A Copper(I) Oxygenation Precursor in the Entatic State: Two Isomers of a Copper(I) Compound of a Rigid Tetradentate Ligand

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Abstract: Oxygenation of $[Cu^{I}(L^{1})(NCCH_3)]^{+}$ (L^{1} = dimethyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-on-1,5-dicarboxylate) leads to a relatively stable μ-peroxo-dicopper(II) product. The stability of this type of oxygenation product has been shown before to be the result of the square pyramidal geometry of L^{1}; preorganization by a dinucleating ligand has been shown to increase the stability of the μ-peroxo-dicopper(II) compound. The structural data presented here indicate that destabilization of the copper(I) precursor is another important factor. There are two isomers of $[Cu^{I}(L^{1})(NCCH_3)]^{+}$; one is yellow, and the other is red. X-ray crystallography indicates that one pyridinyl donor is not coordinated in the yellow compound and that the red compound is 5-coordinate. In the light of the X-ray structure of the metal-free ligand and that of the corresponding copper(II) compound, it emerges that the ligand cavity is well suited for copper(II), whereas the copper(I) compounds are highly strained. This is supported by ^{1}H NMR spectra of the copper(I) species where a fast dynamic process leads to line broadening and by electrochemical data, which indicate that the copper(II) products are exceptionally stable. Also presented are structural (copper(II)), electrochemical, and spectroscopic data (^{1}H NMR, copper(I)) of the derivative $[Cu(L^{2})(X)]^{n+}$ with a methyl substituent at the α-carbon atom of the two coordinated pyridinyl groups (L^{2} = dimethyl 2,4-bis(2-pyridinyl-6-methyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-on-1,5-dicarboxylate). There are two structural forms of $[Cu^{II}(L^{2})(X)]^{n+}$ ($X = NCCH_3$, Cl), which depend on the steric demand of the fifth donor X. For both, van der Waals repulsion leads to a destabilization of the copper(II) products, and this is also evident from an increase in the reduction potential (-110 mV vs. -477 mV, $Ag/AgNO_3$).

Keywords: alterdentate ligand · copper · entatic state · oxygenations · preorganization · rigid ligands

Introduction

Structural, spectroscopic, and functional model compounds for copper-containing proteins that transport or activate dioxygen have recently attracted much interest.[1–5] Hemocyanin and tyrosinase have dinuclear copper sites with a $[Cu_2(\mu\text{-}\eta\text{:}\eta\text{-}O_2)]^{2+}$ core (side-on peroxo bridge).[6, 7] Based on model studies, a number of other binding modes have been proposed, and these include mono-,[8] di-,[9–11] tri-,[12] and tetranuclear[13] copper sites. Dicopper(II) model compounds with μ-peroxo bridges (end-on) have been studied extensively.[3, 4, 14–16] Although the side-on dicopper(II)-peroxo[1, 2, 5, 17] and the dicopper(III)-dioxo modes[5, 11, 17] might, in terms of natural systems, be more relevant, the end-on μ-peroxo bridged compounds have been assumed to be important intermediates in oxygen transport and oxygen activation systems,[14, 15] and these might therefore also be of relevance for industrial processes.[18–21]

End-on μ-peroxo-dicopper(II) compounds have been found to be generally unstable, and only recently there have been a number of reports on carefully designed experiments to stabilize these and other peroxo dicopper(II) compounds at ambient temperature. These include stabilization by preorganized dinucleating ligands,[15, 16, 22, 23] with a careful choice of solvents,[15, 24] and by enforcing electronically preferred coordination geometries.[23] These experiments have all concentrated on the stability of the products, and a destabilization of the copper(I) precursor complexes that drives the equilibrium towards the peroxo-dicopper(II) products [Eq. (1)] has not been discussed so far.

$$2\,Cu^{I}L \overset{O_2}{\rightleftharpoons} LCu^{II}O_2{}^{-1}Cu^{II}L \qquad (1)$$

We have used the very rigid bispidine-type ligands with bispyridinyl – bis-amine donor sets (see given structure, L^{1} = dimethyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-

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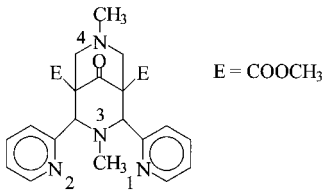

