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Synthesis, characterization and crystal structures of copper(II) complexes containing multidentate polypyridine ligands †

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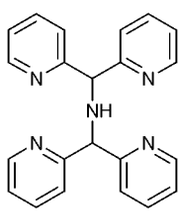
Three mononuclear copper(II) complexes of the tetrapyridyl ligand bis[di(2-pyridyl)methyl]amine have been synthesised and crystallized. The corresponding X-ray crystal structures displayed different geometries around the metal ion, which are mainly induced by the nature of the anionic ligands of the copper(II) salt. $Cu(BDPMA)Cl_2$ **1**, $Cu(BDPMA)(SO_4)MeOH$ **2** and $[Cu(BDPMA)(BF_4)CH_3CN]BF_4$ **3** exhibited distorted trigonal bipyramidal, square pyramidal and octahedral geometries, respectively. FAB mass spectra and ESR spectra of crystalline samples and frozen solutions suggested that the overall structures are not modified for complexes **1**–**3** on going from the solid to the solution states.

Introduction

Coordination chemistry of copper complexes constitutes a wide field of research. Copper-containing proteins are involved in dioxygen metabolism and have a variety of physiological functions such as dioxygen carriers, oxidases, oxygenases and superoxide dismutase.[1] Due to the redox behavior of Cu(II)/Cu(I) couples and the interaction of copper complexes with O_2, biomimetic models of copper-containing proteins have been prepared. These mono- and di-nuclear copper complexes are based on macrocyclic, capping multidentate (di-, tri- and tetra-dentate) or binucleating ligands. These ligands often contain pyridine, imidazole, pyrazole, quinoline or histidine groups (for a recent review, see ref. 2). Among these, Tanaka *et al.* reported a series of $[Cu^{II}X(Me_ntpa)]^{m+}$ complexes (X = Cl, H_2O; tpa = tris(2-pyridylmethyl)amine; n = 1,2,3; m = 1,2) and their ability to reduce NO_2^- ions.[3] Masuda *et al.* described the first mononuclear example of a crystallographically isolated copper–hydroperoxo complex cation $[Cu^{II}(bppa)(OOH)]^+$, in which bis(6-pivalamide-2-pyridylmethyl)(2-pyridylmethyl)-amine (bppa) acts as a tetradentate ligand.[4] Tolman has established that the two isomers of dicopper(II) complexes, namely $[(L^{iPr_3}Cu_2)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}O_2)]^{2+}$ and $[(L^{iPr_3}Cu_2)(\mu\text{-}O_2)]^{2+}$ (L^{iPr_3} = 1,4,7-triisopropyl-1,4,7-triazacyclononane), can interconvert, illustrating for the first time reversible scission and formation of the dioxygen O–O bond in a binuclear complex.[5]

In our group, we have focused our interest on a non-heme tetrapyridyl ligand bis-[di(2-pyridyl)methyl]amine (BDPMA)[6] (Fig. 1) and corresponding mononuclear first-row transition metal complexes,[7] in order to investigate their capacities as non-heme biomimetic catalysts. The BDPMA ligand was synthesised in a one-pot two step reaction from di(2-pyridyl)-methylamine and di(2-pyridyl)ketone on a large scale and with a good yield (70%). The preparation of manganese, iron and cobalt complexes of BDPMA led to two different classes of compounds, that have been crystallographically characterised.[7] The two complexes of general formula $Mn^{II}(BDPMA)Cl_2$ and $[Fe^{III}(BDPMA)_2(O)Cl_2]Cl_2$ constituted the first category. The second one corresponded to oxidative degradation products of the starting BDPMA ligand, namely the cationic species TPIP or one of the starting materials used in the preparation



BDPMA

Fig. 1 Structure of BDPMA.

of BDPMA, di(2-pyridyl)ketone (for a proposed mechanism, see ref. 7). The latter compounds were illustrated by the X-ray crystal structures of $[TPIP]NO_3$,[8] when starting from BDPMA and $Fe^{III}(NO_3)_3{\cdot}9H_2O$, and $[Co^{III}(DPKH)_2(MeO)(MeOH)]$ [DPKH = di(2-pyridyl)ketone hydrate], when using BDPMA and $Co^{II}(OAc)_2{\cdot}4H_2O$.

In this paper, we describe the preparation, characterization and crystal structures of mononuclear copper(II) complexes containing the intact BDPMA ligand. The present work illustrates the modifications of the ligand geometry around the metal centre, depending on the nature of the copper salt used in the preparation of the different complexes. Additionally, the crystal structures of a metal-catalysed oxidative degradation product of BDPMA, namely 1,3,3-tris(2-pyridyl)-3*H*-imidazo-[1,5-*a*]pyridin-4-ium (see Scheme 1 for the representation of TPIP) and a copper(II) complex obtained when starting from the cationic TPIP ligand are also described.

