

Catechol Oxidation with Dinuclear Copper Complexes of Aliphatic Tripodal Amino Alcohols

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A set of unsymmetrical tripodal (aminoalkyl)bis(hydroxyalkyl)-amine ligands **H₄-2** to **H₄-6** with either ethyl or propyl ligand arms has been prepared and characterized. These ligands react with copper hydroxide and ammonium hexafluorophosphate, copper(II) bromide or tris(triphenylphosphane)copper(I) bromide to give di- and polynuclear complexes. The dinuclear copper complexes **9a-f** catalyze the oxidation of 3,5-di-*tert*-butylcatechol (DTBC). The coordination geometry at the copper center is influenced by the length of the side arms resulting in a different reactivity of complexes **9a-f** in the DTBC oxidation. Alternative preparation procedures lead in selected cases to the formation of coordination polymers

10a and **10b**. The reversible formation of the poly(dinuclear) cations in **10a** illustrates that the apical alcohol groups are labile. The solid-state structures are neither necessarily identical with solution structure nor do they represent the catalytically active species. Electronic spectra, however, agree with a dinuclear structures in solution as indicated by the characteristics of the oxygen-copper-CT. The observation of comparable catalytic activities for complexes **9a-9d** renders the bridging coordination of the catechol by both copper ions of a dinuclear complex moiety unlikely.

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Introduction

The diverse applications of tripodal tetraamine ligands in coordination chemistry have been reviewed recently.^[1] Several transition metal complexes of triethanolamine illustrate the application of aliphatic tripodal ligands in supramolecular chemistry.^[2] Furthermore, unsymmetrical tripodal ligands are used in modeling active metal sites in enzymes. For example, a variety of aromatic tripodal NN₂O and NNO₂ ligands have been prepared to model the metal site in the copper enzyme galactose oxidase.^[3] The field of aliphatic tripodal ligands with unsymmetrical donor functions developed more recently. Some complexes of the unsymmetrical aliphatic tripodal ligands NN₂O-222 (**H₅-A**),^[4] NN₂O-332 (**H₅-1**), NN₂O-333 (**H₅-B**),^[5] NNO₂-222 (**H₄-2**),^[4c] NNO₂-233 (**H₄-4**),^[3] NNO₂-223 (**H₄-3**),^[6] and NNO₂-322 (**H₄-5**)^[7] have been prepared (Figure 1). Complexes of sulfur containing unsymmetrical tripodal ligands have also been reported.^[8]

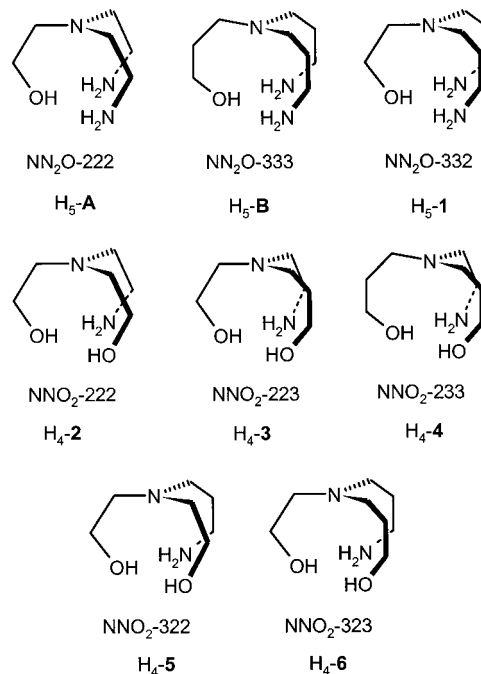


Figure 1. Aliphatic tripodal amino alcohols.

Others and we have studied the correlation between the topology of tripodal ligands and the reactivity of their complexes. A remarkable example for the influence of ligand topology on complex reactivity is the phosphate ester cleavage promoted by tris(3-aminopropyl)amine (trpn) com-

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plexes of cobalt while the tris(2-aminoethyl)amine (tren) complexes are 300 times less active.^[9] Other studies found interrelations between the ligand topology and complex properties for copper(II)^[10] and nickel(II)^[11] complexes of the tetraamine ligands tren, (3-aminopropyl)bis(2-aminoethyl)amine (baep), (2-aminoethyl)bis(3-aminopropyl)amine (abap), and trpn.

In this contribution, we present a study on copper complexes of a set of NNO_2 ligands and extend the relation between ligand shape and complex properties to catalysis. To allow for a fine-tuning of the geometric strain the flexible aliphatic ligands $\text{H}_4\text{-2}$ to $\text{H}_4\text{-6}$ (Figure 1) and their copper(II) complexes were studied. The copper complexes of ligands $\text{H}_5\text{-1}$ to $\text{H}_4\text{-6}$ (**9a–f**) may serve as models of the metal site in type 3 copper proteins. One member of this group is the ubiquitous plant enzyme catechol oxidase (CO, E.C.1.10.3.1) that converts catechols under consumption of molecular oxygen into *o*-quinones, which auto-polymerize to protect the plant from damage.^[12] Many models for the active center in CO have been prepared,^[13] but so far conversion rates of the model compounds are lower by four orders of magnitude compared to the enzyme.^[14] In our study 3,5-di-*tert*-butylcatechol (DTBC) was chosen as model substrate (Figure 2). To date different mechanisms for the oxidation of this substrate are discussed controversially based on measurements on model compounds.^[15]

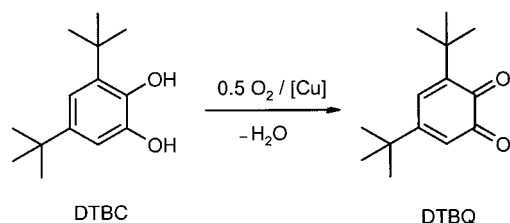


Figure 2. Oxidation of DTBC to 3,5-di-*tert*-butylquinone (DTBQ).

Results and Discussion

Ligand Synthesis

Ethanolamine, propanolamine and diethanolamine, respectively are employed as starting materials for the synthesis of ligands $\text{H}_5\text{-1}$ to $\text{H}_4\text{-6}$. A Strecker synthesis^[16] or Michael addition of acrylic acid derivatives^[17] is applied to assemble the tripodal backbone. The ester or nitrile functions of the protected ligands are reduced with aluminum hydride prepared in situ.^[18] Alternative synthetic pro-

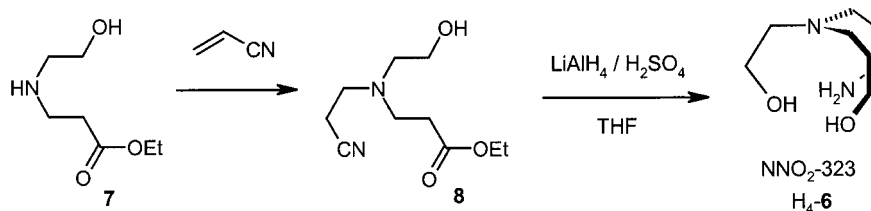
cedures described for the preparation of ligands $\text{NNO}_2\text{-222}$ ($\text{H}_4\text{-2}$),^[19] $\text{NN}_2\text{O-222}$ ($\text{H}_5\text{-A}$),^[20] $\text{NN}_2\text{O-332}$ ($\text{H}_5\text{-1}$)^[21] were found to be less efficient in our hands.