E = $COOCH_3$

on-1,5-dicarboxylate),[23, 25–27] which enforce a square pyramidal (or octahedral) coordination geometry when one (or two) additional ligands (substrates) are coordinated to the metal center. One of the tertiary amine donors (N4 in the given structure) generally is the axial ligand with M–N4 > M–N3.[23, 27–29] Thus, this ligand is highly preorganized for Jahn–Teller active systems, such as μ-peroxo-bridged dicopper(II) compounds. As expected, $[Cu_2(L^1)_2O_2]$ is stable up to approximately $-20\,^{\circ}C$, and the oxygenation product of the corresponding dicopper(I) compound with a preorganized bis-bispidine-type ligand, in which the two cavities are linked by an ethylene spacer group between the two tertiary amine donors N4 (see structure), is stable at room temperature. Raman spectra indicate that the stabilization of the Cu–O bonds is at the expense of a O–O bond weakening.[23]

We now present X-ray structural data which indicate that the stabilization of the μ-peroxo-dicopper(II) compounds is not only due to an electronic stabilization (enforced square-pyramidal structure, in-plane bonding of the μ-peroxo group[23]), and ligand preorganization (entropic effects[23]), but also to destabilization of the copper(I) precursor. Energization or entasis (the entatic state principle) has been much discussed in biochemistry, in particular in the context of metalloproteins, and few examples in the area of classical coordination compounds and technical processes have been presented so far.[30–32]

Abstract in German: *Die Oxygenierung von $[Cu^I(L^1)(NCCH_3)]^+$ (L^1 = Dimethyl 2,4-bis(2-pyridinyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-on-1,5-dicarboxylat) liefert ungewöhnlich stabile μ-peroxo-dikupfer(II) Produkte. Diese Stabilität wurde in einer früheren Arbeit darauf zurückgeführt, dass L^1 eine quadratisch pyramidale Koordinationsgeometrie erzwingt; durch Ligandenpräorganisation für eine zweikernige Einheit kann die Stabilität noch weiter erhöht werden. In der vorliegenden Arbeit wird gezeigt, dass die Destabilisierung des Kupfer(I) Edukts ein weiterer entscheidender Faktor ist. Von $[Cu^I(L^1)(NCCH_3)]^+$ existieren zwei Isomere, ein gelbes, bei dem nur einer der zwei Pyridinyldonoren koordiniert ist und ein rotes, das fünffach koordiniert ist. Aus diesen Strukturdaten, jenen des metallfreien Liganden und des Chloro-Kupfer(II) Komplexes von L^1 folgt, dass L^1 für Kupfer(II) gut vororganisiert ist und mit Kupfer(I) zu relativ gespannten Verbindungen führt. Dies wird durch ^{1}H-NMR Spektren der Kupfer(I) Spezies, welche von einer schnellen Dynamik dominiert werden und elektrochemischen Daten, die zeigen, dass die Oxidationsprodukte stark stabilisiert sind, unterstützt. ortho-Methylierung der Pyridinyl-Donoren (L^2 = Dimethyl 2,4-bis-(2-pyridinyl-6-methyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-on-1,5-dicarboxylat) führt zu einer Destabilisierung der Kupfer(II)produkte ($E^{\circ} = -110$ mV vs. -477 mV, Ag/$AgNO_3$). Abhängig vom sterischen Anspruch des fünften Donors ergeben sich zwei isomere Formen von $[Cu^{II}(L^2)X]^{n+}$ (X = $NCCH_3$, Cl).*

Results and Discussion

Copper(I) has a preference for tetrahedral coordination geometry, and acetonitrile is one of its favorite ligands. Thus, it is not surprising that the reaction of copper(I) trifluoromethanesulfonate $[Cu(CH_3CN)_4](O_3SCF_3)$[33] with the potentially tetradentate bispidine-type ligand L^1 (see structure) in acetonitrile yields a pale yellow product, whose crystal structural analysis indicates that the copper(I) center is coordinated by the two amine donors, one of the two pyridinyl groups, and the nitrogen donor of an acetonitrile molecule (Figure 1a; selected bond lengths and angles are given in Table 1). An interesting feature of this crystal structural analysis is that the orientation of the uncoordinated second pyridinyl donor is not much different from the coordinated one (Figure 1a). Thus, L^1 is an alterdentate ligand in this structure,[34] and a fast dynamic process is expected to occur in solution (see below).

Reaction of copper(I) tetrafluoroborate $[Cu(CH_3CN)_4](BF_4)$[35] with L^1 in acetonitrile yields a dark red product, and the elemental analyses indicate that the molecular cations of the yellow and red copper(I) compounds, $[Cu(L^1)(NCCH_3)]^+$, are isomers. The crystal structural analysis of the red isomer reveals that the copper(I) center is five-coordinate (two tertiary amine, two pyridinyl, and an acetonitrile donor, Figure 1b). Relevant structural data are given in Table 1.