Results and discussion

We present herein the complexation of BDPMA with different copper(II) salts, *i.e.* $CuCl_2$, $CuSO_4{\cdot}5H_2O$ and $Cu(BF_4)_2{\cdot}6H_2O$. Three stable mononuclear complexes were obtained by mixing stoichiometric amounts of the tetrapyridyl ligand and the desired metallic salt in MeOH or in a mixture of MeOH and CH_3CN and they were crystallized in an ethyl acetate atmosphere. All the copper(II) complexes contained the intact BDPMA ligand, so they belong to the first class of compounds described in the Introduction. The geometry of these complexes is controlled by the copper salt used and three different coordination spheres around the metallic centre have been obtained.

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3989/

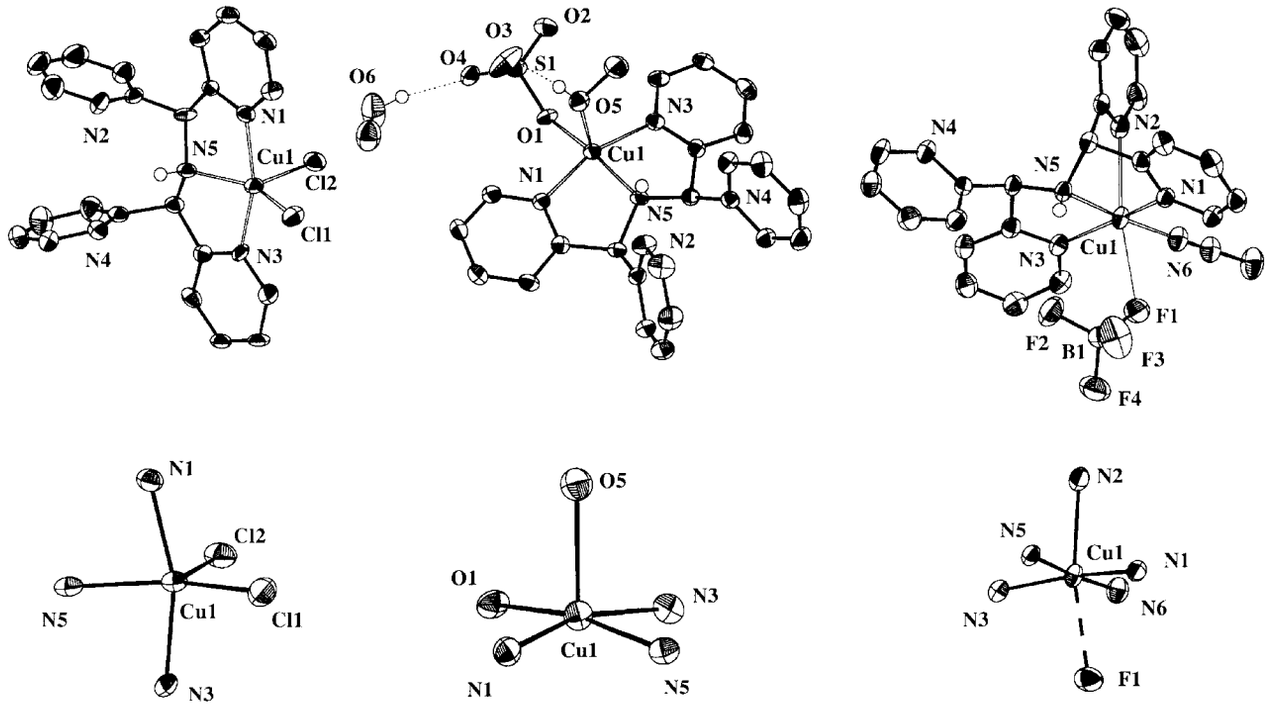


Fig. 2 X-Ray structures of Cu(BDPMA)Cl_2 **1**, Cu(BDPMA)(SO_4)MeOH **2** and [Cu(BDPMA)(BF_4)CH_3CN]BF_4 **3** (noncoordinated BF_4 and H atoms are omitted for clarity) and representation of the geometries around the copper(II) for complexes **1**–**3**.

X-Ray structures of complexes Cu(BDPMA)Cl_2 1, Cu(BDPMA)(SO_4)MeOH 2 and [Cu(BDPMA)(BF_4)CH_3CN]BF_4 3

Three different crystallographic structures of the copper(II) complexes **1**–**3** are shown in Fig. 2 and selected bond distances and angles are given in Tables 1–3, respectively.

