

Coordination Alternatives in Dinuclear Bis(pyridin-2-ylalkyl)-benzylaminecopper(II) Complexes with OH⁻, RO⁻, F⁻, or Cl⁻ Bridges: Experimental Structures and DFT Preferences

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The compounds [L¹Cu(μ-OH)₂CuL¹](ClO₄)₂ (**1**), [L²Cu(μ-OH)₂CuL²](ClO₄)₂ (**2**), [L³Cu(μ-OH)₂CuL³](ClO₄)₂ (**3**), [L³Cu(μ-OMe)₂CuL³](ClO₄)₂ (**4**), [L³Cu(μ-F)₂CuL³](BF₄)₂ (**5**), [L⁴Cu(μ-Cl)₂CuL⁴](ClO₄)₂ (**6**), and [Cu(μ-L⁵)₂Cu](ClO₄)₂ (**7**), where L¹ = bis(pyridin-2-ylmethyl)benzylamine, L² = (6-methylpyridin-2-ylmethyl)(pyridin-2-ylmethyl)benzylamine, L³ = bis(6-methylpyridin-2-ylmethyl)benzylamine, L⁴ = (pyridin-2-ylethyl)(pyridin-2-ylmethyl)benzylamine, and L⁵ = (6-oxidomethylpyridin-2-ylmethyl)(6-methylpyridin-2-ylmethyl)benzylamine, were structurally characterized and studied by low-temperature EPR spectroscopy. The formation of compound **5** involved fluoride abstraction from BF₄⁻ and that of **7** involved O₂-assisted C–H (methyl) activation/monooxygenation of L³. Whereas the dications of **1–4** and **7** possess a square-pyramidal configuration at the copper(II) centers with hydroxide or alkoxide bridges in equatorial positions, the dications of **5** and **6** exhibit equatorial/axial arrangements for the bridging halide ions. In the dication of **5**, the tridentate ligand binds in a meridional fashion and includes two adjacent five-membered chelate rings. Such a situation has been observed previously only with chloride, alk-

oxide, or aqua bridges. In contrast to the *syn* configuration of the dication of **2**, the dications of complexes **1**, **3**, **4**, and **7** adopt an *anti* configuration with respect to the binding of Lⁿ. The dications of **1**, **2**, and **7** have the pyridinyl or 6-methylpyridinyl groups in the axial position, whereas those of **3** and **4** feature the tertiary amine N atom at that site. DFT calculations of various configurations of the dications of **1–6** reproduce the experimentally observed structural alternatives in complexes **1–4**, but they do not predict the axial/equatorial structure of **5** as the lowest-energy configuration. The systematic overestimation of repulsive forces and thus of distances by DFT may result in an underestimation of the π–π interaction between the largely coplanar *mer*-L³ ligands separated by about 3.6 Å in **5**, which probably affects its structure. By incorporating these and previous results, the *syn* versus *anti*, equatorial/equatorial versus equatorial/axial, and axial pyridine versus axial amine structural alternatives are discussed.

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Introduction

Bis(hydroxido)-bridged dicopper(II) complexes are among the most typical products from reactions between copper(I) compounds and molecular oxygen.^[1–8] The reac-

tions of Cu^I with O₂ have found interest in synthesis because of their potential use in the hydroxylation of aromatic and other organic compounds.^[9] In O₂ transport proteins^[10] and oxygenation or oxidoreductase enzymes,^[11,12] however, the formation of bis(hydroxido)dicopper(II) products is usually avoided to ensure reversibility. Among the most widely used copper coligands in this context are the tridentate bis(pyridin-2-ylalkyl)amines,^[2,3,6,7a] which can be modified in terms of their steric bulk, electronic effects, and alkyl chain lengths, which thus allows tridentate coordination in both facial^[2a,2b,13] and meridional fashions.^[2b–2d] In contrast, the equally popular^[6] tris(pyrazolyl)borate,^[4] tris(pyrazolyl)methane,^[7b] and triazacyclononane ligands^[5] are restricted to facial coordination.

The formation of copper(II) [or copper(III)]^[6] species after the interaction of O₂ and Cu^I is accompanied by the typical structural peculiarities of the d⁹ (or d⁸) configuration, that is, the tendency to form approximately square-

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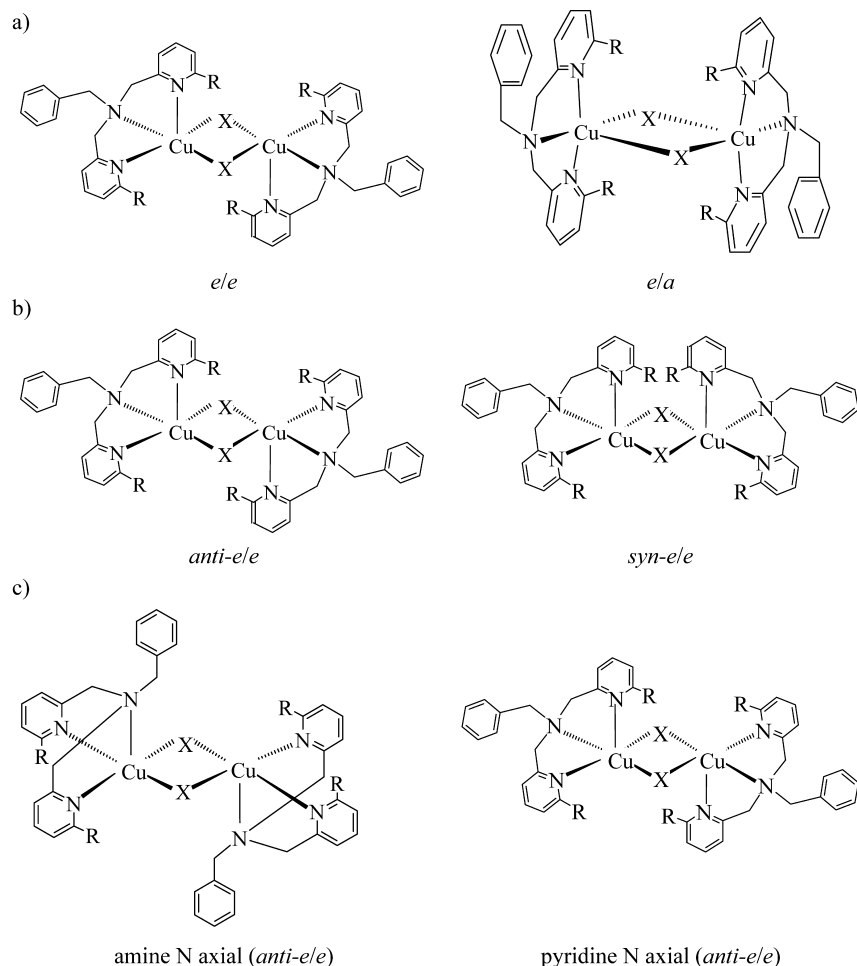
pyramidal structures with significantly different equatorial (*e*) and axial (*a*) binding sites.^[6] Because tridentate chelating ligands restrict rapid interconversion, there are clear structural alternatives for doubly bridged dicopper(II) systems, viz., the *ele* or *ela* situations (Scheme 1a). Whereas the *ele* conformation typically shows a rather symmetrical bridging arrangement with Cu^{II}–OH distances of about 1.93 Å,^[2a,2b,3–5,7a,13] the much longer axial bonds extend to 2.25–2.30 Å for the few *ela* examples described so far.^[2b–2d,14] These isolated examples were formulated as containing six-membered chelate rings with relaxed N–Cu–N bite angles of about 90°.^[2b–2d] Examples with smaller chelate rings were restricted to chlorido-, alkoxido-, and aqua-bridged species.^[7a,15]

In a detailed analysis of the original assertion of a bis(hydroxido)-bridged dicopper(II) complex with an *ela* arrangement,^[2b] Lee and Holm showed^[14] that bridging by two fluoride ions abstracted from PF₆[–] – perhaps by a Cu/O₂/H₂O-assisted process – may instead account for the observed configuration. In addition, these authors reported the formation of small amounts of a dicopper(II) complex doubly bridged by a tetradentate anionic monooxygenated ligand generated by the activation of benzylic CH₂.^[14]