The preparation of the diamino-dihydroxy ligand $\text{NNO}_2\text{-323}$ ($\text{H}_4\text{-6}$) (Scheme 1) starts with the Michael addition of one equivalent ethyl acrylate to ethanolamine.^[8a] A small amount of methanol and excess acrylonitrile were added to the wax-like solid **7**. The mixture was heated to 60 °C for 24 h. After removal of volatiles compound **8** was isolated and the ester and nitrile group were reduced with aluminum hydride at temperatures increasing from 0 °C to ambient temperature. The reaction mixture was carefully hydrolyzed after eight hours and $\text{H}_4\text{-6}$ was obtained by Soxhlet extraction with methanol for 24 h. The extract was dried with sodium sulfate, filtered through celite® and volatiles were removed. Bulb to bulb distillation affords ligand $\text{NNO}_2\text{-323}$ ($\text{H}_4\text{-6}$) as colorless viscous oil.

Solid State Structure of Dinuclear Copper Complexes

Copper complexes of the tripodal amino alcohols were prepared as described for complex $[\text{Cu}(\text{H}_3\text{-4})_2(\text{PF}_6)_2 \cdot 2\text{MeOH}]$ **9c**·2MeOH.^[2e,3i] For the preparation of the copper complexes, one equivalent of ligand was added to an equimolar suspension of copper(II) hydroxide in deionized water. After stirring for one hour two equivalents NH_4PF_6 were added. The solutions were concentrated to approximately 1 mol/L by warming to 40 °C. Blue solids precipitated upon cooling of these solutions to 5 °C. Diffusion of diethyl ether into an ethanol (**9a**), acetonitrile (**9b**, **9e**, **9f**), or methanol (**9d**) solutions of these residues gave crystals of $[\text{Cu}(\text{H}_3\text{-2})_2(\text{PF}_6)_4 \cdot 0.5\text{EtOH} \cdot 0.5\text{H}_2\text{O}]$ (**9a**·0.5EtOH·0.5H₂O), $[\text{Cu}(\text{H}_3\text{-3})_2(\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}]$ (**9b**·2H₂O), $[\text{Cu}(\text{H}_3\text{-5})_2(\text{PF}_6)_2 \cdot \text{CH}_3\text{OH}]$ (**9d**·CH₃OH), $[\text{Cu}(\text{H}_3\text{-6})_2(\text{PF}_6)_2]$ (**9e**), and $[\text{Cu}(\text{H}_4\text{-1})_2(\text{PF}_6)_2]$ (**9f**). The molecular structures of these complexes were determined by X-ray diffraction (Figure 2 and Figure 3). The dinuclear complexes of type **9** were the dominant species under the reaction conditions selected. All attempts to isolate and characterize mononuclear complexes by adding more NH_4PF_6 or NaPF_6 failed.

The structure determinations on **9a**, **9b**, **9d**, **9e**, and **9f** in the solid state show dinuclear dicationic complexes $[\text{Cu}_2\text{L}_2]^{2+}$ as were previously observed for **9c**, in which one deprotonated alcohol group of each ligand serves as bridging donor to the second copper ion in a μ^3 -fashion (Figure 3 and Figure 4). The second hydroxyl arm of each ligand remains protonated as indicated by much longer copper–oxygen distances relative to the bridging alkoxide (com-



Scheme 1. Synthesis of the ligand $\text{NNO}_2\text{-323}$ ($\text{H}_4\text{-6}$).

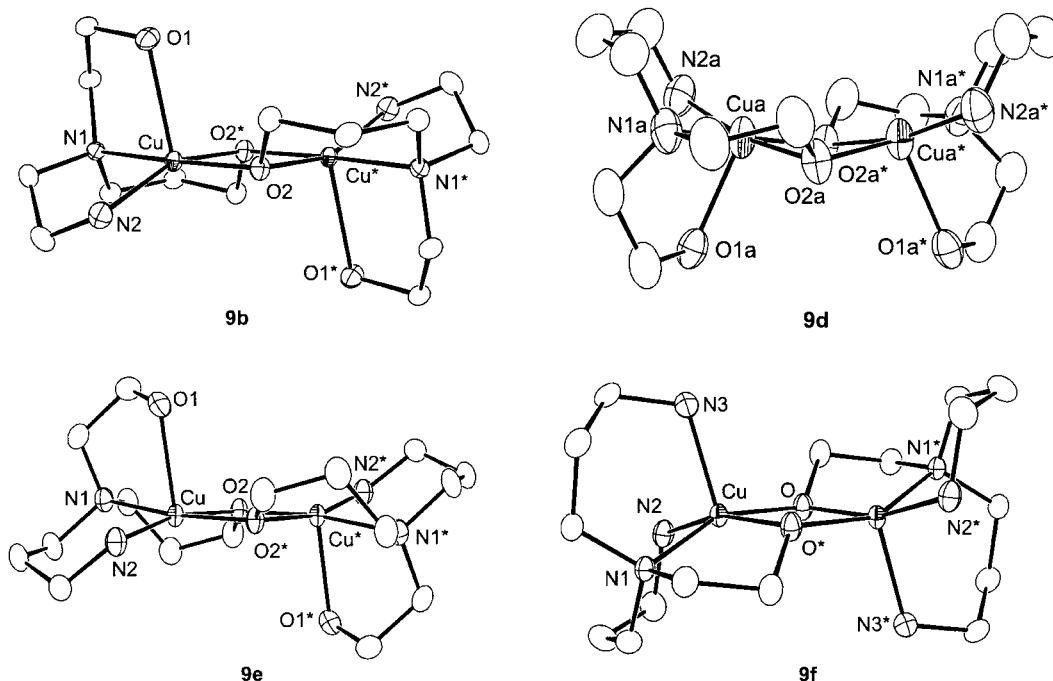


Figure 3. Molecular structures of the dinuclear cations of **9b** and **9d–f**.

pare Cu–O1 and Cu–O2 in Table 1). Comparison of the various structures reveals that propylalkoxide ligand arms, if available, preferably act as bridging donors. Complexes **9b**, **9e**, and **9f** form centrosymmetric complex ions with a planar $[\text{Cu}_2(\text{OR})_2]^{2+}$ moiety and with *trans*-arrangement of the apical alcohol functions.