The crystal structure of complex **1** consists of a mononuclear neutral Cu(BDPMA)Cl_2 entity and contains a CuN_3Cl_2 core in a slightly distorted trigonal bipyramidal geometry. BDPMA provides one equatorial and two axial nitrogen donor atoms, coming from the secondary amine and two pyridine groups respectively, the two other pyridines being uncoordinated. The coordination sphere is completed by two chloride anions, in equatorial positions. The axial distances 1.997(4) for Cu–N(1) and 2.003(4) for Cu–N(3) Å respectively, are usual values for $Cu–N_{(pyridine)}$ bonds. The equatorial distances at 2.022(5) for Cu–N(5), 2.271(2) for Cu–Cl(1) and 2.477(2) Å for Cu–Cl(2), are slightly longer especially for the latter example. The N_{ax}–Cu–L_{eq} angles vary in a range from 81.0(2) for N(3)–Cu–N(5) to 97.6(1) for N(1)–Cu–Cl(1), all being within 10° of the ideal 90°. The equatorial angles are 144.2(2) for N(5)–Cu–Cl(1), 103.9(1) for N(5)–Cu–Cl(2) and 112.0(1) for Cl(1)–Cu–Cl(2). In complex **1**, the BDPMA ligand acts only as a tridentate mononucleating ligand. In order to facilitate the possible coordination of the two other pyridine units, we decided to use other copper(II) salts in which the anions, *i.e.* SO_4^{2-} and BF_4^-, should have less binding properties.

The crystal structure of complex **2** consists of a mononuclear neutral Cu(BDPMA)(SO_4)MeOH entity and a lattice methanol molecule. But as for complex **1**, BDPMA provides only three nitrogen donor atoms in complex **2**, one amine and two pyridine nitrogens, the two other pyridine groups remaining free. The sulfate dianion acts as a monodentate ligand and is stabilized through hydrogen interactions arising from two methanol molecules, one of which is coordinated to the copper(II). The coordination around the metal ion is best described as a distorted square pyramidal geometry CuN_3O_2, in contrast to the trigonal bipyramidal geometry found for complex **1**. Three BDPMA nitrogen donor atoms and one sulfate oxygen atom constitute the basal plane and the fifth coordination position is occupied by a weakly coordinated methanol oxygen atom, with a Cu–O(5) distance of 2.278(2) Å. The four equatorial bonds to the copper(II) lie in the range of 1.932(2) to 1.989(3) Å.

Table 1 Selected bond distances (Å) and angles (°) for Cu(BDPMA)Cl_2 **1**

Cu–N(1)	1.997(4)	Cu–Cl(1)	2.271(2)
Cu–N(3)	2.003(4)	Cu–Cl(2)	2.477(2)
Cu–N(5)	2.022(5)		
N(1)–Cu–N(3)	161.9(2)	N(3)–Cu–Cl(1)	96.4(1)
N(1)–Cu–N(5)	81.0(2)	N(3)–Cu–Cl(2)	92.2(1)
N(3)–Cu–N(5)	81.0(2)	N(5)–Cu–Cl(1)	144.2(2)
N(1)–Cu–Cl(1)	97.6(1)	N(5)–Cu–Cl(2)	103.9(1)
N(1)–Cu–Cl(2)	93.2(1)	Cl(1)–Cu–Cl(2)	112.0(1)

Table 2 Selected bond distances (Å) and angles (°) for Cu(BDPMA)(SO_4)MeOH **2**

Cu–N(1)	1.989(3)	S(1)–O(1)	1.520(2)
Cu–N(3)	1.972(3)	S(1)–O(2)	1.446(3)
Cu–N(5)	1.989(3)	S(1)–O(3)	1.472(3)
Cu–O(1)	1.932(2)	S(1)–O(4)	1.465(3)
Cu–O(5)	2.278(2)		
N(1)–Cu–N(3)	162.3(1)	N(3)-Cu–O(5)	100.5(1)
N(1)–Cu–N(5)	82.3(1)	N(5)–Cu–O(1)	168.6(1)
N(3)–Cu–N(5)	83.2(1)	N(5)–Cu–O(5)	93.5(1)
N(1)–Cu–O(1)	95.4(10)	O(1)–Cu–O(5)	97.7(1)
N(1)–Cu–O(5)	90.5(1)	S(1)–O(1)–Cu	131.1(1)
N(3)–Cu–O(1)	96.8(1)		

The crystal structure of [Cu(BDPMA)(BF_4)CH_3CN]BF_4 **3** indicates that the copper atom is in a distorted octahedral coordination environment, consisting of four nitrogen donor atoms of the BDPMA ligand, a fluorine atom from a BF_4^- ion and one nitrogen atom from an acetonitrile molecule. The square plane is formed by four nitrogen donor atoms, two pyridine nitrogens arising from each di(2-pyridyl)methyl moiety, the secondary amine nitrogen of BDPMA and the nitrogen of the solvent molecule. The equatorial bond distances within the plane are in the range of 1.974(3) to 2.010(2) Å. The

Table 3 Selected bond distances (Å) and angles (°) for [Cu(BDPMA)-$(BF_4)CH_3CN]BF_4$ **3**