For the more common^[16] [LⁿCu(μ-X)₂CuLⁿ]²⁺ systems with *ele* configurations of the bridging ligands, two further

kinds of structural alternatives are established: the axial ligands may be arranged in an *anti* or *syn* orientation relative to the Cu(μ-X)₂Cu plane (Scheme 1b),^[7a] and the unsymmetrical tridentate bis(pyridin-2-ylalkyl)amine ligands may bind with the pyridine or the amine N atoms in the axial position (Scheme 1c).^[2a]

In this contribution we describe seven additional examples of these kinds of [LⁿCu(μ-X)₂CuLⁿ]²⁺ complexes, which may shed light on the structural alternatives delineated above. Of the compounds [L¹Cu(μ-OH)₂CuL¹](ClO₄)₂ (**1**), [L²Cu(μ-OH)₂CuL²](ClO₄)₂ (**2**), [L³Cu(μ-OH)₂CuL³](ClO₄)₂ (**3**), [L³Cu(μ-OMe)₂CuL³](ClO₄)₂ (**4**), [L³Cu(μ-F)₂CuL³](BF₄)₂ (**5**), [L⁴Cu(μ-Cl)₂CuL⁴](ClO₄)₂ (**6**) and [Cu(μ-L⁵)₂Cu](ClO₄)₂ (**7**), where L¹ = bis(pyridin-2-ylmethyl)benzylamine, L² = (6-methylpyridin-2-ylmethyl)-(pyridin-2-ylmethyl)benzylamine, L³ = bis(6-methylpyridin-2-ylmethyl)benzylamine, L⁴ = (pyridin-2-ylethyl)(pyridin-2-ylmethyl)benzylamine, and L⁵ = (6-oxidomethylpyridin-2-ylmethyl)(6-methylpyridin-2-ylmethyl)benzylamine, complexes **1–3** and **7** were obtained from treatment of in situ generated copper(I) precursors [LⁿCu(L')]⁺ with air (L': solvent). The ligands except for L⁵ were described in the literature,^[7a,17] as were some of the copper(I) precursors.^[17] An additional copper(I) compound, [L³Cu(PPh₃)](BF₄), is described here for comparison with the recently



Scheme 1.

reported $[\text{L}^3\text{CuL}'](\text{BF}_4)$ species, where $\text{L}' = \text{CH}_3\text{CN}$ or CO .^[17] Whereas the oligomethylene chain length in the ligands controls the chelate ring sizes,^[18] the 6-methyl substitution at the pyridin-2-yl ring has been reported to decrease its donor ability and slow down the reaction rate due to steric repulsion.^[17] Within the L^1 , L^2 , and L^3 ligand series, substitution at the pyridin-2-yl rings was increased while the five-membered chelate rings were maintained, which thus resulted in a largely planar ligand geometry relative to some previously studied systems.^[2b,2d] In the course of these studies we not only encountered the well-established^[14,19] fluoride abstraction from BF_4^- to yield an unusual structure for **5**, we also observed small amounts of dimeric product complex **7**, which contained a tetradentate anionic monooxygenated ligand L^5 , from the reaction involving L^3 . In contrast to a previous observation,^[14] however, the attack had not occurred at the connecting benzylic methylene functionality, but at the α -methyl group of the pyridine ring. Such CH activation by Cu/O_2 resembles enzymatic processes^[14,20] and is studied in the context of synthetic transformations;^[9] an alkylperoxidocopper(II) complex resulting from the attack on an α -picolyl methyl group was reported recently.^[9e]

To investigate the metal–metal interaction (coupling) and the possible dissociation of the dinuclear complexes in solution,^[2b] we studied compounds **1–6** by EPR spectroscopy. The dications of compounds **1–6** were subjected to DFT calculations of various coordination alternatives in order to confirm their configurational preferences and to understand the stereochemically relevant factors involved.

Results and Discussion

Synthesis

Bis(hydroxido)-bridged dicopper(II) complexes **1–3** were typically obtained as final products from reactions between in situ generated copper(I) complexes of the ligands after exposure to atmospheric conditions [Equation (1)]. One Cu^{I} compound, $[\text{L}^3\text{Cu}(\text{PPh}_3)](\text{BF}_4)$, was isolated for NMR spectroscopic analysis and structural characterization (cf. below).



The lability of the bis(hydroxido)-bridged dicopper(II) complexes in certain solvents allowed simple conversion of **3** into bis(methoxido)-bridged **4** containing the $[\text{L}^3\text{Cu}(\mu\text{-OMe})_2\text{CuL}^3]^{2+}$ dication. The use of the $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{BF}_4)$ precursor led to bis(fluorido)-bridged **5** by well-established^[14,19] F^- abstraction from tetrafluoroborate, where the remaining BF_3 can act as a Lewis acidic partner for amines. This reactivity has been observed even with PF_6^- , a supposedly more inert anion.^[14] Both the unambiguous crystallographic signature of F^- versus OH^- and the much more pronounced asymmetry of the central four-membered ring is typical for bis(fluorido)- versus bis(hydroxido)-bridged dicopper(II) complexes (cf. below).^[14] Otherwise, halide-bridged complexes such as **6** can be obtained by using the

corresponding copper salt. In the absence of an available halide ion for bridging, a secondary reaction may occur that presumably involves the metal-assisted monooxygenation of a partially activated C–H bond. These reactions proceed in low yields.^[14] However, whereas Lee and Holm found a product with a monooxygenated benzylic CH_2 group from a pyridyl–amine linkage,^[14] we observed the monooxygenation of a CH_3 group in the α position of the pyridine. The resulting complex **7** thus contains two anionic, tetradentate (6-oxidomethylpyridin-2-ylmethyl)(6-methylpyridin-2-ylmethyl)benzylamine bridges. CH activation by Cu/O_2 is currently studied in the context of synthetic transformations^[9] and within attempts to elucidate the mechanisms of corresponding enzymes,^[20] that is, tyrosinases,^[21] for aromatic CH groups and dopamine β monooxygenase or peptidylglycine α -hydroxylating monooxygenase (PHM) for nonaromatic CH groups.^[22] These reactions may proceed via mononuclear (Cu^{II} -superoxido)^[23] or dinuclear (Cu^{II} -peroxido)^[6,9e] precursor intermediates to yield the reactive copper–oxyl ($\text{O}^\cdot$) species that effects the necessary H abstraction before rebound.^[24]

Structure Description

The crystallographic data of the systems studied by X-ray diffraction are summarized in Tables 5 and 6.

Despite the poor data quality, the structure results (bond lengths and angles; Tables 1 and 2) for $[\text{L}^3\text{Cu}(\text{PPh}_3)](\text{BF}_4)$ indicate that the corresponding complex cation possesses an intermediate structure between those of $[\text{L}^3\text{Cu}(\text{CH}_3\text{CN})]^+$ and $[\text{L}^3\text{Cu}(\text{CO})]^+$.^[17] This reflects the moderately lower π -acceptor ability of PPh_3 relative to that of CO . The overall structure of this complex (Figure 1) remains that of a highly distorted tetrahedron,^[17] which can be alternatively described as a trigonal pyramid with the more weakly bonded amine N atom at the apex.

Among the bis(hydroxido)-bridged dicopper(II) complexes with nearly square-pyramidal configurations ($\tau < 0.20$),^[25] compounds **1–3** (Figures 2, 3, and 4; Table 1) exhibit the familiar *ele* configuration^[2a,2b,3–5,7a] for the rather symmetrically bonded hydroxide bridges. However, whereas **1** and **3** show *anti*-positioned axial (6-methyl)pyridin-2-yl ligands, the 6-methylpyridin-2-yl axial ligands in **2** were found in a *syn* configuration and face each other with the smallest distance between the methyl-substituted ring C6' and C6'' carbon atoms measuring 3.57 Å (Figure 3). The least-squares planes defined by the apical rings (N1', C2', C3', C4', C5', C6' and N1'', C2'', C3'', C4'', C5'', C6'') are not completely parallel; they adopt a small dihedral angle of 4.2(1)°. The distances between the centroids of each ring and the neighboring planes are 3.44 and 3.50 Å, respectively.

