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Reaction behaviour of dinuclear copper(I) complexes with *m*-xylyl-based ligands towards dioxygen

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Intramolecular ligand hydroxylation was observed during the reactions of dioxygen with the dicopper(I) complexes of the ligands L^1 (L^1 = α,α′-bis[(2-pyridylethyl)amino]-*m*-xylene) and L^3 (L^3 = α,α′-bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-*m*-xylene). The dinuclear copper(I) complex $[Cu_2L^3](ClO_4)_2$ (**3**) and the dicopper(II) complex $[Cu_2(L^1–O)(OH)(ClO_4)]ClO_4$ (**1**) were characterized by single-crystal X-ray structure analysis. Furthermore, phenolate-bridged complexes were synthesized with the ligand L^2–OH (structurally characterized $[Cu_2(L^2–O)Cl_3]$ (**7**) with L^2 = α,α′-bis[*N*-methyl-*N*-(2-pyridylethyl)amino]-*m*-xylene; synthesized from the reaction between $[Cu_2(L^2–O)(OH)](ClO_4)_2$ (**2**) and Cl^-) and Me–L^3–OH: $[Cu_2(Me–L^3–O)(\mu\text{-}X)](ClO_4)_2 \cdot nH_2O$ (Me–L^3–OH = 2,6-bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-4-methylphenol and X = $C_3H_3N_2^-$ (prz) (**4**), $MeCO_2^-$ (**5**) and N_3^- (**6**)). The magnetochemical characteristics of compounds **4–7** were determined by temperature-dependent magnetic studies, revealing their antiferromagnetic behaviour [$-2J$ (in cm^{-1}) values: −92 for **4**, −86 for **5** and −88 for **6**; −374 for **7**].

Introduction

Modelling of the copper enzyme *tyrosinase* (a monooxygenase causing hydroxylation of monophenols and subsequent oxidation of catechols to quinones)[1–5] was first performed successfully by Karlin and coworkers who found that an intramolecular ligand hydroxylation of the complex $[Cu_2(R–XYL–H)]^{2+}$ during its reaction with dioxygen occurred (Fig. 1).[6,7]

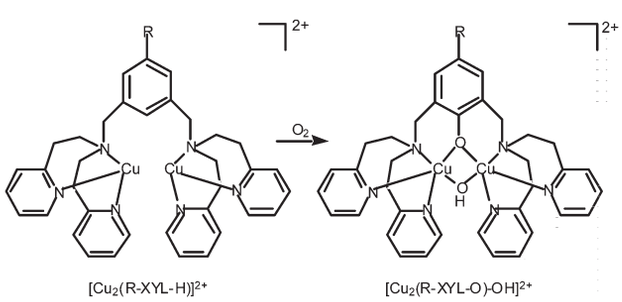

Fig. 1 Intramolecular ligand hydroxylation of $[Cu_2(R–XYL–H)]^{2+}$.

A detailed kinetic analysis performed at low temperature as well as a resonance Raman study revealed the formation of a μ-η^2:η^2-peroxo complex as an intermediate.[8–11] However, it has been shown that bis-μ-oxo copper units are also capable of performing ligand hydroxylation reactions.[12]

At present it remains unclear why substitution of the pyridine groups in $[Cu_2(R–XYL–H)]^{2+}$ with pyrazole or benzimidazole donors completely suppresses the above reaction, while with triazacyclononane units the intramolecular ligand hydroxylation reaction occurs.[13–21]

Furthermore, similar and structurally related binuclear copper(I) imine complexes also showed intramolecular ligand hydroxylation when reacted with dioxygen (Fig. 2), however, in these cases the intramolecular hydroxylation reaction was less sensitive towards ligand modifications.[15,22–32]

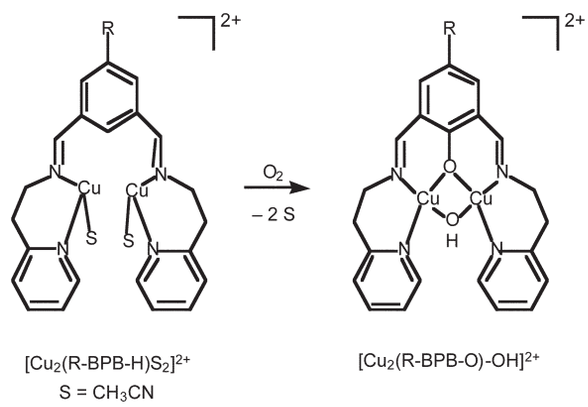

Fig. 2 Intramolecular ligand hydroxylation of $[Cu_2(H–BPB–H)S_2]^{2+}$.