From the rms overlay in Figure 1c, it emerges that the only significant structural differences are a torsional twist around N3–C–C–N of one of the pyridinyl donors of approximately 19°, a displacement of the copper(I) center of approximately 0.3 Å, and a twist of the acetonitrile molecule (N3–Cu–NA(acetonitrile) angle: 135° vs. 150°). In the yellow, four-coordinate structure, the bond lengths are not unusual for four-coordinate Cu^I–N_4 compounds (typical Cu^I–N_{amine} and Cu^I–$N_{pyridine}$ bond lengths are around 2.1–2.2 Å).[36–40] Unlike TMPA-type ligands (TMPA = tris(pyridylmethyl)amine), which have an intrinsic C_{3v} symmetry, our bispidine-type ligands possess C_{2v} symmetry. This implies that, if a metal ion is coordinated by all four donors, the complex itself should also have C_{2v} symmetry; if one of the donors is not coordinated, the symmetry is neither tetrahedral nor trigonal pyramidal. This is what actually is found for the yellow, four-coordinate copper(I) compound. In the red, five-coordinate structure, the rigid ligand is fully coordinated to copper(I), and this enforces a (distorted) square pyramidal coordination geometry. In other five-coordinate Cu^I–N_4X compounds, such as $[Cu(TMPA)(NCCH_3)]^+$,[41–43] $[Cu(py_2DAP)]^+$[44] (py_2DAP = bis-2,6-[1-((2-pyridine-2-ylethyl)imino)ethyl]pyridine), $[Cu(imidH_2DAP)]^+$[39] ($imidH_2DAP$ = 2,6-bis-[1-((2-imidazol-4-ylethyl)imino)ethyl]pyridine), a (distorted) trigonal-bipyramidal geometry is adopted due to the greater flexibility of the metal-free ligand. The average bond lengths in our red isomer are slightly longer than those in other

Table 1. Structural parameters[a] of the yellow, 4-coordinate isomer (a), and the red, 5-coordinate isomer (b) of $[Cu^{I}(L^{1})(NCCH_3)]^+$, $[Cu^{II}(L^{1})Cl]^{+}$[23] (c), L^1 (d), L^2 (e), $[Cu^{II}(L^{2})(NCCH_3)]^{2+}$ (f), and $[Cu^{II}(L^{2})(Cl)]^+$ (g).

	a	b	c	d	e	f	g
Cu–N1	2.0661(0.0026)	2.250(5)/2.169(4)	2.0204(0.0025)			2.052(0.004)	2.0614(0.0033)
Cu–N2	3.117	2.280(6)/2.247(5)	2.0240(0.0025)			2.075(0.004)	2.0640(0.0032)
Cu–N3	2.2030(0.0026)	2.244(5)/2.292(4)	2.0423(0.0025)			2.004(0.004)	2.1474(0.0033)
Cu–N4	2.1597(0.0026)	2.158(5)/2.186(4)	2.2725(0.0025)			2.376(0.004)	2.1200(0.0033)
Cu–X	1.8729(0.0031)	1.893(6)/1.937(5)	2.2320(0.0013)			1.950(0.005)	2.2208(0.0015)
N1–N2[b]	4.945	4.213/4.412	3.971	6.965(4.844)	7.203(4.642)	4.034	4.084
N3–N4	2.913	2.972/2.948	2.921	2.899	2.867	2.928	2.930
N3–C–C–N	– 61.1/ – 41.5	– 40/ – 40.9	– 37.2	130.5	151.9	– 29.8	– 46
N1–Cu–N2	144.31	144.71(19)/145.07(18)	158.13(0.10)			155.62(0.16)	163.82(0.13)
N3–Cu–X	134.18(0.11)	149.3(2)/155.0(2)	165.02(0.07)			174.32(0.17)	112.97(0.09)
N2–Cu–N4	85.13	95.34(18)/94.66(17)	95.36(0.10)			95.66(0.14)	90.26(0.13)
N3–Cu–N4	83.77(0.09)	84.07(17)/83.13(15)	85.03(0.09)			83.68(0.14)	86.71(0.12)
N4–Cu–N1	99.80	95.43(18)/96.33(15)	95.96(0.10)			99.04(0.15)	91.18(0.13)

[a] Bond lengths in Å, angles in degrees. [b] Cl–C2 in parentheses.

