Electron Transfer

Copper Complexes of New Redox-Active 4,5-Bisguanidino-Substituted Benzodioxole Ligands: Control of the Electronic Structure by Counter-Ligands, Solvent, and Temperature

David Fridolin Schrempp, Elisabeth Kaifer, Hubert Wadepohl, and Hans-Jörg Himmel*^[a]

Abstract: Herein, we analyze the possibility of controlling the electronic structure of mononuclear copper complexes featuring new redox-active 4,5-bisguanidino-substituted benzodioxole ligands. The nature of the guanidino groups, the anionic counter-ligands, the applied solvent (polarity), and the temperature are the parameters that decide if a Cu^{II} complex with neutral ligand unit or a Cu^I complex with radical monocationic ligand unit is the adequate description.

Introduction

Transition-metal complexes with redox-active ligands are currently intensively studied. Research in this field is spurred by a variety of different potential applications, spanning from molecular catalysis^[1] to the design of advanced materials for "spintronics",^[2] which allow switching between different spin states on a molecular level. Intramolecular electron-transfer processes influence the reactivity and magnetic properties of these complexes. In some cases, the complexes exhibit two or more isomeric (valence tautomeric) forms. It is particularly attractive to switch between the valence tautomers by means of light irradiation or temperature.^[3] Most work on valence tautomeric complexes is focused on dioxolene-type ligands.^[4] Such ligands can also be found in biological systems. In particular, switching from one to the other valence tautomeric form of the copperdioxolene complex in the enzyme amine-oxygenase was identified as a key step in the catalytic cycle.^[5] The barrier between the two valence tautomers in a mononuclear complex can be influenced by changes in the spin multiplicity at the metal center (e.g., Co^{II}/Co^{III}) and/or structural changes (e.g. Cu^I/Cu^{II}).^[4] A temperature-dependent equilibrium between two valence tautomers Cu^{II}/semiguinolato and Cu^I/catecholato has been reported for a few complexes with hybrid ligands (see Scheme 1 a for an example).^[6] It was also shown that the electronic structure can be controlled by the choice of the counter-ligand. $^{\left[7\right] }$ Hence, soft ligands stabilize the Cul/catecholato

[a] D. F. Schrempp, Dr. E. Kaifer, Prof. H. Wadepohl, Prof. H.-J. Himmel Anorganisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg Im Neuenheimer Feld 275, 69120 Heidelberg (Germany) Fax: (+ 49)6221-545707 E-mail: hans-jorg.himmel@aci.uni-heidelberg.de

E-mail: nans-jorg.nimmei@aci.uni-neiaeiberg.a

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201602402. Under special conditions, a temperature-dependent equilibrium of the two valence tautomeric forms (Cu^{II} /neutral ligand and Cu^{I} /radical monocationic ligand) is achieved. Removal of a ligand-centered electron from a paramagnetic Cu^{II} complex with a neutral ligand unit leads to a diamagnetic Cu^{II} complex with a dicationic ligand unit through a redoxinduced electron-transfer (RIET) process.



Scheme 1. a) Example of a synthesized mononuclear copper complex for which a temperature-dependent equilibrium between two valence tautomeric forms was reported. b) Example of the influence of the counter-ligands on the electronic structure of copper-dioxolene complexes. c) Selected guanidino-substituted aromatic compounds. The synthesis of compounds 3 and 4 is shown for the first time in this work. Compounds 1, 2, and 5 were previously reported.

form, whereas hard ligands favor the Cu^{II} /semiquinolato valence tautomer (see Scheme 1 b).

Guanidino-substituted aromatic compounds (GFAs) constitute a relatively new class of redox-active ligands developed

Chem. Eur. J. 2016, 22, 1-14

Wiley Online Library

These are not the final page numbers! **77**

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



by our group.^[8] Examples comprise 1,2,4,5-tetrakis-(N,N,N',N'tetramethylguanidino)benzene (1, see Scheme 1 c) and 1,4,5,8tetrakis-(N,N,N',N'-tetramethyl-guanidino)naphthalene (2).^[9] All known GFA compounds are thermally stable and can be sublimed without decomposition. Also, salts of the GFA compounds decompose at high temperatures without explosion.^[10,11] Late transition metals such as copper strongly bind to the imino nitrogen atoms of the guanidino groups in three charge states of the ligands (neutral, radical monocationic, and dicationic).^[12] Furthermore, we recently showed that the electronic structures of dinuclear copper complexes of ligand 2 depend on the counter-ligands at the copper atoms.^[13] As expected, hard counter-ligands prefer the Cu^{II}/neutral ligand form and soft ligands prefer the Cul/dicationic ligand form. Very recently, we reported a dinuclear Cu-GFA-Cu complex, in which two valence tautomers (diamagnetic Cu¹-GFA²⁺-Cu¹ and paramagnetic Cu^{II}–GFA–Cu^{II}) are in a temperature-dependent equilibrium in acetone solution.^[14] It was also shown that the electronic structure is extremely sensitive to the environment, especially the solvent polarity. Whereas tetraoxolene-type bridging ligands are typically negatively charged in complexes,^[15] the GFA ligands could adopt neutral or positive charges in complexes. Therefore, tetraoxolene and GFA ligands are complementary to each other. Guanidines are versatile ligands, and, for example, Cu^{II} complexes of the bisguanidine 5 catalyze atomic transfer radical polymerization (ATRP), but in this case ligand-metal electron transfer does not take place.^[16]

Herein, we report the synthesis and coordination chemistry of two new redox-active 4,5-bisguanidino-substituted benzodioxole ligands (**3** and **4**, see Scheme 2). The two compounds



Scheme 2. Oxidation of 3 to $3(PF_6)_2$ (similar reaction from 4 leads to $4(PF_6)_2$).

can be used for the preparation of 4,5-bisguanidino-substituted o-dioxolene ligands, and thereby the oxolene and the guanidine "concepts" could be merged in one ligand. We show that the redox-active ligands **3** and **4** function in Cu^{II} complexes as electron reservoirs. They are excellent model ligands for studying the possibility of controlling the electronic structure by choice of the guanidino groups and the counter-ligands, as well as parameters such as solvent and temperature.

Results and Discussion

Ligand synthesis and characterization

In situ deprotonation of 5,6-diamino-2,2-dimethyl-[1,3]-benzodioxole hydrochloride (for details of its synthesis see ref. [17]

2

and the Supporting Information) followed by guanidinylation with either 2-chloro-*N*,*N*,*N'*,*N'*-tetramethyl-formamidinium chloride^[18] or 2-chloro-1,3-dimethyl-4,5-dihydro-1*H*-imidazolium chloride^[18] afforded the new redox-active 4,5-bisguanidino-substituted benzodioxoles **3** and **4** in greater than 70% isolated yield (see Experimental Section and the Supporting Information, Scheme SI2). The new ligands **3** and **4** were structurally characterized (see Figure 1 and the Supporting Information,



Figure 1. Visualization of the solid-state structure of **4** (structure of **3** shown in the Supporting Information, Figure SI3). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity.

Figure SI3). Their structures show no peculiarities. The N1-C7/ N4-C12 bond lengths (1.295(1)/1.292(1) Å for 3 and 1.293(2)/ 1.287(2) Å for 4) are in line with the imino C=N bond length found in known guanidines.^[9] Cyclic voltammetry (CV) experiments show that 3 and 4 are oxidized in solution either in a single reversible two-electron redox process or in two reversible one-electron redox processes at different potentials, depending on the applied solvent. In tetrahydrofuran (THF) or acetonitrile (CH₃CN), the CV curves show a single two-electron wave (Figures SI5 and SI6 in the Supporting Information). On the other hand, in dichloromethane (CH₂Cl₂), two separated one-electron waves appeared. From the potential difference of the two redox steps, the Gibbs free energy change ΔG_{com} for comproportionation (e.g., $3^{2+}+3\rightarrow 23^{+}$) was estimated to be -13.5 kJmol^{-1} for **3** and -12.5 kJmol^{-1} for **4**. In contrast to 1,2-bis(*N*,*N*,*N*',*N*'-tetramethyl-guanidino)benzene (5, see Scheme 1), the redox processes are fully reversible. The adiabatic ionization energies calculated with density functional theory (DFT) are included in Table 1.^[17] The four compounds can be ordered with respect to their first ionization potential I_1

Table 1. Redox potentials ($E_{1/2}$ vs. Fc/Fc ⁺ , in CH ₂ Cl ₂) and calculated adia-
batic first and second ionization energies I_1 and I_2 (B3LYP and BP86 func-
tionals, def2-TZVPP basis set) for guanidino-substituted aromatic com-
pounds (n.r. means non-reversible in CV experiments).

	E _{1/2} [V]		<i>I</i> ₁ [eV]		<i>I</i> ₂ [eV]	
	0/+	+/2+	B3LYP	BP86	B3LYP	BP86
1	-0.67	-0.67	4.66 ^[19]	4.70	7.31 ^[19]	7.44
4	-0.46	-0.33	5.17	5.20	8.42	8.52
3	-0.25	-0.11	5.26	5.28	8.51	8.59
5	n.r.	n.r.	5.83	5.78	9.14	9.33



in the order 1 (4.66 eV) <4 (5.17 eV) <3 (5.26 eV) <5 (5.83 eV), and the measured $E_{1/2}$ values follow the same trend. The CV curves are displayed in Figure SI5 in the Supporting Information.

Chemical oxidation with two equivalents of ferrocenium hexafluorophosphate, $Fc(PF_6)$, leads to the salts $3(PF_6)_2$ and $4(PF_6)_2$ in good yield (see Scheme 2). A visualization of their solid-state structures and a table with a comparison of selected bond parameters can be found in the Supporting Information, Figures SI7 and SI8 and Table SI1. As expected, oxidation leads to an increase of the former imino C=N double bonds N1-C7 and N4-C12 (from 1.295(1)/1.292(1) Å in 3 to 1.381(3)/ 1.385(3) Å in 3(PF₆)₂ and from 1.293(2)/1.287(2) Å in 4 to 1.373(4)/1.385(4) Å in 4(PF₆)₂). All other C-N bond lengths decrease (Table SI1). In both $3(PF_6)_2$ and $4(PF_6)_2$, the guanidino groups (the plane defined by atoms N2, C7, and N3 and that defined by N5, C12, and N6) are oriented almost perpendicular to the benzodioxole core. Such a conformation seems at first to be unfavorable, since it prohibits formation of an extended π -conjugated system. However, steric constraints prohibit a planar conformation, and the π -interaction of the lone pairs on N1 and N4 with the aza-allyl systems N5, C12, N6 and N2, C7, N3, respectively, favors the orthogonal conformation (a detailed analysis of this issue was recently performed for p-bisguanidino-benzenes).^[20]

Two-electron oxidation clearly changes the electronic excitation spectra. In the UV/Vis spectra, a new band at 450 nm appeared for $\mathbf{3}^{2+}$ and $\mathbf{4}^{2+}$, which was absent in the spectra of the neutral compounds (Figures SI12 and SI13 in the Supporting Information), and is responsible for the orange color of the dicationic compounds (the neutral compounds are pale-yellow colored).

As discussed above, the CV experiments in CH₂Cl₂ solution indicate that the formation of the radical monocation from the neutral compound and its dication is exergonic for 3 and 4. Indeed, the radical monocationic compounds 3^{+} and 4^{+} can be generated by mixing the neutral and dicationic compounds together. The radical monocation is not only present in CH₂Cl₂ solutions (leading to a brown-colored solution), but also in CH₃CN and other solvents. Upon addition of equimolar ratios of neutral **3** to a solution of $3(PF_6)_2$ in CD₃CN, the ¹H NMR spectra were free of distinct signals, in line with formation of a paramagnetic compound.