The reaction of dioxygen with complexes derived from reduction of the imine bonds of such complexes (*e.g.* $[Cu_2(H–BPB–H)S_2]^{2+}$ in Fig. 2) has not been studied so far in detail, although phenolate bridged binuclear copper(II) complexes with such amine ligands are well known (a few examples are given in the references).[33–37]

Therefore, in our efforts to gain a better understanding of the intramolecular ligand hydroxylation reactions of xylyl-bridged dicopper complexes, we investigated the reactivity of dioxygen towards the dinuclear copper(I) complex of the ligand α,α′-bis[(2-pyridylethyl)amino]-*m*-xylene (L^1, Scheme 1), the reduced form of the imine H–BPB–H (Fig. 2). Additionally we analysed the reaction of dioxygen with the copper(I) complex of the ligand α,α′-bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-*m*-xylene (L^3) (Scheme 1) which differs from R–XYL–H (Fig. 1) by two shorter ligand "arms", leading to the formation of two smaller chelate rings in the metal complex.

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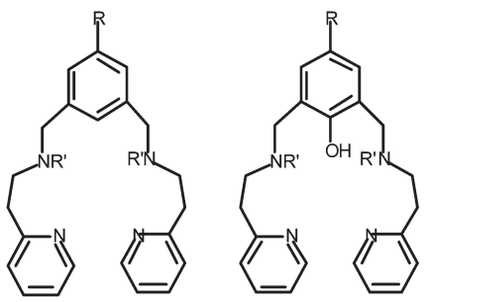
Table 1 Crystallographic data for **1, 3** and **7**

	1	**3**	**7**
Molecular formula	$C_{22}H_{28}Cl_2Cu_2N_4O_{11}$	$C_{37}H_{42}Cl_2Cu_2N_6O_9$	$C_{24}H_{29}Cl_3Cu_2N_4O$
M_r	722.46	912.75	622.94
T/K	183(2)	100(2)	293(2)
Radiation used (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	10.570(5)	8.8457(5)	9.931(4)
b/Å	12.130(5)	12.839(2)	16.66(2)
c/Å	12.360(5)	18.430(2)	17.64(2)
α/°	68.590(5)	75.861(6)	61.26(5)
β/°	73.080(5)	78.533(5)	87.52(5)
γ/°	71.198(5)	85.776(6)	87.59(5)
V/Å^3	1369(1)	1988.5(4)	2557(4)
Z	2	2	4
D_c/g cm^{-3}	1.752	1.524	1.618
μ/mm^{-1}	1.814	1.265	2.002
Reflections measured	9128	51968	7019
Unique reflections, R_{int}	5370, 0.1048	8770, 0.0952	6583, 0.0987
Refined parameters	384	507	609
Goodness-of-fit on F^2	1.029	1.049	1.031
$R(F, F^2 > 2\sigma)$	0.0836	0.0447	0.0964
$R_w(F^2$, all data)	0.2358	0.0926	0.3169



L¹: R' = H, R = H **L¹-OH:** R' = H, R = H
L²: R' = CH_3, R = H **L²-OH:** R' = CH_3, R = H
L³: R' = CH_2py, R = H **Me-L³-OH:** R' = CH_2py, R = CH_3

Scheme 1 Ligands used in this study.

Results and discussion

L^1, L^3 and Me–L^3–OH were readily prepared using standard synthetic procedures (see experimental section; however, alternative methods for the syntheses of L^3 and Me–L^3–OH have been used as well: *e.g.* L^3 can be prepared from L^1 using 2-picolyl chloride and base or by an *in situ* reductive alkylation[38,39] with 2-pyridinecarbaldehyde and $NaBH(OAc)_3$). The crude oils were purified by chromatography.