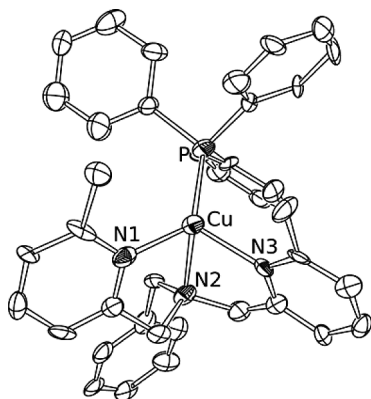
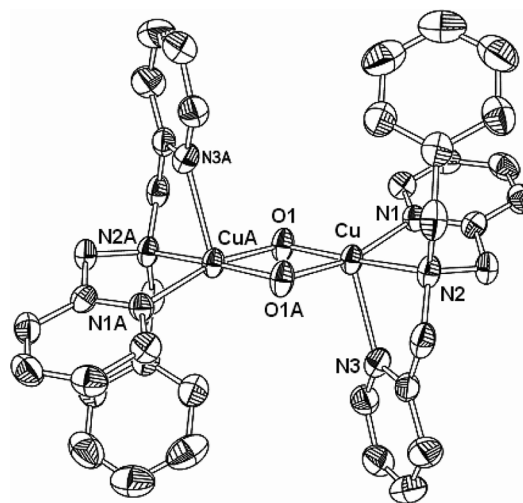
The preference of the sterically more demanding 6-methylpyridin-2-yl group for the axial position is not unexpected, and the tendency of unactivated pyridines to adopt this position has been reconfirmed recently.^[2a] However, with strong donor substituents such as OR or NR_2 in the *para*

Table 1. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for compounds **1**·CH₃COCH₃, **2**·H₂O, and **3**.

1 ^[a]		2 ^[b]		3 ^[c]	
Cu–O1	1.921(4)	Cu'–O1'	1.952(5)	Cu'–N2'	2.054(6)
Cu–O1A	1.947(4)	Cu'–O1''	1.948(5)	Cu''–N2''	2.043(5)
Cu–N1	1.983(5)	Cu''–O1'	1.919(4)	Cu'–N3i	2.013(6)
Cu–N2	2.058(4)	Cu''–O1''	1.960(5)	Cu''–N3''	1.993(6)
Cu–N3	2.280(5)	Cu'–N1'	2.279(7)	Cu'–Cu''	2.955(1)
Cu–CuA	2.922(1)	Cu''–N1''	2.332(6)		
N1–Cu–N2	83.4(2)	N3'–Cu'–N2'	83.6(3)	N1''–Cu''–O1''	94.8(2)
N1–Cu–N3	101.4(2)	N3''–Cu''–N2''	84.4(2)	N3''–Cu''–O1'	97.9(2)
N2–Cu–N3	77.3(2)	N3'–Cu'–N1'	96.8(3)	N3''–Cu''–O1''	167.2(2)
N1–Cu–O1	97.6(2)	N3''–Cu''–N1''	97.6(2)	N2''–Cu''–O1'	173.8(2)
N2–Cu–O1	176.2(2)	N2'–Cu'–N1'	76.0(3)	N2''–Cu''–O1''	95.5(2)
N3–Cu–O1	106.0(2)	N2''–Cu''–N1''	76.0(2)	N1'–Cu'–O1'	98.1(2)
N3–Cu–O1A	93.7(2)	N3'–Cu'–O1'	164.1(2)	N1'–Cu'–O1''	111.2(3)
N2–Cu–O1A	96.2(2)	N3''–Cu''–O1''	99.3(2)	Cu'–O1'–Cu''	99.5(2)
N1–Cu–O1A	164.4(2)	N2'–Cu'–O1'	94.6(2)	Cu'–O1''–Cu''	98.2(2)
O1–Cu–O1A	81.9(2)	N2''–Cu''–O1''	171.6(3)	O1'–Cu'–O1''	80.4(2)
Cu–O1–CuA	98.1(2)	N1'–Cu'–O1'	109.2(2)	O1'–Cu''–O1''	80.9(2)
				Cu–O1–CuA	104.9(6)

[a] A: $-x, -y + 2, -z$. [b] The symbols ' and '' refer to two crystallographically nonequivalent molecule halves. [c] A: $0.5 - x, 1.5 - y, 1 - z$.Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for compounds **4**–**7**.

4 ^[a]		5 ^[b]		6 ^[c]		7 ^[d]	
Cu–O1A	1.930(2)	Cu–F1	1.878(1)	Cu–N1	1.994(4)	Cu–O1A	1.948(3)
Cu–O1	1.933(2)	Cu–F1A	2.268(1)	Cu–N2	2.088(4)	Cu–O1	1.962(3)
Cu–N1	2.040(2)	Cu–N1	2.016(2)	Cu–N3	2.008(4)	Cu–N1	2.186(4)
Cu–N2	2.254(2)	Cu–N2	2.011(2)	Cu–Cl1	2.298(1)	Cu–N2	2.102(3)
Cu–N3	2.019(2)	Cu–N3	2.031(2)	Cu–Cl1A	2.791(1)	Cu–N3	1.923(3)
Cu–CuA	3.0520(7)	Cu–CuA	3.134(1)	Cu–CuA	3.714(1)	Cu–CuA	2.9067(10)
N1–Cu–N2	80.61(9)	N1–Cu–N2	84.12(7)	N1–Cu–N2	90.7(2)	N1–Cu–N2	80.42(13)
N1–Cu–N3	98.11(9)	N1–Cu–N3	163.79(7)	N1–Cu–N3	172.0(2)	N1–Cu–N3	114.15(15)
N2–Cu–N3	78.45(9)	N2–Cu–N3	81.90(7)	N2–Cu–N3	81.3(2)	N2–Cu–N3	81.75(14)
N1–Cu–O1	94.47(9)	N1–Cu–F1	97.02(6)	N1–Cu–Cl1	93.5(1)	N1–Cu–O1	112.90(13)
N2–Cu–O1	105.44(9)	N2–Cu–F1	169.10(6)	N2–Cu–Cl1	166.3(1)	N2–Cu–O1	162.24(13)
N3–Cu–O1	167.31(9)	N3–Cu–F1	98.27(6)	N3–Cu–Cl1	94.5(1)	N3–Cu–O1	81.98(13)
N3–Cu–O1A	91.69(9)			N1–Cu–Cl1A	95.3(1)	N3–Cu–O1A	144.81(14)
N2–Cu–O1A	107.91(9)			N2–Cu–Cl1A	105.9(1)	N2–Cu–O1A	105.63(12)
N1–Cu–O1A	168.22(9)			N3–Cu–Cl1A	85.8(1)	N1–Cu–O1A	101.03(13)
O1–Cu–O1A	75.62(8)	F1–Cu–F1A	82.26(5)	Cu–Cl1–CuA	93.2(1)	O1–Cu–O1A	83.95(12)
Cu–O1–CuA	104.38(8)	Cu–F1–CuA	97.74(5)	Cl1–Cu–Cl1A	86.8(1)	Cu–O1–CuA	96.05(12)

[a] A: $-x, 2 - y, -z$. [b] A: $1 - x, 1 - y, 1 - z$. [c] A: $1 - x, 1 - y, 1 - z$. [d] A: $2 - x, -y, 1 - z$.Figure 1. Molecular structure of the cation in the crystal of [L³Cu(PPh₃)](BF₄). Selected bond lengths [$\text{\AA}$] and angles [$^\circ$]: Cu–P 2.178(4), Cu–N1 2.007(11), Cu–N2 2.202(10), Cu–N3 2.074(10); P–Cu–N1 129.1(3), P–Cu–N2 119.2(3), P–Cu–N3 116.9(3), N1–Cu–N2 80.9(4), N1–Cu–N3 112.8(4), N2–Cu–N3 78.0(4).Figure 2. Molecular structure of the dication in the crystal of [L¹Cu(μ-OH)₂CuL¹](ClO₄)₂·2Me₂CO (**1**).