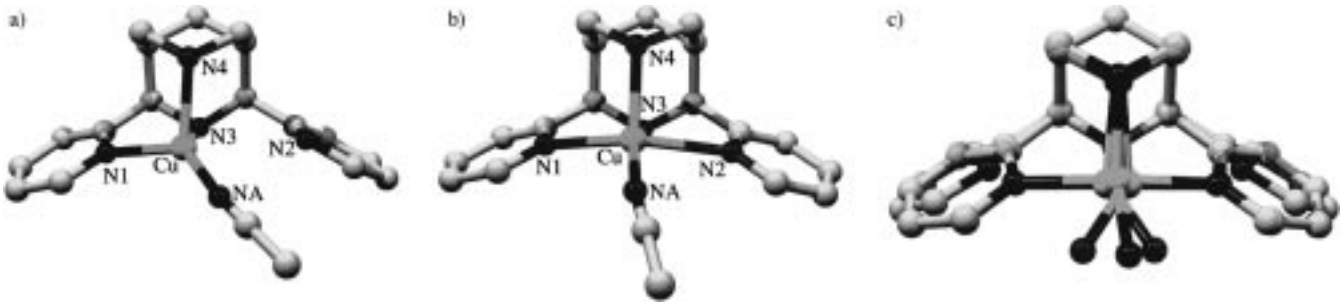

Figure 1. Plots of the crystallographically determined structures of $[Cu^{I}(L^{1})(NCCH_3)]^+$ (substituents of the bispidine backbone and H atoms omitted): a) yellow, four-coordinate isomer, b) red, five-coordinate isomer, and c) rms overlay of the two isomers.

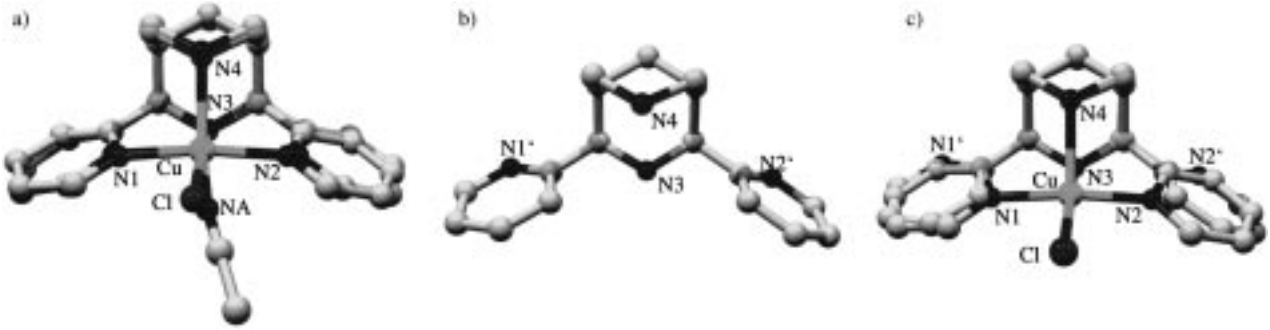

Figure 2. Plots of the crystallographically determined structures of $[Cu^{I}(L^{1})(NCCH_3)]^+$, $[Cu^{II}(L^{1})(Cl)]^{+}$,[23] and L^1 (substituents of the bispidine backbone and H atoms omitted): a) rms overlay of $[Cu^{I}(L^{1})(NCCH_3)]^+$ and $[Cu^{II}(L^{1})(Cl)]^+$, b) L^1 (metal-free ligand), and c) rms overlay of L^1 and $[Cu^{II}(L^{1})(Cl)]^+$.

$Cu^{I}N_4X$ compounds (2.17 – 2.21 Å compared with 2.11 – 2.14[39, 44] and 2.14 – 2.15 Å[41–43]). It emerges that the tetradentate ligand L^1 leads to significantly strained copper(I) compounds, and that the five-coordinate structure is similar to that of the corresponding copper(II) product. This is shown in Figure 2a, which is an rms overlay of the experimental structures of the red isomer of $[Cu^{I}(L^{1})(NCCH_3)]^+$ and of $[Cu^{II}(L^{1})(Cl)]^+$ (structural parameters of the copper(II) product are also given in Table 1).[23] The instability of $[Cu^{I}(L^{1})(NCCH_3)]^+$ might therefore be one of the reasons for the formation of a stable μ-peroxo-dicopper(II) oxygenation product[23] [Eq. (1)], and this has been discussed as the entatic state principle.[30–32]

The basis for these interesting structural properties and for the resulting reactivity of the copper(I) compound is the rigidity of the metal-free ligand, which is highly preorganized for coordination to copper(II).[23] This emerges also from the X-ray crystal structural analysis of the metal-free ligand (Figure 2b and Table 1) and an rms overlay with the previously reported[23] copper(II) structure (Figure 2c).

