dinuclear complex **4**, which was synthesized to model the copper site in galactose oxidase, also shows a distorted square-pyramidal coordination geometry ($\tau = 0.205$ and $\tau = 0.101$) around both copper(II) atoms. Complex **4** contains two uncoordinated primary alcohol functionalities of the ligands. In addition, both the ligand H_4-**2** and its dinuclear copper complex $[(\eta^3\text{-}H_3\text{-}\mathbf{2})Cu(\mu\text{-}OAc)_2(\eta^3\text{-}H_3\text{-}\mathbf{2})]{\cdot}2CH_3CN$ can easily be oxidized to yield free or coordinated phenoxyl radicals, which are stable on the time scale of cyclic voltammetry.

Introduction

Redox reactions involving a transition metal ion and a redox-active amino acid side chain, e.g. tyrosine, play a key role in many biochemical processes.[1] Some years ago, Ito et al.[2] have shown that the reactive site in galactose oxidase (E.C. 1.1.3.9) GO, a copper enzyme that was isolated from the parasitic fungus *Fusarium dendroides*, contains a tyrosyl radical which is coordinated to a copper(II) center. Galactose oxidase catalyzes the stereospecific oxidation of D-galactose and various primary alcohols to the corresponding aldehydes, coupled to the simultaneous reduction of O_2 to H_2O_2 [Equation (1)].

$$RCH_2OH + O_2 \rightarrow RCH{=}O + H_2O_2 \quad (1)$$

The X-ray crystal structure analysis of the inactive form of galactose oxidase at a 1.7 Å resolution showed a mononuclear copper(II) center that is surrounded by a square-pyramidal N_2O_3 coordination environment.[2] As depicted in Figure 1, two histidine residues (His-496, His-581), one tyrosinate (Tyr-272) and one water or acetate molecule reside in the equatorial plane, while the remaining apical position is occupied by the oxygen atom of another tyrosinate ligand (Tyr-495). A unique characteristic of the copper site in galactose oxidase is that the equatorial tyrosinate residue Tyr-272 is covalently linked to a sulfur atom of the neighboring cysteine Cys-228. This leads to a lowering of the oxidation potential and significantly facilitates the formation of a tyrosyl radical from Tyr-272.[3] Furthermore, in the oxidized form of GO, antiferromagnetic coupling of the single electron in the copper(II) $d_{x^2-y^2}$ orbital with the tyrosyl radical is observed, giving a diamagnetic and EPR silent ($S = 0$) ground state of oxidized, active galactose oxidase.[4]

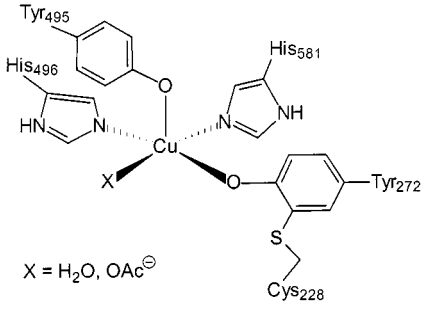

Figure 1. The active site in galactose oxidase

Several attempts have been made in the last years to mimic the geometric, spectroscopic and catalytic properties of native galactose oxidase. Functional model complexes have been presented by Tolman[5] and by Stack and coworkers.[6] Recently, Wieghardt et al.[7] described a functional model of galactose oxidase derived from a

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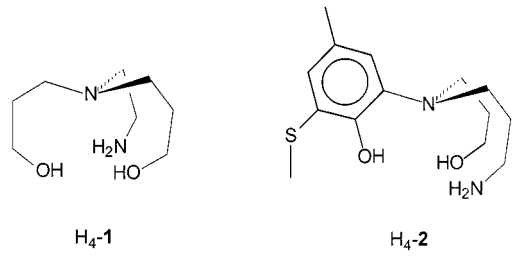
Cu^{II}−iminosemiquinone with a square-planar $[Cu(O-N-O)(NEt_3)]$ (O−N−O = dianionic ligand with one imine and two two phenolate donors) reaction center, which showed a high catalytic activity despite the lack of most structural features found at the active center of native galactose oxidase.

Various Cu^{II} complexes have been prepared in order to model the structural features of the reactive center in galactose oxidase. Mostly tripodal tetradentate ligands that contain one or two phenol and pyrazole or pyridine donor groups were used, providing an N_3O[3a,8,9] or N_2O_2[10,11] coordination environment for the copper center. Pentacoordination is normally achieved by coordination of a counterion or a solvent molecule. Unfortunately, all of the model compounds lack significant features found in the reactive site of native galactose oxidase. These features include a Cu^{II} atom coordinated in a square-pyramidal fashion which exhibits a thioether-functionalized phenoxyl donor in the equatorial plane and another O-donor in the apical position. Two more N-donors and one labile (possibly solvent molecule) O-donor in the equatorial plane should complete the overall N_2O_3 coordination environment.

If a GO model is to be built from a tetradentate tripodal ligand, certain restrictions apply. Such ligands, together with a monodentate coligand, form trigonal-bipyramidal or square-pyramidal complexes with Cu^{II}. For example $[Cu(tren)(NH_3)]^{2+}$ in the solid state is an almost perfect trigonal bipyramid.[12] A systematic study with higher homologues of tren, e.g. with ligands where methylene groups were added stepwise to the three ligand arms, revealed that the tripod with one ethyl and two propyl ligand arms $N(CH_2CH_2CH_2NH_2)_2(CH_2CH_2NH_2)$ forms a square-pyramidal Cu^{II} complex where the apical position is occupied by a donor linked to the central nitrogen atom by a propyl chain.[13] Thus, the topology of the tetradentate tripod determines both the overall geometry of the Cu^{II} complex (sqp vs. tbp), as well as the position of the donors in the complex (donor group at the end of a propyl chain in the apical position). Studies with unsymmetrical tetradentate tripods providing an N_3O donor set for Cu^{II} [8,9] gave similar results. Again, it was found that the formation of square-pyramidal Cu^{II} complexes is preferred when the ligand is capable of forming a 5,6,6-membered chelate ring sequence.[8]

These observations can be used to design ligands for the preparation of GO model compounds. Any tetradentate tripod with a central nitrogen atom capable of forming a 5,6,6-membered chelate ring sequence should give a more or less perfectly coordinated square-pyramidal Cu^{II} complex with a donor at the end of a propyl chain in the apical position.

The aliphatic tripodal ligand H_4-**1** (Figure 2) was synthesized to investigate the extent to which the above mentioned results for N_4 and N_3O ligands (control of complex geometry vs. ligand topology) are transferable to a N_2O_2 donor set. Ligand H_4-**1** should form a square-pyramidal Cu^{II} complex with one of the oxygen donors in the apical and the other in an equatorial position.