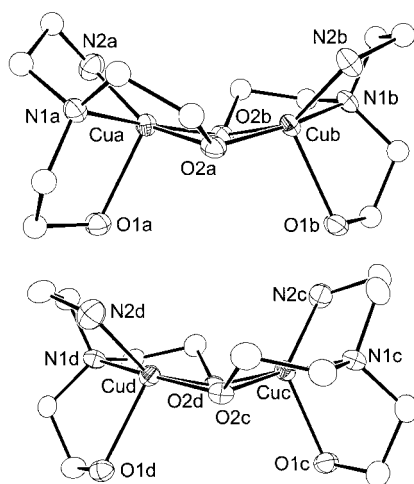


Figure 4. Molecular structure of the two dinuclear isomeric dications in **9a**.

Complexes **9a** and **9d** with ligands **H₄-2** and **H₄-5**, respectively, adopt a rather bowl-shaped geometry with a butterfly-like distorted $[\text{Cu}_2(\text{OR})_2]^{2+}$ core and *cis*-constitution of the coordinated alcohol groups. The short ligand arms of the ethyl alcohol lead to geometric strain and a distortion of the angles at the copper atom (Table 1). Hence, metal ions with a different coordination environment are found in the crystal structures of **9a** and **9d**. The

unit cell of **9d** contains two not related halves of the dinuclear complex ion $[\mathbf{9d}]^{2+}$. Complex **9a** crystallizes in a polar space group ($P2_1$) and the unit cell contains four different copper atoms of two dinuclear complex dications $[\mathbf{9a}]^{2+}$. The observation of the polar space group $P2_1$ for **9a** can be rationalized by the helicity of the dinuclear units and by the fact that the diamino chelate rings adopt different configurations in the two dinuclear complexes ($\lambda\lambda$ and $\lambda\delta$, respectively) (Figure 4).

Bond lengths and angles differ between the two dinuclear units in crystals of **9a**. Consequently, four different τ -values^[22] (0.21, 0.32, 0.51, 0.36) were observed for the four copper atoms in the asymmetric unit, indicating a distorted tetragonal-pyramidal coordination environment for the metal ions. The Cu–O distances range from 2.177(4) Å to 2.265 Å for the alcohol functions in the apical position. Within the $\text{Cu}(\mu\text{-O})_2\text{Cu}$ core the Cu–O2 distances in *trans*-position to the tertiary nitrogen donor are distinctively shorter [1.939(3) Å to 1.956(4) Å] than the Cu–O2 bond lengths *trans* to the primary nitrogen donor [1.998(4) Å to 2.075(4) Å, Table 1].

While **9d** exhibits an almost ideal tetragonal-pyramidal copper environment ($\tau = 0.03$), **9e** and **9f** are also close to such a coordination geometry ($\tau = 0.10$ and $\tau = 0.12$, respectively). The highest τ -value is observed for **9a** and **9b** ($\tau = 0.3$) which can be attributed to the shorter ethyl ligand arms leading to a distortion towards a trigonal-bipyramidal coordination geometry.

An interesting structural feature of these dinuclear complexes is the angle at the bridging oxygen atoms. Often, the magnetic coupling between two paramagnetic Cu^{II} centers is antiferromagnetic for angles larger than 96° while a ferromagnetic interaction is observed for smaller angles.^[23a,23b]

Table 1. Selected bond lengths [Å] and angles [°] for **9a**·0.5EtOH·0.5H₂O, **9b**·2H₂O, **9d**·2CH₃OH, **9e**, **9f**, and **10a**.

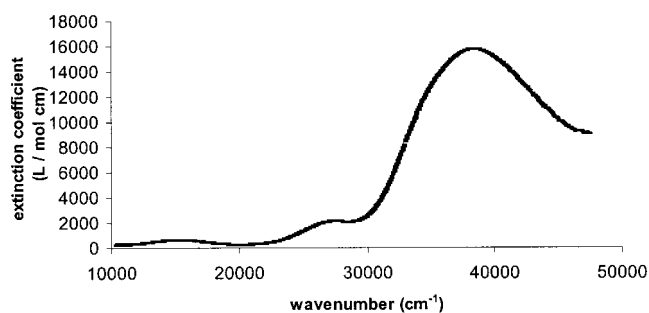
	9a ^[a]	9b	9c ^[b]	9d ^[c]	9e	9f	10a
Cu–O1	2.220(4), 2.255(4) 2.177(4), 2.265(4)	2.337(2)	2.338(4)	2.279(5) 2.283(4)	2.358(2)	–	2.500(1)
Cu–O2	1.998(4), 2.005(3) 2.075(4), 2.019(4)	1.9423(15)	1.919(3)	1.957(3) 1.955(3)	1.9231(12)	1.965(2)	1.927(3)
Cu–O2*	1.956(4), 1.947(4) 1.939(3), 1.945(3)	1.9357(14)	1.941(3)	1.966(3) 1.960(3)	1.9525(12)	1.952(2)	1.940(3)
Cu–N1	2.009(5), 2.028(5) 2.000(5), 2.018(4)	2.018(2)	2.030(4)	2.036(4) 2.026(4)	2.0410(14)	2.058(2)	2.024(4)
Cu–N2	1.996(4), 1.994(5) 2.025(4), 2.005(5)	1.997(2)	1.990(4)	1.971(5) 1.978(4)	1.9859(15)	2.009(2)	1.987(4)
Cu–N3	–	–	–	–	–	2.171(3)	–
Cu–Cu	2.8929(9) 2.9060(9)	2.9368(5)	3.0009(11)	2.9278(10) 2.9364(11)	3.0129(4)	2.9692(7)	2.9821(12)
Largest angle	O2*–Cu–N1 166.7(2), 168.3(2) 168.3(2), 169.5(2)	O2*–Cu–N1 175.38(6)	O2*–Cu–N1 172.77(14)	O2–Cu–N2 168.0(2) 168.6(2)	O2*–Cu–N1 171.21(5)	O–Cu–N2 161.84(10)	O2–Cu–N2 174.9(2)
2 nd largest angle	O2–Cu–N2 154.0(2) 149.3(2) 137.7(2), 147.9(2)	O2–Cu–N2 157.15(8)	O2–Cu–N2 162.0(2)	O2*–Cu–N1 166.2(2) 166.57(14)	O2–Cu–N2 164.93(7)	O*–Cu–N1 154.85(8)	O2*–Cu–N1 169.93(15)
Cu–O2–Cu*	94.30(15), 93.80(15) 94.45(15), 92.55(14)	98.45(6)	102.01(13)	96.91(13) 96.83(13)	102.05(5)	98.57(8)	100.91(15)

[a] The asymmetric unit contains for copper atoms in two dinuclear complexes **9a**. [b] Published data.^[31] [c] Atoms labeled with an asterisk denote atoms from different ligands not necessarily related by a symmetry element.