Ortho-methylation of the pyridinyl donors leads to the sterically more demanding bispidine-based ligand L^2 (L^2 = dimethyl 2,4-bis(2-pyridinyl-6-methyl)-3,7-diazabicyclo-[3.3.1]-nonane-9-on-1,5-dicarboxylate). From preliminary oxygenation experiments of the corresponding copper(I) compound, it emerges that the +1 oxidation state is stabilized with respect to $[Cu(L^{1})X]^{n+}$, and no peroxo-dicopper(II) intermediates were observed. There is slow, direct oxidation to the corresponding mononuclear copper(II) product. The crystal structural analyses of two $[Cu^{II}(L^{2})(X)]^{n+}$ compounds (X = $NCCH_3$, Cl) and of the metal-free ligand L^2 are shown in Figure 3, and relevant parameters are given in Table 1. As a

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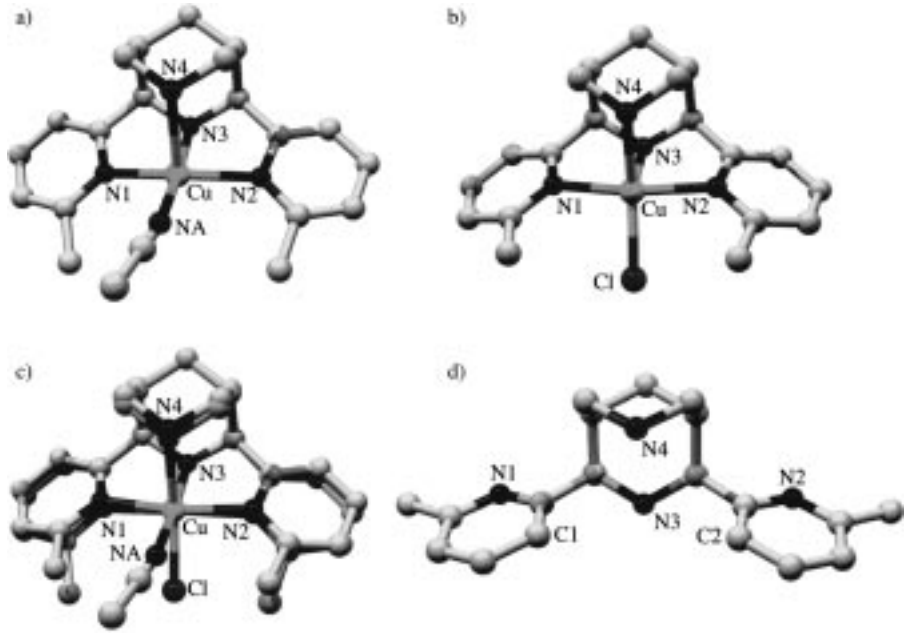

Figure 3. Plots of the crystallographically determined structures of $[Cu^{II}(L^2)(X)]^{n+}$ (substituents of the bispidine backbone and H atoms omitted): a) $[Cu^{II}(L^2)(NCCH_3)]^{2+}$, b) $[Cu^{II}(L^2)(Cl)]^{+}$, c) rms overlay of $[Cu^{II}(L^2)(NCCH_3)]^{2+}$ and $[Cu^{II}(L^2)(Cl)]^{+}$, and d) L^2 (metal-free ligand).

result of the steric demand of the methyl substituents, coordination of a monodentate ligand in the CuN_3 plane is difficult, and this probably is the major reason for the destabilization of the +2 oxidation state (products, peroxo-intermediates).

As both a four- and a five-coordinate structure of $[Cu^{I}(L^1)(NCCH_3)]^{+}$ are observed in the solid state, we assume that the energy difference between both structures is very small. Therefore, in solution (in the absence of crystal packing forces), both species and dynamic behavior should be observed. In the room-temperature ^{1}H NMR spectra of the copper(I) compounds of L^1, broad signals are observed. At $-40\,^{\circ}C$, the spectra sharpen, and all signals are well resolved. The low-temperature spectra are similar to those of the metal-free ligand (except for the expected chemical shift differences). This indicates that the ligand backbone in its coordinated form is symmetric, as expected from the crystal structure analysis (Figure 1), that is, the pyridinyl groups are equivalent. The ^{1}H NMR spectrum of the copper(I) compound of L^2 is well resolved at room temperature, that is, there is no fast dynamic process, and again the two pyridinyl groups are equivalent. This is in agreement with the structural observations (see above) and suggests that both pyridinyl groups are coordinated.