H_4-**1** H_4-**2**

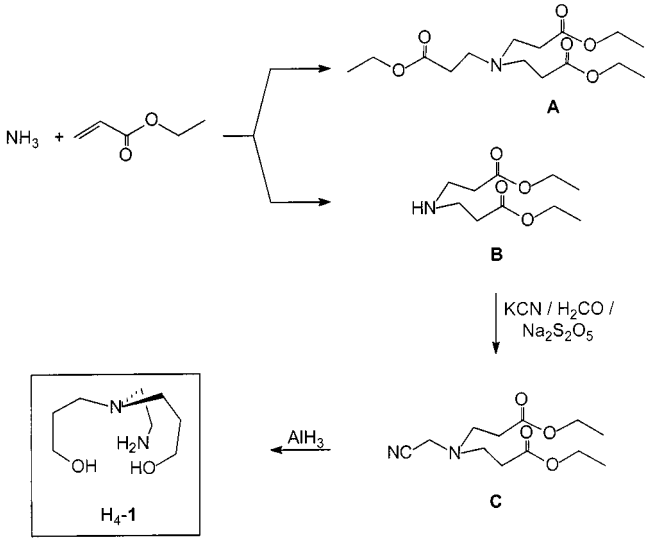
Figure 2. Topology of the tripodal N_2O_2 ligands H_4-**1** and H_4-**2**

The second ligand H_4-**2** (Figure 2), providing an N_2O_2 donor set, was designed for a more accurate structural modeling of the reactive site in GO. This ligand is expected to form a square-pyramidal Cu^{II} complex with a 5,6,6-membered chelate ring sequence. The phenolate oxygen donor, linked by a C_2 chain to the central nitrogen atom, is expected to occupy an equatorial coordination site. In addition, the aromatic ring is functionalized with an *o*-(methylthio) group which in native GO is essential for the formation of a tyrosyl radical on oxidation. The mode of coordination of the two donors linked by C_3 chains to the central nitrogen atom can be elucidated by X-ray crystallography. One of them is expected to occupy an apical coordination site in a Cu^{II} complex. Overall, ligand H_2-**2** possesses an N_2O_2 donor set. It differs from N_2O_2 ligands previously reported[10,11] by possessing aliphatic amine and alcohol donor groups in the presence of an *o*-(methylthio)-functionalized phenol.

Results and Discussion

Ligand Syntheses

Our strategy for the preparation of the unsymmetrical N_2O_2 ligand H_4-**1** involves three reaction steps as depicted in Scheme 1. For the condensation of the C_3 chains to



Scheme 1. Preparation of ligand H_4-**1**

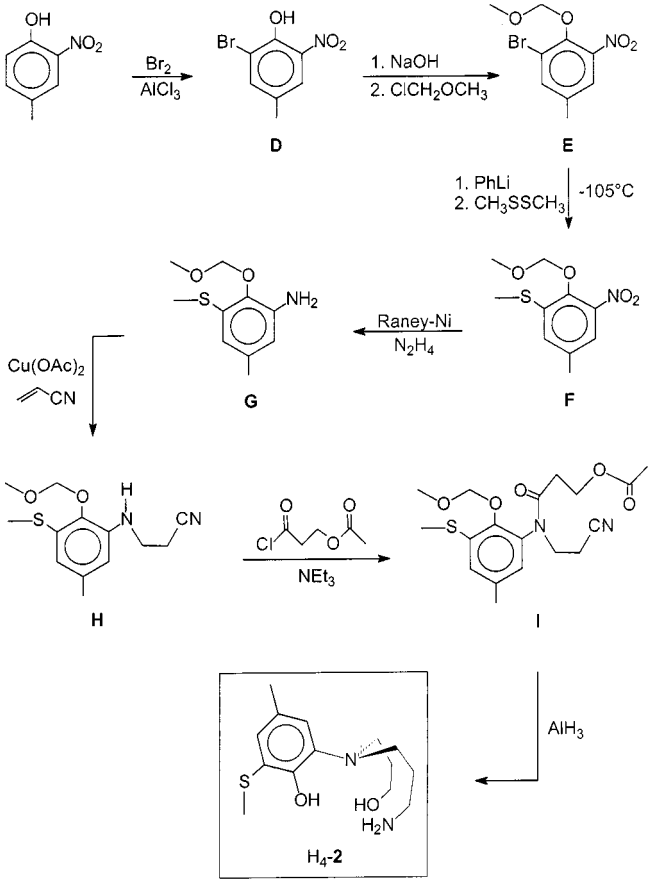
ammonia, the Michael addition of ethyl acrylate had previously proved useful.[14] However, this reaction leads to a mixture of the tertiary (**A**) and secondary amines (**B**), which can be separated by distillation.[14a] Cyanomethylation of the secondary amine **B** by the Strecker synthesis according to the modification of Knoevenagel,[15] yielded the α-nitrilamine **C**. Finally, all protected donor groups were simultaneously liberated by reduction with AlH_3, which led directly to the free ligand H_4-**1**.

Ligand H_4-**1** contains one NH_2- and two OH-substituted ligand arms in addition to the central tertiary nitrogen atom. Furthermore, the ligand possesses an unsymmetrical topology with regard to the three alkyl chains, containing one C_2 and two C_3 arms. This allows for the formation of both five- and six-membered chelate rings yielding a 5,6,6 ring sequence on complex formation. Due to the flexibility and lengths of the alkyl arms, the ligand should be capable of providing an N_2O_2 coordination environment for a copper(II) ion without any steric strain.

Ligand H_4-**2** (Figure 2) was developed on the basis of simple force field calculations and molecular modeling experiments. It was assumed that a tripod, which could form a 5,6,6-chelate ring sequence, would form a square-pyramidal Cu^{II} complex with one of the C_3-linked donors in the apical position. Linking the phenol group directly to the central nitrogen atom should force the oxygen atom of this group in the equatorial position of the expected square-pyramidal complex. Taking into account the significance of the equatorial (*RS*)-substituted Tyr-272 for galactose oxidase activity, an *o*-(methylthio)phenol group was selected. In addition, the *para* position relative to the phenolic OH group was blocked by a methyl group in order to prevent dimerization when a radical intermediate is formed after one-electron oxidation. A similar N_2O_2 ligand capable of forming a 5,6,6-chelate ring sequence and possessing an *o*-(methylthio)phenol group was presented by Whittaker.[10] However, this ligand like all other tripods providing an N_2O_2 donor set and a 5,6,6-chelate ring sequence,[11] contains a phenol group connected to the central nitrogen atom in a way that the phenolic oxygen atom will be part of a six-membered chelate ring.

For the synthesis of H_4-**2**, *o*-nitro-*p*-cresol was selected as a suitable starting material. This molecule contains, at least in the protected form, all three of the desired functional groups for the construction of the aromatic part of H_4-**2**. The complete reaction sequence for the preparation of H_4-**2** is depicted in Scheme 2.