Instead, a signal was detected in the EPR spectrum (with clear signs of hyperfine coupling (HFC) in the case of compound 3⁺⁺, see Figure 2 and Figure SI9 in the Supporting Information). In line with the nuclear spin and its relative natural abundances, the HFC pattern is dominated by coupling to nitrogen nuclei, and the experimental spectrum can be fitted satisfactorily with two pairs of equally treated nitrogen nuclei (see Figure 2). This spin system is in line with the calculated spin density distribution in the radical monocation 3⁺, displayed in Figure SI11 in the Supporting Information. Two of the amino N atoms carry only a small percentage of the spin density, explaining the nuclei spin system of two pairs of equally treated nitrogen atoms in the EPR spectrum (see the results of the natural bond orbital (NBO) analysis in the Sup-



Paper

Figure 2. Second derivative of an EPR spectrum (9.631859 GHz) for an equimolar mixture of $3 + 3(PF_6)_2$ in diglyme at room temperature together with a simulated spectrum. Fit parameters: $g_{iso} = 2.0035$, $A_{N1}(2N) = 4.1$ G, $A_{N2}(2N) = 2.3 \text{ G}, \text{ FWHM}_{iso} = 2.3 \text{ G}.$

porting Information, caption of Figure SI11). Deviations from the simulated spectra are presumably due to weak HFC to the two nitrogen nuclei with small atomic spin density and to the ¹³C nuclei. The spin density distribution in **4**^{+•} is comparable, but the spin density on the imino N atoms (N1 and N4) is slightly lower (see caption of Figure SI11 in the Supporting Information), and that on the amino N2, N3, and N6 (but not N5) atoms is slightly higher. For some reason, in the EPR spectra of 4^{+•} no comparable HFC is visible (Figure SI10 in the Supporting Information).

The presence of the radical monocationic ligands is also visible in the UV/Vis spectra. Upon addition of equimolar ratios of neutral **3** to a solution of $3(PF_6)_2$ in CH₃CN, the electronic transition at 450 nm diminished and a new band around 370 nm appeared in the UV/VIS spectra (Figure SI12 in the Supporting Information), with a long tail extending into the visible region. In the spectra recorded for an equimolar mixture of 4 and $4(PF_6)_2$, a strong band at approximately 370 nm with a shoulder at around 385 nm and a broad band with a double maximum structure at 675 and 733 nm could be assigned to the radical monocation **4**^{+•} (Figure SI13 in the Supporting Information).

Synthesis of copper complexes and solid-state characterization

Reaction of the new ligands with CuX_2 (X = Cl, Br) yielded the mononuclear complexes [3(CuX₂)] and [4(CuX₂)] in greater than 80% yield. Moreover, reaction between Cu(OAc)₂ and 3 or 4 gave [3{Cu(OAc)₂}] and [4{Cu(OAc)₂}]. The complexes were structurally characterized by single-crystal X-ray diffraction, and their electronic structures further analyzed by EPR, UV/VIS spectroscopy, and cyclic voltammetry (CV) measurements. Finally, quantum chemical calculations were drawn on to complete the analysis of the complexes, which could either be described as Cu^{II} complexes with neutral ligand units or as Cu^{II} complexes with radical monocationic ligand units. The structural characterization (Figure 3 and Figures SI15-SI16 in the

Chem. Eur. J. 2016, 22, 1 – 14



Figure 3. Molecular structure of $[3(CuCl_2)]$. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms omitted for clarity. Visualizations of the structures of the other complexes $[3(CuX_2)]$ and $[4(CuX_2)]$ can be found in the Supporting Information, Figures SI13–SI16.

Supporting Information) showed that the geometry around the copper atom in the complexes is in between that commonly expected for Cu^{II} (square planar) and Cu^I (tetrahedral), as shown by Figure 3 and the dihedral angles given in Table 2. Such geometries were also observed for other dinuclear complexes with quanidine ligands (e.g., 2),^[12-14] and deviations from square-planar coordination geometries in Cu^{II} complexes could be explained by π -bonding contributions to the Culigand bonding.^[21] Therefore, the small dihedral angles at the copper atoms are not in dissonance with a Cu^{II} complex description. The C=N (imino) bond lengths N1-C7 and N4-C12 increase upon coordination (see Table 2), as is typical for guanidine-metal complexes.^[9] A structural comparison of the free neutral and oxidized ligands 3/4 and $3^{2+}/4^{2+}$ (Table SI1 in the Supporting Information) with the ligands in the copper complexes [3(CuCl₂)], [4(CuCl₂)], and [3(CuBr₂)] (Table SI3 in the Supporting Information) is also in harmony with a description in terms of Cu^{II} complexes with neutral ligands. As expected, the hard acetate counter-ligands in [3{Cu(OAc)₂}] and [4{Cu(OAc)₂}] also favor the Cu^{II}/neutral ligand form (Table SI4 in the Supporting Information). In the solid state, the copper atoms of [3{Cu(OAc)₂}] and [4{Cu(OAc)₂}] are weakly coordinated by the second oxygen atom of each acetate group ($O_{C=0}$ - $\text{Cu}\,{\approx}\,2.7$ Å, Figures SI17 and SI18 and Table SI4 in the Supporting Information).

The calculated structures (B3LYP functional, def2-TZVPP basis set, Table SI5 in the Supporting Information) are generally in good agreement with the experimental solid-state structures. The dihedral angle \measuredangle (CuN₂, CuX₂) shows some deviations (Table SI5 in the Supporting Information). But for [4(CuCl₂)] there are different independent molecules in one elementary cell, the dihedral angles of which range from 50.70° to 64.35° (see Table 2) and the DFT-calculated dihedral angle of 61.17° is in this range. In line with the description as Cu^{II} complexes, the calculated spin density distribution in all four complexes shows that the copper states contribute most to the singly occupied molecular orbital (SOMO, $Cu \approx 60\%$, $X \approx 20\%$, $N\!\approx\!15\,\%$ atomic spin densities from NBO analysis, Table SI6 in the Supporting Information). EPR measurements at room temperature confirm the Cu^{II} isomer in the solid state (Figure SI19– SI20 in the Supporting Information). Hence, it can be concluded that all the studied complexes, without any interaction with the environment or with the weak intermolecular interactions present in the solid state, should be described as Cu^{II} complexes with neutral ligand units.

Electronic structure in solution

As demonstrated in a number of seminal contributions,^[22] EPR is particularly suited for the analysis of the electronic structure of complexes with redox-active ligands in solution. A g-factor near the free-electron value typically indicates an organic (ligand) radical (bound to Cu¹), whereas a significantly higher g-factor argues for a metal (Cu^{II}) radical (with a neutral ligand).^[23] For [3(CuCl₂)] dissolved in THF, CH₂Cl₂, or CH₃CN, a relatively broad signal centered at g = 2.11 was measured, indicating a metal-centered radical (Cu^{II}/neutral ligand). Weakly anisotropic spectra lacking a clear HFC structure were recorded (Figure SI23 in the Supporting Information) at room temperature. By contrast, the EPR spectrum at 120 K in a frozen THF solution is a typical anisotropic Cu^{II} spectrum, and a fit of the spectrum returned a HFC constant $A_{Cu} = 117$ G and g-factors of 2.059, 2.146, and 2.292 (Figure SI24 in the Supporting Information). Even at 35 K, the resolution was unfortunately not sufficient to determine the other HFC constants.

Replacing the chlorido ligand by the softer bromido counter-ligand clearly affects the electronic structure. Besides the main signal at g=2.11, a weak signal at g=2.003 with a distinct HFC pattern was observed in the EPR spectrum of [**3**(CuBr₂)] at

Table 2. Selected structural parameters for the copper halide complexes. Bond distances in Å, dihedral angle at the copper atom in degrees. For [4(CuCl₂)] and [3(CuBr₂)] (Figures SI15 and SI16 in the Supporting Information, for more structural parameters see Table SI3) the atom numbering equals that used in Figure 3 for [3(CuCl₂)].

	$[3(CuCl_2)]^{[a]}$	[4 (CuCl ₂)] ^[b]	[3 (CuBr ₂)]	3
C1–C2/C4–C5	1.396(4)/1.379(4)	1.408(4)/1.379(4)	1.410(6)/1.377(6)	1.410(2)/1.377(2)
N1-C1/N4-C2	1.423(3)/1.421(3)	1.408(4)/1.413(4)	1.418(5)/1.407(5)	1.410(1)/1.418(2)
N1-C7/N4-C12	1.352(4)/1.325(3)	1.343(6)/1.341(6)	1.341(6)/1.334(6)	1.292(1)/1.295(1)
ム (CuN₂, CuX₂)	45.0	50.7-64.4	48.9	
[a] Crystal structure with	out THE solvent molecule Edd2 sn	ace group [b] Crystals with two d	lifferent space groups are obtained	Two independent mole-

[a] Crystal structure without THF solvent molecule, *Pad2* space group. [b] Crystals with two different space groups are obtained. Two independent molecules are found for the $P2_1/n$ crystal structure and three independent molecules for the $Pca2_1$ crystal structure. Average bond lengths are listed. For the dihedral angle significant deviation is observed, and therefore the angle range is given.

Chem. Eur. J. 2016, 22, 1 – 14

www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



room temperature ($A_N = 5.2$ G, Figure SI25 in the Supporting Information). The quintet pattern measured in CH₃CN or THF fits to two equivalent nitrogen nuclei, assignable to the two imino nitrogen nuclei, in line with the calculated atomic spin density distribution (caption of Figure SI22 in the Supporting Information). The weak signal with the low *g*-factor near the free-electron value is assigned to $[3^+(Cu^{l}Br_2)]$, which is generated in small amounts by intramolecular charge transfer from its $[3(Cu^{ll}Br_2)]$ isomer in solution. The stabilization of the Cu^l/radical monocationic ligand form for the bromido counter ligand is in line with the hard-and-soft-acid-and-bases (HSAB) concept.

For the complexes [4(CuCl₂)] and [4(CuBr₂)] with the stronger electron-donor ligand 4, two EPR signals were detected at room temperature, a broad one at $q \approx 2.11$ (≈ 3250 G) and a sharp one at q = 2.003 (≈ 3450 G; see Figure 4 and Figure SI26 in the Supporting Information). The appearance of these two signals could be interpreted as the co-existence of both valence tautomeric complexes (the form with Cu^{II} and neutral ligand and its valence tautomer with Cu^I and radical monocationic ligand). Interestingly, the relative intensity of the two signals heavily depends on the applied solvent (see Figure 4 and Figure SI26 in the Supporting Information). The signal intensities from double integration (area of the first derivative signal) are compared in Table 3. Please note that the values arising from quantitative analysis of the EPR spectra by double integration are afflicted by a large error of about 10%.^[6a, 24] The solvent effect is larger for the chloro complexes



Figure 4. EPR spectra (9.633 GHz) measured for [4(CuCl₂)] in different solvents at room temperature. The ligand-centered signal increases relative to the metal-centered signal with increasing solvent polarity.

These are not the final page numbers! 77

Table 3.Solvent ofgration of the EPR	lependence o signals. Cont	f the electronic ribution of radi	structure by cal character i	double inte- n %.
	$[4(Cu^{II}Cl_2)]$	[4 ⁺ •(Cu ^I Cl ₂)]	[4(Cu ^{II} Br ₂)]	[4 ⁺ •(Cu ^I Br ₂)]
THF ($\epsilon_{\rm r} = 7.58$)	97	3	84	16
$CH_2CI_2 \ (\varepsilon_r = 8.93)$	88	12	71	29
$CH_3CN (\varepsilon_r = 37.5)$	18	82	33	67

than for the bromido complexes, but in both cases an increase in the solvent polarity stabilizes the electronic structure $[\mathbf{4}^+$ '(Cu¹X₂)] (see Table 3).

This trend is in accordance with the larger degree of charge separation in the $[4^+(Cu^{I}X_2)]$ complex compared with the $[4(Cu^{II}X_2)]$ isomeric form, which leads to a larger solvent effect.