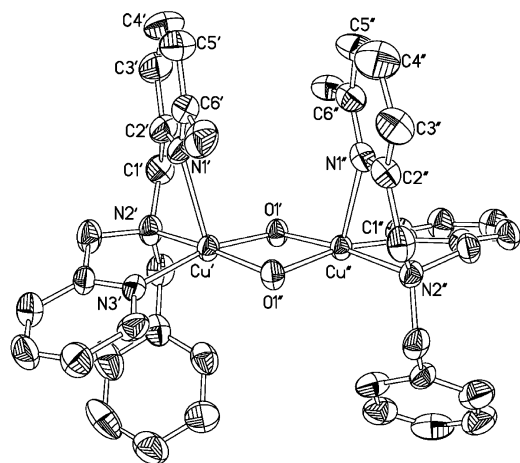


Figure 3. Molecular structure of the dication in the crystal of $[L^2Cu(\mu-OH)_2CuL^2](ClO_4)_2 \cdot H_2O$ (**2**).

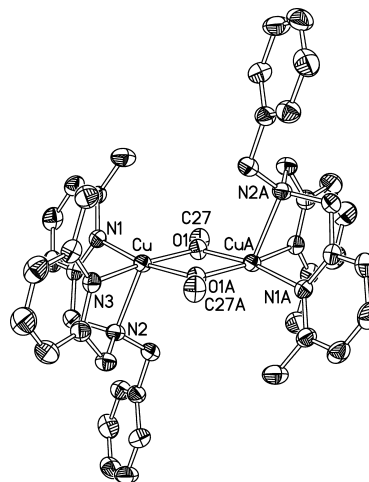


Figure 5. Molecular structure of the dication in the crystal of $[L^3Cu(\mu-OMe)_2CuL^3](ClO_4)_2$ (**4**).

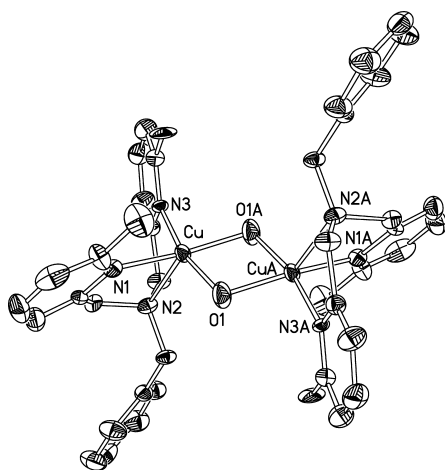


Figure 4. Molecular structure of the dication in the crystal of $[L^3Cu(\mu-OH)_2CuL^3](ClO_4)_2$ (**3**).

position, the pyridines may prefer the equatorial coordination, leaving the axial binding site for the trialkylamine N atom.^[2a] The *syn* configuration for **2** is reminiscent of that of a 6-trifluoromethyl-substituted analogue,^[7a] which suggests that there is an attractive interaction.

The related hydroxido- and methoxido-bridged structures **3** and **4** (Figures 4 and 5, respectively) are very similar in their *anti* configurations, which are almost superimposable. The Cu–O distances are a bit shorter for **3** [1.891(2), 1.905(2) Å] than for **4** [1.930(2), 1.933(2) Å]. The methoxy carbon atoms of the OMe groups lie at opposite sides of the central Cu_2O_2 plane in **4** and are almost coplanar. The C–O vector defines an angle of only 7.9° with the plane.

As pointed out before,^[2d] bis(chlorido)-bridged dicopper(II) complexes can readily adopt the *ela* arrangement for the bridges with long axial Cu–Cl distances of about 2.8 Å. A previous study of $[L^1Cu(\mu-Cl)_2CuL^1](ClO_4)_2$ (**8**) showed^[7a] that this also holds when two five-membered chelate rings are formed in the L^nCu moiety. Compound

6, $[L^4Cu(\mu-Cl)_2CuL^4](ClO_4)_2$, described here shows that the same kind of structure is obtained after lengthening either one of the alkyl chains that connects the amine N atom or the pyridin-2-yl moiety from CH_2 to CH_2CH_2 (Figure 6, Table 2).

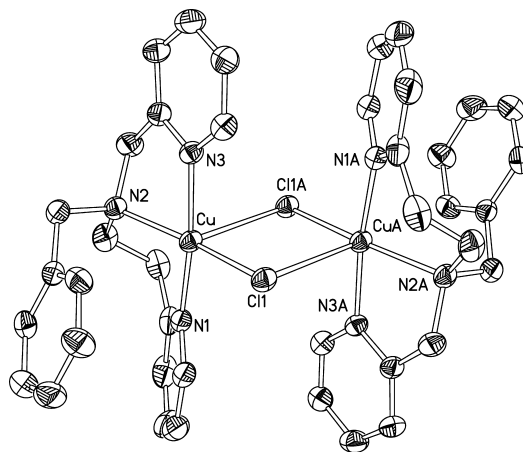


Figure 6. Molecular structure of the dication in the crystal of $[L^4Cu(\mu-Cl)_2CuL^4](ClO_4)_2$ (**6**).

In contrast to $\mu-Cl^-$, $\mu-OR^-$, and $\mu-OH_2$, the smaller $\mu-OH^-$ bridges typically favor the *ele* configuration in dinuclear $[(\eta^3-L)Cu(\mu-OH)_2Cu(\eta^3-L)]^{2+}$ complexes. The tridentate ligands will then coordinate in a facial mode. This rule is not only confirmed by the revision of the initially assigned hydroxido-bridged complex with the *ela* configuration^[2b] to a fluorido-bridged species,^[14] but it is also corroborated by the examples presented here, viz., an *ele* configuration for **3** and **4** but an *ela* configuration for fluorido-bridged **5** (Figure 7). Nevertheless, the latter is surprising because meridional binding of tridentate ligands such as L^3 is less favorable due to the necessity to form two adjacent five-membered chelate rings (Table 2).

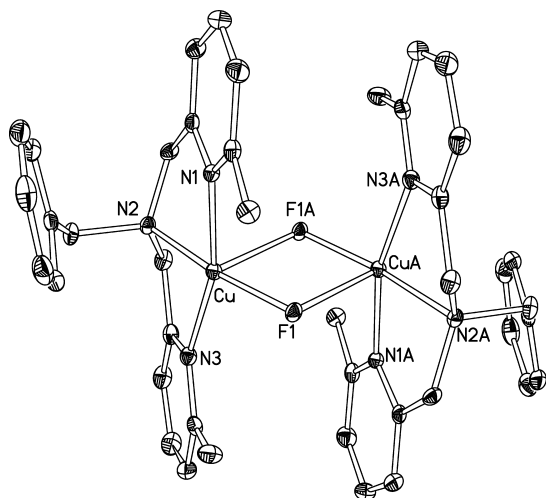
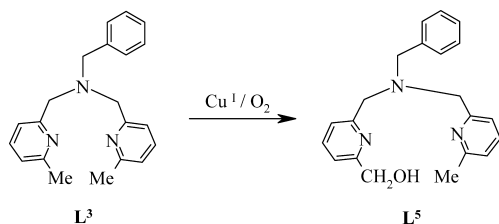


Figure 7. Molecular structure of the dication in the crystal of $[L^3Cu(\mu-F)_2CuL^3](BF_4)_2 \cdot 2CH_2Cl_2$ (**5**).

According to the five-membered chelate ring situation, the N–Cu–N angles in **5** have decreased to about 83° and the *trans*-N1–Cu–N3 angle to $163.79(7)^\circ$. Measuring $169.10(6)^\circ$, the other *trans*-N2–Cu–F1 angle is distinctly more linear, as is the N1–Cu–N3 angle for the *mer*-coordinated L^4 in compound **6**, which measures $172.0(2)^\circ$. All Cu–N bond lengths in **5** lie around $2.02 \text{ \AA}$; the typically weaker bonding to the amine N atom is compensated for



Scheme 2.