In a first reaction, the aromatic core of *o*-nitro-*p*-cresol was brominated by treatment with bromine in the presence of the Lewis acid catalyst $AlCl_3$.[16] The position *ortho* to the OH group is exclusively brominated, yielding compound **D**, due to the *ortho*- and *meta*-directing effect of the OH and the NO_2 substituents, respectively. Subsequently, **D** was deprotonated with NaOH, and the resulting phenolate was treated with (chloromethoxy)methane to give the MOM-protected derivative **E**.[17] Halogen/metal exchange of the bromine substituent, by use of phenyllithium at −105 °C resulted in the formation of a reactive aryllithium species that was not isolated.[18] This *ortho*-lithiated intermediate was quenched with dimethyl disulfide.[19] The *o*-(methylthio)-substituted compound **F** was isolated in good yield. According to a literature procedure,[20] the nitro group in **F** can be reduced quantitatively to the amine by an excess of hydrazine in the presence of Raney nickel to yield the aniline derivative **G**. Subsequently, a β-cyanoethyl group which will serve as the synthon for the 3-aminopropyl arm, was introduced by a copper(II) acetate catalyzed Michael addition of acrylonitrile to **G**. This resulted in the formation of compound **H**.[21] Finally, a C_3 chain (the precursor for the 3-hydroxypropyl arm) was added to the central nitrogen atom by acylation of **H** with β-acetoxypropionyl chloride, which was synthesized as described.[22] After chromatographic purification, amide **I** was obtained as a crystalline white solid. Reduction of **I** with AlH_3 yielded the ligand H_4-**2**. Under these conditions even the MOM-protected phenolic OH group is liberated. This is quite surprising since MOM ethers are known to be stable in basic media and are normally cleaved under acidic conditions. Ligand H_4-**2** is a sticky white solid which is slightly air-sensitive.



Scheme 2. Preparation of ligand H_4-**2**

Ligand H_4-**2**, like H_4-**1**, possesses an N_2O_2 donor set and an unsymmetrical topology. It is capable of forming a 5,6,6-membered chelate ring sequence and should be suitable for the preparation of square-pyramidal Cu^{II} complexes. H_4-**2** contains an *o*-(methylthio)-substituted phenol which is

directly connected to the central nitrogen atom of the ligand backbone. This is in contrast with tripodal N_2O_2 ligands published to date with regard to the modeling of the copper site in galactose oxidase. The electron-donating *o*-(methylthio) and the *p*-methyl substituents and the direct linkage of the aromatic ring to the central nitrogen atom should significantly lower the redox potential for the oxidation of this phenol group, while the substituents in the *ortho* and *para* positions relative to the OH group will prevent the formed phenoxyl radical from dimerizing.

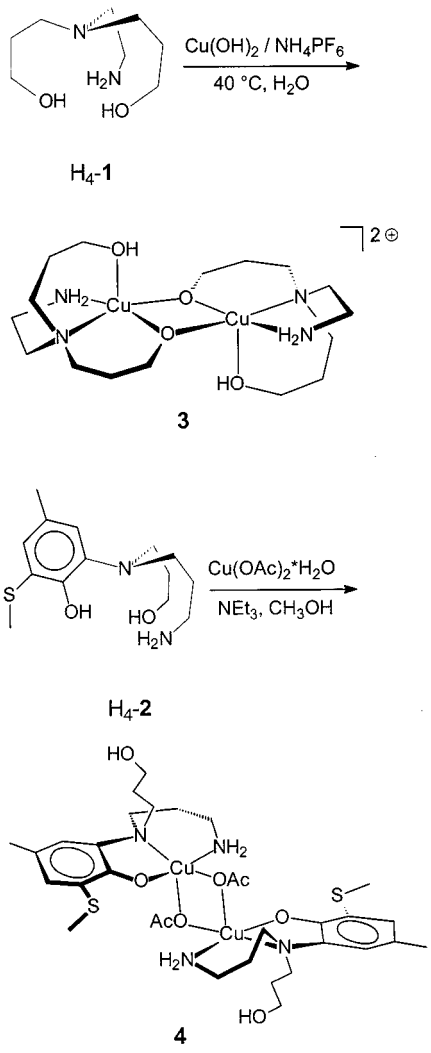
Preparation of Copper Complexes

Freshly prepared $Cu(OH)_2$, suspended in water, reacted at 40 °C with a stoichiometric amount of ligand H_4-**1** to give a blue suspension which contained unidentified copper species (probably hydroxides). Addition of 2 equiv. of NH_4PF_6 to such a suspension yielded a deep blue solution. From this solution complex **3** crystallized over a period of 6 h (Scheme 3). The complex is air-stable and can be recrystallized from water as deep blue prisms. The reaction of $[HNEt_3]^+[H_3$-**2**$]^-$ with an equimolar amount of $[Cu(OAc)_2{\cdot}H_2O]_2$ in methanol at room temperature yielded a dark green solution. On addition of a mixture of acetonitrile and *tert*-butyl methyl ether, and on cooling to −30 °C, air-sensitive blue plates crystallized, which were identified as **4**·2CH_3CN by X-ray crystallography (Scheme 3).

Molecular Structures of 3

The X-ray crystal structure analysis shows the formation of the dinuclear complex $[Cu(\eta^4\text{-}\mu\text{-O-}H_3\text{-}\mathbf{1})_2Cu](PF_6)_2$ (**3**) from $Cu(OH)_2$ and the ligand H_4-**1**. The dication of complex **3** resides on a crystallographic inversion center in the unit cell. Each copper(II) ion is coordinated by two nitrogen atoms, one terminal propyloxy group (O1) and two μ^2-propyloxo groups (O2) (Figure 3). The bridging oxygen atom O2 is deprotonated while the monodentate oxygen atom O1 remains protonated in the complex. The charge distribution was assigned based on the presence of only two PF_6^- anions which make the complex a dication with two monodeprotonated ligands H_3-**1**$^-$. The most acidic functions of the ligand are the alcohol groups. We concluded that O2 is the deprotonated alcohol group, based on the difference in the Cu−O distances [Cu−O1 2.339(3) Å, Cu−O2 1.920(3) Å].

The coordination geometry around the copper centers is best described by the use of the τ-criterion,[23] which indicates that the coordination geometry in **3** is only slightly distorted (τ = 0.181) from square-pyramidal. Atom O1 occupies the apical position. The Cu_2O_2 core shows a significant rhombic distortion. The angle O2−Cu−O2* is 78.10(13)°, while for Cu−O2−Cu* an angle of 101.90(13)° is observed. The Cu and Cu* distance is 3.001(1) Å. The Cu−N and $Cu-O_{eq}$ bond lengths are only slightly different [Cu−N1 2.033(3), Cu−N2 1.992(4) and Cu−O2 1.920(3), Cu−O2* 1.944(3) Å], leading to an almost symmetrical bridge between the copper atoms.



Scheme 3. Preparation of complexes **3** and **4**

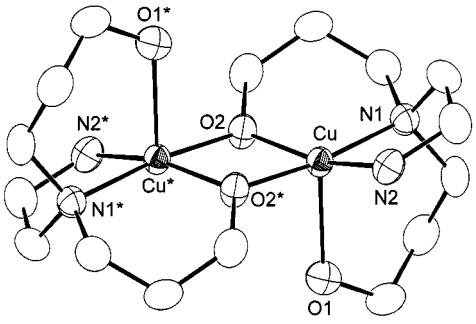


Figure 3. ORTEP plot of one complex dication of **3** (hexafluorophosphate anions are not shown); selected bond lengths [Å] and angles [°]: Cu···Cu 3.001(1), Cu−O1 2.339(3), Cu−O2 1.920(3), Cu−O2* 1.944(3), Cu−N1 2.033(3), Cu−N2 1.992(4); O1−Cu−O2 90.91(14), O1−Cu−O2* 91.77(13), O1−Cu−N1 94.74(14), O1−Cu−N2 106.3(2), O2−Cu−O2* 78.10(13), O2−Cu−N1 98.66(13), O2−Cu−N2 161.9(2), O2*−Cu−N1 172.79(14), O2*−Cu−N2 95.43(15), N1−Cu−N2 85.7(2), Cu−O2−Cu* 101.90(13)

A 5,6,6-chelate ring sequence is observed in the dication of **3**. This should and does lead to a square-pyramidal coordination geometry, with a donor atom of a six-membered

chelate ring (O1) in the apical position. In this regard, the molecular structure of **3** meets our expectations and experiences gained from related aliphatic tripodal N_4 ligand systems.[13] However, complex **3** cannot serve as a GO model compound since GO contains a mononuclear square-pyramidal copper center and not a binuclear one.