Cu–N(1)	2.010(2)	Cu–F(1)	2.534(2)
Cu–N(2)	2.333(2)	B(1)–F(1)	1.392(4)
Cu–N(3)	1.990(2)	B(1)–F(2)	1.379(4)
Cu–N(5)	2.006(2)	B(1)–F(3)	1.366(4)
Cu–N(6)	1.974(3)	B(1)–F(4)	1.375(4)
N(1)–Cu–N(2)	84.7(1)	N(2)–Cu–F(1)	166.8(1)
N(1)–Cu–N(3)	159.8(1)	N(3)–Cu–N(5)	82.7(1)
N(1)–Cu–N(5)	80.8(1)	N(3)–Cu–N(6)	99.0(1)
N(1)–Cu–N(6)	98.3(1)	N(3)–Cu–F(1)	90.2(1)
N(1)–Cu–F(1)	82.2(1)	N(5)–Cu–N(6)	176.0(1)
N(2)–Cu–N(3)	103.0(1)	N(5)–Cu–F(1)	102.1(1)
N(2)–Cu–N(5)	77.5(1)	N(6)–Cu–F(1)	81.7(1)
N(2)–Cu–N(6)	98.5(1)	Cu–F(1)–B(1)	121.6(2)

axial positions are occupied by another pyridine nitrogen of the BDPMA ligand, with a long Cu–N(2) distance of 2.333(2) Å, and a weakly coordinated BF_4^- anion. The Cu–F(1) bond distance of 2.534(2) Å is similar to interactions of this type observed previously[9] [*i.e.* $[Cu^{II}L][BF_4]_2$ L = bis[4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole] with a Cu–F distance of 2.515(3) Å] and has been designated as 'semi-coordination'.[10] The BF_4^- ion shows no disorder and is nearly regular tetrahedral, with mean B–F distance 1.377 Å and mean angle 109.5°. The electroneutrality of complex **3** is ensured by an ionic BF_4^-.

Properties of complexes 1–3

The FAB mass spectra were consistent with the X-ray data and demonstrated that the structures of the copper(II) complexes involving BDPMA are maintained in solution. The expected molecular ion peaks were observed at $m/z = 451$ for $[Cu^{II}(BDPMA)(Cl^-)]^+$ (100%), $m/z = 513$ for $[Cu^{II}(BDPMA)(SO_4^{2-}) + H^+]^+$ (100%) and $m/z = 503$ for $[Cu^{II}(BDPMA)(BF_4^-)]^+$ (11%). In the case of complex **3**, the major peak $[Cu^{II}(BDPMA)(F^-)]^+$ (100%) still contained a fluorine ligand released possibly from the BF_4^- anion.

The room temperature X-band ESR spectra of powder samples of **2** and **3** are best described as isotropic signals centered at 2.07 and 2.06 respectively, suggesting that the copper(II) centers of these two complexes are not magnetically diluted. Lowering the temperature to 90 K did not modify the spectra. In contrast, the X-band ESR spectrum of a powder sample of complex **1** at 90 K showed anisotropic absorptions with three g values ($g_1 = 2.241$, $g_2 = 2.108$ and $g_3 = 2.026$), consistent with the presence of magnetically isolated copper(II) centers. ESR spectra of complexes **1**, **2** and **3** in 80/20 mixtures of CH_2Cl_2–DMF glasses at 90 K are quite similar and resolved into parallel and perpendicular components. They exhibited two identifiable magnetic g values along with the corresponding copper ($I = 3/2$) hyperfine splitting constants with the following values: $g_\parallel = 2.24$, $A_\parallel = 172$ G and $g_\perp = 2.05$ for **1**; $g_\parallel = 2.27$, $A_\parallel = 174$ G and $g_\perp = 2.04$ for **2**; $g_\parallel = 2.27$, $A_\parallel = 175$ G and $g_\perp = 2.07$ for **3**. A poorly resolved super-hyperfine coupling was observed on the perpendicular component for complexes **2** and **3**: seven lines can be detected with a spacing comprised between 20 and 15 G, suggesting interactions of the unpaired spin with three nitrogen nuclei ($I = 1$). Practically, observed axial spectra with $g_\parallel > g_\perp$ were consistent with the X-ray crystal structures of complexes **1**–**3**. The similarity of the g values in the solid and solution states corroborated the mass spectra results and indicated that the overall structures of these three complexes are probably retained in solution.

Electrochemical measurements on the copper(II) complex **1** were investigated. A cyclic voltammogram of **1** in CH_3CN (0.1 M tetrabutylammonium hexafluorophosphate, scan rate 100 mV s^{-1}) showed a one-electron (confirmed by bulk electrolysis) quasi-reversible (peak to peak separation ΔEp: 136 mV) electrochemical reduction at −207 mV/SCE. The i_{pc}/i_{pa} ratio of 0.56 is indicative of a poor chemical stability of the reduced copper(I) species. This fact was confirmed after electrolysis: the cyclic voltammogram contained a new quasi-reversible wave close to −800 mV/SCE and the UV-visible spectrum showed no characteristic MLCT band, both in favor of a demetalation. The electrochemical investigations of complex **1** revealed that BDPMA was not able to stabilize the low oxidation state in the corresponding copper complexes. This is probably due to the involvement of strong configuration changes and the too short arms of BDPMA probably does not allow a tetrahedral geometry around the copper(I) cation.