The bridging alkoxide groups lead to angles below this value for complex **9a**, while the Cu–O–Cu angles fall in the range 98° and 102° (Table 1) for the other complexes. However, temperature dependent measurements of the magnetic susceptibility for **9b–f** indicate that the coupling between the copper centers is antiferromagnetic in all cases.

Electronic Spectra

The electronic spectra of the dinuclear copper complexes **9a–f** show three transitions (Table 2, Figure 5 for **9f**). The most intense absorption is observed between 36 500 cm^{−1} (**9a**) and 39 400 (**9e**) cm^{−1} with extinction coefficients between 4900 L/mol·cm (**9c**) to 15700 L/mol·cm (**9f**). This absorption is assigned to a nitrogen-centered ligand-to-metal charge transfer (LMCT) by comparison with a variety of copper amine complexes.^[23c] Hence, a distinct difference in intensity appears between the complex with the triamine NN₂O ligand (**9f**) and the complexes with the diamine NNO₂ ligands (**9a–9e**).

Figure 5. Electronic spectrum of **9f** in acetonitrile solution.

The second absorption is observed between 27300 cm^{−1} (**9c**, **9e**, **9f**) and 27800 cm^{−1} (**9a**) with extinction coefficients around 2000 L/mol·cm (Table 2). As the intensity of this band is similar in all complexes and as the common feature of complexes of type **9** is the dialkoxy bridge, this band is associated with a charge transfer from the alkoxy oxygen atoms to the copper centers.^[24] This assignment is sup-

Table 2. Listing of τ -values, parameters of the electronic spectra, redox potentials, DTBQ yields and turnover numbers upon catalytic oxidation with complexes **9a–f**.

	9a	9b	9c	9d	9e	9f
τ -value ^[22]	0.21, 0.32, 0.51, 0.36	0.30	0.18	0.03	0.10	0.12
UV/Vis [cm ^{−1}]	36500	37300	37000	38800	39400	38230
(ϵ [L/mol·cm])	(6700)	(7900)	(4900)	(7100)	(8700)	(15700)
	27800	27400	27300	27500	27300	27300
	(540)	(1800)	(2000)	(1000)	(2300)	(2080)
	15250	16580	17090	16100	16500	15150
	(170)	(160)	(120)	(150)	(180)	(580)
Oxidation vs. Fc/Fc ⁺ [V]	1.15/1.27	1.01	0.90	1.05	1.42	0.87/1.50
Reduction vs. Fc/Fc ⁺ [V]	−1.43/−1.31	−1.10/−1.00	−1.42	−1.07	−1.33	−1.78
Yield DTBC [%]	15	83	99	80	50	36
TON [h ^{−1}]	180	216	227	94	140	504

ported by the intensity decrease observed for complexes **9a** and **9d**. Within these two complexes the $\text{Cu}(\mu\text{-O})_2\text{Cu}$ rings are distorted, because five-membered chelate rings are involved in the formation of the bridging four-membered ring (Figure 4). Apparently, the planarity of this four-membered ring is responsible for an optimum absorption. The observed difference of the extinction coefficient for the band around 27000 cm^{-1} between the *cis* structures **9a** and **9d** and the *trans* structures **9b**, **9c**, and **9e** support retention of the dinuclear structures in solution.

The absorptions with the lowest intensity and energy result from $d \rightarrow d$ transitions. They fall in the range between 15150 cm^{-1} (**9f**) and 17090 cm^{-1} (**9c**) with extinction coefficients from $120\text{ L/mol}\cdot\text{cm}$ (**9c**) to $580\text{ L/mol}\cdot\text{cm}$ (**9f**). The increased extinction coefficient in **9f** is most likely associated with the extra nitrogen atom present which causes a stronger mixing of ligand orbitals and metal d -orbitals in **9f**.

The energy of the $d \rightarrow d$ bands is consistent with either a trigonal-bipyramidal or a square-pyramidal geometry around the copper atoms. The coordination geometry at the copper center has been derived from the energy of the $d \rightarrow d$ absorption band for CuN_4 ,^[10b] CuN_5 and CuN_6 complex fragments or complexes.^[25] However, with compounds **9a–9e** no significant correlation was observed between τ -value and energy of the low energy transition. A comparison of different methods to determine the distortion of the trigonal-bipyramidal towards the tetragonal-pyramidal geometry showed the τ -value to be a sufficient criteria to distinguish between the two geometries for CuN_5 chromophores.^[26] In general, the $d \rightarrow d$ transitions of complexes of type **9** shift hypsochromic with an increasing number of six-membered chelate rings as well as for a change in the donor set from NNO_2 to NN_2O ligands (Table 2).

Cyclic Voltammetry

Cyclic voltammetry experiments show one irreversible reduction and one irreversible oxidation peak for the copper complexes **9b–9e** in acetonitrile solution (Table 2). The CV's of complex **9e** are shown as an example in Figure 6. The presence of four reduction peaks for **9a** can be attributed to four different copper centers displaying different τ -values as found in the solid-state structure. For the oxidation process two peaks are observed for compounds **9a** (1.15 V and 1.27 V) and **9f** (0.87 V and 1.50 V). In general, reduction of complexes of type **9** occurs between -1.78 V and -1.07 V while oxidations are observed between 0.87 and 1.50 V vs. Fc/Fc^+ .

Compound **9f** with an NN_2O ligand exhibits the strongest ligand field, which is reflected by the lowest reduction potential (-1.78 V) in the series of complexes of type **9**. The precipitation of copper metal during this reduction suggests that Cu^{II} is reduced to Cu^{I} , whose complexes are unstable. The irreversibility of the reduction process with complexes of type **9** is thus explained with the instability of Cu^{I} within a strong ligand field generated by the alkoxide and amine

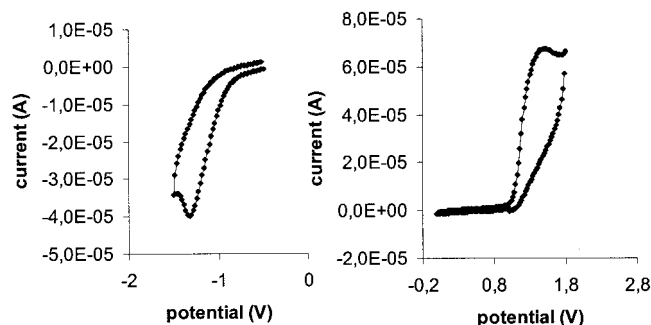


Figure 6. Irreversible reduction and oxidation peaks for **9e**. CV data were recorded in a 0.1 M solution of Bu_4NPF_6 in acetonitrile against Fc/Fc^+ .

functions. A sharp reoxidation peak is observed around -0.4 V resulting from the oxidation of metallic copper to Cu^{II} in the presence of ligand. A limited number of stable $\text{Cu}^{\text{I}}\text{-OR}$ species is known.^[27] While the Cu^{I} alkoxide can be stabilized in the absence of air or water either sterically or by conjugated π -systems in phenolates or enolates, $\text{Cu}^{\text{I}}\text{-OMe}$ species decomposes vigorously into copper metal, formaldehyde and methanol.