At 35 K, a HFC is observed in the EPR spectra of [4(CuCl₂)] in THF solution. The A_{cu} value of 88 G derived from curve fitting (Figure SI27 in the Supporting Information) is in line with a tetrahedrally coordinated copper atom.[22] Direct coordination of THF solvent molecules is therefore improbable. In frozen solutions of CH₂Cl₂ and CH₃CN at 35 K, Cu^{II} EPR spectra were measured with a broad signal at g = 2.11. For the bromido complexes [3(CuBr₂)] and [4(CuBr₂)], the signals in the EPR spectra at 35 K are broader and less anisotropic than for the chlorido complexes [3(CuCl₂)] and [4(CuCl₂)]. The EPR spectrum of [4(CuCl₂)] at 35 K in CH₃CN solution indicates that the Cu^{II} radical character dominates (with only small ligand radical character), whereas at higher temperature the signal at $g \approx 2.003$ increases, signaling a temperature-induced conversion to a ligand-centered radical. Reversible temperature-dependent intramolecular electron-transfer processes are observed for both complexes of ligand 4, interconverting the two valence tautomers. Figure 5 reproduces the EPR spectra measured at different temperatures for [4(CuCl₂)] in CH₃CN. The spectrum recorded at 242 K shows a HFC pattern with five discrete lines ($A_{\rm N} \approx 4.7$ G), consistent with coupling to the two imino nitrogen nuclei (see also the calculated atomic spin density from the NBO analysis in the Supporting Information, caption to Figure SI22). At room temperature, the signal at $g \approx$ 2.003 clearly dominates. This ligand-centered EPR signal of [4(CuCl₂)] shows no HFC, like the signal of the free radical ligand 4^{+*}. The EPR spectra recorded for the complex [4(CuBr₂)] show a similar temperature-dependent equilibrium of both valence tautomeric forms $[4(Cu^{II}X_2)]$ and $[4^+(Cu^{II}X_2)]$ (see the EPR spectra in Figure SI28 in the Supporting Information).

The temperature-dependent equilibrium between the two valence tautomers implies that their interconversion is subject to a significant barrier. For copper complexes, such a barrier is generally caused by the structural differences of the two isomers (e.g., coordination geometry changes).^[4] Previous studies on dinuclear copper complexes also suggest that the processes are entropy-driven (like most thermal equilibria between valence tautomers),^[4,14] and that the reorganization of the solvent cage upon interconversion has a major contribution.^[21,25]

An unambiguous discrimination between the two valence tautomeric forms of the copper complexes on the basis of their UV/Vis spectra is less straightforward (see the UV/Vis

Chem. Eur. J. **2016**, 22, 1–14

www.chemeurj.org





Figure 5. EPR spectra (9.639260 GHz) recorded for $[4(CuCl_2)]$ in CH₃CN solution at different temperatures.

spectra in the Supporting Information, Figures SI29–SI34). Nevertheless, in the variable-temperature UV/Vis spectra of [4(CuCl₂)] and [4(CuBr₂)] in CH₃CN (see Figures SI35–SI36 in the Supporting Information) the conversion between the two valence tautomers is clearly visible. The presence of isosbestic points (at 352, 545, and 792 nm for [4(CuCl₂)] and at 493 nm for [4(CuBr₂)]) confirms clean and reversible isomerization, and an equilibrium between the two valence tautomeric forms. An estimation of the reaction enthalpy and Gibbs free energy for interconversion (as carried out for a dinuclear copper complex with a bridging GFA ligand)^[14] is unfortunately hampered by the heavy band overlap.

As expected, the acetato complex $[4{Cu^{II}(OAc)_2}]$ is clearly a Cu^{II} complex with neutral ligands in all applied solvents. The EPR spectra at room temperature in CH₃CN show a quartet structure (g=2.123, A_{iso} =56 G) and no signal near the freeelectron g-factor (Figure SI37 in the Supporting Information). The EPR signal in THF solution is similar. Thus, the electronic structure of the acetato complexes could not be altered by solvent variations (Figure SI37–SI38 in the Supporting Information). This result is in line with the HSAB concept. The harder oxygen ligand stabilizes the Cu^{II}/neutral ligand form with respect to the Cu^I/radical monocationic ligand form.

The nature of the guanidino groups, the counter-ligands, the solvent polarity, and the temperature are parameters that clearly affect the electronic structure of the copper–bisguanidine complexes. **Oxidation of copper complexes**

For applications, it is important that the ligand units (**3** or **4**) can provide the copper atoms with electrons. The CV measurements showed that the complexes $[\mathbf{3}(\text{CuX}_2)]$ (X = Cl or Br) could be oxidized reversibly in two separate one-electron steps at different potentials (Figure 6a and Figure SI40 in the Supporting Information). The potential of the first one-electron redox step of the ligand **3** is similar for the chlorido ($E_{1/2}$ = -0.12 V) and bromido (-0.15 V) complexes and only slightly higher than for the free ligand **3** (-0.25 V). A potential $E_{1/2}$ = 0.36 V for X = Cl and 0.42 V for X = Br for the second one-electron redox step could be deduced from the CV curve. The potential difference ΔE between the first and second one-electron redox events is 0.48 V for X = Cl and 0.57 V for X = Br, and



6



Figure 6. Comparison between the CV curves of a) the free ligand **3** and the complexes [**3**(CuX₂)] and b) the free ligand **4** and the complexes [**4**(CuX₂)] (X = Cl or Br) in CH₂Cl₂ solution (0.001 M, measured with Bu₄NPF₆ (0.01 M) as supporting electrolyte, a Ag/AgCl electrode, and with potentials given vs. Fc/Fc⁺).

Chem. Eur. J. 2016, 22, 1 – 14 www.chemeurj.org

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FF These are not the final page numbers!



a Gibbs free energy change of 46.3 kJ mol⁻¹ for X=Cl and 55.0 kJ mol⁻¹ for X=Br could be estimated for the disproportionation of the monocationic complex into neutral and dicationic complexes. This means that the monocationic ligand is stabilized by complex formation. A similar observation was made for dinuclear complexes of ligand 1.^[26] The complexes could also be reduced (Cu^{II} \rightarrow Cu^I at E_{red} =-1.04 V for [3(CuCl₂)] and -0.86 V for [4(CuBr₂)]), but this copper-centered redox process is irreversible (Figure SI41 in the Supporting Information). A corresponding oxidation wave was observed at -0.27 V for the chlorido and at -0.22 V for the bromido complex.

The CV curves recorded for the [4(CuX₂)] complexes look significantly different. They show only one reversible redox step at $E_{1/2} = -0.30$ V for X = Cl and at -0.34 V for X = Br (see Figure 6b and Figure SI42 in the Supporting Information). From its potential, this redox process might be ligand-centered. However, a clear copper redox wave at negative potential is not visible, and therefore the assignment is not straightforward. The temperature-dependent equilibrium between both valence tautomers of $[4(CuX_2)]$ (X = Cl or Br) might affect the redox processes in the CV curve. To differentiate between copper- and ligand-based redox processes and motivated by the observation of reversible redox processes in the CV curves and their negative potential relative to the Fc/Fc⁺ redox couple, chemical oxidation was carried out on a preparative scale with Fc(PF₆) as the oxidizing reagent. These chemical oxidation experiments were successful and led to the synthesis of the two salts [4(CuCl₂)]PF₆ and [4(CuBr₂)]PF₆ as dark-colored solids in good yield. Elucidation of the electronic structure of these compounds and their descriptions either as diamagnetic Cu^{l} compounds with dicationic ligand units ([$4^{2+}(Cu^{l}X_{2})$]PF₆) or as paramagnetic Cu^{II} complexes with radical monocationic ligand units ([4⁺ (Cu^{II}X₂)]PF₆) required again a detailed structural and spectroscopic analysis.

Figure 7 visualizes the solid-state structure of the $[4(CuCl_2)]^+$ cation in $[4(CuCl_2)]PF_6$ (for $[4(CuBr_2)]PF_6$, the small crystal size unfortunately prohibited structural characterization). Table 4 compares some structural parameters of the cationic complex



Figure 7. Molecular structure of the $[4(CuCl_2)]^+$ cation in the salt $[4(CuCl_2)]^{PF_6}$ as determined by single-crystal X-ray diffraction at 120 K. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the co-crystallized CH₃CN solvent molecule were omitted for clarity.

Table 4. Selected structural parameters of $[4(CuCl_2)]PF_6$ and $4(PF_6)_2$ (bond distances in Å, angles in degrees) in comparison with the calculated bond lengths (B3LYP/def2-TZVPP). Atom numbering from Figure 7 for $[4(CuCl_2)]PF_6$.

	4 +• (calcd)	$4(PF_6)_2$ (X-ray)	[4(CuCl ₂)]PF ₆ (X-ray)
C1-C2/C4-C5 N1-C1/N4-C2 N1-C7/N4-C12 Հ (CuN ₂ , CuX ₂)	1.472/1.460 1.333/1.343 1.301/1.310	1.523(4)/1.448(4) 1.279(4)/1.294(4) 1.373(4)/1.385(4)	1.485(8)/1.432(9) 1.336(8)/1.320(8) 1.384(8)/1.378(8) 89.8

with those of the free monocationic ligand (from DFT calculations, Table SI2 in the Supporting Information) and for the free dicationic ligand in the hexafluorophosphate salt. The dihedral angle \measuredangle (CuN₂, CuX₂) measures 89.94° and thus adopts a value typical for Cu¹. The C1–C2, C4–C5, N1–C1, and N4–C2 bond lengths are similar to the DFT-calculated bond lengths for free **4**⁺, but the N1–C7 and N4–C12 bond lengths clearly argue for a dicationic ligand unit (see Table 4 and Table SI1 in the Supporting Information). Super-conducting quantum interference device (SQUID) measurements of solid [**4**(CuCl₂)]PF₆ show diamagnetic behavior at *T*=100 K and 300 K (d*M*/d*H* < 0; see Figure SI45 in the Supporting Information). Hence, in solid [**4**(CuCl₂)]PF₆ the electronic structure could be described in terms of a Cu¹ complex with a dicationic ligand unit, [**4**²⁺ (Cu^lCl₂)]⁺.

The electronic excitation bands in the UV/Vis spectra of [4(CuCl₂)]PF₆ and [4(CuBr₂)]PF₆ are quite similar and comparable to those found in the spectrum for the salt $4(PF_6)_2$ (Figure SI46 in the Supporting Information). However, the two complexes differ in the visible region between 500-950 nm, which explains the color differences (dark blue for [4(CuCl₂)]PF₆ and dark green for [4(CuBr₂)]PF₆ in solution and in the solid state). In CD₃CN solution, broad ¹H NMR signals for $[4(CuCl_2)]PF_6$ were observed at room temperature, and a weak signal in the EPR spectra (Figure SI48 in the Supporting Information). Temperature-dependent NMR experiments in CD₂Cl₂ and CD₃CN (Figure SI47 and SI48 in the Supporting Information) indicate that for X = CI the diamagnetic form $[4^{2+}]$ $(Cu^{I}X_{2})]PF_{6}$ is energetically preferred over its valence tautomeric form $[4^+(Cu^{\parallel}X_2)]PF_6$. With increasing temperature, a paramagnetic shift of the ¹H NMR signals is observed and the signals become broader, indicating the presence of small quantities of the paramagnetic $[\mathbf{4}^+ (Cu^{II}CI_2)]PF_6$ valence tautomer. In CD_2CI_2 solution the shift is more distinct than in CD₃CN solution. EPR measurements in CH₃CN are in line with the ¹H NMR measurements, and at room temperature weak signals are observed for ligand- as well as copper-centered radicals, which are virtually extinguished at low temperatures (Figures SI49 and SI50 in the Supporting Information).