X-Ray structure of $[TPIP]BF_4$ 4

The obtention of crystal of complexes **1**–**3** indicated that the BDPMA ligand remains intact in the presence of copper(II) salts, since corresponding complexes are rapidly formed. These results contrast with those obtained when exposing this ligand, in solution, to iron or cobalt salts, namely $Fe(NO_3)_3 \cdot 9H_2O$[8] or $Co(OAc)_2 \cdot 4H_2O$.[7] The corresponding crystallized products evidenced only oxidative degradation products of the starting BDPMA ligand. BDPMA alone is stable in solution but the activation of the fragile benzylic C–H bonds in a position α to the heteroatom can occur in the presence of a Lewis acid. There is a kinetic competition between the rapid formation of stable complexes containing BDPMA and metal-catalysed reactions that occurred in solution and led to the decomposition of the starting tetrapyridyl ligand. In fact, the degraded products $[TPIP]NO_3$,[8] $[Co^{III}(DPKH)_2(MeO)(MeOH)]$[7] (DPKH: di(2-pyridyl)ketone hydrate) crystallized over a period from two weeks to two months while the presently described copper(II) complexes were isolated as single crystals within a day. This competition between ligand coordination or ligand degradation is well illustrated in the case of $Cu(BF_4)_2 \cdot 6H_2O$. The first crop of blue crystals (46%) corresponded to complex **1** involving the BDPMA ligand and, from the mother liquor, red crystals **4** (8%) were isolated after one further week. It is interesting to note that stable BDPMA complexes were more easily isolated when metallic salts containing strong binding anions like chlorides were used. On the other hand, the use of metallic salts having anions like nitrates, acetates or tetrafluoroborates, favored the degradation of the initial BDPMA ligand. This could be explained by the fact that since BDPMA acts as a tri- or a tetra-dentate ligand, no well defined saturated coordination sphere around the metal centre can be fully stabilized.

The crystal structure of the cationic containing ligand $[TPIP]BF_4$ **4** is shown in Fig. 3 and selected bond lengths and angles are given in Table 4. As mentioned above, the cationic ligand TPIP has been already obtained with a nitrate as counter ion.[8] The main feature of **4** is the presence of an imidazopyridinium entity, in which the positively charged nitrogen N(2) is both connected to a six- and a five-membered ring. Three free pyridines complete the ligand and are branched at the C(1) and C(7) carbon atoms of the five-membered ring. The C(7)–N(1) bond of the five-membered ring has a short length of 1.282(3) Å, which is in good agreement with a double bond in this position.

X-Ray structure of $Cu(DPMMDPI)Cl_2$ 5

The coordination ability of the TPIP ligand was investigated with several first-row transition metals. Two categories of products were thus obtained, the first one corresponding to the already described cation TPIP, with a simple exchange of the counter ion: $[TPIP](Fe^{III}Cl_4)$, $[TPIP]_2(Mn^{II}Cl_4)$ and $[TPIP]_2(Co^{II}Cl_4)$, when starting from $FeCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$

Table 4 Selected bond distances (Å) and angles (°) for [TPIP]BF_4 **4**

C(1)–N(1)	1.442(3)	C(2)–N(2)	1.343(3)
C(7)–N(1)	1.282(3)	C(6)–N(2)	1.359(3)
C(1)–N(2)	1.494(3)		
C(1)–N(1)–C(7)	109.8(2)	C(1)–N(2)–C(6)	109.1(2)
C(2)–N(2)–C(6)	122.4(2)	N(1)–C(1)–N(2)	103.9(2)
C(1)–N(2)–C(2)	128.5(2)		

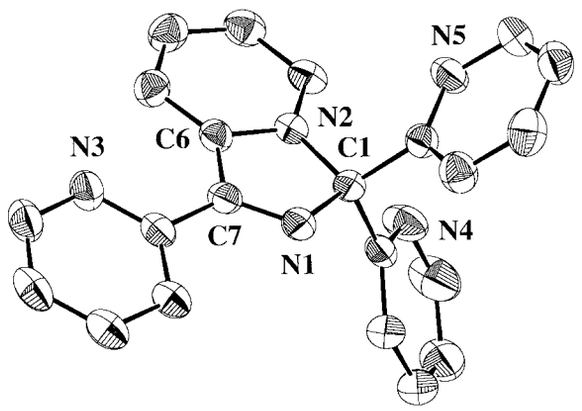


Fig. 3 X-Ray structure of [TPIP]BF_4 **4**, noncoordinated BF_4 and H atoms are omitted for clarity.

and $CoCl_2 \cdot 6H_2O$ as metallic salts respectively.[7] In contrast, mononuclear complexes crystallized upon mixing stoichiometric amounts of TPIP (as nitrate form) and $FeCl_2 \cdot 4H_2O$[7] or $CuCl_2$ in methanol. The X-ray analyses of the two corresponding complexes show analogous structures, which is illustrated by the neutral entity Cu(DPMMDPI)Cl_2 (DPMMDPI stands for *N*-[di(2-pyridyl)methoxymethyl][di(2-pyridyl)]imine) **5** in Fig. 4. Corresponding selected bond distances and angles are given in Table 5.