As described above it is well known that intramolecular ligand hydroxylation occurs when $[Cu_2(R–XYL–H)]^{2+}$ is reacted with dioxygen (Fig. 1). The different reaction pathways of related xylyl-bridged copper complexes during oxidation raised the question about the basic essential requirements for the occurrence of an intramolecular ligand hydroxylation. That intramolecular ligand hydroxylation was observed when the Schiff base complex $[Cu_2(H–BPB–H)S_2]^{2+}$ (Fig. 2) was reacted with dioxygen demonstrated that only two of the four "ethyl-pyridine arms" in $[Cu_2(R–XYL–H)]^{2+}$ are required for this kind of oxidation. However, it was not clear from the above finding if the imine donor atoms present in $[Cu_2(H–BPB–H)S_2]^{2+}$ are essential. It had been demonstrated by some of us earlier that imine donor atoms are not prerequisite by analyzing the oxidation of the dinuclear copper(I) complex with L^2.[40,41] Once again intramolecular ligand hydroxylation was observed and therefore suggesting that only two nitrogen donor atoms of the ligand (per copper ion) are sufficient for intramolecular ligand hydroxylation reactions. Our findings were confirmed furthermore by the observations of Tolman and coworkers who observed ligand hydroxylations using bidentate ligands with nitrogen donor atoms.[12] However, the question remained and is addressed herein, as to whether the methyl group (or more generally an alkyl group) needs to be attached to the secondary amine nitrogen donor atoms for intramolecular ligand hydroxylation to be observed.

Unfortunately we were unsuccessful in isolating the copper(I) complex of L^1 as a pure solid material. Therefore, solutions of this complex employed in the oxygenation experiments were prepared *in situ* by mixing $[Cu(CH_3CN)_4]ClO_4$ with L^1 in methanol (or dichloromethane) under an inert atmosphere. The yellow complex $[Cu_2L^1(CH_3CN)_{2x}](ClO_4)_2$ (x = 1 or 2) is most likely formed, where one or two acetonitrile molecules are coordinated additionally as co-ligands to each copper(I) ion. After the reaction with dioxygen the green phenolate-bridged product $[Cu_2(L^1–O)(OH)(ClO_4)]ClO_4$ (**1**) was isolated in good yield, clearly demonstrating again that intramolecular ligand hydroxylation had occurred. Crystals of complex **1** suitable for a single-crystal X-ray structure analysis were obtained by slow diffusion of Et_2O into a MeOH solution containing **1**. The quality of the crystals was poor and could not be improved by varying the crystallization conditions. This seems to be a general problem when six-membered chelate rings are present in this type of ligands (see below) while in contrast it was much easier obtaining crystals of high quality for diffraction studies if only five-membered chelate rings are present.[37] This might be a consequence of the fact that copper(II) ions usually prefer five-membered chelate rings in their complexes. We obtained acceptable diffraction data for $[Cu_2(L^1–O)(OH)(ClO_4)]ClO_4$ (**1**) at 183(2) K. A summary of the crystallographic data, bond lengths and angles for **1** can be found in Tables 1 and 2. An ORTEP[42] view of the cation of **1** is shown in Fig. 3.

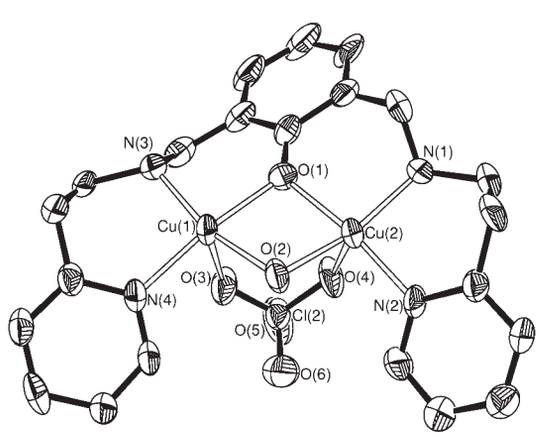


Fig. 3 ORTEP[42] representation (50% probability displacement ellipsoids) of the cation of **1**. Hydrogen atoms omitted for clarity.