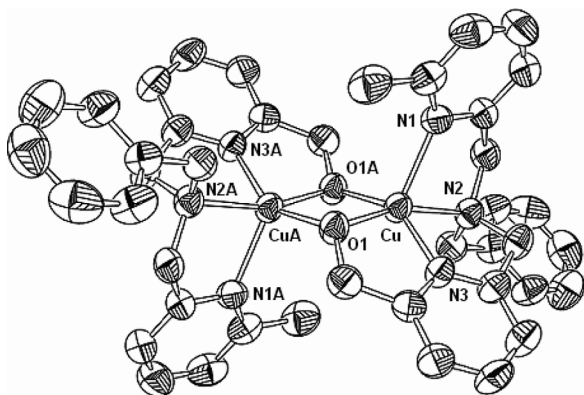


Figure 8. Molecular structure in the crystal of $[Cu(\mu-L^5)_2Cu]$ (**7**).

by its preferred central position in *mer*- L^3 . In contrast, the difference between the short equatorial Cu–F bond length and the typically^[14] long axial Cu–F distance is almost $0.4 \text{ \AA}$. The molecular dication of **5** has inversion symmetry (Figure 7), and the central Cu_2F_2 ring approaches a rectangular geometry because the bond lengths differ widely but the Cu–F1–CuA and F1–Cu–F1A angles [$97.74(5)$ and $82.26(5)^\circ$, respectively] do not strongly deviate from 90° . Measuring $3.134(1) \text{ \AA}$, the Cu–CuA distance is longer than the corresponding distances in the *ele*-configured hydroxido

Table 3. Relative energies (most stable isomer = 0 kcal mol^{-1}) calculated for the different coordination alternatives of compounds **1–6**, **8**, and $[L^2Cu(\mu-OMe)_2CuL^2]^{2+}$.^[a]

Compound number	Bridge configuration	Orientation	Axial ligand	Relative energy [kcal mol^{-1}]
1	<i>ele</i>	<i>anti</i>	Pyridine-N	0.1
	<i>ele</i>	<i>anti</i>	Amine-N	0
	<i>ele</i>	<i>syn</i>	Pyridine-N	0.9
	<i>ele</i>	<i>syn</i>	Amine-N	2.8
	<i>ela</i>	<i>syn</i>	OH	16.7
2	<i>ele</i>	<i>anti</i>	Pyridine-N	0.3
	<i>ele</i>	<i>anti</i>	Amine-N	2.1
	<i>ele</i>	<i>syn</i>	Pyridine-N	0.1
	<i>ele</i>	<i>syn</i>	Amine-N	0
	<i>ela</i>	<i>syn</i>	OH	17.9
3	<i>ele</i>	<i>anti</i>	Pyridine-N	9.5
	<i>ele</i>	<i>anti</i>	Amine-N	0
	<i>ele</i>	<i>syn</i>	Pyridine-N	9.7
	<i>ele</i>	<i>syn</i>	Amine-N	0.3
	<i>ela</i>	<i>syn</i>	OH	23.8
4	<i>ele</i>	<i>anti</i>	Pyridine-N	12.5
	<i>ele</i>	<i>anti</i>	Amine-N	0
	<i>ele</i>	<i>syn</i>	Pyridine-N	15.2
	<i>ele</i>	<i>syn</i>	Amine-N	1.0
	<i>ela</i>	<i>syn</i>	OMe	2.4
$[L^2Cu(\mu-MeO)_2]$	<i>ele</i>	<i>anti</i>	Pyridine-N	3.6
	<i>ele</i>	<i>anti</i>	Amine-N	0
	<i>ele</i>	<i>syn</i>	Pyridine-N	4.2
	<i>ele</i>	<i>syn</i>	Amine-N	5.9
$[CuL^2]^{2+}$	<i>ela</i>	<i>syn</i>	OMe	19.7
5	<i>ele</i>	<i>anti</i>	Pyridine-N	0
	<i>ele</i>	<i>anti</i>	Amine-N	0.1
	<i>ele</i>	<i>syn</i>	Pyridine-N	0.8
	<i>ele</i>	<i>syn</i>	Amine-N	1.1
	<i>ela</i>	<i>syn</i>	F	6.3
6	<i>ele</i>	<i>anti</i>	Pyridine-N	10.6
	<i>ele</i>	<i>anti</i>	Amine-N	8.0
	<i>ele</i>	<i>syn</i>	Pyridine-N	9.8
	<i>ele</i>	<i>syn</i>	Amine-N	47.5
	<i>ela</i>	<i>syn</i>	Cl	0
8	<i>ele</i>	<i>anti</i>	Pyridine-N	1.7
	<i>ele</i>	<i>anti</i>	Amine-N	7.8
	<i>ele</i>	<i>syn</i>	Pyridine-N	0.9
	<i>ele</i>	<i>syn</i>	Amine-N	9.2
	<i>ela</i>	<i>syn</i>	Cl	0

[a] *ele*: equatorial/equatorial; *ela*: equatorial/axial; in bold: experimentally observed geometry.

derivatives **1–3** (<3.01 Å), but much smaller than those in the chlorido-bridged **6** [$3.714(1)$ Å] and **8** [$3.566(1)$ Å],^[7a] and that reported for a complex involving nonplanar, six-membered chelate rings (3.271 Å).^[2d] In fact, the virtually planar L^3Cu^{II} moieties in **5** are arranged in a parallel stacked structure (dihedral angle of 4.5°) with partially overlapping pyridyl-ring π systems and oppositely oriented methyl groups. The interplanar distance of about 3.6 Å (vs. 3.35 Å in graphite) indicates a π – π interaction that probably induces and stabilizes^[2b] the structure. π – π interactions have been implicated before in similar complexes,^[2b] and relatively long interplanar distances are typical for nitrogen-containing aromatic molecules.^[26] The aromatic rings of the benzyl substituents in **5** also overlap with the pyridyl rings (dihedral angle of 21.4°) with interplanar distances (e.g. 3.068 Å for N1–C21) that allow such π – π interactions. In total, a π – π – π arrangement (pyridyl, pyridyl, benzyl) results that is reminiscent of a recently described dicopper(I) complex involving phenylphosphane and bipyrimidine π systems.^[27]

Complex **7** in which the L^3 ligand has undergone monooxygenation at a picolyl methyl group and then deprotonation to yield tetradentate anionic L^5 (Scheme 2) shows the familiar *anti* configuration of the *ele* arrangement, with the nonmonooxygenated 6-methylpyridyl group in the axial position (Figure 8). Because of the restriction by tetrachelation, the square planar configuration is slightly more distorted ($\tau = 0.28$) than in the other cases ($\tau < 0.20$). Table 3 summarizes the experimentally observed coordination situations, and the following discussion is concerned with the possible predictability of such structural preferences.

DFT Calculations for the $[L^nCu(\mu-X)_2CuL^n]^{2+}$ Dications

The variety of structural alternatives for these complexes (Scheme 1, Table 3) and their realization under different conditions have prompted us to undertake a DFT calculation study to rationalize the experimental results and to explore the predictive potential of the method. Table 3 summarizes the energies calculated for the different stereoisomers, and the DFT-calculated structure parameters are found in Table S1 (Supporting Information).

As can be expected just by considering steric hindrance, dicopper(II) complexes sharing an edge of the two square-based pyramids favor the *anti* arrangement for the apical ligands. For the dication of **1**, $[L^1Cu(\mu-OH)_2CuL^1]^{2+}$, the *anti-ele* structure with pyridine or amine nitrogen atoms in the apical position should be expected. The X-ray structure shows a pyridyl *anti-ele* geometry for this complex (as a perchlorate salt). DFT results predict this isomer to be 0.006 eV higher in energy than the most stable *anti-ele* amine configuration. Both these isomers are practically of the same energy, so packing could play an important role in determining the observed crystal structure. The *syn-ele* isomers for the complex are 0.041 and 0.121 eV higher in energy than the most stable configuration. The *ela* isomer

was computed to be 0.723 eV less stable than the *anti-ele* pyridyl isomer. Interestingly, the *anti-ele* pyridyl configuration is preserved when complex **2** is crystallized as an aqua solvate instead of the acetone solvate described in the text, where the packing interactions must be completely different.