The irreversible nature of the oxidation process suggests that hypothetical Cu^{III} species are highly reactive and might lead to ligand degradation. Within the functional groups present, the bridging alkoxide functions are most susceptible for oxidation, which can produce aldehydes, carboxylic acid derivatives or CC coupled products.

DTBC Oxidation

Acetonitrile solutions of complexes of type **9** and DTBC (30 equiv.) were mixed in a shaking device under an oxygen atmosphere. The amount of oxygen consumed was monitored by an experimental set up described by one of us previously for similar experiments.^[28] Typically, green solutions were obtained upon mixing of the catalyst and the DTBC solution. The addition of one equivalent sodium methoxide initiated oxygen consumption, otherwise complexes of type **9** were found catalytically inactive. The order of mixing of the solutions influenced the yield of the oxidation product DTBQ. For example, mixing of **9b** and DTBC followed by addition of base gave lower yields (25%–30%) than mixing **9b** and base followed by DTBC addition (83% yield, Table 2). In general, complexes **9a–f** show a variation in catalytic activity giving yields from 15 to 99% with a TON from 90 to 500 h^{-1} (Table 2). A plot of the oxygen consumption during the oxidation of DTBC with complex **9f** as the catalyst is depicted in Figure 7. The experimental data confirm our assumption that a nitrogen (amine) rich coordination environment improves the catalytic activity of the copper center for the DTBC oxidation. Unfortunately, compound **9f** is less stable than **9a–e** under the required basic conditions. The coordination geometry described by the τ -value and catalytic activity do not correlate. Reaction rates and yields are best in the presence of six-membered chelate

rings for the alcohol functions and five-membered chelate rings for the terminal amine functions.

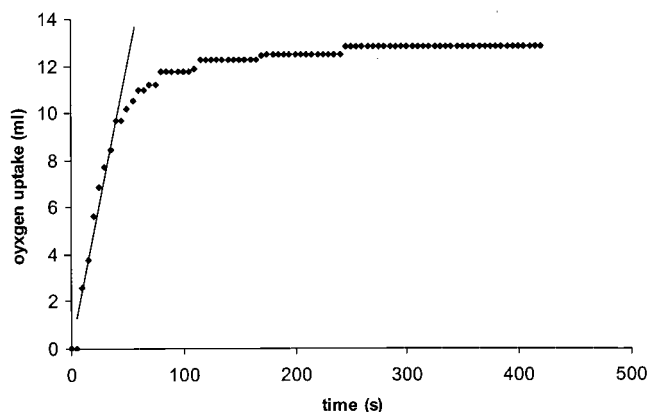


Figure 7. Consumption of O_2 (mL) vs. time (s) for the catalytic oxidation of DTBC (3 mmol) with **9f** in acetonitrile (maximum oxygen uptake: 33.6 mL).

Additional Copper Complexes

The stability of the copper(II) complexes of type **9** was corroborated by the formation of a purple Cu^{II} species upon reaction of $[Cu^I(PPh_3)_3Br]$ with ligand NNO_2 -233 (**H₄-4**). Equimolar amounts of the copper(I) compound and the ligand were mixed at air in a dichloromethane solution. The initially colorless solution turned blue rapidly and a purple solid **10a** precipitated. The elemental analysis suggested a ratio of Cu/Br/ligand of 1:1:1. The purple color of **10a** differs from the blue color of the dinuclear hexafluorophosphate salts **9a–9e**. Compound **10a** can be obtained directly by reaction of anhydrous copper(II) bromide and **H₄-4** in methanol. The X-ray structure analysis revealed that a polymer chain consisting of dinuclear dicationic units, which are bridged by alkoxy functions of the singly deprotonated ligand had formed (Figure 8). The remaining alcohol function of the ligand binds to a copper atom of an adjacent dinuclear unit in the apical position. The coordination geometry around the copper atoms is square-pyramidal with $\tau = 0$ (Table 1).

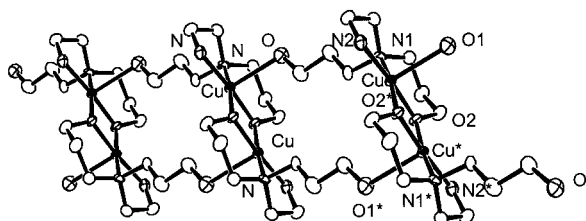


Figure 8. Fraction of the poly(dinuclear) coordination polymer built from $[Cu_2(H_3-4)_2]^{2+}$ cations of complex **10a**.

In an attempt to exchange the apical protonated alcohol function in the dinuclear complex $[Cu(H_3-4)]_2(PF_6)_2$ (**9c**) against 2,4,6-trimethylphenol (TMP), purple $[Cu(H_3-4)(TMP)]_2(PF_6)_2$ (**10b**) precipitated from a green solution. We assume that the TMP ligand substituted the protonated

(apical) alcohol function at the copper center. Apparently, this apical alcohol function is the most labile in the complex and can be substituted for other ligands. Furthermore, **10b** can be reconverted to **9c** in the absence of competing ligands such as methanol or TMP. Dissolving the purple complex $[Cu(H_3-4)(TMP)]_2(PF_6)_2$ (**10b**) in acetonitrile gives a blue solution. Addition of diethyl ether to this solution leads to precipitation of the dark blue dinuclear complex **9c**.

In conclusion, the energy difference between the two solid-state structures of type **9** and type **10** is small enough to allow interconversion. Apparently, the apical alcohol ligands in the dinuclear copper complexes of type **9** are labile and can be substituted for the catechol substrate without breaking up the dinuclear units immediately. The Cu–Cu distances in complexes of type **9** fall in the range between 2.89 Å (**9a**) and 3.01 Å (**9e**). However, the observation of comparable catalytic activity for both the *cis* complexes **9a** and **9d** and the *trans* complexes **9b** and **9c** renders the bridging coordination of the catechol by both copper ions of a dinuclear complex moiety unlikely. We therefore assume that during the catalytic cycle catechol substitutes one of the apical alcohol groups in the dinuclear copper complexes and eventually η^1 -coordinated catechol replaces one of the bridging alkoxide arms with the second oxygen donor atom.^[29] This process is aided by addition of a base which deprotonates the catechol ligand thereby enhancing its basicity. The addition of bases to the dinuclear complexes of type **9** in the absence of catechol leads to decomposition of the dinuclear complexes to a brown insoluble substance.