DFT calculations (BP86 and B3LYP) for the closed-shell singlet state (CS, with electronic structure $[4^{2+}(Cu^{I}Cl_{2})]^{+})$ and the triplet state (T1, with electronic structure $[4^{++}(Cu^{II}Cl_{2})]^{+})$ show that the calculated CS state structure (especially the C–N and C–C bonds) fits better to the experimentally derived solid-state structure than the calculated triplet structure (Tables SI7–SI10 in the Supporting Information). Only the dihedral angle

These are not the final page numbers! **77**

www.chemeurj.org

Chem. Eur. J. 2016, 22, 1 – 14



 \measuredangle (CuN₂, CuX₂) fits better to the T1 state (81.7° for B3LYP/def2-SVP) than to the CS state (63.1°), but it was already shown for the neutral complex that this angle varies to a large extent in the solid-state structures, indicating a flat potential. The energies of the closed-shell singlet and triplet states are very similar. For calculations with the BP86 functional, the closed-shell singlet state is slightly below the triplet state (16 kJ mol⁻¹ with the def2-SVP and 21 kJ mol⁻¹ with the def2-TZVPP basis set), in agreement with the experimental results. As already discussed, the energy difference between the two states heavily depends on the applied functional and particularly the amount of exact electron exchange.^[14,27] For B3LYP, the closed-shell singlet state energy is slightly higher than that of the triplet state (25 kJ mol⁻¹ with the def2-SVP and 21 kJ mol⁻¹ with the def2-TZVPP basis set, see the Supporting Information). The energy of the BS (broken symmetry) state is slightly lower than that of the T1 state, indicating weak antiferromagnetic coupling.

Compound [4(CuBr₂)]PF₆ dissolved in CD₃CN shows sharp signals at room temperature in the ¹H NMR spectrum (Figure SI51 in the Supporting Information), so that the diamagnetic valence tautomer $[\mathbf{4}^{2+}(Cu^{l}Br_{2})]PF_{6}$ dominates in CD₃CN solution even at room temperature. EPR experiments show that only a tiny amount of the paramagnetic $[4^{+}(Cu^{II}Br_2)]^+$ valence isomer exists in CH₃CN solution at room temperature (Figure S52 in the Supporting Information). On the basis of the experimental results, we can exclude halide dissociation upon oxidation of the complex. In the solid state, the complex [4(CuCl₂)]PF₆ was proven by structural characterization. In solution the cations $[4(CuX_2)]^+$ (X = Cl, Br) prevail. Hence, similar ¹H NMR spectra were recorded in CD₃CN and CD₂Cl₂ solutions (Figures SI47 and SI48 in the Supporting Information), indicating the presence of the same diamagnetic complex in both solutions. In particular, equilibria as expected from dissociation and/or substitution processes leading to the presence of different complexes in solution and in the solid state, could be excluded on the basis of these NMR data. Halide dissociation from the cationic complex is also unlikely as it would increase the charge. Finally, our CV experiments show reversible redox processes, which should not occur if the redox process is accompanied by ligand dissociation or exchange.

It can be concluded, then, that one-electron oxidation of $[4(Cu^{II}X_2)]$, which under the same conditions is in a temperature-dependent equilibrium with its valence tautomer $[4^{+}(Cu^{I}X_2)]$, gives $[4^{2+}(Cu^{I}X_2)]PF_6$. Oxidation is therefore accompanied by a redox-induced electron transfer (RIET) from the ligand to the copper atom. Consequently, the second redox process in the CV experiment (Figure 6 b), involving the monocationic complex $[4^{2+}(Cu^{I}X_2)]^+$ as the reduced form and the dicationic complex as the oxidized form, should be an irreversible copper-centered redox step.

Conclusion

New redox-active 4,5-bisguanidino-substituted benzodioxole ligands were synthesized, and their redox properties studied. In cyclic voltammetry measurements, two electrons are removed either at the same potential in a single reversible two-electron redox process, or in two separate reversible one-electron redox processes at different potentials, depending on the applied solvent. Their dications were synthesized by oxidation with ferrocenium salts, and the radical monocationic ligands were generated in a comproportionation equilibrium in solutions containing both the neutral ligand and its dication. Having studied systematically all three possible charge states of the free ligands, the electronic structure in copper complexes, synthesized by reaction of the neutral ligands with Cu^{II} compounds, was investigated.

The results show that the electronic structure of these complexes subtly depends on the guanidino group, the counter-ligands at the copper atom, the applied solvent (polarity), and on the temperature, stabilizing either a Cu^{II} complex with neutral ligand unit or a Cu^{II} complex with radical monocationic ligand unit. The conditions were then fine-tuned to achieve a temperature-dependent equilibrium between the two valence tautomeric forms (Cu^{II}/neutral ligand and Cu^I/radical monocationic ligand). Finally, it was demonstrated that redoxinduced electron-transfer (RIET) processes could be induced by oxidation of the copper complexes. Scheme 3 summarizes the characterized complexes with the Lewis structures that fit best their experimentally verified electronic structures.

The results presented and discussed in this work are the basis for ongoing research activities in our group. First, the results show that the new redox-active ligands are involved in intramolecular electron-transfer processes with the attached metal atoms, and could stimulate their application in molecular catalysis (e.g., oxidation of unsaturated hydrocarbons). Moreover, the removal of the acetal protection group from **3** and **4** leads to new bisguanidino-substituted catechol ligands, which could be applied as bridging ligands in hetero-bimetallic transition-metal complexes.



Scheme 3. Electronic structures of copper complexes featuring the new redox-active 4,5-bisquanidino-substituted benzodioxole ligands 3 and 4.

Chem. Eur. J. 2016, 22, 1–14 www.ch

www.chemeurj.org

FF These are not the final page numbers!

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Experimental Section

All synthetic work was carried out under inert gas (Ar) atmosphere by using standard Schlenk techniques. Solvents were dried prior to their use by using a MB-SPS-800 from MBraun, degassed, and stored over molecular sieves. Diamino-2,2-dimethyl-[1,3]-benzodioxole hydrochloride,^[17] 2-chloro-N,N,N',N'-tetramethyl-formamidinium, and 1,3-dimethyl-4,5-dihydro-1H-imidazolium chloride were synthesized as described in the literature.^[18] 2,2-Dimethyl-[1,3]-benzodioxole, N,N,N',N'-tetramethylurea, and 1,3-dimethyl-2-imidolidinone were purchased from ABCR. Oxalyl chloride, all applied copper salts, and ferrocenium hexafluorophosphate were acquired from Sigma-Aldrich. NMR spectra were recorded with Bruker DRX 200, Bruker Avance II 400, or Bruker Avance III 600 spectrometers. High-resolution electrospray ionization (HR-ESI) spectra were measured with a Finnigan LCQ quadrupole ion trap. High-resolution fast atom bombardment (HR-FAB) mass spectrometric data were recorded with a JEOL JMS-700 magnetic sensor aperture. IR spectroscopic measurements relied on an FTIR Biorad Merlin Excalibur FT 300 spectrometer. Elementary analysis was carried out at the Microanalytical Laboratory of the University of Heidelberg. CV measurements were recorded with an E&G Princeton 273 apparatus with Ag/AgCl as the reference electrode and (nBu)₄NPF₆ (Fluka, electrochemical grade) as the supporting electrolyte. Cyclic voltammograms were referenced to Fc/Fc⁺. Helium-cooled X-band EPR spectra were measured with a Bruker ESP 300 E. In figures with several EPR spectra, one referenced frequency is given for reasons of comparability. The dc-SQUID measurements were taken with a MPMS-XL apparatus from LOT Quantum Design. CCDC 1476843-1476855 and 1476859—1476861 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre. Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, surrounded by perfluorinated polyether oil, and fixed on a cyro loop. The crystals of the compounds 3 (CCDC 1476860), **4** (CCDC 1476859), **3**(PF₆)₂ (CCDC 1476855), [**3**(CuCl₂)] (CCDC 1476851), [**3**(CuCl₂)]•0.6 THF (CCDC 1476850), [3(CuBr₂)] (CCDC 1476854), [4(CuCl₂)] (CCDC 1476853), 2,2-dimethyl-5-nitro-[1,3]-benzodioxole (CCDC 1476849), 2,2-dimethyl-5-nitro-[1,3]-benzodioxole (CCDC 1476852), **3**(BF₄)₂ (CCDC 1476861), and [3{Cu^{ll}(OAc)₂}] (CCDC 1476848) were measured with a Nonius-Kappa CCD diffractometer with $\text{Mo}_{\text{K}\alpha}$ radiation. $^{\text{[28]}}$ Crystal structure determination was performed by using the SHELXT-PLUS software. SHELXS-97 and SHELXS-2014 were used to solve the structure by direct methods and refined with SHELXS-97 and SHELXS-2014.^[29,30] Graphical handling of the structural data during solution and refinement were performed with XPMA.^[31] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.^[31] For the crystals of [4CuCl₂] (CCDC 1476844), [4CuCl₂](PF₆) (CCDC 1476846), [4(Cu(OAc)₂)]•1.25 H₂O (CCDC 1476845), [4(PF₆)] (CCDC 1476843), and [4(BF₄)] (CCDC 1476847) full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Cu_{\mbox{\tiny K}\alpha} radiation, microfocus X-ray tube, multilayer mirror optics). Data were corrected for air and detector absorption, Lorentz, and polarization effects;^[32] absorption by the crystal was treated with a semiempirical multiscan method (complex $[\text{4CuCl}_2])^{\scriptscriptstyle[33,34]}$ or numerically (Gaussian grid, $[\text{4CuCl}_2](\text{PF}_6)$ and $[4(Cu(OAc)_2)]$ -1.25 H₂O)).^[32,35] The structures were solved by the charge flip procedure^[36] and refined by full-matrix least-squares methods based on F² against all unique reflections.^[37] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. When justified by the quality of the data, the positions of some hydrogen atoms (those on the arene ring carbon atoms in $[4(BF_4)_2]$) were taken from difference Fourier syntheses and refined. Hydrogen atoms of solvent water molecules were placed tentatively, as implemented in the Olex2 software.^[38] When found necessary, disordered groups and/or [BF₄]⁻ and [PF₆]⁻ anions were subjected to suitable geometry and adp restraints. Owing to severe disorder and fractional occupancy, electron density attributed to solvents of crystallization (n-hexane and/or diethyl ether) was removed from the structure of [4CuCl₂] with the BYPASS procedure,^[39] as implemented in PLATON (SQUEEZE).^[40] Partial structure factors from the solvent masks were included in the refinement as separate contributions to F_{calc} . Crystals of [4Cu(OA $c)_2$]-1.25 H₂O were twinned by merohedry. Twin refinement of the possible cases (rotation and reflection combined with or without inversion) revealed the twin operation to be a reflection (twin matrix $M = (010\ 100\ 001)$; det. M = -1). Final two-component refinement was carried out with this matrix to give twin fractions 0.75:0.25).^[37] DFT calculations were carried out with the TURBO-MOLE program package.^[41] The BP86^[42] or B3LYP^[43] functional was used, in combination with the def2-SVP and def2-TZVPP basis set.^[44] The structures, MOs, and spin density functions were visualized with the Gaussian 09 software.[45]

5,6-Bis-(*N*,*N*,*N*',*N*'-tetramethylguanidino)-2,2-dimethyl-[1,3]benzodioxole (3)