Cyclic voltammetry revealed quasireversible electron transfer for $[Cu(L^1)](PF_6)_2$ and $[Cu(L^2)](BF_4)_2$. The former compound exhibits a reduction wave at -477 mV against Ag/$AgNO_3$ and a relatively broad oxidation wave at -144 mV. Similar behavior (reduction at -110 mV, broad oxidation wave at $+100$ mV, shoulder (adsorption phenomenon) at $+50$ mV) is observed for $[Cu(L^2)](BF_4)_2$. The peak separations are relatively large (333 mV and 210 mV for $[Cu(L^1)](PF_6)_2$ and $[Cu(L^2)](BF_4)_2$, respectively; scan rate: 100 mV s^{-1}); this suggests a kinetic barrier to electron transfer at the surface of the glassy carbon electrode.[45] The positive shift of the electrochemical waves of $[Cu(L^2)]^{n+}$ relative to $[Cu(L^1)]^{n+}$ indicates a destabilization of the copper(I) oxidation state in $[Cu(L^1)]^{n+}$, and this is in agreement with the observed structural properties and reactivities of these compounds with respect to oxygen (see above).

Experimental Section

Measurements: ^{1}H NMR spectra were recorded on a Bruker AS200 (200.13 MHz), a General Electric QE300 (300.13 MHz), or a OMEGA600 (600 MHz) spectrometer in CD_3CN and referenced to internal TMS. Cyclic voltammetry (CV) measurements were recorded on a BAS100B instrument with a standard three electrode cell (a glassy carbon working electrode, a Ag/$AgNO_3$ reference electrode, and a Pt wire as auxiliary electrode) at room temperature in degassed CH_3CN, tetrabutylammonium hexafluorophosphate (0.1M), and copper complex (2×10^{-3}M). There was no difference in the measured potential at different scan rates.

X-ray structure analyses: ORTEP plots of all structurally characterized compounds have been made available as Supporting Information, and the crystallographic data have been submitted to CCDC. Crystallographic data are given in Table 2.

Single crystals of $[Cu(L^1)(NCCH_3)](O_3SCF_3)$ (a), $[Cu(L^1)(NCCH_3)](BF_4)$ (b), and $[Cu^{II}(L^2)(Cl)]Cl\cdot H_2O$ (g) were grown by slow diffusion of Et_2O into a solution of the complex in acetonitrile. Those of L^1 (d), L^2 (e), and $[Cu^{II}(L^2)(NCCH_3)](BF_4)_2$ (f) were grown by slow evaporation of a solution of the complex in acetonitrile. The data for a, b, d, and e were collected on a Bruker P4/RA (XSCANS-V2.2) instrument at $T=223$ K (a, b, and e) or 301 K (d). The data for f were collected on a BrukerAXS (CCD) at 173 K, and those for g on a Siemens-Stoe AED2 diffractometer at 218 K. Structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 with SHELXL-97.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120651, 120652, 120653, 119697, 119698, and 127339. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Materials: Reagents and solvents were used without purification; deoxygenation of solvents was done by bubbling N_2 through the solutions; preparation and handling of air-sensitive materials was done in a glovebox (N_2). L^1, L^2, and the piperidone precursors were prepared by published procedures.[25]

NMR spectral data for L^1 and L^2

Ligand L^1: ^{1}H NMR (200 MHz, CD_3CN): $\delta=8.45$ (d, $^3J_o=4.5$ Hz, 2H; py–CH3), 8.06 (d, $^3J_o=7.8$ Hz, 2H; py–CH6), 7.84 (t, $^3J_o=7.7$ Hz, 2H; py–CH5), 7.27 (t, $^3J_o=6.1$ Hz, 2H; py–CH4), 4.61 (s, 2H; bis–CH2, bis–CH4), 3.69 (s, 6H; OCH_3), 2.92 (d, $^2J_o=12$ Hz, 2H; bis–$CH6_{eq}$, bis–$CH8_{eq}$), 2.43 (d, $^2J_o=12$ Hz, 2H; bis–$CH6_{ax}$, bis–$CH8_{ax}$), 2.199 (s, 3H; N3–CH_3), 1.92 (s, 3H; N7–CH_3).