To the best of our knowledge **3** is one of two examples of a clearly square-pyramidal copper complex with an apical O-donor derived from a tripodal N_2O_2 ligand. Previously described tripodal N_2O_2 ligands with pyridyl and phenolate donors gave dinuclear copper complexes which deviate significantly from the square-pyramidal geometry, towards a trigonal-bipyramidal geometry.[10][11b] However, one tripodal N_2O_2 ligand with bulky substituents at its pyridyl and phenolate donors[11c] forms a distorted square-pyramidal mononuclear copper complex ($\tau = 0.273$) with a 5,6,6-chelate ring sequence and with an oxygen donor at the end of a C_3 chain in the apical position. These results together with the molecular structure of **3** indicate again, that the coordination geometry of copper complexes with tripodal ligands can at least partly be controlled and manipulated by the ligand topology.

Molecular Structures of 4·2CH_3CN

The X-ray structure analysis of **4**·2CH_3CN revealed that the oxygen-bridged, inversion-symmetric, dinuclear complex [(η^3-H_3-**2**)Cu(μ-OAc)$_2$Cu(η^3-H_3-**2**)]·2CH_3CN had formed (Scheme 3, Figure 4). The asymmetric unit contains two halves of the complex, which are not related by crystallographic symmetry.

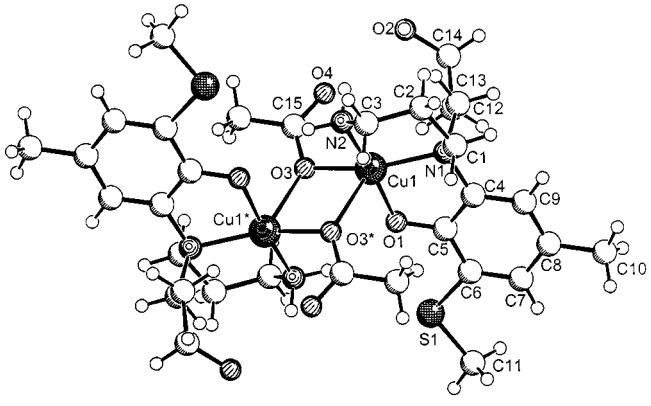


Figure 4. SCHAKAL plot of one molecule of complex **4** (the asymmetric unit contains two nearly identical halves of a molecule); selected bond lengths [A] and angles [°] for molecule A [molecule B]: Cu1···Cu1 3.2729(11) [3.2375(12)], Cu1−O1 1.916(3) [1.909(3)], Cu1−O3 1.999(3) [1.993(3)], Cu1−O3* 2.374(3) [2.529(3)], Cu1−N1 2.056(3) [2.056(4)], Cu1−N2 1.980(4) [1.970(3)]; O1−Cu1−O3 92.15(12) [92.21(12)], O1−Cu1−O3* 88.18(12) [85.33(12)], O1−Cu1−N1 86.09(13) [86.21(14)], O1−Cu1−N2 171.36(14) [169.21(14)], O3−Cu1−O3* 83.47(12) [89.36(12)], O3−Cu1−N1 159.04(14) [163.13(14)], O3−Cu1−N2 88.95(13) [88.74(14)], O3*−Cu1−N1 117.30(12) [107.23(12)], O3*−Cu1−N2 83.42(13) [83.93(13)], N1−Cu1−N2 95.91(15) [95.92(15)], Cu1−O3−Cu1* 96.53(12) [90.64(12)]

In complex **4** both copper(II) ions reside in a square-pyramidal ($\tau = 0.205$ and $\tau = 0.101$) N_2O_3 coordination environment, but in contrast to the situation in **3**, the μ^2-oxy bridges in **4** result from the bridging coordination of acetate oxygen atoms. The two acetate oxygen atoms occupy equatorial (O3) and apical (O3*) positions at the copper atom. Each Cu^{II} ion is coordinated by two nitrogen and three oxygen donors (one phenolate and two acetate oxygen atoms), while the hydroxypropyl arm (O2) of the ligand remains uncoordinated. Like in **3**, both copper atoms are coordinated in a square-pyramidal fashion, but again a dinuclear complex was obtained and hence it cannot act as an acceptable GO model compound.

The apical Cu−O bond is not exactly perpendicular to the equatorial plane which also leads to a rhombic distortion of the Cu_2O_2 core [O3−Cu−O3* 83.47(12)° and 89.36(12)°, Cu−O3−Cu* 96.53(12)° and 90.64(12)°]. For the same reason all O3*−Cu−L_{eq} angles significantly deviate from the ideal value of 90° expected for a perfect tetragonal pyramid.

The Cu−N bond lengths are almost equal, as found in **3** [Cu1−N1 2.056(3) Å and 2.056(4) Å, Cu1−N2 1.980(4) Å and 1.970(3) Å]. The Cu−O_{eq} distances [Cu−O1 1.916(3) Å and 1.909(3) Å, Cu−O3 1.999(3) Å and 1.993(3) Å] are similar. However, the separation Cu−O_{apical} is much more pronounced [Cu−O3* 2.374(3) Å and 2.529(3) Å], a behavior observed in all square-pyramidal copper complexes with an O-donor in the apical position.

Due to reasons we do not exactly know yet, and in contrast with the coordinated ligand (H_3-**1**)$^-$ in **3**, each (H_3-**2**)$^-$ ligand anion in complex **4** uses only three of the four donor groups for binding to the copper atom, while the hydroxypropyl arm is not coordinated and remains protonated. We believe that this is not exclusively due to the steric situation in **4**, but also to the low stability of the six-membered chelate ring which would have formed with the hydroxypropyl ligand arm. A similar behavior of related aliphatic tripodal ligands has been reported recently.[24] In addition it has been shown that the stability of the copper complex with the ligand trpn, which exclusively forms six-membered chelate rings is about 10^5 times lower than the stability of the corresponding tren complex that contains only five-membered chelate rings.[13b] The acetate oxygen atoms are apparently better donors than the hydroxypropyl group when competing for the coordination site at the copper center. Similar behavior has been reported for copper complexes with a tripodal ligand capable of forming a 5,6,6-chelate ring sequence, where the presence of chloride ions prevents the formation of the chelate complex, and a copper complex with chloride ligands was obtained.[11c] Table 1 lists some structural parameters for **3** and **4**.