It is important to note that TPIP is highly stable in a methanolic solution. So, as also observed for the transformation of BDPMA to TPIP,[8] the starting ligand TPIP can also undergo a metal-assisted modification, leading this time to the new tetrapyridyl ligand DPMMDPI. The first step is probably a coordination of copper(II) to the two pyridine nitrogens N(3) and N(5) and to the imidazole nitrogen N(1) of TPIP, leading to a significant constraint in the molecule due to a pinching effect (Scheme 1). The ring system then became more electrophilic and this allowed an attack of the weak nucleophilic methanol molecule, followed by the opening of the imidazolium ring (Scheme 1).

In the crystal structure of complex **5**, the copper atom is in a distorted square pyramidal environment like in complex **2**, in which the square plane is formed by two pyridine N(1) and N(3) and one imine N(5) nitrogen atoms and the chloride anion Cl(2). The equatorial Cu–N bond distances are comparable to those of complex **2**. The second chloride Cl(1) occupies the axial position with a longer distance of 2.423(1) Å. The two noticeable characteristics of the DPMMDPI ligand are the presence of (i) an imine function with a short bond length C(6)–N(5) of 1.299(6) Å, and (ii) a methoxy group attached at the C(17) carbon and adjacent to the imine function.

Conclusion

The present study demonstrates that stable mononuclear copper(II) complexes containing the tetrapyridyl ligand BDPMA rapidly crystallize. The X-ray crystal structures of complexes **1**–**3** show three different coordination spheres around the metallic centre, which strongly depends on the nature of the anions of the copper(II) salt used in the preparation of these complexes. BDPMA behaves as a tri- or tetradentate ligand and the coordination spheres are completed by anions and/or solvent molecules, thus affording labile sites on the metal centre. Moreover, from FAB mass spectrometry and ESR measurements, complexes **1**–**3** are also stable in solution, without breaking down the general core of the corresponding molecules. These BDPMA copper(II) complexes will be tested in various catalytic oxidation reactions, in particular as a DNA cleaver by activation with ascorbate in the presence of dioxygen and with hydrogen peroxide.

Table 5 Selected bond distances (Å) and angles (°) for Cu^{II}(DPMMDPI)Cl_2 **5**

Cu–N(1)	2.006(4)	Cu–Cl(1)	2.423(1)
Cu–N(3)	1.997(4)	Cu–Cl(2)	2.259(1)
Cu–N(5)	1.987(4)	C(6)–N(5)	1.299(6)
N(1)–Cu–N(3)	158.7(2)	N(5)–Cu–Cl(1)	103.8(1)
N(1)–Cu–N(5)	80.3(2)	N(1)–Cu–Cl(2)	96.3(1)
N(3)–Cu–N(5)	80.0(2)	N(3)–Cu–Cl(2)	97.5(1)
N(1)–Cu–Cl(1)	94.5(1)	N(5)–Cu–Cl(2)	152.8(1)
N(3)–Cu–Cl(1)	98.0(1)	Cl(1)–Cu–Cl(2)	103.4(1)

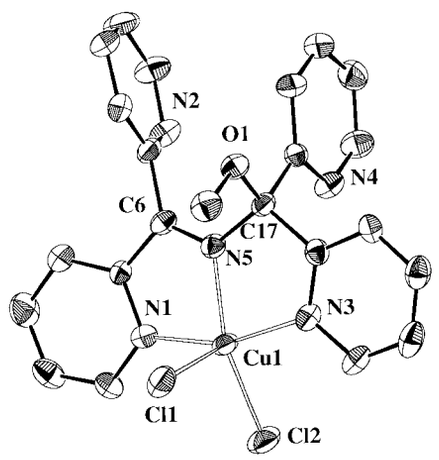
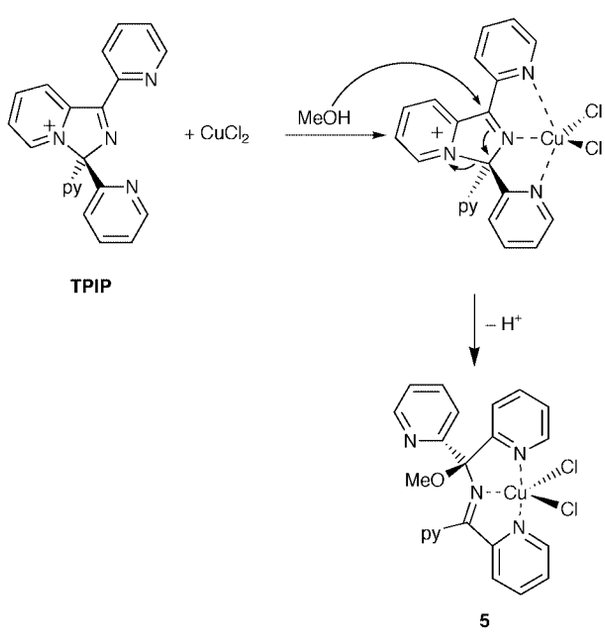


Fig. 4 X-Ray structure of Cu^{II}(DPMMDPI)Cl_2 **5**, H atoms are omitted for clarity.