A cooled solution of 2-chloro-N,N,N',N'-tetramethyl-formamidinium chloride (1.507 g, 8.813 mmol, 2.5 equiv) in acetonitrile (22 mL) was added to an ice-cooled suspension of 5,6-diamino-2,2-dimethyl-1,3benzodioxole dihydrochloride (0.892 g, 3.525 mmmol). NEt₃ (4.9 mL, 10 equiv) was added to the resulting red solution. The reaction mixture was stirred for 5 h and then slowly warmed to room temperature. A methanolic solution of NaOMe (5.4 m, 3.9 mL, 6 equiv) was added to the filtrate and the volatile compounds were removed in vacuo. Subsequently, distilled water (10 mL) was added to the residue. After 3 h of stirring, the precipitated product was isolated by filtration. The crude product was dissolved in Et₂O (30 mL) and dried over Na2SO4. After solvent removal, the product was obtained as a pale yellow solid (1.110 g, 2.978 mmol, 84% yield). Crystals were grown from Et₂O solutions. Elemental analysis calcd (%) for C₁₉H₃₄N₆O₂ (376.50 g mol⁻¹): C 60.61, H 8.57, N 22.32; found: C 60.79, H 8.70, N 22.13; ¹H NMR (600.13 MHz, CD₂Cl₂): $\delta =$ 5.93 (s, 2H, H_{ar}), 2.64 (s, 24H, -NMe), 1.67 (s, 6H, -CMe) ppm; ¹³C NMR (150.90 MHz, CD₂Cl₂, HSQC, HMBC): δ = 158.8 (C7, C12), 141.6 (C1, C2, C4, C5), 137.2 (C1, C2, C4, C5), 116.4 (-CMe), 102.7 (C3, C6), 39.6 (-NMe), 25.2 (-CMe) ppm; HR-MS (ESI+, CH₂Cl₂/ CH₃OH): m/z (%) = 377.26600 (100) $[M + H]^+$; IR (CsI): v = 2991 (w), 2935 (w), 2877 (w), 2800 (w), 1606 (s), 1586 (s), 1485 (s), 1373 (s), 1258 (m), 1221 (s), 1155 (s), 1136 (s), 979 (s), 884 (s), 851 (s), 789 (m) cm⁻¹; UV/Vis (CH₃CN, $c = 5.65737 \times 10^{-5}$ M, d = 1 cm): λ (ε in Imol⁻¹ cm⁻¹) = 227 (40601), 300 (10236), 334 (11527) nm; CV in CH_2Cl_2 (100 mV s⁻¹): $E_{1/2} = -0.25$ (rev. 1 e⁻, -0.19/-0.31), -0.11 (rev. $1e^{-}$, -0.05/-0.17) V; Crystal data for 1: $M_r = 376.51$, $0.33 \times 0.55 \times$ 0.50 mm³, monoclinic, space group $P2_1/c$, a=8.999(2) Å, b=20.263(4) Å, c = 11.951(2) Å, $\beta = 97.03(3)^{\circ}$, V = 2162.90 Å³, Z = 4, $d_{\text{calcd}} = 1.156 \text{ Mgm}^{-3}$, $2\theta = 4.6$ to 58.3° , $Mo_{K\alpha}$ radiation (graphitemonochromated, $\lambda = 0.71073$ Å), T = 100 K, measured reflections 11645, independent 5818, $R_{int} = 0.0313$, final *R* indices $[l > 2\sigma(l)]$: $R_1(F) = 0.043, wR_2(F^2) = 0.130.$

Chem. Eur. J. 2016, 22, 1 – 14 www.chemeurj.c

@ 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77**



5,6-Bis-(*N*,*N*'-dimethyl-*N*,*N*'-ethylene-guanidino)-2,2-dimethyl-[1,3]-benzodioxole (4)

A suspension of CH₃CN (20 mL) and 5,6-diamino-2,2-dimethyl-1,3benzodioxole dihydrochloride (0.878 g, 3.469 mmol) was cooled with ice. A solution of 2-chloro-1,3-dimethyl-4,5-dihydro-1H-imidazolium chloride (9 mL, 0.961 M, 8.671 mmol, 2.5 equiv) was added to this suspension. NEt₃ (4.9 mL, 10 equiv) was added to the resulting red solution. The reaction was slowly warmed up and stirred for 5 h. A methanolic solution of NaOMe (3.9 mL, 5.4 M, 6 equiv) was added to the filtered solution. Shortly afterward, the solvent was removed and the residue treated with water (10 mL). After 2 h of stirring, the precipitated product was isolated by filtration. The product was dried over Na2SO4 and extracted with Et2O. Solvent residues were extricated with *n*-hexane from the product. After solvent removal, a pale-yellow solid was obtained (0.940 g, 2.573 mmol, 73% yield). Crystals were grown from Et₂O solution at ambient conditions. Elemental analysis calcd (%) for C10H30N6O2 (372.46 g mol⁻¹): C 61.27, H 7.58, N 22.56; found: C 61.35, H 7.60, N 22.86; ¹H NMR (399.89 MHz, CD₂Cl₂): $\delta = 6.16$ (s, 2H, H_{ar}), 3.16 (s, 8H,-NCH₂-), 2.60 (s, 12H, -MMe), 1.59 (s, 6H, -CMe) ppm; ¹³C NMR (150.90 MHz, CD₂Cl₂, HSQC, HMBC): $\delta = 154.0$ (C7, C12), 141.6 (C1, C2, C4, C5), 134.9 (C1, C2, C4, C5), 116.6 (-CMe), 103.4 (C3, C6), 48.9 (-NCH2-), 34.9 (-NMe), 25.6 (-CMe) ppm; HR-MS (ESI+, CH3OH): m/z (%) = 373.23464 (100) $[M + H]^+$; IR (CsI): $\nu = 2988$ (w), 2933 (w), 2843 (w), 1655 (s), 1605 (m), 1482 (s), 1441 (w), 1412 (m), 1390 (m), 1352 (w), 1281 (m), 1245 (m), 1215 (m), 1189 (m), 1140 (s), 1072 (w), 1035 (s), 969 (s), 891 (s), 846 (s), 805 (s), 788 (m), 730 (s), 712 (m), 663 (m), 625 (m), 545 (w), 514 (m), 471 (w), 407 (m) cm⁻¹; UV/ Vis (CH₃CN, $c = 2.214 \times 10^{-5}$ m, d = 1 cm): λ (ε in Imol⁻¹ cm⁻¹) = 220 (shoulder), 277 (9823), 336 (13212) nm; CV in CH₂Cl₂, (100 mV s⁻¹): $E_{1/2} = -0.46$ (rev. 1e⁻, -0.37/-0.55), -0.33 (rev. 1e⁻, -0.27/-0.39) V; Crystal data for 4·H₂O: M_r=390.49, 0.60×0.40×0.30 mm³, monoclinic, space group $P2_1/c$, a=8.022(16) Å, b=13.315(3) Å, c=18.984(4) Å, $\beta = 97.51(3)^{\circ}$, $V = 2010.3(7) \text{ Å}^3, Z = 4,$ $d_{\text{calcd}} =$ 1.290 Mgm⁻³, 2θ = 3.7 to 61.1°, Mo_{Ka} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, measured reflections 11386, independent 5813, $R_{int} = 0.0680$, final R indices $[I > 2\sigma(I)]$: $R_1(F) = 0.053$, $wR_2(F^2) = 0.141.$

3(PF₆)₂

Compound 3 (51.4 mg, 0.137 mmol) was dissolved in CH₃CN (5 mL). FcPF₆ (90.4 mg, 0.274 mmol) was added to the yellow solution. The resulting orange-colored solution was mixed at room temperature for 5 h. Then, the solvent was removed under vacuum. The residue was washed with $2 \times 2 \text{ mL}$ toluene and $4 \times$ 4 mL n-hexane. The residue was dissolved in CH₃CN (3 mL) and the solution was filtered. Then, this solution was overlaid by Et₂O (18 mL). The crystalline orange product (50.1 mg, 0.075 mmol, 55% yield) was isolated by filtration and washed with 2×2 mL Et₂O. Elemental analysis calcd (%) for $C_{19}H_{32}F_{12}N_6O_2P_2$ (666.43 g mol⁻¹): C 34.24, H 4.84, N 12.61; found: C 34.73, H 4.76, N 12.98; ¹H NMR (399.89 MHz, CD_3CN): $\delta\!=\!6.01$ (s, 2 H, H_{\rm C3}, H_{\rm C6}), 3.02 (s, 24 H, -NMe), 1.82 (s, 6H, -CMe) ppm; ^{13}C NMR (100.55 MHz, CD_3CN, HSQC, HMBC): $\delta = 165.9$ (C7, C12), 161.1 (C1, C2, C4, C5), 159.8 (C1, C2, C4, C5), 127.8 (-CMe), 97.3 (C3, C6), 42.3 (-NMe), 25.8 (-CMe) ppm; $^{19}{\rm F}~{\rm NMR}$ (376.23 MHz, CD_3CN): $\delta\!=\!-72.84$ (d, J=706.6 Hz) ppm; ³¹P NMR (161.88 MHz, CD₃CN): $\delta = -144.64$ (sept, J = 706.6 Hz) ppm; IR (CsI): v = 2957 (w), 1621 (s), 1590 (m), 1520 (w), 1473 (w), 1408 (s), 1311 (m), 1292 (w), 1261 (m), 1221 (m), 1191 (w), 1176 (w), 1158 (w), 1093 (w), 1070 (w), 1024 (w), 986 (w), 838 (vs), 782 (m), 705 (w), 672 (w), 558 (s), 503 (w), 471 (w) cm⁻¹; UV/Vis (CH₃CN, c =1.068 × 10⁻⁴ M, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 225 (27488), 300 (12733), 450 (3255) nm; Crystal data for [1a](PF₆)₂: M_r =666.45, 0.40×0.30×0.15 mm³, monoclinic, space group $P2_1/n$, a= 8.1660(16) Å, b=12.125(2) Å, c=28.503(6) Å, β =97.72(3)°, V= 6244.96 Å³, Z=12, d_{calcd} =1.580 Mgm⁻³, 2θ =3.66 to 60.12°, Mo_{Kα} radiation (graphite-monochromated, λ =0.71073 Å), T=100 K, measured reflections 16150, independent 8220, R_{int} =0.0415, final R indices [$I > 2\sigma(I)$]: $R_1(F)$ =0.052, $wR_2(F^2)$ =0.148.

4(PF₆)₂·CH₃CN

Compound 4 (50.1 mg, 0.135 mmol) was dissolved in CH₃CN (5 mL). FcPF₆ (89.0 mg, 0.269 mmol) was added to the solution. The resulting orange solution was stirred at room temperature for 16 h. Then, the solvent was removed under vacuum. The residue was washed with 4×3 mL Et₂O. Then, it was dissolved in CH₃CN (3 mL) and the solution was filtered. This solution was overlaid by Et₂O (36 mL). The crystalline orange product (83.2 mg, 0.118 mmol, $88\,\%$ yield) was isolated by filtration and washed with $2{\times}2.5\,mL$ Et₂O. Elemental analysis calcd (%) for C₁₉H₂₈F₁₂N₆O₂P₂·CH₃CN (703.47 g mol⁻¹): C 35.86, H 4.44, N 13.94; found: C 35.98, H 4.04, N 14.34; ¹H NMR (399.89 MHz, CD₃CN): $\delta = 6.13$ (s, 2H, H_{C3}, H_{C6}), 3.85 (m, 8H, -NCH₂-), 2.78 (s, 12H, -MMe), 1.96 (s, 3H, CH₃CN), 1.82 (s, 6H, -CMe) ppm; $^{\rm 13}{\rm C}$ NMR (100.55 MHz, CD $_{\rm 3}{\rm CN}$, HSQC, HMBC): $\delta\!=$ 163.8 (C7, C12), 128.5 (-CMe), 49.8 (-NCH2-), 33.0 (-NMe), 25.8 (-CMe) ppm; no signals found for C1-C6; ¹⁹F NMR (376.23 MHz, CD₃CN): $\delta = -72.86$ (d, J=706.6 Hz) ppm; ³¹P NMR (161.88 MHz, CD₃CN): $\delta = -144.63$ (sept, J = 706.6 Hz) ppm; IR (CsI): v = 3091 (w), 2950 (w), 2910 (w), 2255 (w), 1636 (s), 1606 (s), 1558 (w), 1473 (w), 1414 (s), 1367 (m), 1301 (m), 1259 (s), 1217 (s), 1157 (w), 1087 (w), 1024 (w), 982 (w), 838 (vs), 785 (m), 694 (w), 652 (w), 558 (s), 503 (w) cm⁻¹; UV/Vis (CH₃CN, $c = 1.560 \times 10^{-4}$ M, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 225 (27488), 300 (12733), 450 (3255) nm; Crystal data for $4(PF_6)_2 \cdot CH_3CN$: $M_r = 703.47$, $0.21 \times 0.04 \times 0.03$ mm³, orthorhombic, space group *Pbca*, *a* = 14.8644(4) Å, *b* = 18.2389(6) Å, *c* = 21.3201(6) Å, V = 5780.1(3) Å³, Z = 8, $d_{calcd} = 1.617$ Mgm⁻³, $2\theta = 4.1$ to 67.6°, Cu_{Ka} radiation ($\lambda = 1.54184$ Å), T = 120 K, measured reflections 152345, independent 5195, $R_{int} = 0.1393$, final R indices [/> $2\sigma(I)$]: R(F) = 0.056, $wR(F^2) = 0.149$.