Cyclic Voltammetry

The cyclic voltammogram of complex **3** recorded in an acetonitrile solution exhibits an irreversible oxidation potential at $E_{pa} = +1375$ mV vs. Ag/AgCl. Complex **3** is quite stable relative to to the corresponding Cu^{III} species which is highly reactive and rapidly decomposes to non-identified

Table 1. Comparison of selected structural details in complexes **3** and **4**·2CH_3CN

Complex	Cu−N_{eq} [Å]	Cu−O_{eq} [Å]	Cu−O_{ap} [Å]	τ
3	1.992(4), 2.033(3)	1.920(3), 1.944(3)	2.339(3)	0.179
4·2CH_3CN	1.980(4), 2.056(3)	1.916(3), 1.999(3)	2.374(3)	0.205, 0.101

products. Upon application of a negative potential an irreversible reduction is observed at $E_{pc} = -725$ mV vs. Ag/AgCl in acetonitrile. This corresponds to the process $Cu^{II} + e^- \rightarrow Cu^{I}$, which is followed by the dissociation of the Cu^{I} complex and disproportionation of Cu^{I} to Cu^{II} and Cu^0.

The results of the cyclic voltammetric analysis of the redox potentials of ligand H_4-**2** and complex **4** are shown in Figure 5. In the cathodic region, the free ligand H_4-**2** displays one quasireversible oxidation peak at $E = +130$ mV vs. Ag/AgCl in acetonitrile (top, solid line).

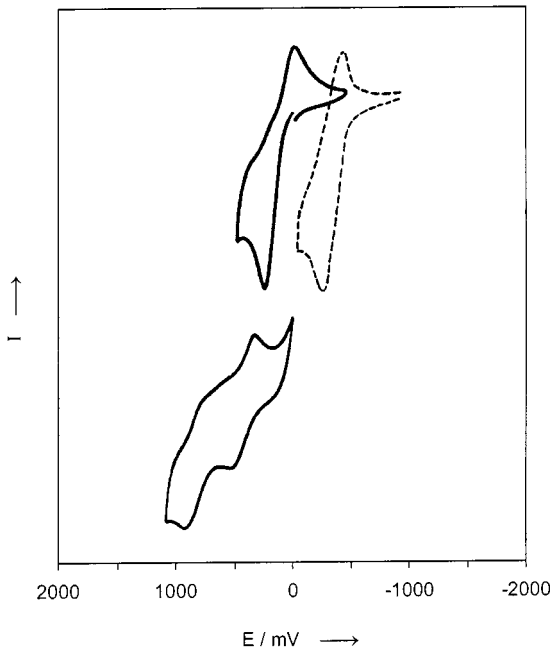


Figure 5. Cyclic voltammograms of H_4-**2** (top, solid line), $(H_3$-**2**$)^-$ (top, dashed line) and of complex **4** (bottom); *E* vs. Ag/AgCl in acetonitrile

This process corresponds to the oxidation of the phenolic moiety, leading to a phenoxyl radical which is prevented from dimerizing. The same process is observed when the phenolic OH group is deprotonated in the presence of $(n\text{Bu})_4N^+OH^-$. The oxidation potential of the phenol group is then shifted towards a more negative potential by about 440 mV than reported previously,[10,11] and is now observed as a quasireversible voltammetric response at $E = -310$ mV vs. Ag/AgCl in acetonitrile (top, dashed line). This low-potential redox step arises from the relatively facile oxidation of the electron-rich thioether and amino-substituted phenol. Recently, such stable, free phenoxyl radicals have also been shown to be essential for enzymes other than galactose oxidase, e.g. glyoxal oxidase[25] and ribonucleotide reductase[1b].

Although the oxidation of the blue dimeric copper complex **4** takes place at a somewhat higher potential than the protonated ligand H_4-**2**, **4** is also easily oxidized. A broad peak, which seems to be the result of the overlapping of two independent redox processes, is observed between 0 and +1000 mV vs. Ag/AgCl in acetonitrile (Figure 5, bottom). The oxidation of the phenolate takes place at a potential of $E^1 = +430$ mV vs. Ag/AgCl, while a second oxidation process occurs at $E^2 = +870$ mV vs. Ag/AgCl. The superimposing cyclic voltammetric responses suggest a quasireversible electron transition, which indicates that in **4** a stable phenoxyl radical is formed on oxidation. In addition, the ligand stabilizes the copper(II) state, since reduction of the complex is observed at a very low potential ($E = -1320$ mV vs. Ag/AgCl in acetonitrile; not shown in Figure 5). This reduction process is irreversible and leads to a deposit of copper(0) on the electrode surface, as concluded from a sharp anodic oxidation peak at $E_{pc} = -60$ mV during the reverse scan with the typical features of a redissolution process.[10]

Conclusion

We have prepared two novel nonsymmetric tripodal ligands which provide an N_2O_2 donor set. Both ligands are capable of coordinating to Cu^{II} to give a 5,6,6-chelate ring sequence. For this chelate ring sequence, square-pyramidal complexes with a donor linked by a C_3 chain in the apical position are expected. Ligand H_4-**1** indeed forms such a complex. However, this complex is dinuclear. With ligand H_2-**2**, we present a tripod with an *o*-amino-*o*-(methylthio)-substituted phenolate donor. This ligand also forms a square-pyramidal Cu^{II} complex, which is also dinuclear. While the dinuclear nature of complexes **3** and **4**·2CH_3CN excludes them from the acceptable mononuclear GO models, they still provide information about the ligand design for the preparation of structural GO models. Among the dinuclear complexes with an N_2O_2 donor set, **3** and **4**·2CH_3CN contain copper atoms which deviate least from the required square-pyramidal coordination geometry, as judged by the τ values of 0.181 for **3** and 0.205 and 0.101 for **4**·2CH_3CN. Thus, the 5,6,6-chelate ring sequence indeed leads to the desired square-pyramidal complexes. Finally, the unique *o*-amino-*o*-(methylthio)-substitution of the phenol donor in ligand H_4-**2** leads to a significant reduction of the redox potential for the oxidation of the free or coor-

dinated phenolate group to the corresponding phenoxyl radical, which is stabilized against dimerization by *p*-methyl substitution of the aromatic ring. Based on these observations we propose that substitution of the aliphatic OH and NH_2 donors in H_4-**2** by aromatic ones (phenol and pyridine) and sterically more bulky substituents at the phenol groups could lead to a square-planar, mononuclear Cu^{II} complex, which would serve as a satisfactory structural GO model.

Experimental Section

General Remarks: All manipulations were carried out under argon. Solvents were purified by standard methods, freshly distilled and degassed prior to use. − Infrared spectra were recorded in KBr using a Perkin−Elmer IR 983 spectrometer. − NMR spectra were recorded with a Bruker AM 250 spectrometer. − Elemental analyses (C,H,N,S) were performed with a Vario EL Elemental Analyzer. − EI and +FAB mass spectra were recorded with Finnigan MAT 112 or Finnigan MAT 711 instruments. − UV/Vis spectra were recorded with a Perkin−Elmer Lambda 9 UV/Vis/NIR spectrophotometer. − Cyclic voltammetric experiments were carried out with a Bank High Power Potentiostat Wenking HP 72 and a Bank Scan Generator Wenking Model VSG 83, using a three-electrode cell configuration (working electrode: Pt; auxiliary electrode: Pt; reference electrode: Ag/AgCl/3 M KCl; $E_{Fc/Fc+}$ = 435 mV). The experiments were performed in acetonitrile with 0.1 M tBu_4NPF_6 as the supporting electrolyte with scan rates of 100 mV/s.