Ligand L^2: ^{1}H NMR (300 MHz, CD_3CN): $\delta=7.89$ (d, $^3J_o=7.8$ Hz, 2H; py–CH6), 7.74 (t, $^3J_o=7.6$ Hz, 2H; py–CH5), 7.15 (d, $^3J_o=7.2$ Hz, 2H; py–CH4), 4.57 (s, 2H; bis–CH2, bis–CH4), 3.74 (s, 6H; OCH_3), 2.84 (d, $^2J_o=12.3$ Hz, 2H; bis–$CH6_{eq}$, bis–$CH8_{eq}$), 2.43 (s, 6H; CH_3(py)), 2.38 (d,

Table 2. Experimental data of the X-ray diffraction studies of a, b, d, e, f, and g (see Table 1 and Experimental Section for the stoichiometries of a to g).

	a	b	d	e	f	g
formula	$C_{26}H_{29}CuF_3N_5O_8S$	$C_{26}H_{29}BCuF_4N_5O_5$	$C_{23}H_{26}N_4O_5$	$C_{25}H_{30}N_4O_5$	$C_{31}H_{39}B_2CuF_8N_7O_5$	$C_{27}H_{35}Cl_2CuN_5O_6$
color	yellow plate	red needle	colorless plate	colorless needle	blue needle	turquoise plate
size [mm]	(0.50 × 0.50 × 0.20)	(0.52 × 0.46 × 0.40)	(0.50 × 0.30 × 0.14)	(0.40 × 0.30 × 0.20)	(0.05 × 0.05 × 0.45)	(0.2 × 0.3 × 0.4)
crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pnma*	$P2_1/n$	$P2_1/c$
a [Å]	11.484(2)	12.470(1)	13.2496(6)	8.0279(16)	8.0763(12)	12.264(6)
b [Å]	12.003(1)	13.159(1)	18.361(1)	23.006(4)	25.367(4)	10.443(6)
c [Å]	12.865(3)	18.161(2)	9.0817(4)	13.4317(10)	17.932(3)	23.047(12)
α	112.85(1)	93.080(8)	90.00	90.00	90.00	90.00
β	107.98(2)	100.117(8)	93.549(7)	90.00	91.159(3)	96.33(4)
γ	101.01(1)	92.851(8)	90.00	90.00	90.00	90.00
V [Å^{-3}]	1453.3(4)	2924.1(5)	2205.1(2)	2480.7(7)	3673.0(9)	2931(3)
Z	2	4	4	4	4	4
ρ_{calcd} [mg m^{-3}]	1.582	1.431	1.321	1.249	1.50	1.50
λ [Å]	$Cu_{K\alpha}$ 1.54178	$Cu_{K\alpha}$ 1.54178	$Cu_{K\alpha}$ 1.54178	$Cu_{K\alpha}$ 1.54178	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073
$2\theta_{max}$ [°]	113.5	113.5	113.5	49.98	46.6	54.0
measured reflections	4323	8790	3703	1807	5259	6404
unique reflections/[$I > 2\sigma(I)$]	3667	7571	2810	1310	3734	3959
$R1$	0.040	0.076	0.050	0.0715	0.064	0.053
w$R2$	0.108	0.215	0.136	0.2075	0.178	0.121
parameters	398 parameters	759 parameters	290 parameters	164 parameters	504 parameters	500 parameters

$^2J_0 = 11.7$ Hz, 2H; bis−$CH6_{ax}$, bis−$CH8_{ax}$), 2.18 (s, 3H; N3−CH_3), 2.008 (s, 3H; N7−CH_3).[46]

Syntheses

[Cu(L¹)(CH₃CN)]BF₄: $[Cu(CH_3CN)_4]BF_4$[35] (72 mg, 0.23 mmol) in CH_3CN (1 mL) was added slowly to a suspension of L^1 (100 mg, 0.23 mmol) in CH_3CN (1 mL). The clear yellow/orange solution was put in a diethylether diffusion bath. After several hours, deep red crystals precipitated from the solution (yield: 83 mg, 0.13 mmol, 57%). ^{1}H NMR (600 MHz, −40 °C, CD_3CN): $\delta = 8.74$ (2H; py−CH3), 7.95 (t, $^3J_o = 7.3$ Hz, 2H; py−CH5), 7.57 (2H; py−CH6), 7.32 (2H; py−CH4), 4.997 (s, 2H; bis−CH2, bis−CH4), 3.79 (s, 6H; OCH_3), 3.08 (d, 2H; bis−$CH6_{eq}$, bis−$CH8_{eq}$), 2.82 (d, 2H; bis−$CH6_{ax}$, bis−$CH8_{ax}$), 2.48 (s, 3H; N3−CH_3), 1.88 (s, 3H; N7−CH_3); IR (KBr): $\tilde{\nu} = 3500-3000$ (w, C_{py}−H), 2954 (m, CH_2), 2868 (w, OC−H), 1738 (s, C=O, ketone), 1597 (m, C=N, py), 1438 (m, CH_2), 1273 (s, C−OCH_3), 1061 (s, B−F_4), 776 cm^{-1} (s, C_{ar}−H); UV/Vis: $\lambda_{max}(\varepsilon) = 345$ (sh, 1944), 300 (sh, 3750), 260 nm (1330); $C_{25}H_{29}N_5O_5CuBF_4$ (629.66): calcd C 47.67, H 4.64, N 11.12; found C 47.40, H 4.70, N 11.17.