[3(CuCl₂)]

Compound 1 (54.1 mg, 0.147 mmol) was dissolved in diethyl ether (3 mL). To this solution, anhydrous CuCl₂ (18.8 mg, 0.140 mmol, 0.95 equiv) was added and stirred for 2 days. The green precipitate was isolated by filtration and washed with diethyl ether (2 mL). Released from solvent remnants in vacuo 68.8 mg (0.134 mmol) of the product was obtained, which corresponds to 96% yield. Crystals were grown by slow diffusion of *n*-hexane into THF. Elemental analysis calcd (%) for $C_{17}H_{32}Cl_2CuN_6O_2$ (510.95 $g\,mol^{-1}$): C 44.66, H 6.31, N 16.45; found: C 44.31, H 6.06, N 16.49; HR-MS (FAB, NPOE): m/z (%) = 377.3 (100) $[L + H]^+$, 513.1244 (22.4) $[L + {}^{63}Cu^{37}L_2]^+$ and $[L + {}^{65}Cu^{37}L^{35}Cl]$, 511.1242 (62.4) $[L + {}^{65}Cu^{35}L_2]^+$ and $[L + {}^{63}Cu^{37}L^{35}Cl]^+$, 509.1266 (54.3) $[L + {}^{63}Cu^{35}L_2]^+$, 478.1580 (12.7) $[L + {}^{65}Cu^{37}Cl]^+$, 476.1589 (58.6) $[L+{}^{65}Cu^{35}Cl]^+$ and $[L+{}^{63}Cu^{37}Cl]^+,$ 474.1593 (74.9) $[L + {}^{63}Cu^{35}Cl]^+$; IR (Csl): $\nu = 3074$ (w), 2998 (w), 2983 (w), 2935 (m), 2886 (w), 2790 (w), 1586 (m), 1546 (m), 1515 (m), 1488 (m), 1464 (w), 1400 (s), 1331 (m), 1275 (m), 1229 (m), 1166 (s), 1137 (m), 1105 (w), 1066 (m), 1020 (m), 981 (s), 935 (w), 916 (m), 894 (s), 857 (m), 816 (m), 803 (m), 784 (w), 731 (w), 702 (w), 629 (w), 512 (w), 486 (w) cm⁻¹; UV/Vis (CH₃CN, $c = 5.010 \times 10^{-4}$ m, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 233 (21001), 324 (12493), 410 (1968, shoulder), 755 (637) nm; CV (CH₂Cl₂, 100 mVs⁻¹): $E = -0.26 E_{ox}$ (Cu) (irrev. 1e⁻), $-1.04 E_{red}(Cu)$ (irrev. 1 e⁻), -0.12 (rev. 1 e⁻, -0.06/-0.18), 0.36 (rev. $1e^-$, 0.29/0.43) V. Crystals grown from Et₂O solution: crystal data

Chem. Eur. J. 2016, 22, 1–14

www.chemeurj.org

10

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

N These are not the final page numbers!



for [3(CuCl₂)]: $M_r = 510.95$, $0.35 \times 0.25 \times 0.20$ mm³, orthorhombic, space group *Fdd*2, a = 20.443(4) Å, b = 37.518(8) Å, c = 12.751(3) Å, $V = 9780(3) \text{ Å}^3$, Z = 16, $d_{\text{calcd}} = 1.388 \text{ Mgm}^{-3}$, $2\theta = 3.92$ to 60.08° , Mo_{ka} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T =100 K, measured reflections 7141, independent 6990, $R_{int} = 0.0309$, final *R* indices $[l > 2\sigma(l)]$: $R_1(F) = 0.039$, $wR_2(F^2) = 0.103$. Crystals grown by diffusion of *n*-hexane into a solution of THF: crystal data for $[3(CuCl_2)]$ ·0.6C₄H₈O: $M_r = 554.21$, $0.30 \times 0.30 \times 0.20$ mm³, monoclinic, space group C2/c, a = 18.354(4) Å, b = 13.463(3) Å, c = $\beta = 102.63(3)^{\circ}$, $V = 5758(2) \text{ Å}^3$, 23.882(5) Å, Z=8, $d_{\text{calcd}} =$ 1.279 Mgm^{-3}, $Mo_{K\!\alpha}$ radiation (graphite-monochromated, $\lambda\!=\!$ 0.71073 Å), T = 100 K, $2\theta = 4.38$ to 59.22° , measured reflections 12872, independent 6616, $R_{int} = 0.0368$, final *R* indices $[l > 2\sigma(l)]$: $R_1(F) = 0.0791, wR_2(F^2) = 0.2540.$

[3(CuBr₂)]

Compound 3 (51.3 mg, 0.136 mmol) was dissolved in THF (4 mL). Then, anhydrous CuBr₂ (30.8 mg, 0.136 mmol) was added. The suspension was stirred for 2 days. Thereafter, the reaction mixture was filtered and the solid residue was dissolved in THF (1 mL). From the collected and filtrated solution, the solvent was removed in vacuo and the residue was washed with Et₂O (2×2 mL). After removal of all solvent traces, a brown powder was obtained (70.3 mg, 0.117 mmol, 85% yield). Crystals were grown from THF solution. Elemental analysis calcd (%) for C₁₉H₃₂CuBr₂N₆O₂ (599.86 g mol⁻¹): C 38.04, H 5.38, N 14.01; found: C 38.34, H 5.38, N 13.97; HR-MS (FAB, NPOE) m/z (%) = 520.1024 (100) $[M-Br]^+$, 603.0225 (14.1) $[L + {}^{65}Cu^{81}Br_2]^+$, 601.03231 (52.3) $[L + {}^{63}Cu^{81}Br_2]^+$ and $[L + {}^{65}Cu^{79}Br^{81}Br]^+$, 599.0234 (67.5) $[L + {}^{63}Cu^{79}Br^{81}Br]^+$ and $[L + {}^{63}Cu^{79}Br^{81}Br]^+$ ${}^{65}Cu^{79}Br_{2}]^{+}$, 597.0214 (28.2) $[L + {}^{63}Cu^{79}Br_{2}]^{+}$, 522.1039 (32.0) [L + ${}^{65}Cu^{81}Br]^+$, 520.1024 (100.0) $[L + {}^{63}Cu^{81}Br]^+$ and $[L + {}^{65}Cu^{79}Br]^+$, 518.1055 (72.5) $[L+{}^{63}{\rm Cu}{}^{79}{\rm Br}]^+;$ IR (CsI): $\nu\!=\!2995$ (w), 2934 (w), 2885 (w), 2791 (w), 1580 (m), 1553 (m), 1515 (m), 1487 (m), 1400 (s), 1330 (m), 1274 (m), 1252 (m), 1229 (s), 1213 (s), 1166 (s), 1136 (m), 1105 (w), 1066 (m), 1020 (m), 980 (s), 935 (w), 915 (m), 893 (s), 856 (m), 817 (s), 803 (m), 793 (w), 699 (w), 629 (w), 510 (w), 483 (w) cm⁻¹; UV/Vis (CH₃CN, $c = 2.00227 \times 10^{-4}$ м, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 221 (24782), 244 (shoulder, 18786), 325 (15501), 345 (13936), 416 (2056), 802 (651) nm; CV (CH₂Cl₂, 100 mV s⁻¹): E = $-0.23 E_{ox}(Cu)$ (irrev. 1 e⁻), $-0.86 E_{red}(Cu)$ (irrev. 1 e⁻), -0.08 (rev. 1e⁻, -0.06/-0.11), 0.42 (rev. 1e⁻, -0.36/-0.48) V; Crystal data for [**3**(CuBr₂)]: $M_r = 599.87$, $0.30 \times 0.20 \times 0.10 \text{ mm}^3$, orthorhombic, space group *Fdd*2, a = 20.739(4) Å, b = 38.076(8) Å, c = 12.761(3) Å, V =10077(3) Å³, Z=16, d_{calcd} =1.582 Mgm⁻³, 2 θ =4.28 to 60.42°, Mo_{Ka} radiation (graphite-monochromated, λ =0.71073 Å), T=100 K, measured reflections 45279, independent 7400, R_{int}=0.0675, final *R* indices $[l > 2\sigma(l)]$: $R_1 = 0.038(F)$, $wR_2(F^2) = 0.081$.

[4{Cu(OAc)₂}]

Compound **4** (67.4 mg, 0.181 mmol) was added to a suspension of anhydrous Cu(OAc)₂ (32.2 mg, 0.177 mmol, 0.98 equiv) and Et₂O (2 mL). The suspension was stirred for 2 days. After removal of the solvent, the residue was dissolved in THF (2.5 mL) and the blue solution was filtered into *n*-hexane (20 mL). The obtained precipitate was separated by filtration and washed with 3×2 mL *n*-hexane. Removed from solvent residues, a blue powder was obtained (74.2 mg, 0.134 mmol, 76% yield). Crystals were gained by diffusion of *n*-hexane into THF. Elemental analysis calcd (%) for C₂₃H₃₄CuN₆O₆ (554.11 g mol⁻¹): C 49.86, H 6.19, N 15.17; found: C 49.92, H 6.33, N 14.69; HR-MS (ESI, CH₃CN): *m/z* (%)=476.18340 (100) [*M*-2OAc+MeCN]⁺, 494.17019 (35.7) [*M*-OAc]⁺; IR (CsI): ν = 3448 (bm), 2988 (w), 2932 (w), 2886 (w), 2804 (w), 1560 (s), 1488

(s), 1413 (s), 1388 (s), 1335 (m), 1292 (m), 1242 (s), 1213 (s), 1163 (s), 1084 (w), 1025 (m), 979 (s), 909 (m), 824 (s), 785 (w), 713 (w), 678 (m), 620 (w), 578 (w), 509 (w), 466 (w) cm⁻¹; UV/Vis (CH₃CN, c=9.051×10⁻⁵ м, d=0.2 cm): λ (ε in Imol⁻¹ cm⁻¹)=232 (24782), 326 (10960), 347 (11841), 481 (161) nm; CV (CH₂Cl₂, 100 mV s⁻¹): E=-1.72 $E_{\rm red}$ (irrev.), -0.27 (rev., 1e⁻, -0.21/-0.32), 0.16 $E_{\rm ox}$ (irrev.) V; Crystal data for [4(Cu(OAc)₂)]·1.25 H₂O (water traces from the applied Cu(OAc)₂)]·H₂O reagent): M_r =576.62, 0.15×0.10×0.09 mm³, tetragonal, space group $P4_1$, a=14.24839(5) Å, b=14.24839(5) Å, c=52.7665(5) Å, V=10712.47(12) Å³, Z=16, $d_{\rm calcd}$ =1.374 Mgm⁻³, 2θ =3.4 to 71.0°, Cu_{Kα} radiation (graphite-monochromated, λ = 1.54184 Å), T=120 K, measured reflections 610708, independent 20526, $R_{\rm int}$ =0.0669, final *R* indices [$I > 2\sigma(I)$]: $R_1(F)$ =0.029, $wR_2(F^2)$ = 0.074.