Conclusions

The rates of catalytic DTBC oxidation by the model compounds **9a–f** are far from modeling the enzyme catechol oxidase. However, **9f** shows an activity which is comparable to some other model compounds.^[13b,13d] The aim of this study was to probe the relation between the particular ligand design of basically similar ligands and the catalytic activity of its Cu^{II} complexes. Complexes **9a** to **9e** show indeed a different catalytic activity manifested in a variation of the yield in DTBC oxidation (15% to 99%) and different TON (94 to 227 h^{−1}). Since complexes **9a** to **9e** contain identical donor sets all differences in the activity can be attributed to different arm length at the tripodal ligands. However, the derivation of linear correlations between structural factors and catalytic activity turns out to be difficult.

Experimental Section

Materials and Methods: All manipulations were carried out in air unless noted otherwise. Solvents were purified by standard methods and freshly distilled prior use. Infrared spectra were recorded in KBr (pellets or thin films) with a Bruker Vector 22 FT spectrometer. ¹H and ¹³C NMR spectra were recorded on Bruker AC 200 or Bruker ARX 300 spectrometers. Elemental analyses (C,H,N) were

performed with a Vario EL III Elemental Analyzer at the Institut für Anorganische und Analytische Chemie, University of Münster. MALDI, ESI and EI mass spectra were measured with Bruker Reflex IV, Micromass Quattro LC and Varian MAT 212 instruments, respectively. UV/Vis spectra were recorded in acetonitrile with a Varian Cary 50 spectrophotometer. Cyclic voltammetry experiments were carried out with a Eco-Chemie PGSTAT 30 potentiostat using a three-electrode cell configuration (working electrode: glassy carbon, auxiliary electrode: platinum, reference electrode: Ag/AgCl/3 M KCl). The experiments were performed in 0.1 M acetonitrile solutions of Bu₄NPF₆ as supporting electrolyte with scan rates of 100 mV/s. A computer-controlled apparatus^[28] was used for oxygen uptake measurements in oxidation experiments with DTBC (Aldrich). Solutions of DTBC were freshly prepared. 30 equivalents of DTBC were mixed with one equivalent catalyst and one equivalent sodium methoxide in acetonitrile at 25 °C.

Ligand Syntheses: Ligands NNO₂-222 (H₄-2),^[4c] NNO₂-223 (H₄-3),^[6b] NNO₂-233 (H₄-4),^[31] NNO₂-322 (H₄-5),^[7] and NN₂O-332 (H₅-1)^[5] were prepared according to previously published procedures.

Ethyl 3-[(2-Cyanoethyl)(2-hydroxyethyl)amino]propanoate (8): 2.0 equivalents of acrylonitrile (5.46 g, 0.10 mol) were added to a solution of ethyl 3-[(2-hydroxyethyl)amino]propanoate (7)^[8a] (8.29 g, 0.0514 mol) in methanol (5 mL). The reaction mixture was heated to 60 °C for 48 h. Excess acrylonitrile and methanol were removed under reduced pressure and **8** remained as a colorless liquid. Yield: 10.6 g (0.049 mol, 96%). ¹H NMR (200 MHz, CDCl₃): δ = 4.07 (q, 2 H, OCH₂CH₃), 3.52 (t, 2 H, CH₃CH₂OH), 2.85–2.70 (m, 4 H, NCH₂), 2.59 (t, 2 H, NCH₂CH₂OH), 2.47–2.33 (m, 4 H, NCH₂CH₂), 1.18 (t, 3 H, OCH₂CH₃). ¹³C NMR (50.3 MHz, CDCl₃): δ = 172.4 [C(O)OEt], 118.7 (CN), 60.6 (CH₂O), 59.4 (CH₂O), 55.6 (NCH₂CH₂OH), 49.6 (NCH₂), 48.8 (NCH₂), 32.7 (NCH₂CH₂CO₂Et), 16.6 (NCH₂CH₂CN), 13.9 (OCH₂CH₃).

N-(2-Hydroxyethyl)-N-(3-hydroxypropyl)propylene-1,3-diamine NNO₂-323 (H₄-6): Dry lithium aluminum hydride (8.36 g, 0.209 mol) was suspended in THF (200 mL). After stirring for 60 minutes and cooling to –5 °C concentrated sulfuric acid (4.80 g, 0.047 mol) was added carefully dropwise (**Caution:** this reaction is extremely exothermic, hydrogen is evolved). The suspension was stirred for 60 min and ethyl 3-[(2-cyanoethyl)(2-hydroxyethyl)amino]propanoate (**8**) (15.0 g, 0.020 mol) dissolved in THF (30 mL) was slowly added. The reaction mixture should not be allowed to boil during the addition of **8**. The suspension was stirred at room temperature for 8 h and then quenched by slow addition of degassed water (15.1 g, 0.84 mol) at 0 °C. The reaction mixture was filtered under an argon atmosphere. The filtrate contained H₄-6 and side products, but most of the ligand was found in the solid residue. It was isolated by continuous extraction with methanol for one day. An immediate work-up after hydrolysis increased the yield of ligand H₄-6 because otherwise aluminum complexes form. The extract and the filtrate were united and dried with sodium sulfate. Removal of the solvent gave a colorless to yellow residue, which was suspended in dichloromethane (200 mL) and dried with sodium sulfate. The drying agent and precipitated lithium salts were separated by filtration through Celite®. Distillation under reduced pressure (180 °C, 0.05 mbar) afforded H₄-6 as colorless oil. Yield: 3.37 g (19.1 mmol, 27%). C₈H₂₀N₂O₂ (176.26): calcd. C 54.52, H 11.44, N 15.89; found C 53.32, H 11.43, N 15.12. ¹H NMR (200.1 MHz, CDCl₃): δ = 3.62 (t, 2 H, NCH₂CH₂CH₂OH), 3.54 (t, 2 H, NCH₂CH₂OH), 3.29 (s br, 4 H, OH + NH₂), 2.68 (t, 2 H, NCH₂CH₂CH₂NH₂), 2.54 (t, 2 H, NCH₂CH₂CH₂OH), 2.48 (t, 2 H, NCH₂CH₂OH), 2.46 (t, 2 H, NCH₂CH₂CH₂NH₂), 1.63 (qi, 2

H, NCH₂CH₂CH₂OH), 1.55 (qi, 2 H, NCH₂CH₂CH₂NH₂). ¹³C NMR (50.3 MHz, CDCl₃): δ = 62.2 (NCH₂CH₂CH₂OH), 59.4 (NCH₂CH₂OH), 55.6 (NCH₂CH₂OH), 53.3 (NCH₂CH₂CH₂OH), 51.8 (NCH₂CH₂CH₂NH₂), 39.8 (NCH₂CH₂CH₂NH₂), 29.6 (NCH₂CH₂CH₂NH₂), 28.7 (NCH₂CH₂CH₂OH). IR (KBr film): ν = 3358 (s, NH), 3285 (s, NH), 2949 (s, CH), 2871 (s, CH), 2829 (s, CH), 1662 (w), 1602 (w, NH), 1464 (m, CH), 1375 (w, CH), 1299 (w), 1060 (s, CO), 910 (m), 870 (w), 750 (w). MALDI-MS (337.0 nm, 3 ns) *m/z*: 177.0 [MH]⁺.