Ligand Syntheses

B: 3,3′-Iminobis(ethyl propionate) **B** was prepared according to a procedure published previously.[14] − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.12 (q, 4 H, $-OCH_2$), 2.92 (t, 4 H, NCH_2), 2.49 (t, 4 H, CH_2COO), 1.84 (s, 1 H, NH), 1.24 (t, 6 H, CH_3). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 172.38 (COO), 60.15 (CH_2O), 44.68 (NCH_2), 34.52 (CH_2COO), 13.97 (CH_3).

C: Formaldehyde (2.027 g, 0.025 mol, 37% in water) was added to a solution of sodium pyrosulfite $Na_2S_2O_5$ (2.376 g, 0.0125 mol) in 10 mL of water. The reaction mixture was heated to 50 °C for a period of 45 min and then cooled to 0 °C. **B** (5.431 g, 0.025 mol) was added slowly while maintaining the temperature below 5 °C. Subsequently, the flask was allowed to warm to room temperature and the reaction mixture was stirred for 2 h. The mixture was again cooled to 0 °C and a solution of KCN (5.431 g, 0.025 mol) in 8 mL of water was added. The resulting solution was stirred overnight at room temperature. During this period an oil had separated, which was extracted with chloroform (3 × 50 mL). The organic phases were combined and dried with anhydrous $MgSO_4$. All solvents were removed in vacuo, and the residue was distilled at 115 °C ($2\cdot10^{-2}$ mbar). Yield: 5.070 g (79.1% relative to **B**) of a colorless oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.12 (q, 4 H, OCH_2), 3.64 (s, 2 H, CH_2CN), 2.90 (t, 4 H, NCH_2), 2.48 (t, 4 H, CH_2COO), 1.24 (t, 6 H, CH_3). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 171.39 (COO), 114.84 (CN), 60.41 (OCH_2), 49.37 (NCH_2), 41.96 (CH_2CN), 32.85 (CH_2COO), 13.99 (CH_3).

H_4-1: All protected donor groups in **C** were liberated simultaneously by reduction with AlH_3. The AlH_3 was prepared from lithium aluminium hydride (LAH) (5.40 g, 0.143 mol) and H_2SO_4 (6.183 g, 60 mmol, 96%) in 150 mL of dry THF as described.[13a] Compound **C** (5.07 g, 19.8 mmol), dissolved in 30 mL of THF, was added dropwise to the vigorously stirred AlH_3 suspension, at room temperature. The reaction mixture was stirred for 24 h at ambient temperature, and residual AlH_3 was carefully hydrolyzed with water (8.2 mL, 0.46 mol). All solids were removed by filtration and repeatedly washed with methanol (6 × 50 mL). The organic layers were combined, all solvents removed in vacuo, and the residue was distilled at 135 °C ($2\cdot10^{-3}$ mbar). Ligand H_4-**1** was obtained as a colorless oil. Yield 2.234 g (64% relative to **C**). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.67 (s + t, 6 H, OH + CH_2O), 2.80 (t, 2 H, $NCH_2CH_2NH_2$), 2.58 (t, 4 H, $NCH_2CH_2CH_2$), 2.50 (t, 2 H, CH_2NH_2), 1.70 (m + s, 6 H, $CH_2CH_2CH_2$ + NH_2). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 61.27 (CH_2O), 56.45 ($NCH_2CH_2NH_2$), 52.27 ($NCH_2CH_2CH_2$), 39.29 (CH_2NH_2), 28.97 ($CH_2CH_2CH_2$). − MS (EI): *m*/*z* (%) = 176 (2.55, $[M]^+$), 146 (100, $[M - H_2O]^+$), 102 (57.38), 58 (70.21). − IR (KBr): $\tilde{\nu}$ = 3343 (br. s, N−H + O−H), 2939, 2869 (s, C−H), 1593 (m, N−H), 1373 (m, O−H), 1464 (s, C−H), 1216 (m, C−N), 1063 (s, C−O).

D: Anhydrous $AlCl_3$ (18.0 g, 0.12 mol) was suspended in 50 mL of dry dichloromethane of. This mixture was treated with a solution of *o*-nitro-*p*-cresol (15.314 g, 0.1 mol) in 20 mL of dichloromethane. When the evolution of HCl had ceased, bromine (17.5 g, 0.11 mol) was added dropwise and the dark green suspension was stirred overnight at room temperature. The mixture was hydrolyzed with 10 g of ice under vigorous evolution of HCl. Subsequently, 50 mL of water and 30 mL of dichloromethane were added and the resulting suspension was mixed with 30 mL of aqueous HCl (32%). The clear orange organic layer was separated, washed twice with acidic water and dried with anhydrous $MgSO_4$. The solvent was stripped in vacuo to give 21.33 g (91%) of a yellow powder. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 11.0 (s, 1 H, OH), 7.92, 7.74 (s, 2 H, Ar-H), 2.38 (s, 3 H, CH_3). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 150.09, 141.76, 132.70, 124.04, 118.94, 112.81 (Ar−C), 20.19 (CH_3).

E: The sodium salt of **D** was obtained by deprotonation of the phenolic OH group with aqueous NaOH. To achieve this **D** (11.6 g, 0.05 mol), dissolved in 24 mL of hot (70 °C) ethanol, was added to a warm solution of NaOH (2.04 g, 0.051mol) in a mixture of 24 mL of ethanol and 3.5 mL of water. Immediately a red precipitate separated, which was collected by filtration and dried in vacuo for several hours. A sample of the sodium salt of **D** (12.7 g, 0.05 mol) was suspended in 70 mL of dry THF. (Chloromethoxy)methane (MOMCl) (4.026 g, 0.05 mol) was then added dropwise to this suspension. ***Warning: (Chloromethoxy)methane (MOMCl) is known to be extremely carcinogenic!*** The mixture was refluxed for 4 h. During this period the color of the suspension changed from red to white. The reaction mixture was extracted three times with a saturated K_2CO_3 solution, and the combined organic layers were dried with anhydrous $MgSO_4$. Removal of the solvent yielded 11.95 g (86.6%) of a pale yellow powder, that was purified by recrystallization from a mixture of hexane/ether (3:1, v:v). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.66, 7.54 (s, 2 H, Ar-H), 5.12 (s, 2 H, OCH_2O), 3.54 (s, 3 H, OCH_3), 2.34 (s, 3 H, CH_3). − $^{13}C\{^1H\}$ NMR (62.90 MHz, $CDCl_3$): δ = 137.89, 136.05, 124.36, 119.13 (Ar−C, only 4 resonances were observed), 100.68 (OCH_2O), 58.01 (OCH_3), 20.36 (CH_3).