[4(CuCl₂)]

Ligand 4 (39.3 mg, 0.106 mmol) was dissolved in Et₂O (3 mL). After addition of anhydrous CuCl₂ (13.4 mg, 0.100 mmol, 0.95 equiv), the suspension was stirred for 2 days at room temperature. The green suspension was filtered and the precipitate washed twice with Et₂O (2 mL). The solvent residues were removed in vacuo and a green solid was obtained (49.9 mg, 0.098 mmol, 98% yield). Elemental analysis calcd (%) for $C_{17}H_{28}Cl_2CuN_6O_2$ (506.92 g mol⁻¹): C 45.02, H 5.57, N 16.58; found: C 44.79, H 5.43, N 16.28; HR-MS (FAB, NPOE): m/z (%) = 377.23 (100) $[L + H]^+$; 509.0946 (6.8) $[L + H]^+$ ${}^{63}Cu^{37}L_2]^+$ and $[L + {}^{65}Cu^{37}L^{35}Cl]$, 507.1025 (7.1) $[L + {}^{65}Cu^{35}L_2]^+$ and $[L + {}^{63}Cu^{37}L^{35}Cl]^+$, 505.0961 (2.5) $[L + {}^{63}Cu^{35}L_2]^+$, 474.1258 (8.6) $[L + {}^{63}Cu^{37}L_2]^+$ ${}^{65}Cu^{37}Cl]^+$, 472.1250 (23.5) $[L + {}^{65}Cu^{35}Cl]^+$ and $[L + {}^{63}Cu^{37}Cl]^+$, 470.1241 (25.0) $[L + {}^{63}Cu^{35}Cl]^+$; IR (Csl): $\nu = 2988$ (w), 2933 (w), 2883 (w), 1612 (m), 1564 (s), 1537 (m), 1481 (m), 1410 (m), 1372 (m), 1297 (m), 1214 (s), 1160 (s), 1087 (m), 1024 (m), 977 (s), 906 (m), 852 (w), 821 (s), 708 (w), 561 (m), 507 (m), 466 (m) cm^{-1} ; UV/Vis (CH₃CN, $c = 1.58567 \times 10^{-4}$ m, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 224 (28631), 315 (9510), 347 (10535), 384 (5134, shoulder), 445 (1771), 612 (shoulder), 675 (886), 736 (955), 816 (568, shoulder) nm; CV (CH₂Cl₂, 100 mV s⁻¹): E = -0.35 (rev. $E_{ox} = -0.26$ and $E_{red} = -0.35/$ -0.53), 0.22 $E_{\rm ox}$ (irrev.), 0.44 $E_{\rm red}$ (irrev.) V; Crystals grown by diffusion of *n*-hexane into a solution of THF: crystal data for [4(CuCl₂)]: $M_r = 506.91, 0.40 \times 0.30 \times 0.25 \text{ mm}^3$, monoclinic, space group $P2_1/n$, a = 11.934(2) Å, b = 33.276(7) Å, c = 12.895(3) Å, $\beta = 110.03(3)^{\circ}$, V =4811.1(17) Å³, Z=8, d_{calcd} =1.400 Mgm⁻³, 2 θ =2.44 to 64.08°, Mo_{Ka} radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, measured reflections 32936, independent 16731, $R_{int} = 0.0504$, final *R* indices $[l > 2\sigma(l)]$: $R_1(F) = 0.049$, $wR_2(F^2) = 0.142$. Crystals grown in diethyl ether: crystal data for [4(CuCl₂)]: $M_r = 506.91$, $0.29 \times 0.04 \times$ 0.03 mm³, orthorhombic, space group $Pca2_1$, a = 32.8250(9) Å, b =17.4668(3) Å, c = 13.3167(3) Å, V = 7635.1(3) Å³, Z = 12, $d_{calcd} =$ 1.323 $Mgm^{-3}\!,~2\theta\!=\!3.70$ to $71.32^\circ\!,~Cu_{K\!\alpha}$ radiation (graphite-monochromated, $\lambda = 1.5418$ Å), T = 110 K, measured reflections 240238, independent 14611, $R_{int} = 0.1175$, final R indices $[I > 2\sigma(I)]$: $R_1(F) =$ 0.065, $wR_2(F^2) = 0.146$.

[4(CuBr₂)]

Compound **4** (50.3 mg, 0.135 mmol) was dissolved in THF (3 mL) and anhydrous CuBr₂ (28.7 mg,0.128 mmol) was added. The suspension was stirred for 3 days at room temperature. After solvent removal, the residue was dissolved in CH₃CN (3 mL) and filtered. The solvent was removed and the product was washed with diethyl ether (2×2 mL). Solvent traces were removed in vacuo, and a brown solid was obtained (61.1 mg, 0.106 mmol, 83 % yield). Elemental analysis calcd (%) for C₁₉H₂₈CuBr₂N₆O₂ (595.83 g mol⁻¹): C 38.30, H 4.74, N 14.11; found: C 38.10, H 4.70, N 14.36; HR-MS (FAB,

Chem. Eur. J. **2016**, 22, 1–14

www.chemeurj.org

11

@ 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! **77**



NBA): m/z (%) = 516.0766 (100) $[M-Br]^+$; 598.9922 (7.3) [L+ ${}^{65}Cu^{81}Br_2]^+$, 596.9910 (26.6) $[L + {}^{63}Cu^{81}Br_2]^+$ and $[L + {}^{65}Cu^{79}Br^{81}Br]^+$, 594.9932 (30.4) $[L + {}^{63}Cu^{79}Br^{81}Br]^+$ or $[L + {}^{65}Cu^{79}Br_2]^+$, 516.0766 (100.0) $[L + {}^{63}Cu^{81}Br]^+$ and $[L + {}^{65}Cu^{79}Br]^+$, 514.0778 (92.3) [L + 63 Cu⁷⁹Br]⁺; IR (CsI): $\nu = 2989$ (w), 2938 (w), 2886 (w), 1609 (s), 1560 (s), 1534 (s), 1481 (s), 1411 (s), 1378 (s), 1297 (m), 1242 (m), 1214 (s), 1158 (m), 1024 (m), 977 (s), 905 (m), 851 (w), 821 (s), 707 (w), 563 (m), 508 (m), 468 (m) cm⁻¹; UV/Vis (CH₃CN, $c = 1.215 \times 10^{-4}$ M, d=0.2 cm): λ (ϵ in Imol⁻¹ cm⁻¹)=204 (49338), 219 (48528), 313 (11256), 345 (11800), 445 (2142, shoulder), 613 (658, shoulder), 673 (860), 736 (936), 824 (624, shoulder) nm; CV (CH₂Cl₂, 100 mV s⁻¹): E = -0.30 (rev., -0.21/-0.38), 0.32 E_{ox} (irrev.), 0.62 E_{ox} (irrev.) V.

[4(CuCl₂)]PF₆

[4(CuCl₂)] (63.3 mg, 0.125 mmol) was dissolved in CH₃CN (7 mL) and ferrocenium hexafluorophosphate (40.5 mg, 0.122 mmol, 0.98 equiv) was added. The reaction mixture was stirred for 16 h and then filtered. The solution of the filtrate was removed. The residue was washed with 5×2 mL diethyl ether. The product was crystallized by diffusion of diethyl ether into an acetonitrile solution. The dark blue-green crystalline needles were washed with 2×2 mL diethyl ether and solvent residues were removed in vacuo. The final product (53.5 mg, 0.082 mmol, 67%) was gained by crystallization. Elemental analysis calcd (%) for C19H28Cl2CuF6N6O2P (651.88 g mol⁻¹): C 35.01, H 4.33, N 12.89; found: C 35.11, H 4.29, N 13.32; ¹H NMR (399.89 MHz, CD₃CN): $\delta = 7.65$ (bs, 2 H, H_{C3}, H_{C6}), 4.65 (bs, 8H, -NCH₂-), 3.41 (s, 12H, -MMe), 1.51 (s, 6H, -CMe) ppm; ¹³C NMR (100.55 MHz, CD₃CN, HSQC, HMBC): $\delta = 49.4$ (-NCH₂-), 33.0 (-NMe) ppm; no signals found for -CMe, -CMe, C1-C7, and C12; ¹⁹F NMR (376.23 MHz, CD₃CN): $\delta = -72.9$ (d, J = 706.4 Hz) ppm; ^{31}P NMR (161.88 MHz, CD_3CN): $\delta\!=\!-144.6$ (sept, J=706.4 Hz) ppm; HR-MS (ESI⁺, CH₃CN): *m*/*z* (%) = 505.09492 (100) [*M*]⁺; 509.09033 (24.4) $[L + {}^{65}Cu^{37}Cl_2]^+$, 507.09209 (66.8) $[L + {}^{63}Cu^{37}Cl_2]^+$ and $[L + {}^{63}Cu^{37}Cl_2]^+$ ${}^{65}Cu^{35}Cl^{37}Cl^{+}$, 505.09492 (100) $[L + {}^{63}Cu^{35}Cl^{37}Cl^{+}$ or $[L + {}^{65}Cu^{35}Cl_{2}]^{+}$; IR (CsI): $\nu = 3055$ (w), 2992 (w), 2938 (w), 2819 (w), 1621 (s), 1569 (s), 1559 (s), 1465 (s), 1400 (s), 1371 (s), 1340 (m), 1310 (m), 1256 (s), 1221 (s), 1161 (m), 1088 (m), 1021 (m), 980 (m), 917 (m), 839 $\,$ (vs), 807 (w), 769 (m), 701 (w), 672 (w), 648 (s), 558 (s), 512 (w), 488 (w) cm⁻¹; UV/Vis (CH₃CN, $c = 1.2347 \times 10^{-4}$ m, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 202 (44432), 214 (34740, shoulder), 261 (8981, shoulder), 329 (15898), 458 (3845), 584 (1352), 786 (701, shoulder) nm; Crystal data for $[4(CuCl_2)]PF_6$ -CH₃CN: $M_r = 692.94$, $0.24 \times 0.06 \times$ 0.04 mm³, monoclinic, space group $P2_1/n$, a=6.53266(8) Å, b=32.9648(5) Å, c = 12.98832(18) Å, $\beta = 91.3298(11)^{\circ}$, V = 2796.25(7) Å³, Z=4, $d_{calcd}=1.646 \text{ Mgm}^{-3}$, $2\theta=3.66$ to 71.15° , $Cu_{K\alpha}$ radiation (graphite-monochromated, $\lambda = 1.5418$ Å), T = 120 K, measured reflections 107179, independent 5359, R_{int}=0.0475, final R indices $[l > 2\sigma(l)]: R_1(F^2) = 0.094, wR_2(F^2) = 0.234.$

[4(CuBr₂)]PF₆

[4(CuBr₂)] (79.3 mg, 0.133 mmol) was dissolved in CH₃CN (6 mL). hexafluorophosphate Ferrocenium (43.2 mg, 0.130 mmol. 0.98 equiv) was added to the solution and the mixture was stirred for 16 h. The solvent of the filtrate was removed and the residue washed with 5×3 mL Et₂O. The product was further purified by diffusion of Et₂O into a CH₃CN solution. The crystalline product was washed with 3×3 mL Et₂O and the solvent residues were removed in vacuo. Dark-green crystalline needles of the product (87.5 mg, 0.118 mmol, 91% yield) were obtained. Elemental analysis calcd (%) for $C_{19}H_{28}Br_2CuF_6N_6O_2P$ (740.79 g mol⁻¹): C 30.81, H 3.81, N 11.34; found: C 30.71, H 4.14, N 11.41; $^1\mathrm{H}\,\mathrm{NMR}$ (399.89 MHz, CD_3CN): $\delta\!=\!6.40$ (s, 2 H, H_{C3}, H_{C6}), 4.05 (m, 8 H, -NCH_2-), 3.04 (s, 12 H,