Synthesis of Copper Complexes. General Procedure: Copper hydroxide was prepared from copper chloride and sodium hydroxide in the presence of a small amount of polyethylene glycol ether at 0 °C. The turquoise solid can be stored at –30 °C for several months without darkening. The preparation of copper complexes of type **9** was carried out according to a published procedure described for the preparation of complex **9c**.^[31] Copper hydroxide was suspended in deionized water (10–20 mL) and the ligand dissolved in water (10 to 20 mL) was added. The reaction mixture was stirred at 40 °C for 2 h. Solid NH₄PF₆ was added and the volume of the solutions was reduced to reach a concentration of approximately 1 M. Crystalline material precipitated upon storage at 5 °C. For further purification, the raw material was recrystallized from ethanol (**9a**·0.5EtOH·0.5H₂O), methanol (**9d**·MeOH), acetonitrile (**9b**·2H₂O, **9e**, **9f**) or dichloromethane (**10a**). Yields and selected analytical data for complexes **9a**·0.5EtOH·0.5H₂O, **9b**·2H₂O, **9d**·MeOH, **9e**, **9f** and **10a** are given below.

[Cu₂(H₃-2)₂](PF₆)₄·0.5EtOH·0.5H₂O (9a**·0.5EtOH·0.5H₂O):** Cu(OH)₂ (425 mg), 4.36 mmol, ligand H₄-2 (647 mg, 4.36 mmol) and NH₄PF₆ (711 mg, 4.36 mmol) were used in the procedure described for the preparation of **9c**.^[31] Yield: 340 mg (0.457 mmol, 21%). IR (KBr): ν = 3364 cm^{–1} (s), 3312 (s), 3208 (s, br), 2990 (s), 2927 (s), 2870 (s), 1597 (m), 1473 (m), 1371 (w), 1269 (w), 1134 (m). MALDI-MS (337.0 nm, 3 ns) *m/z*: 482 (45, [Cu₂(H₃-2)₂]⁺), 416 (75, [Cu₂(H₃-2)₂(CH₃CN)]⁺), 419 (100, [Cu₂(H₃-2)₂]⁺).

[Cu₂(H₃-3)₂](PF₆)₂·2H₂O (9b**·2H₂O):** Cu(OH)₂ (195 mg, 2.00 mmol), ligand H₄-3 (330 mg, 2.00 mmol) and NH₄PF₆ (530 mg, 4.00 mmol) were used. Yield: 308 mg (0.397 mmol, 40%). **9b**·2H₂O C₁₄H₃₈N₄Cu₂F₁₂O₆P₂ (775.52): calcd. C 21.68, H 4.94, N 7.22; found C 21.59, H 4.35, N 6.91. ¹⁹F NMR (188.3 MHz, CD₃CN): δ = –66.8 (¹J_{FP} = 710 Hz). IR (KBr): ν = 3627 cm^{–1} (m), 3327 (s), 3128 (m), 2919 (m), 2861 (m), 2821 (m), 1594 (m), 1472 (m), 1320 (m), 1120 (s), 1084 (s), 1062 (s), 830 (s, PF₆). MALDI-MS (337.0 nm, 3 ns) *m/z*: 447 (100, [Cu₂(H₃-3)₂]⁺), 592.9 (30, [Cu₂(H₃-3)₂](PF₆)⁺).

[Cu₂(H₃-5)₂](PF₆)₂·CH₃OH (9d**·CH₃OH):** Cu(OH)₂ (292 mg, 3.00 mmol), ligand H₄-5 (487 mg, 3.00 mmol) and NH₄PF₆ (980 mg, 6.00 mmol) were used. Yield: 550 mg (0.713 mmol, 48%). IR (KBr): ν = 3666 cm^{–1} (s), 3448 (s), 3343 (s), 3297 (s), 3131 (s), 2951 (m), 2921 (m), 2880 (m), 2765 (m), 1604 (s), 1463 (m), 1333 (m), 1286 (m), 1265 (m), 1161 (s), 1072 (s), 1044 (s), 1015 (s), 833 (s, PF₆).

[Cu₂(H₃-6)₂](PF₆)₂ (9e**):** Cu(OH)₂ (211 mg, 2.18 mmol), ligand H₄-6 (383 mg, 2.18 mmol) and NH₄PF₆ (711 mg, 4.36 mmol) were used. Yield: 350 mg (0.456 mmol, 42%). IR (KBr): ν = 3591 cm^{–1} (s), 3358 (s), 3305 (s), 2951 (m), 2871 (m), 2803 (w), 2712 (w), 1602 (m), 1463 (m), 1311 (w), 1089 (s), 1048 (s), 839 (s, PF₆). MALDI-MS (337.0 nm, 3 ns) *m/z*: 475 (100, [Cu₂(H₃-6)₂]⁺), 659 (10, [Cu₂(H₃-6)₂](PF₆·CH₃CN)]⁺), negative ions *m/z*: 910 ([Cu₂(H₃-6)₂](PF₆)₃)[–].

[Cu₂(H₄-1)₂](PF₆)₂ (9f**):** Cu(OH)₂ (390 mg, 4.00 mmol), ligand H₅-1 (701 mg, 4.00 mmol) and NH₄PF₆ (1.30 g, 8.00 mmol) were used.

Yield: 330 mg (0.431 mmol, 22%). IR (KBr): $\tilde{\nu}$ = 3373 cm⁻¹ (m), 3355 (m), 3324 (m), 3304 (m), 2974 (m), 2946 (m), 2933 (m), 2892 (m), 2857 (m), 1603 (m), 1487 (w), 1457 (w), 1244 (w), 1150 (m), 1056 (m), 1022 (m), 835 (s, PF₆). MALDI-MS (337.0 nm, 3 ns) *m/z*: 238 (24, [Cu(H₅-1)]⁺), 422 (24, [Cu(H₅-1)(PF₆)(CH₃CN)]⁺), 606 (100, [Cu(H₅-1)(PF₆)₂(CH₃CN)₂]⁺).