Scheme 1 Metal-assisted opening of the imidazolium ring of TPIP to generate Cu^{II}(DPMMDPI)Cl_2 **5**.

Table 6 Crystal structure data of **1** to **5**

	1	**2**	**3**	**4**	**5**
Chemical formula	$C_{22}H_{19}Cl_2CuN_5$	$C_{24}H_{27}CuN_5O_6S$	$C_{24}H_{22}B_2CuF_8N_6$	$C_{22}H_{16}BF_4N_5$	$C_{23}H_{19}Cl_2CuN_5O$
Formula weight	487.86	577.11	631.64	437.21	515.87
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/n$
μ/mm^{-1}	1.283	1.014	0.913	0.115	1.289
R ($I > 2\sigma(I)$)	0.0433	0.0324	0.0362	0.0462	0.0387
$wR2$[a] (all data)	0.1051	0.0640	0.1015	0.1218	0.0813
a/Å	8.374(1)	12.506(1)	15.009(1)	8.405(1)	8.184(1)
b/Å	21.546(3)	12.998(1)	15.807(2)	8.828(1)	17.278(2)
c/Å	11.939(2)	15.891(2)	22.516(2)	14.235(2)	15.242(2)
α/°				76.23(2)	
β/°	92.98(2)	105.98(1)	99.45(1)	80.61(2)	90.61(2)
γ/°				77.32(2)	
V/Å^3	2151.2(5)	2483.3(4)	5269.4(9)	994.0(2)	2155.1(5)
Temp. of data collection/K	173(2)	173(2)	173(2)	163(2)	173(2)
Z	4	4	8	2	4
Measured reflections	13704	19178	16999	8094	17548
Independent reflections	3102	3558	4140	3003	3003
$R_{(int)}$	0.1067	0.0626	0.0403	0.0408	0.1030

[a] $wR2 = \{[\Sigma w(F_c^2 - F_o^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Experimental

General

Commercially available reagents and all solvents were purchased from standard chemical suppliers and used without further purification. BDPMA[6] and TPIP[8] were synthesized according to literature methods. Instrumentation used for routine characterizations has been described previously.[7] Electrochemical measurements were carried out on a home-made potentiostat, using the interrupt method to minimize the uncompensated resistance (IR) drop.[11] Electrochemical experiments were performed at room temperature in an airtight cell connected to a vacuum-argon line. Cyclic voltammograms were obtained with a three-electrode cell comprised of a platinum working electrode (1 mm diameter), a platinum spiral counter electrode (1 cm² apparent surface area, 8 cm long and 0.5 cm diameter) and a reference electrode. The reference electrode consisted of a saturated calomel electrode (SCE), separated from the non-aqueous solution by a bridged compartment containing the electrolyte support and the solvent described below. Linear voltammograms were performed with a platinum rotating disc. For electrolysis experiments, a platinum gauze was used. The supporting electrolyte was $(nBu_4N)PF_6$ 0.1 M and the solvent used CH_3CN.

Dichloro{bis[di(2-pyridyl)methyl]amine}copper(II) Cu(BDPMA)Cl$_2$ 1. To a solution of 94.5 mg (0.27 mmol) of BDPMA in 2 cm^3 of MeOH, a methanolic solution (1 cm^3) of 36 mg (0.27 mmol) of $CuCl_2$ was added. The mixture was stirred at room temperature for 1 h after which the solution was allowed to stand in an ethyl acetate bath for one day. Turquoise blue crystals of **1** were collected, washed with ethyl acetate and dried under vacuum (45 mg, 35%) (Found: C, 53.36; H, 4.24; N, 13.64. $C_{22}H_{19}CuCl_2N_5 \cdot MeOH$ requires C, 53.33; H, 4.44; N, 13.50%); *m*/*z* 451 ([Cu^{II}(BDPMA)(Cl$^-$)]$^+$, 100%), 416 ([Cu^I(BDPMA)]$^+$, 18); UV-Visible λ_{max}/nm (CH_3CN): 608 (ε/dm^3 mol^{-1} cm^{-1} 320), 712 (220).