[Cu(L¹)(CH₃CN)]OTF: $[Cu(CH_3CN)_4]OTF$[35] (86 mg, 0.23 mmol) in CH_3CN (1 mL) was added slowly to a suspension of L^1 (100 mg, 0.23 mmol) in CH_3CN (1 mL). The clear yellow/orange solution was put in a diethylether diffusion bath. After several hours, pale yellow crystals precipitated from the solution (yield: 93 mg, 0.13 mmol, 58.5%). IR (KBr): $\tilde{\nu} = 3500-3000$ (w, C_{py}−H), 2952 (m, CH_2), 2869 (w, OC−H), 1739 (s, C=O, ketone), 1599 (m, δ C=N, py), 1440 (m, CH_2), 1288, 1260 (s, C−OCH_3), 780 cm^{-1} (s, C_{ar}−H); UV/Vis: $\lambda_{max}(\varepsilon) = 390$ (1375), 300 (sh, 2750), 260 nm (12100); $C_{26}H_{29}N_5SO_8CuF_3$ (691.92): calcd C 45.12, H 4.22, N 10.12; found C 44.90, H 4.07, N 9.87.

[Cu(L²)]OTF: $[Cu(CH_3CN)_4]OTF$[35] (79 mg, 0.21 mmol) in CH_3CN (1 mL) was added slowly to a suspension of L^2 (100 mg, 0.21 mmol) in CH_3CN (1 mL). The clear orange solution was put in a diethylether diffusion bath. After several hours, orange crystals precipitated from the solution (yield: 60 mg, 0.09 mmol, 42.1%). ^{1}H NMR (300 MHz, CD_3CN): $\delta = 7.78$ (t, $^3J_o = 7.8$ Hz, 2H; py−CH6), 7.38 (d, $^3J_o = 7.5$ Hz, 2H; py−CH5), 7.19 (d, $^3J_o = 7.5$ Hz, 2H; py−CH4), 4.70 (s, 2H; bis−CH2, bis−CH4), 3.89 (d, $^2J_0 = 13.2$ Hz, 2H; bis−$CH6_{eq}$, bis−$CH8_{eq}$), 3.67 (s, 6H; OCH_3), 2.88 (d, $^2J_0 = 14.7$ Hz, 2H; bis−$CH6_{ax}$, bis−$CH8_{ax}$), 2.69 (s, 6H; CH_3(py)), 2.68 (s, 3H; N3−CH_3), 1.998 (s, 3H; N7−CH_3); $C_{26}H_{30}N_4SO_8CuF_3$ (678.5): calcd C 45.98, H 4.45, N 8.25; found C 45.88, H 4.42, N 8.41.

[Cu(L²)Cl]Cl·H₂O: $CuCl_2 \cdot 2H_2O$ (17 mg, 0.1 mmol) in CH_3CN (0.7 mL) was added slowly to a suspension of L^2 (47 mg, 0.1 mmol) in CH_3CN (0.7 mL). The blue/green solution was put in a diethylether diffusion bath. After one day, blue crystals precipitated from the solution (yield: 50 mg, 0.08 mmol, 81%). $C_{25}H_{32}N_4O_6CuCl_2$ (618.75): calcd C 48.50, H 5.21, N 9.05; found C 47.80, H 4.92, N 8.93.

[Cu(L²)(NCCH₃)](BF₄)₂: $[Cu(CH_3CN)_4]BF_4$[35] (34 mg, 0.105 mmol) in CH_3CN (0.5 mL) was added slowly to a suspension of L^2 (50 mg, 0.105 mmol) in CH_3CN (0.5 mL). Slow oxygenation by air led to a blue/green solution, which was put in an diethylether diffusion bath. After two days, turquoise needles precipitated from the solution. They were recrystallized from CH_3CN (1 mL) and vacuum dried (yield: 20 mg, 0.03 mmol, 53%).

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