Replacement of one α -hydrogen atom on one of the pyridyl groups of L^1 by a methyl group leads to L^2 . The dication of **2**, $[L^2Cu(\mu-OH)_2CuL^2]^{2+}$, crystallizes in the *syn-ele* pyridyl geometry (with perchlorate counteranions); this was also observed for the trifluoromethyl derivative of L^2 .^[7a] DFT calculations for **2** show that the energy of the *syn-ele* pyridyl isomer lies just 0.002 eV above that of the most stable *syn-ele* amine alternative. The *anti* configurations are a bit higher in energy, whereas the energy of the *ela* isomer lies about 0.7 eV above that of the most stable isomer. The observed structure may result from CX_3 ···ring interactions that could occur in the *syn* configuration between the substituted pyridine rings. The replacement of the other α -hydrogen atom by a methyl group to give $[L^3Cu(\mu-OH)_2CuL^3]^{2+}$ (dication of **3**) has a strong effect on the relative energies. In this complex, the *anti-ele* amine configuration is computed to be the most stable isomer, and this result coincides with the X-ray determined structure for the perchlorate salt.

Changing the hydroxy bridge into a methoxy one leads to $[L^2Cu(\mu-OMe)_2CuL^2]^{2+}$ ^[7a] and $[L^3Cu(\mu-OMe)_2CuL^3]^{2+}$ (dication of **4**), where again the *anti-ele* amine form is calculated to be the most stable isomer, and this is confirmed by the X-ray diffraction results. Moreover, the computed energy differences between the most stable isomer and the others are now larger, which suggests that the incorporation of a methyl group on the bridge produces enhanced repulsion.

The complexes $[L^3Cu(\mu-F)_2CuL^3]^{2+}$ (dication of **5**), $[L^4Cu(\mu-Cl)_2CuL^4]^{2+}$ (dication of **6**), and $[L^1Cu(\mu-Cl)_2CuL^1]^{2+}$ (dication of **8**) were studied to test the effect of halide bridges. Their experimental structures correspond to the *ela* isomer. The most stable isomer computed for the dication of **5** is the *anti-ele* pyridyl form. Although this result does not fit the experimental observations (*ela* isomer), the difference in energy of this isomer relative to the most stable one at 0.275 eV is noticeably diminished in comparison to the hydroxy or methoxy analogues, where the energy differences between the *ele* and *ela* configurations are of the order of 1 eV. The computational results for the dications of **6** and **8** show that the most stable isomers possess *ela* configurations, which is in agreement with the experimental results.

In conclusion, the DFT method makes a clear distinction between the *ele* and *ela* configurations. Although the calculated energy differences are not very large in the case of some *syn*- and *anti-ele* isomers, the DFT method has correctly reproduced the experimentally favored complex configurations except in the case of the dication of **5** where additional, highly distance-dependent π – π interactions are obviously underestimated^[26,27] because of the systematic overestimation of distances.

EPR Spectroscopy

The EPR method is suited to study intramolecular spin–spin interactions of copper(II) ions in dinuclear complexes and to investigate their possible dissociation into mononuclear species in solution.^[2b] We therefore studied the compounds by this method in the solid state and in frozen solutions at 110 K (Figure 9, Table 4).

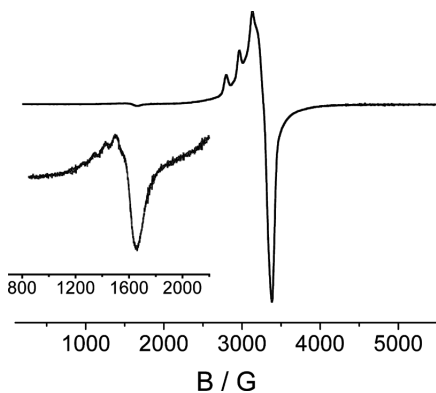


Figure 9. EPR signal of compound $[L^4Cu(\mu-Cl)_2CuL^4](ClO_4)_2$ (**6**) with half-field component (insert).

Table 4. EPR parameters of complexes in CH_2Cl_2/CH_3CN (x/y) at 110 K.

Complex	(x/y)	$g_{ }$	$g_{\perp}$	g_{av}	$A_{ }^{[a]}$
1	2/1			2.10 ^[b] 4.10 ^[b,c]	
3	4/1	2.260	2.050	2.120 4.27 ^[b-d]	15.0
4	4/1	2.270	2.057	2.128 4.26 ^[b-d]	14.6
5	1/0	2.270	2.056	2.127 4.21 ^[b-d]	15.6
6	4/1	2.206 4.91 ^[c]	2.040 4.21 ^[c]	2.075 4.44 ^[c]	17.6 8.3 ^[c]
8	5/1	2.224 4.86 ^[c]	2.015 4.16 ^[c,e]	2.085 4.39 ^[c]	17.7 8.7 ^[c]

[a] In mT. [b] Unresolved signal. [c] Half-field signal. [d] Weak signal. [e] $A_{\perp} = 2.0$ mT.

The complexes show typical^[2] EPR signals for $Cu^{II}(\mu-X)_2-Cu^{II}$ cores in both cases with the spectra in frozen solutions being better resolved (Figure 9). Under both sets of conditions we could observe half-field transitions for certain compounds, especially for the halide-bridged species possessing a pronounced asymmetry of the $Cu(\mu-X)Cu$ core and possible triplet ground states.^[7a] The fact that both solid samples and frozen solutions exhibit the half-field signals for the triplet excited states suggests that the dinuclear arrangement remains largely intact in the chosen CH_2Cl_2/CH_3CN solvent mixtures. Preliminary UV/Vis spectroscopic experiments have shown that association and ligand substitution equilibria can occur in media such as alcohols. The differences between the complexes are rather small except for the somewhat higher $A_{||}$ ($^{63,65}Cu$) and lower g values for the chloride-bridged species **6** and **8** (Table 4). The increased copper–halide covalency and the higher spin-

orbit coupling contributions from Cl^- are held responsible for these differences.

Conclusions

During this study of $[L^nCu(\mu-X)_2CuL^n]^{2+}$ complex dications, we encountered a remarkable structural variety (Table 3). Nevertheless, DFT calculations were able to confirm the preferred configuration of most of these structures by their computed relative energies except in the case of the F-bridged complex **5**, where the systematic overestimation of repulsive forces and thus of distances led to wrong predictions as a result of underestimated π – π interactions. Whereas some effects such as the preference of the more weakly basic halide ligands for the axial position are easily rationalized, the differences between the *anti* and *syn* orientations or the preferred N donor for the axial position are not readily obvious. Karlin and coworkers noted that “such structural differences or variations may need to be considered to explain certain aspects of [...] reactivity patterns”,^[2a] and therefore, a detailed computational approach may provide increased efficiency in the design and development of ligands for broader interest such as in metal/ O_2 -induced CH activation;^[9] an example encountered accidentally is presented here as doubly monooxygenated complex **7**.

Experimental Section

Instrumentation: EPR spectra in the X band were recorded with a Bruker System EMX. 1H NMR spectra were recorded in $CDCl_3$ with a Bruker AMX-300 NMR spectrometer. IR spectra were obtained with a Bruker Vector 22 instrument.

Syntheses of Ligands: The ligands L^1 = bis(pyridin-2-ylmethyl)benzylamine, L^2 = (6-methylpyridin-2-ylmethyl)(pyridin-2-ylmethyl)benzylamine, L^3 = bis(6-methylpyridin-2-ylmethyl)benzylamine, and L^4 = (pyridin-2-ylethyl)(pyridin-2-ylmethyl)benzylamine were prepared according to the literature^[7a,17] by reaction of the appropriate secondary amine with benzyl bromide in CH_3CN as the solvent.

Synthesis of Copper Complexes

Caution: Perchlorate complexes are potentially explosive and should be handled with care.