Sulfatomethanol{bis[di(2-pyridyl)methyl]amine}copper(II), Cu(BDPMA)(SO$_4$)MeOH 2. To a solution of 117 mg (0.33 mmol) of BDPMA in 2 cm^3 of MeOH, a methanolic solution (2 cm^3) of 83 mg (0.33 mmol) of $CuSO_4 \cdot 5H_2O$ was added. After 1 h stirring at room temperature, **2** precipitated as an ultramarine blue microcrystalline solid. The complex was filtered, washed with ethyl acetate and dried under vacuum (120 mg, 67%) (Found: C, 48.99; H, 4.26; N, 12.67; S, 5.19. $C_{23}H_{23}CuN_5O_5S \cdot H_2O$ requires C, 49.06; H, 4.47; N, 12.43; S, 5.69%); *m*/*z* 513 ([Cu^{II}(BDPMA)(SO$_4^{2-}$) + H$^+$]$^+$, 100), 416 ([Cu^I(BDPMA)]$^+$, 18); UV-Visible λ_{max}/nm (CH_3CN): 682 (144). Slow evaporation of a methanolic solution of **2** in an ethyl acetate atmosphere gave deep blue crystals suitable for X-ray diffraction.

Tetrafluoroboratoacetonitrile{bis[di(2-pyridyl)methyl]amine}copper(II) tetrafluoroborate, [Cu(BDPMA)(BF$_4$)CH$_3$CN]BF$_4$ 3. To a solution of 164 mg (0.46 mmol) of BDPMA in 2 cm^3 of CH_3CN, a methanolic solution (2 cm^3) of 110 mg (0.46 mmol) of $Cu(BF_4)_2 \cdot 6H_2O$ was added. The resulting solution was stirred for 1 h at room temperature and upon addition of diethyl ether (50 cm^3), **3** precipitated as a blue green powder. After filtration and drying under vacuum, the complex was recrystallized by dissolving the solid in a MeOH–CH_3CN mixture. The resulting solution was allowed to stand in an ethyl acetate bath for one day. Blue crystals of **3** were collected (136 mg, 46%) (Found: C, 45.25; H, 3.38; N, 13.71; $C_{24}H_{22}CuB_2F_8N_6$ requires C, 45.64; H, 3.51; N, 13.30%); *m*/*z* 503 ([Cu^{II}(BDPMA)(BF4$^-$)]$^+$, 11), 435 ([Cu^{II}(BDPMA)(F$^-$)]$^+$, 100), 416 ([Cu^I(BDPMA)]$^+$, 91); UV-Visible λ_{max}/nm (CH_3CN): 672 (133).

1,3,3-Tris(2-pyridyl)-3*H*-imidazo[1,5-*a*]pyridin-4-ium tetrafluoroborate [TPIP]BF$_4$ 4. After one further week, the mother liquors of **3** gave red crystals **4**. They were washed with ethyl acetate and dried under vacuum (17 mg, 8%) (Found: C, 59.43; H, 3.59; N, 15.62. $C_{22}BF_4H_{16}N_5 \cdot 0.5H_2O$ requires C, 59.62; H, 3.87; N, 15.80%); *m*/*z* 350 ([TPIP]$^+$, 100).

Dichloro{[di(2-pyridyl)methoxymethyl][di(2-pyridyl)]imine}copper(II), Cu(DPMMDPI)Cl$_2$ 5. 50 mg (0.12 mmol) of [TPIP](NO_3) and 20 mg (0.15 mmol) of $CuCl_2 \cdot 4H_2O$ were dissolved separately in a total volume of 2 cm^3 of MeOH. The resulting solution was stirred for 15 min and then allowed to stand in a methyl *tert*-butyl ether bath. A precipitation started instantaneously and after 2 h the solution was almost colorless. The solid was filtered off and partially redissolved in 8 cm^3 of MeOH. The resulting solution was placed in a methyl *tert*-butyl ether bath. After 3 weeks, green needles of **5** were collected and dried under vacuum (15 mg, 24%) (Found: C, 53.46; H, 3.55; N, 13.52. $C_{23}H_{19}Cl_2CuN_5O$ requires C, 53.55; H, 3.71; N, 13.58%); *m*/*z* 478.8 ([Cu^{II}(DPMMDPI)Cl]$^+$, 100). UV-Visible λ_{max}/nm (CH_3CN): 680 (96).

Crystallography

Crystal data for all structures are presented in Table 6. All data were collected at low temperatures using an oil-coated shock-cooled crystal[12] on a Stoe-IPDS with Mo-Kα (λ = 0.71073 Å) radiation. The structures were solved by direct methods using SHELXS-97[13] and refined with all data on F^2 using SHELXL-97.[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealised and refined using a riding model. Disorders of the noncoordinated BF_4^- anions in **3** and **4** were refined anisotropically using ADP and distance restraints with the occupancies of 64/46 and 53/47, respectively. Selected bond lengths and angles of **1**–**5** can be found in Tables 1–5.

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See http://www.rsc.org/suppdata/dt/1999/3989/ for crystallographic files in .cif format.

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