[Cu₂(H₃-4)₂]Br₂ (10a): Preparation starting from Cu^I: A solution of H₄-4 (162 mg, 1.0 mmol) in dichloromethane (10 mL) was added to a colorless solution of [Cu^I(PPh₃)₃Br] (930 mg, 1.0 mmol) in dichloromethane (20 mL). Within several minutes the solution turned blue upon stirring under air. Purple crystals precipitated, which were suitable for X-ray diffraction analysis. Yield: 65 mg (0.10 mmol, 20%). [Cu₂(H₃-4)₂]Br₂ **10a** C₇H₁₈Br₂Cu₂N₂O₂ (318.66): calcd. C 30.15, H 6.01, N 8.79; found C 30.78, H 6.04, N 8.90%.

Preparation Starting from Cu^{II}: A solution of H₄-4 (353 mg, 2.0 mmol) in methanol (10 mL) was added to a brown solution of copper bromide (447 mg, 2.0 mmol) in methanol (10 mL). Immediately upon mixing the color of the solution changed to blue. Purple crystals formed upon standing in air. More crystals were precipitated by diffusion of diethyl ether into this solution. Yield: 227 mg (0.356 mmol, 36%). C₇H₁₈Br₂Cu₂N₂O₂ (318.66): calcd. C 30.15, H 6.01, N 8.79; found C 30.19, H 6.01, N 8.72%.

Crystal Structure Analyses: Blue crystals of **9a**·0.5EtOH·0.5H₂O, **9b**·2H₂O, **9d**·MeOH, **9e** and **9f** and purple crystals of **10a** were obtained by recrystallization from ethanol (**9a**·0.5EtOH·0.5H₂O), methanol (**9d**·MeOH), acetonitrile (**9b**·2H₂O, **9e**, **9f**) or dichloromethane (**10a**) at 5 °C. Diffraction data were measured at low temperature (Table 3 and Table 4) on a Bruker APEX diffractometer

Table 3. Summary of crystallographic data for **9a**·0.5EtOH·0.5H₂O, **9b**·2H₂O, and **9d**·2CH₃OH.

	9a ·0.5EtOH·0.5H ₂ O	9b ·2H ₂ O	9d ·MeOH
Crystal size [mm]	0.18 × 0.05 × 0.4	0.26 × 0.21 × 0.18	0.21 × 0.13 × 0.10
Formula	C ₁₃ H ₃₄ Cu ₂ F ₁₂ N ₄ O ₅ P ₂	C ₁₄ H ₃₈ Cu ₂ F ₁₂ N ₄ O ₆ P ₂	C ₁₅ H ₃₈ Cu ₂ F ₁₂ N ₄ O ₅ P ₂
<i>f</i> _w , amu	743.36	775.50	771.51
<i>a</i> [Å]	12.9766(13)	7.4536(7)	11.6574(5)
<i>b</i> [Å]	15.2839(15)	10.6827(10)	19.2777(8)
<i>c</i> [Å]	13.5796(14)	17.0136(16)	26.3811(11)
<i>a</i> [deg]	90	90	90
<i>β</i> [deg]	96.874(2)	91.398(1)	90
<i>γ</i> [deg]	90	90	90
<i>V</i> [Å ³]	2673.9(5)	1354.3(2)	5928.6(4)
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> ccn
<i>Z</i>	4	2	8
<i>d</i> _{calcd.} [g cm ⁻³]	1.847	1.902	1.729
<i>μ</i> [mm ⁻¹]	1.826	1.810	1.651
<i>T</i> [K]	173(2)	153(2)	173(2)
Unique data	9414	2375	5233
Observed data [<i>I</i> ≥ 2σ(<i>I</i>)]	8217	2254	4247
<i>R</i> (observed data)	0.0420	0.0246	0.0553
<i>wR</i> (observed data)	0.0933	0.0596	0.1386
GOF	1.004	1.048	1.043
2θ-range [deg]	3.0–50.1	4.5–50.0	3.7–50.1
Residual electron density [e/Å ³]	0.751/–0.308	0.774/–0.241	1.395/–1.042

Table 4. Summary of crystallographic data for **9e**, **9f**, and **10a**.

	9e	9f	10a
Crystal size [mm]	0.10 × 0.08 × 0.02	0.20 × 0.07 × 0.02	0.07 × 0.04 × 0.03
Formula	C ₁₆ H ₃₈ Cu ₂ F ₁₂ N ₄ O ₄ P ₂	C ₁₆ H ₄₀ Cu ₂ F ₁₂ N ₆ O ₂ P ₂	C ₁₆ H ₃₈ Br ₂ Cu ₂ N ₄ O ₄
<i>f</i> _w , amu	767.52	765.56	637.40
<i>a</i> [Å]	7.9889(5)	7.7147(8)	8.316(2)
<i>b</i> [Å]	8.3591(5)	9.6178(10)	16.212(3)
<i>c</i> [Å]	11.0443(7)	9.6401(10)	8.671(2)
<i>a</i> [deg]	76.1580(10)	77.686(2)	90
<i>β</i> [deg]	76.2270(10)	85.577(2)	91.179(4)
<i>γ</i> [deg]	79.0790(10)	89.414(2)	90
<i>V</i> [Å ³]	688.63(7)	696.73(13)	1168.7(4)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	1	1	2
<i>d</i> _{calcd.} [g cm ⁻³]	1.851	1.825	1.811
<i>μ</i> [mm ⁻¹]	1.774	1.750	5.267
<i>T</i> [K]	153(2)	173(2)	123(2)
Unique data	3139	4002	2675
Observed data [<i>I</i> ≥ 2σ(<i>I</i>)]	2859	3087	2159
<i>R</i> (observed data)	0.0265	0.0477	0.0573
<i>wR</i> (observed data)	0.0685	0.0886	0.1108
GOF	1.019	0.969	1.107
2θ-range [deg]	3.9–55.0	4.3–60.2	5.0–50.0
Residual electron density [e/Å ³]	0.350/–0.336	0.605/–0.501	1.265/–0.907

equipped with a rotating molybdenum anode ($\lambda = 0.71073 \text{ \AA}$) and a CCD area detector. Empirical absorption corrections were applied to all data sets. The structures were solved and refined by standard Patterson- and Fourier-techniques.^[30] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were added to the structure model on calculated positions. Selected crystal, data collection and refinement details are listed in Table 3 and Table 4.

Supplementary Material: CCDC-276044 (for **9a**·0.5EtOH·0.5H₂O), -276045 (for **9b**·2H₂O), -276046 (for **9d**·MeOH), -276047 (for **9e**), -276048 (for **9f**), and -276049 (for **10a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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