$[L^3Cu(PPh_3)](BF_4)$: To a solution of L^3 (55 mg, 0.173 mmol) in CH_2Cl_2 (10 mL) was added $[Cu(CH_3CN)_3(PPh_3)]BF_4$ (83 mg, 0.155 mmol). The mixture was stirred at room temperature overnight. After reducing the solvent 3 mL, a bright yellow product precipitated in 79% yield (89 mg) by adding hexane/toluene (1:1). Crystals were obtained by recrystallization from CH_2Cl_2 at $-20^\circ C$. Single crystals were covered with a layer of viscous hydrocarbon oil (Paratone N, Exxon), attached to a glass fiber, and instantly placed in a low-temperature N_2 stream. 1H NMR (300 MHz, CD_3CN): δ = 2.62 (s, 6 H), 3.56 (s, 2 H), 3.67 (AB-m, 4 H), 7.08 (br., 2 H), 7.21–7.33 (m, 15 H), 7.37–7.54 (m, 7 H), 7.80 (pt, J = 7.7 Hz, 2 H) ppm. $C_{39}H_{38}BCuF_4N_3P$ (730.07): calcd. C 64.16, H 5.25, N 5.76; found C 63.92, H 5.93, N 5.12.

$[L^3Cu(CH_3CN)](BF_4)$: To a solution of L^3 (100 mg, 0.315 mmol) in CH_2Cl_2 (10 mL) was added $[Cu(CH_3CN)_4]BF_4$ (100 mg,

0.318 mmol). The mixture was stirred for 2 h at room temperature. After reducing the solvent to 2 mL and adding hexane a partially crystalline and highly air-sensitive precipitate was obtained and dried. Yield: 69 mg (43%). ^1H NMR (300 MHz, CD_3CN): δ = 2.71 (s, 6 H), 3.81 (AB-m, 4 H), 3.93 (s, 2 H), 7.11 (d, J = 8 Hz, 2 H), 7.25–7.40 (m, 7 H), 7.68 (pt, J = 7.7 Hz, 2 H) ppm.

[$\text{L}^1\text{Cu}(\mu\text{-OH})_2\text{CuL}^1](\text{ClO}_4)_2 \cdot 2\text{CH}_3\text{COCH}_3$ ($1 \cdot 2\text{CH}_3\text{COCH}_3$): To a suspension of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ (654 mg, 2 mmol) in acetone (10 mL) was added an acetone solution of the ligand (579 mg, 2 mmol) under an atmosphere of nitrogen. The mixture was stirred for 30 min to give a yellow solution, and then the flask was opened to the atmosphere. The solution turned blue, and the solid product separated with time. Crystals suitable for X-ray diffraction studies were obtained by recrystallization from boiling acetone. Yield: 697 mg (66%). IR (KBr pellet): $\tilde{\nu}$ = 3570 (sharp, shoulder), 3450 (br., OH), 1604, 1574, 1481, 1444 (sharp, py), 1100 (vs, ClO_4^-) cm^{-1} . $\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{12}$ (1054.9): calcd. C 50.1, H 5.0, N 8.0, Cu 12.0; found C 48.8, H 4.9, N 8.1, Cu 12.3.

[$\text{L}^2\text{Cu}(\mu\text{-OH})_2\text{CuL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ($2 \cdot \text{H}_2\text{O}$): To a suspension of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ (654 mg, 2 mmol) in CH_2Cl_2 (10 mL) was added a dichloromethane solution of the ligand (607 mg, 2 mmol) under an atmosphere of nitrogen. The mixture was stirred for 30 min after which the flask was opened to the atmosphere. After several hours a blue solid separated. Recrystallization from boiling ethanol gave crystals suitable for X-ray diffraction studies. Yield: 460 mg (45%). IR (KBr pellet): $\tilde{\nu}$ = 3600 (sharp, shoulder), 3500 (br., OH), 1603, 1577, 1473, 1458 (sharp, py), 1100 (vs, ClO_4^-) cm^{-1} . $\text{C}_{40}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{11}$ (1020.9): calcd. C 48.8, H 4.7, N 8.5, Cu 12.9; found C 48.2, H 4.6, N 8.5, Cu 13.4.

[$\text{L}^3\text{Cu}(\mu\text{-OH})_2\text{CuL}^3](\text{ClO}_4)_2$ (3**):** To a suspension of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{ClO}_4)$ (654 mg, 2 mmol) in CH_2Cl_2 (10 mL) was added a dichloromethane solution of the ligand (635 mg, 2 mmol) under an atmosphere of nitrogen. The mixture was stirred for 30 min after which the flask was opened to the atmosphere. Blue crystals of **3** suitable

for X-ray studies were obtained by slow evaporation of the solvent. Yield: 448 mg (45%). IR (KBr pellet): $\tilde{\nu}$ = 3560 (sharp, shoulder), 3500 (br., OH), 1610, 1579, 1469, 1441 (sharp, py), 1095 (vs, ClO_4^-) cm^{-1} . $\text{C}_{42}\text{H}_{48}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{10}$ (994.9): calcd. C 50.7, H 4.9, N 8.5, Cu 12.8; found C 52.1; H 4.8; N 8.2; Cu 13.1.

[$\text{L}^3\text{Cu}(\mu\text{-OMe})_2\text{CuL}^3](\text{ClO}_4)_2$ (4**):** This compound was obtained by recrystallization of compound **3** in boiling methanol. IR (KBr pellet): $\tilde{\nu}$ = 1609, 1578, 1468, 1441 (sharp, py), 1090 (vs, ClO_4^-) cm^{-1} . $\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{10}$ (1022.9): calcd. C 51.6, H 5.1, N 8.2, Cu 12.4; found C 50.8, H 5.0, N 7.9, Cu 12.6.

[$\text{L}^3\text{Cu}(\mu\text{-F})_2\text{CuL}^3](\text{BF}_4)_2 \cdot 2\text{CH}_2\text{Cl}_2$ ($5 \cdot 2\text{CH}_2\text{Cl}_2$): To a cooled (-20°C) solution of $[\text{L}^3\text{Cu}(\text{CH}_3\text{CN})]\text{BF}_4$ (89 mg, 0.175 mmol) in CH_2Cl_2 (5 mL) was added O_2 -saturated CH_2Cl_2 solution (5 mL). The initially bright-yellow solution turned deep green spontaneously. The mixture was stirred for 1 h at -20°C . Removal of the solvent gave a deep green residue that was recrystallized from CH_2Cl_2 at -10°C to afford a green product. Yield: 30 mg (36%). $\text{C}_{44}\text{H}_{50}\text{B}_2\text{Cl}_4\text{Cu}_2\text{F}_{10}\text{N}_6$ (1143.42): calcd. C 47.68, H 4.69, N 8.20; found C 45.71, H 4.64, N 8.67.

[$\text{L}^4\text{Cu}(\mu\text{-Cl})_2\text{CuL}^4](\text{ClO}_4)_2$ (6**):** This complex was obtained by the reaction of a 1:1 mixture of copper(II) perchlorate hexahydrate (370 mg) and anhydrous copper(II) chloride (135 mg) with the L^4 ligand in methanol. Recrystallization from boiling methanol afforded crystals suitable for X-ray diffraction. Yield: 442 mg (44%). IR (KBr pellet): $\tilde{\nu}$ = 1610, 1570, 1485, 1448 (sharp, py), 1100 (vs, ClO_4^-) cm^{-1} . $\text{C}_{40}\text{H}_{42}\text{Cl}_4\text{Cu}_2\text{N}_6\text{O}_8$ (1003.7): calcd. C 47.8, H 4.2, N 8.4, Cu 12.7; found C 47.1, H 4.0, N 8.3, Cu 12.5.

[$\text{Cu}(\mu\text{-L}^5)_2\text{Cu}](\text{ClO}_4)_2$ (7**):** Evaporation of the residual solution resulting from the synthesis of compound **3** gave a blue-green syrup that was dissolved in acetonitrile. Slow evaporation of this solution gave a small amount of green crystals identified as compound **7** by X-ray diffraction.

X-ray Data Collection and Refinement Details: Single crystals of the compounds were glued to the tip of glass capillaries and then

Table 5. Crystallographic and refinement details for compounds [$\text{L}^3\text{Cu}(\text{PPh}_3)](\text{BF}_4)$, $1 \cdot 2\text{CH}_3\text{COCH}_3$, $2 \cdot \text{H}_2\text{O}$, and **3**.