Table 2 Selected bond lengths (Å) and interbond angles (°) for **1, 3** and **7**

1					
Cu(1)–N(1)	2.026(8)	Cu(1)–N(2)	1.946(8)	Cu(1)–O(1)	1.973(7)
Cu(1)–O(2)	1.918(7)	Cu(1)–O(3)	2.528(8)	Cu(2)–N(3)	2.028(8)
Cu(2)–N(4)	1.941(8)	Cu(2)–O(1)	1.916(6)	Cu(2)–O(2)	1.943(7)
Cu(2)–O(4)	2.499(7)	Cu(1)···Cu(2)	3.006(2)		
N(1)–Cu(1)–N(2)	96.3(3)	N(1)–Cu(1)–O(1)	172.3(3)	N(1)–Cu(1)–O(2)	97.6(3)
N(2)–Cu(1)–O(1)	90.1(3)	N(2)–Cu(1)–O(2)	165.3(3)	O(1)–Cu(1)–O(2)	76.4(3)
N(3)–Cu(2)–N(4)	94.7(3)	N(3)–Cu(2)–O(1)	93.9(3)	N(3)–Cu(2)–O(2)	165.1(3)
N(4)–Cu(2)–O(1)	171.4(3)	N(4)–Cu(2)–O(2)	94.4(3)	O(1)–Cu(2)–O(2)	77.1(3)
3					
Cu(1)–N(1)	2.334(2)	Cu(1)–N(2)	1.909(2)	Cu(1)–N(3)	1.921(2)
Cu(1)–O(40)	2.835(2)	Cu(2)–N(4)	2.308(2)	Cu(2)–N(5)	1.902(2)
Cu(2)–N(6)	1.916(2)	Cu(2)–O(24)	3.087(2)		
N(1)–Cu(1)–N(2)	96.40(9)	N(1)–Cu(1)–N(3)	83.50(9)	N(2)–Cu(1)–N(3)	172.8(1)
N(1)–Cu(1)–O(40)	123.55(8)	N(2)–Cu(1)–O(40)	92.14(9)	N(3)–Cu(1)–O(40)	93.92(9)
N(4)–Cu(2)–N(5)	97.2(1)	N(4)–Cu(2)–N(6)	83.74(9)	N(5)–Cu(2)–N(6)	171.2(2)
N(4)–Cu(2)–O(24)	136.90(8)	N(5)–Cu(2)–O(24)	93.42(9)	N(6)–Cu(2)–O(24)	91.80(9)
7					
Cu(1)–N(1)	2.03(2)	Cu(1)–N(2)	2.06(2)	Cu(1)–O(1)	1.92(2)
Cu(1)–Cl(1)	2.339(5)	Cu(1)–Cl(2)	2.457(6)	Cu(2)–N(3)	2.03(2)
Cu(2)–N(4)	2.00(2)	Cu(2)–O(1)	1.95(2)	Cu(2)–Cl(2)	2.426(5)
Cu(2)–Cl(3)	2.421(5)	Cu(1)···Cu(2)	3.293(5)		
N(1)–Cu(1)–O(1)	168.2(5)	N(1)–Cu(1)–Cl(1)	94.5(5)	N(2)–Cu(1)–Cl(2)	126.9(4)
N(2)–Cu(1)–O(1)	91.2(6)	N(2)–Cu(1)–Cl(1)	118.5(4)	Cl(1)–Cu(1)–Cl(2)	114.0(2)
N(1)–Cu(1)–N(2)	93.6(6)	O(1)–Cu(1)–Cl(2)	79.1(4)	N(1)–Cu(1)–Cl(2)	89.3(4)
O(1)–Cu(1)–Cl(1)	92.7(4)	N(3)–Cu(2)–O(1)	90.3(6)	N(4)–Cu(2)–O(1)	167.6(5)
N(3)–Cu(2)–N(4)	93.1(6)	O(1)–Cu(2)–Cl(3)	94.6(4)	N(4)–Cu(2)–Cl(3)	95.5(4)
N(3)–Cu(2)–Cl(3)	110.0(4)	O(1)–Cu(2)–Cl(2)	79.4(4)	N(4)–Cu(2)–Cl(2)	90.7(4)
N(3)–Cu(2)–Cl(2)	142.8(4)	Cl(2)–Cu(2)–Cl(3)	106.4(2)		