F: Compound **E** (16.565 g, 0.06 mol) was dissolved in 250 mL of dry THF and cooled to −105 °C with a mixture of diethyl ether/liquid nitrogen as described previously.[18b] Over a period of 30 min phenyllithium (37 mL, 0.066 mol, 1.8 M solution in hexane/ether, 70:30) was slowly added via a syringe maintaining the temperature below −100 °C. When all the phenyllithium had been added, the

red suspension was stirred for 1 h at −105 °C and subsequently quenched with dry, degassed dimethyl disulfide (11.3 mL, 0.12 mol). After 15 min, the mixture was allowed to warm to −78 °C. After stirring at this temperature for an additional 30 min, the orange suspension was carefully hydrolyzed with 15 mL of degassed water and slowly brought to 0 °C. Toluene (150 mL) was added and the total volume of the solution was reduced to 100 mL in vacuo. Ether (150 mL) was then added. The resulting organic phase was repeatedly extracted with water until the aqueous layer remained colorless. After drying with anhydrous $MgSO_4$ and removal of the solvents in vacuo, a brown oily residue was obtained. Column-chromatographic purification (SiO_2, hexane/ethyl acetate, 4:1, R_f = 0.29) yielded 10.05 g (72.3%) of an intense orange oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.30, 7.10 (s, 2 H, Ar-H), 5.02 (s, 2 H, OCH_2O), 3.50 (s, 3 H, OCH_3), 2.42 (s, 3 H, SCH_3), 2.32 (s, 3 H, CH_3). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 144.82, 144.18, 136.14, 135.03, 130.12, 121.11 (Ar-C), 100.06 (OCH_2O), 57.88 (OCH_3), 20.80 (CH_3), 14.89 (SCH_3).

G: A solution of **F** (7.298 g, 0.03 mol) in 100 mL of methanol was cooled to 0 °C and mixed with hydrazine (6 g, 0.12 mol, 100%). After addition of three small portions of Raney nickel, it was stirred until the evolution of gas had ceased and the mixture decolorized. In order to decompose the excess hydrazine an additional portion of Raney nickel was added and the suspension was heated to reflux for 90 min. The solid metal was separated by filtration under argon, and all solvents were removed in vacuo. The oily residue obtained was dissolved in 50 mL of degassed dichloromethane and the solution was dried with anhydrous $MgSO_4$. Removal of the solvent in vacuo yielded 5.77 g (90.2%) of **G** as a yellow oil. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.37, 6.34 (s, 2 H, Ar-H), 5.04 (s, 2 H, OCH_2O), 3.94 (br. s, 2 H, NH_2), 3.62 (s, 3 H, OCH_3), 2.40 (s, 3 H, SCH_3), 2.24 (s, 3 H, CH_3). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 139.80, 139.51, 135.04, 132.04, 115.88, 113.95 (Ar-C), 99.11 (OCH_2O), 57.58 (OCH_3), 21.07 (CH_3), 14.71 (SCH_3).

H: Acrylonitrile (3.188 g, 0.06 mol) and **G** (8.535 g, 0.04 mol) were mixed with the catalyst $Cu(OAc)_2 \cdot H_2O$ (0.839 g) and the polymerization inhibitor quinone (0.17 g). The mixture was heated to 110 °C and the reaction was monitored by chromatography (SiO_2, hexane/ethyl acetate, 4:1, $R_f^{\mathbf{G}}$ = 0.18, $R_f^{\mathbf{H}}$ = 0.13). The reaction was complete after 4 h, otherwise additional portions of acrylonitrile and copper catalyst had to be added. The resulting brown residue was purified by column chromatography (SiO_2, hexane/ethyl acetate). Yield 7.55 g (70.9%) of a brown crystalline solid. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.36, 6.25 (s, 2 H, Ar-H), 5.02 (s, 2 H, OCH_2O), 4.88 (br. s, 1 H, NH), 3.62 (s, 3 H, OCH_3), 3.50 (q, 2 H, NHC*H*$_2$), 2.62 (t, 2 H, CH_2CN), 2.40 (s, 3 H, SCH_3), 2.24 (s, 3 H, CH_3). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 139.74, 135.36, 132.00, 118.05, 115.31 (Ar-C, only 5 resonances were observed), 108.87 (CN), 99.32 (OCH_2O), 57.71 (OCH_3), 39.56 ($NHCH_2$), 21.56 (CH_3), 18.04 (CH_2CN), 14.68 (SCH_3).

I: H (5.332 g, 20 mmol) was dissolved in a mixture of dry diethyl ether (25 mL) and chloroform (5 mL) and treated with acetoxypropionyl chloride (3.09 g, 20.5 mmol) which was synthesized according to a published procedure.[22] On reaction the mixture slightly warmed and became darker in color. After 30 min, triethylamine (2.086 g, 20.6 mmol) was added, and the solution was stirred for one additional hour at room temperature. Washing of the reaction solution with water, drying of the organic phase with anhydrous $MgSO_4$ and removal of the solvents in vacuo yielded a brown oil that was purified chromatographically (SiO_2, hexane/ethyl acetate, 1:1, $R_f^{\mathbf{I}}$ = 0.15). The product crystallized as colorless needles. Yield: 4.95 g (65%). − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.99, 6.86 (s, 2 H, Ar-H), 5.01 (q, 2 H, OCH_2O), 4.52 + 4.41 (dd, 2 H, $NC(O)CH_2$), 4.37 + 4.30 (dd, 2 H, $NC(O)CH_2CH_2$), 3.48 (s, 3 H, OCH_3), 2.77 (q, 2 H, NCH_2), 2.60 (t, 2 H, CH_2CN), 2.46 (s, 3 H, SCH_3), 2.36 (s, 3 H, CH_3), 2.02 (s, 3 H, $C(O)CH_3$). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 170.78 [C(O)O + C(O)N], 147.24, 135.69, 134.93, 134.24, 126.74, 126.70 (Ar-C), 117.89 (CN), 99.35 (OCH_2O), 60.32 (OCH_3), 47.51 [$NC(O)CH_2CH_2O$], 44.42 [$NC(O)CH_2$], 33.26 (NCH_2), 21.00 (Ar-CH_3), 20.88 [$C(O)CH_3$], 16.41 (CH_2CN), 14.70 (SCH_3).