	[$\text{L}^3\text{Cu}(\text{PPh}_3)](\text{BF}_4)$	$1 \cdot 2\text{CH}_3\text{OCH}_3$	$2 \cdot \text{H}_2\text{O}$	3
Formula	$\text{C}_{39}\text{H}_{38}\text{BCuF}_4\text{N}_3\text{P}$	$\text{C}_{44}\text{H}_{52}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{12}$	$\text{C}_{40}\text{H}_{46}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{11}$	$\text{C}_{42}\text{H}_{48}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{10}$
F_w	730.04	1054.91	984.82	994.85
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_12_12_1$	$C2/c$
a [Å]	16.225(7)	10.530(1)	12.1372(7)	18.979(5)
b [Å]	9.925(4)	11.019(1)	16.777(1)	8.7256(18)
c [Å]	23.327(9)	11.390(1)	22.710(1)	27.449(6)
α [°]	90	67.289(2)	90	90
β [°]	105.79(1)	87.113(2)	90	104.854(8)
γ [°]	90	86.747(2)	90	90
Volume [Å ³]	3615(3)	1216.6(3)	4624.2(5)	4393.7(17)
Z	4	1	4	4
$F(000)$	1512	546	2028	2072
$D_{\text{calcd.}}$ [g cm ⁻³]	1.341	1.440	1.413	1.519
Crystal size [mm]	$0.5 \times 0.05 \times 0.01$	$0.45 \times 0.13 \times 0.05$	$0.50 \times 0.34 \times 0.16$	$0.38 \times 0.18 \times 0.02$
T [K]	173	293	293	293
2θ range	3.15 to 27.04	3.88 to 50.20	3.02 to 50.16	1.53 to 25.04
μ [mm ⁻¹]	0.701	1.049	1.097	1.156
Index ranges	$-19 \leq h \leq 20$ $-10 \leq k \leq 12$ $-27 \leq l \leq 26$	$-12 \leq h \leq 12$ $-13 \leq k \leq 13$ $-13 \leq l \leq 13$	$-14 \leq h \leq 14$ $-20 \leq k \leq 19$ $-26 \leq l \leq 27$	$-22 \leq h \leq 22$ $-10 \leq k \leq 10$ $-32 \leq l \leq 32$
No. reflections collected	4214	4272	8211	3887
No. reflections observed	2355	2737	6010	2768
R , R_w [a]	0.1184, 0.2100	0.0738, 0.1676	0.0728, 0.1926	0.1625, 0.3581
Final difference [e Å ⁻³]	0.530, -0.548	0.665, -0.552	0.852, -0.743	1.043, -1.531

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$. $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å.

Table 6. Crystallographic and refinement details for compounds **4**, **5**·2CH₂Cl₂, **6**, and **7**.

	4	5 ·2CH ₂ Cl ₂	6	7
Formula	C ₄₄ H ₅₂ Cl ₂ Cu ₂ N ₆ O ₁₀	C ₄₄ H ₅₀ B ₂ Cl ₄ Cu ₂ F ₁₀ N ₆	C ₄₀ H ₄₂ Cl ₄ Cu ₂ N ₆ O ₈	C ₄₂ H ₄₄ Cl ₂ Cu ₂ N ₆ O ₁₀
<i>F</i> _w	1022.92	1141.83	1003.70	990.83
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> [Å]	10.8139(11)	11.9814(3)	9.1595(8)	10.4493(11)
<i>b</i> [Å]	16.8512(18)	13.4624(3)	17.762(2)	17.0095(18)
<i>c</i> [Å]	13.4087(14)	15.7738(4)	12.557(1)	12.8309(13)
<i>α</i> [°]	90	90	90	90
<i>β</i> [°]	109.745(2)	112.168(1)	91.305(2)	109.945(2)
<i>γ</i> [°]	90	90	90	90
Volume [Å ³]	2299.8(4)	2356.22(10)	2042.5(3)	2143.7(4)
<i>Z</i>	2	4	2	2
<i>F</i> (000)	1060	1168	1028	1020
<i>D</i> _{calcd.} [g cm ^{−3}]	1.477	1.614	1.632	1.535
Crystal size [mm]	0.30 × 0.20 × 0.17	0.46 × 0.2 × 0.06	0.27 × 0.24 × 0.12	0.42 × 0.20 × 0.07
<i>T</i> [K]	293	293	293	293
2θ range	2.02 to 25.10	3.88 to 28.28	3.98 to 50.16	2.07 to 25.07
<i>μ</i> [mm ^{−1}]	1.104	1.21	1.365	1.182
Index ranges	−12 ≤ <i>h</i> ≤ 12 −20 ≤ <i>k</i> ≤ 20 −15 ≤ <i>l</i> ≤ 15	−15 ≤ <i>h</i> ≤ 15 −17 ≤ <i>k</i> ≤ 17 −20 ≤ <i>l</i> ≤ 19	−10 ≤ <i>h</i> ≤ 10 −21 ≤ <i>k</i> ≤ 21 −14 ≤ <i>l</i> ≤ 14	−12 ≤ <i>h</i> ≤ 12 −20 ≤ <i>k</i> ≤ 20 −15 ≤ <i>l</i> ≤ 15
No. reflections collected	4087	5784	3610	3808
No. reflections observed	3323	4850	2557	2661
<i>R</i> , <i>R</i> _w ^[a]	0.0438, 0.1067	0.0375, 0.0805	0.0593, 0.1452	0.0573, 0.1498
Final difference [e Å ^{−3}]	0.633, −0.209	0.487, −0.477	0.817, −0.487	0.566, −0.285

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$. $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$.

mounted on either a Bruker SMART-APEX^[28a] (**1–4**, **6**, **7**), or a Bruker-Nonius Kappa CCD diffractometer [$\{\text{L}^3\text{Cu}(\text{PPh}_3)\}(\text{BF}_4)$ and **5**]. Intensity data for **1–4**, **6**, and **7** were collected by using 10 s by frame (except for **4** where 30 s was used), separated by 0.3°. Data integration and cell refinement was made by using SAINTPLUS.^[28b] The structures were solved by direct methods with the use of XS and XL in SHELXTL,^[28c] or the program system SHELXL-97 in connection with absorption correction.^[28d] Anisotropic thermal parameters were included for all non-hydrogen atoms. H atoms were placed geometrically and refined by using a riding model, including free rotation of methyl groups and variable isotropic displacement parameters. Final *R* values and important bond parameters are listed in Tables 1, 2, 5, and 6.

Analysis of the raw data for complex **3** clearly suggested that the crystal had two identifiable components, related by a 180° rotation around <−1, −2, 0>. Data reduction using both components shows one major component (mean $I/\sigma = 2.0$) and a minor one (mean $I/\sigma = 0.5$). A rather small amount of reflections (≈5%) corresponds to overlapped data. Structure solution and structure refinement were finally performed considering just the major component.

During the last stages of refinement some disorder of the perchlorate anions for complexes **1**, **2**, **3**, **4**, and **6** was obvious. This was modeled by using partially occupied positions, which were first refined and then held constant for the final refinement.

DFT Calculations: DFT calculations were carried out by using the Amsterdam Density Functional package^[29a] developed by Baerends and coworkers.^[29b–29f] The local density approximation for electron correlation was treated with the Vosko–Wilk–Nusair parametrization.^[30a] The nonlocal corrections of Becke^[30b,30c] and Perdew^[30d,30e] (BP86) were added to the exchange and correlation energies, respectively. The numerical integration procedure applied for the calculations was developed by te Velde et al.^[29f] The standard ADF STO TZP basis set was used.^[29a] The frozen-core approximation^[30f] was considered for Cu, 3p; Cl, 2p; F, O, N, and

C, 1s. Geometry optimization and single point calculations were done for $[\text{Cu}_2\text{L}_2\text{X}_2]^{2+}$ by considering a unrestricted singlet state involving *C*_i or *C*₂ symmetry as constraints for *anti* and *syn* models, respectively.

CCDC-647370 to -647377 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.

Supporting Information (see footnote on the first page of this article): Selected DFT optimized distances and angles for model complexes **1–6**, **8**, and $[\text{L}^2\text{Cu}(\mu\text{-MeO})_2\text{CuL}^2]^{2+}$, bond lengths and angles for $[\text{L}^3\text{Cu}(\text{PPh}_3)](\text{BF}_4)$.

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