The two copper(II) centres (intramolecular separation Cu(1)···Cu(2) 3.006(2) Å) in **1** are both penta-coordinate; Cu(1) is ligated by pyridyl nitrogen atom N(4), aliphatic amine N(3), phenolate oxygen O(1) and oxygen atoms O(2) and O(3) of the respective bridging hydroxo and perchlorate moieties. The bond angle between Cu(1), the μ-phenolate oxygen and Cu(2) [Cu(1)–O(1)–Cu(2)] = 101.1(3)°; the bond angle between Cu(1), the μ-hydroxo moiety and Cu(2) [Cu(1)–O(2)–Cu(2)] = 102.2(3)°. The coordination geometry about Cu(1) and Cu(2) is best described as close to square pyramidal with values of the trigonality index[43] (τ) equal to 0.12 for Cu(1) and 0.11 for Cu(2) (where $\tau = (\beta - \alpha)/60$, with α and β being the two largest coordination angles around the metal centre: $\tau = 0$ for square pyramidal geometry and $\tau = 1$ for trigonal bipyramidal geometry). The basal plane of the square pyramid around Cu(1) contains O(1), O(2), N(3) and N(4) with O(3) occupying the axial coordination site. Metric parameters around Cu(2) are similar to Cu(1). A non-coordinating water solvent molecule and perchlorate anion (not shown in Fig. 3) complete the structure of **1**.

Phenolate bridged complexes similar to **1** are well known and their properties have been studied extensively (a few examples are provided in the references).[17,18,33,35,37] A structurally related complex to **1** has been characterized by Grzybowski *et al.*[34] The ligand employed differed from L^1–OH in that a *para*-methyl group was present on the central aromatic ring (Scheme 1, L^1–OH, however with R = CH_3 instead of H). Although the authors presented detailed physicochemical studies no crystal structure of the complex was described probably due to the same difficulties we had with obtaining crystals of **1** suitable for X-ray crystal structure determination.

Comparison of the crystal structure of **1** with the complex $[Cu_2(L^2–O)(OH)](ClO_4)_2$ (**2**) described previously[40] shows that bond lengths and angles around the copper(II) centres are similar, with the distance between the two copper(II) ions being close to 3 Å. The situation is different if we compare the crystal structure of **1** with an analogous complex described earlier by some of us, where the chelate ring sizes are smaller.[37] There are significant differences in bond lengths and bond angles between the two complexes. The most striking effect of the smaller chelate ring size is reflected in the bond angles N(1)–Cu(1)–N(2) and N(3)–Cu(2)–N(4): these values are 84.8(4) and 84.1(4)° in the structure with the smaller chelate rings present and 96.3(3) and 94.7(3)° for **1**.

Karlin and coworkers and some of us observed that reducing the chelate ring sizes in $[Cu_2(R–XYL–H)]^{2+}$ by substituting the "ethylpyridine arms" with "methylpyridine arms" completely suppressed intramolecular ligand hydroxylation.[41,44] Therefore, it was an obvious question to address as to whether partial substitution, *i.e.* the substitution of only two "arms", would support or suppress the intramolecular ligand hydroxylation reaction.

Reaction of L^3 (Scheme 1) and $[Cu(CH_3CN)_4]ClO_4$ in acetone led to the formation of $[Cu_2L^3](ClO_4)_2$ (**3**) that could be crystallographically characterized. A summary of the crystallographic data, bond lengths and angles for **3** is presented in Tables 1 and 2. An ORTEP[42] view of the cation of **3** (including the weak interaction of an acetone molecule and a perchlorate anion) is shown in Fig. 4.