H_4-2: All protected donor groups in **I** were liberated simultaneously by use of AlH_3. The AlH_3 was prepared from lithium aluminium hydride (LAH) (2.73 g, 72 mmol) and H_2SO_4 (3.065 g, 30 mmol, 96%) in 70 mL of dry THF as described.[13a] Ligand precursor **I** (3.75 g, 10 mmol), dissolved in 30 mL of THF, was added dropwise to the vigorously stirred AlH_3 suspension. The reaction mixture was stirred for 24 h at ambient temperature, residual AlH_3 was carefully hydrolyzed with water (5.4 mL, 0.3 mmol), and all solids were removed by filtration. The solid residue was repeatedly extracted with methanol under argon. All organic phases were combined and all solvents were removed in vacuo. The oily residue obtained was dissolved in a small portion of dichloromethane and this solution was filtered and dried with anhydrous $MgSO_4$. Removal of the solvent in vacuo yielded a yellow sticky oil that crystallized at −30 °C. Alternatively, addition of diethyl ether to oily H_4-**2** gave a white powder. Yield: 1.51 g (84.8%). − $C_{14}H_{24}N_2O_2S$ (284.42): calcd. C 59.12, H 8.51, N 9.85, S 11.27; found C 58.24, H 8.49, N 9.58, S 11.37. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.66 (s, 2 H, Ar-H), 5.64 (br. s, 4 H, Ar-OH, CH_2-OH, NH_2), 3.58 (t, 2 H, CH_2OH), 2.98 (t + t, 4 H, NCH_2), 2.84 (t, 2 H, CH_2NH_2), 2.36 (s, 3 H, SCH_3), 2.22 (s, 3 H, Ar-CH_3), 1.60 (m + m, 4 H, $CH_2CH_2CH_2$). − ^{13}C{^{1}H} NMR (62.90 MHz, $CDCl_3$): δ = 152.96, 136.99, 125.52, 124.34, 120.77, 118.36 (Ar-C), 60.95 (CH_2OH), 52.99 ($NCH_2CH_2CH_2OH$), 48.41 ($NCH_2CH_2CH_2NH_2$), 38.69 (CH_2NH_2), 29.06, 26.35 ($CH_2CH_2CH_2$), 20.95 (Ar-CH_3), 14.94 (SCH_3). − MS (EI), *m*/*z* (%) = 284 (38.79) $[M]^+$, 240 (20.22) $[M - CH_2CH_2NH_2]^+$, 196 (100), 182 (21.11), 134 (6.95). − IR (KBr): ṽ: 3504 (s, N−H), 3337 (s, O−H), 2950, 2918, 2848, 2799 (s, C−H), 1547 (m, N−H), 1448 (m, O−H), 1265 (m, C−N), 1077 (s, C−O), 830, 871 (m, C−H of a 1,2,3,5-substituted aromatic ring).

Preparation of Copper Complexes

3: For the preparation of **3** freshly precipitated $Cu(OH)_2$ (195 mg, 2 mmol) was suspended in water (10 mL) and ligand H_4-**1** (370 mg, 2.1 mmol) was added dropwise with a syringe. The blue suspension was stirred at 40 °C for 60 min, and then solid NH_4PF_6 (652 mg, 4 mmol) was added, resulting in a deep blue solution. The solution was reduced to a volume of 5 mL and cooled to 5 °C. After 24 h, deep blue crystals had formed. The crystals were collected by filtration and recrystallized from warm acetonitrile/diethyl ether. Yield 596 mg (68.9%). − $C_{16}H_{38}Cu_2F_{12}N_4O_4P_2$ (767.52): calcd. C 25.04, H 4.99, N 7.30; found C 25.09, H 5.17, N 7.46. − MS (FAB, positive ions, 3-nitrobenzyl alcohol/DMSO), *m*/*z* (%) = 475 (18.95, $[M - H]^+$), 301 (37.67, $[Cu(H_3$-**1**$) + Cu]^+$), 239 (33.19, $[$**3** $+ H]^{2+}$). − IR (KBr): ṽ: 3549, 3378, 3330 (w, O−H + N−H), 2970, 2875, 2833 (m, C−H), 1596 (m, NH_2), 1473, 1459, 1433 (m, C−H), 1065, 1046 (s, C−O); 833, 558 (s, PF_6). − UV/Vis (CH_3OH): λ_{max} [nm] (ε) = 270 (4900), 366 (2000), 585 (120).

4: H_4-**2** (62.6 mg, 0.22 mmol) was mixed with triethylamine (44.4 mg, 0.44 mmol). The mixture was added dropwise to a solution of $Cu(OAc)_2 \cdot H_2O$ (43.9 mg, 0.22 mmol) in 10 mL of methanol, resulting in the formation of a green solution. After stirring for 30 min, the solvent was removed in vacuo and the residue suspended

in acetonitrile and filtered. To the clear, deep green solution was added *tert*-butyl methyl ether. Cooling the solution to −30 °C yielded blue plate-shaped crystals. Yield 8.3 mg (4.6%) of **4**·2CH_3CN. − $C_{36}H_{58}Cu_2N_6O_8S_2$ (894.08): calcd. C 47.33, H 6.45, N 6.90, S 7.89; found C 47.48, H 6.53, N 7.09, S 8.13. − MS (FAB, positive ions, 3-nitrobenzyl alcohol/DMSO), *m/z* (%) = 409 (11.34) $[Cu_2(H_3\text{-}\mathbf{2})]^+$, 346 (18.20) $[Cu(H_3\text{-}\mathbf{2})]^+$. − UV/Vis ($CH_3OH$): λ_{max} [nm] (ε) = 310 nm (15360), 400 (sh, 220), 650 (140).

Crystal Structure Analyses: Crystallographic data for complexes **3** and **4**·2CH_3CN are presented in Table 2. Crystals of **3** are air-stable. Diffraction data were collected at room temperature with an Enraf−Nonius CAD-4 diffractometer. No absorption correction was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at geometrically idealized positions and were refined using a riding model. Complex **4**·2CH_3CN rapidly degenerates in air under loss of co-crystallized solvent. Suitable specimens were mounted at 198 K on a Nonius Kappa CCD diffractometer with a rotating anode generator. Diffraction data were collected at 198 K. An absorption correction via SORTAV was applied to the raw data ($0.85 \leq T \leq 0.99$). All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at geometrically idealized positions and were refined using a riding model. The following programs were used: Data collection EXPRESS and COLLECT, data reduction MolEN and DENZO-SMN, absorption correction for CCD data SORTAV, structure solution SHELXS-86 and SHELXS-97, structure refinement SHELXL-97, graphical presentation ZORTEP and SCHAKAL-92. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-150423 and -150424 for **3** and **4**·2CH_3CN, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Summary of crystallographic data for **3** and **4**·2CH_3CN

	3	**4**·2CH_3CN
Empirical formula	$C_{16}H_{38}N_4CuF_{12}P_2O_4$	$C_{36}H_{58}N_6Cu_2O_8S_2$
M_r	767.52	894.08
T [K]	293(2)	198(2)
Crystal size [mm]	0.31×0.22×0.20	0.15×0.10×0.05
a [Å]	9.041(6)	9.978(1)
b [Å]	13.356(2)	13.433(1)
c [Å]	11.990(2)	16.398(1)
α [°]	90	97.87(1)
β [°]	98.54(3)	94.94(1)
γ [°]	90	90.36(1)
V [Å^3]	1419.8(10)	2168.7(3)
Z	2	2
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
$\rho_{calcd.}$ [g cm^{-3}]	1.795	1.369
μ Mo-K_α [mm^{-1}]	1.721	1.130
Diffractometer	Enraf−Nonius CAD-4	Enraf−Nonius Kappa CCD
λ [Å]	0.71073	0.71073
2θ range [°]	$2.3 \leq 2\theta \leq 26.4$	$2.05 \leq 2\theta \leq 25.0$
Index range	$h, k, \pm l$	$\pm h, \pm k, \pm l$
Unique data	2918	7597
Observed data [$I \geq 2\sigma(I)$]	2003	5092
R	0.0414	0.0597
wR	0.0952	0.1111
No. of variables	257	735
GOF	1.050	1.022

Acknowledgments

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