-MMe), 1.81 (s, 3H, CH₃CN), 1.82 (s, 6H, -CMe) ppm; ¹³C NMR (100.55 MHz, CD₃CN, HSQC, HMBC): $\delta = 127.4$ (-CMe), 49.9 (-NCH₂-), 33.9 (NMe), 25.3 (-CMe) ppm; no signals found for C1-C7 and C12; ¹⁹F NMR (376.23 MHz, CD₃CN): $\delta = -72.86$ (d, J = 706.6 Hz) ppm; ³¹P NMR (161.88 MHz, CD₃CN): $\delta = -144.63$ (sept, J = 706.6 Hz) ppm; HR-MS (ESI⁺, CH₃CN): *m/z* (%) = 594.99242 (100) [*M*]⁺; 598.98892 (16.6) $[L + {}^{65}Cu^{81}Br_2]^+$, 596.99051 (77.5) $[L + {}^{63}Cu^{81}Br_2]^+$ and $[L + {}^{65}Cu^{79}Br^{81}Br]^+$, 594.99242 (100) $[L + {}^{63}Cu^{79}Br^{81}Br]^+$ and $[L + {}^{63}Cu^{79}Br^{81}Br]^+$ ${}^{65}Cu^{79}Br_{2}]^{+}$, 592.99463 (40.6); IR (CsI): $\nu = 3058$ (w), 2964 (w), 2905 (w), 1617 (s), 1570 (s), 1465 (s), 1465 (s), 1400 (s), 1369 (s), 1340 (w), 1308 (m), 1257 (s), 1222 (s), 1158 (m), 1088 (w), 1020 (m), 841 (vs), 807 (s), 769 (m), 741 (w), 699 (w), 673 (w), 647 (m), 558 (s), 502 (w), 486 (w) cm⁻¹; UV/Vis (CH₃CN, $c = 1.31666 \times 10^{-4}$ m, d = 0.2 cm): λ (ε in Imol⁻¹ cm⁻¹) = 218 (47591, shoulder), 328 (14700), 456 (3515), 786 (874) nm.

Acknowledgments

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG). We thank Christoph Krämer for SQUID measurements, and Dr. Marion Kerscher for the introduction to helium-cooled EPR measurements.

Keywords: copper complexes · electron transfer · electronic structures · redox-active ligands · valence tautomerism

- [1] a) O. R. Luca, R. H. Crabtree, Chem. Soc. Rev. 2013, 42, 1440-1459; b) V. Lyaskovskyy, B. de Bruin, ACS Catal. 2012, 2, 270-279
- [2] a) O. Sato, J. Tao, Y.-Z. Zhang, Angew. Chem. Int. Ed. 2007, 46, 2152-2187; Angew. Chem. 2007, 119, 2200-2236; b) D. A. Shultz in Magnetism Molecules to Materials II (Eds.: J. S. Miller, M. Drillon), Wiley-VCH, Weinheim, 2001, pp. 281-306.
- [3] C. Carbonera, A. Dei, J.-F. Létard, C. Sangregorio, L. Sorace, Angew. Chem. Int. Ed. 2004, 43, 3136-3138; Angew. Chem. 2004, 116, 3198-3200.
- [4] Reviews exclusively on catecholato/semiguinolato/guinone ligands: a) C. G. Pierpont, Coord. Chem. Rev. 2001, 216-217, 99-125; b) A. Dei, D. Gatteschi, C. Sangregorio, L. Sorace, Acc. Chem. Res. 2004, 37, 827-835; c) D. N. Hendrickson, C. G. Pierpont, Top. Curr. Chem. 2004, 234, 64-95.
- [5] D. M. Dooley, M. A. McGuirl, D. E. Brown, P. N. Turowski, W. S. McIntire, P. F. Knowles, Nature 1991, 349, 262-264.
- [6] a) J. Rall, M. Wanner, M. Albrecht, F. M. Hornung, W. Kaim, Chem. Eur. J. 1999, 5, 2802-2809; b) W. Kaim, M. Wanner, A. Knödler, S. Záliš, Inorg. Chim. Acta 2002, 337, 163-172.
- [7] J. Rall, W. Kaim, J. Chem. Soc. Faraday Trans. 1994, 90, 2905-2908.
- [8] A. Peters, E. Kaifer, H.-J. Himmel, Eur. J. Org. Chem. 2008, 5907-5914.
- [9] H.-J. Himmel, Z. Anorg. Allg. Chem. 2013, 639, 1940-1952.
- [10] B. Eberle, H. Hermann, E. Kaifer, H.-J. Himmel, Eur. J. Inorg. Chem. 2013, 3671-3679.
- [11] H. Herrmann, A. Ziesak, U. Wild, S. Leingang, D. Schrempp, N. Wagner, J. Beck, E. Kaifer, H. Wadepohl, H.-J. Himmel, ChemPhysChem 2014, 15, 351-365.
- [12] C. Trumm, O. Hübner, P. Walter, S. Leingang, U. Wild, E. Kaifer, B. Eberle, H.-J. Himmel, Eur. J. Inorg. Chem. 2014, 6039-6050.
- [13] A. Ziesak, T. Wesp, O. Hübner, E. Kaifer, H. Wadepohl, H.-J. Himmel, Dalton Trans. 2015, 44, 19111-19125.
- S. Wiesner, A. Wagner, E. Kaifer, H.-J. Himmel, Chem. Eur. J. 2016, 22, [14] 10438-10445.
- [15] a) A. Dei, D. Gatteschi, L. Pradi, U. Russo, Inorg. Chem. 1991, 30, 2589-2594; b) S. Kitagawa, Coord. Chem. Rev. 2002, 224, 11-34.
- [16] A. Hoffmann, O. Bienemann, I. dos Santos Viera, S. Herres-Pawlis, Z. Naturforsch. Sect. B 2014, 69, 589-595.

Chem. Eur. J. 2016, 22, 1-14

www.chemeuri.org

KR These are not the final page numbers!

© 2016 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

12

^[17] J. E. Sundeen, P. H. Ermann, ER SQUIBB & SONS, EP 0342423A2, 16.05.1988





- [18] A. Peters, H. Herrmann, M. Magg, E. Kaifer, H.-J. Himmel, Eur. J. Inorg. Chem. 2012, 1620–1631.
- [19] B. Eberle, O. Hübner, A. Ziesak, E. Kaifer, H.-J. Himmel, Chem. Eur. J. 2015, 21, 8578-8590.
- [20] H. Hornung, O. Hübner, E. Kaifer, H.-J. Himmel, RCS Adv. 2016, 6, 39323–39329.
- [21] a) P. Roquette, A. Maronna, A. Peters, E. Kaifer, H.-J. Himmel, Ch. Hauf, V. Herz, E.-W. Scheidt, W. Scherer, *Chem. Eur. J.* 2010, *16*, 1336–1350; b) A. Hoffmann, S. Binder, A. Jesser, R. Haase, U. Flörke, M. Gnida, M. S. Stagni, W. Meyer-Klaucke, B. Lebsanft, L. E. Grünig, S. Schneider, M. Hashemi, A. Goos, A. Wetzel, M. Rübhausen, S. Herres-Pawlis, *Angew. Chem. Int. Ed.* 2014, *53*, 299–304; *Angew. Chem.* 2014, *126*, 305–310.
- [22] A. Bencini, D. Gatteschi in *Inorganic Electronic Structure and Spectroscopy, Vol.* 1 (Eds.: E. I. Solomon, A. B. P. Lever), Wiley, Hoboken, **2006**, pp. 93–160.
- [23] W. Kaim, Dalton Trans. 2003, 761-768.
- [24] G. R. Eaton, S. S. Eaton, D. P. Barr, R. T. Weber in *Quantitative EPR*, Springer, Wien, 2010.
- [25] J. Winkler, P. Wittung-Stafshede, J. Leckner, B. Malmström, H. Gray, Proc. Natl. Acad. Sci. USA 1997, 94, 4246-4249.
- [26] B. Eberle, M. Damjanovic, M. Enders, S. Leingang, J. Pfisterer, C. Krämer, O. Hübner, E. Kaifer, H.-J. Himmel, *Inorg. Chem.* 2016, *55*, 1683–1696.
- [27] S. Wiesner, A. Wagner, O. Hübner, E. Kaifer, H.-J. Himmel, Chem. Eur. J. 2015, 21, 16494–16503.
- [28] DENZO-SMN, data processing software, Nonius 1998; http://www.nonius.nl.
- [29] a) G. M. Sheldrick, SHELXS-97 and SHELXS-2014, Program for Crystal Structure Solution, University of Göttingen, 1997 and 2014; http://shelx.uni-ac.gwdg.de/SHELX/index.php; b) G. M. Sheldrick, SHELXL-97 and SHELX-2014, Program for Crystal Structure Refinement, University of Göttingen, 1997 and 2014; http://shelx.uni-ac.gwdg.de/SHELX/index.php.
- [30] International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.
- [31] L. Zsolnai, G. Huttner, XPMA, University of Heidelberg, 1994; http:// www.uni-heidelberg.de/institute/fak12/AC/huttner/software/software.html.
- [32] CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK, 2011 2014 and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland, 2015.
- [33] R. H. Blessing, Acta Crystallogr. Sect. A 1995, 51, 33-38.
- [34] SCALE3 ABSPACK, CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK, 2011–2014, and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland, 2015.

- [35] W. R. Busing, H. A. Levy, Acta Crystallogr. 1957, 10, 180-182.
- [36] a) L. Palatinus, SUPERFLIP, EPF Lausanne, Switzerland, and Fyzikální ústav AV ČR, v.v.i., Prague, Czech Republic, 2007–2014; b) L. Palatinus, G. Chapuis, J. Appl. Crystallogr. 2007, 40, 786–790.
- [37] a) G. M. Sheldrick, SHELXL-20xx, University of Göttingen, Germany, and Bruker AXS GmbH, Karlsruhe, Germany, 2012–2014; b) G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112–122; c) G. M. Sheldrick, Acta Crystallogr. Sect. C 2015, 71, 3–8.
- [38] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2, Durham University, UK, and OlexSys Ltd., Durham, UK; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
- [39] a) P. van der Sluis, A. L. Spek, Acta Crystallogr. Sect. A 1990, 46, 194–201;
 b) A. L. Spek, Acta Crystallogr. Sect. C 2015, 71, 9–18.
- [40] a) A. L. Spek, PLATON, Utrecht University, The Netherlands; b) A. L. Spek, J. Appl. Crystallogr. 2003, 36, 7–13.
- [41] TURBOMOLE V6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007.
- [42] a) J. P. Perdew, Phys. Rev. B 1986, 33, 8822–8824; b) A. D. Becke, Phys. Rev. A 1988, 38, 3098–3100.
- [43] a) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. **1994**, 98, 11623–11627; b) A. D. Becke, J. Chem. Phys. **1993**, 98, 5648–5652; c) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B **1988**, 37, 785– 789.
- [44] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
- [45] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford, CT, **2009**.

Received: May 19, 2016 Published online on ■■ ■, 0000

www.chemeurj.org

Chem. Eur. J. 2016, 22, 1-14



FULL PAPER

Electron Transfer

D. F. Schrempp, E. Kaifer, H. Wadepohl, H.-J. Himmel*

Copper Complexes of New Redox-Active 4,5-Bisguanidino-Substituted Benzodioxole Ligands: Control of the Electronic Structure by Counter-Ligands, Solvent, and Temperature



Redox-active guys: The electronic structure of mononuclear copper complexes featuring new redox-active 4,5bisguanidino-substituted benzodioxole ligands can be controlled by several parameters and a temperature-dependent equilibrium between two tautomeric forms (Cu^{II}/neutral ligand and Cu^I/radical monocationic ligand) can be achieved. One electron removal leads to a redoxinduced electron transfer (RIET; see figure).

14