Similar to the crystal structure of $[Cu_2(R–XYL–H)]^{2+}$ acetonitrile molecules are not coordinated to the copper(I) ions as additional ligands.[7] However, bond distances and angles are clearly different due to the "replacement" of a six-membered chelate ring with a five-membered chelate ring [*e.g.* Cu–N(amine) distances: Cu(1)–N(1) 2.334(2) and Cu(2)–N(4) 2.308(2) Å are longer in **3** compared with Cu(1)–N(1) 2.121(8) and Cu(2)–N(4) 2.196(7) Å in $[Cu_2(R–XYL–H)]^{2+}$].[7]

Oxidation of the solution-generated dicopper(I) complex of the *m*-xylyl-based dinucleating ligand L^3 and $[Cu(CH_3CN)_4]ClO_4$ in MeOH at 298 K with O_2 again led to an intramolecular ligand hydroxylation. This was proved by isolation and characterization of the hydroxylated ligand L^3–OH according to the published procedure for the hydroxylation of $[Cu_2(R–XYL–H)]^{2+}$.[7] No crystals of the product complex suitable for an X-ray crystal structure

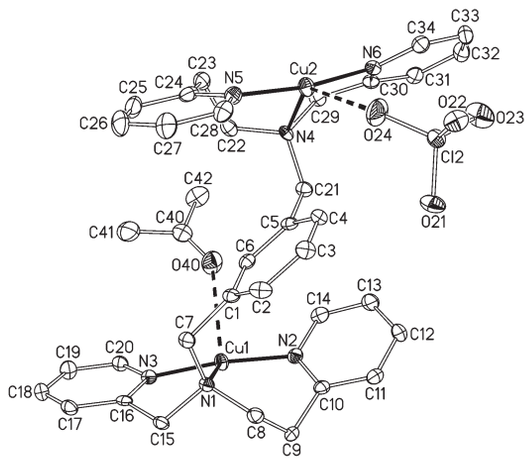


Fig. 4 ORTEP[42] representation (50% probability displacement ellipsoids) of the cation of **3** (including the weakly coordinated acetone molecule and perchlorate anion). Hydrogen atoms omitted for clarity.

analysis were obtained (however, see below: independent synthesis of phenolate-bridged complexes derived from Me–L^3–OH).

As described above, it was possible to observe a peroxo intermediate complex spectrophotometrically when $[Cu_2(R–XYL–H)]^{2+}$ was oxidized with dioxygen using low temperature stopped-flow techniques.[8–10] However, our efforts to detect such a transient "dioxygen adduct" with the dinuclear copper complexes of the ligands L^1, L^2 and L^3 using stopped-flow techniques were unsuccessful. Even at low temperatures only the formation of the final products was observed spectroscopically. This finding is in agreement with our earlier results on the related imine complex $[Cu_2(H–BPB–H)S_2]^{2+}$ described above (Fig. 2) and a dinuclear macrocyclic copper Schiff base compound; in both cases no "dioxygen adduct" was observed.[29–31] Furthermore, Murthy *et al.* could not detect spectroscopically such an intermediate during the analysis of the reaction of dioxygen with $[Cu_2(UN2–H)]^{2+}$ where the unsymmetric ligand UN2–H consists of one half of R–XYL–H and one half of L^2.[45] The probable reason in all these cases most likely is based on the kinetics of the reaction: the rate of formation of any "dioxygen adduct" is slower than its consecutive reactions and therefore cannot be detected.

Phenolate-bridged complexes

As described above, the phenolate-bridged complexes $[Cu_2(L^1–O)(OH)(ClO_4)]ClO_4$ (**1**) and $[Cu_2(L^2–O)(OH)](ClO_4)_2$ (**2**) could be readily prepared in good yields by oxidizing the copper(I) complexes of L^1 and L^2 with dioxygen, while this was not possible with the ligand L^3. Therefore, we prepared three copper(II) complexes $[Cu_2(Me–L^3–O)X](ClO_4)_2{\cdot}nH_2O$ (Me–L^3–OH = 2,6-bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-4-methylphenol) (Scheme 1) with X = $C_3H_3N_2^-$ (prz) (**4**), $MeCO_2^-$ (**5**) and N_3^- (**6**); n = 1 for **4** and n = 2 for **5** and **6**. Microanalytical data, IR spectra and solution electrical conductivity measurements are in conformity with our proposed formulations. The IR data demonstrates that in complex **6** the azide group most likely is present in a μ-1,1-bridging mode. So far we have been unsuccessful in determining the three-dimensional X-ray crystal structures of the complexes **4**–**6** because of the poor quality of crystals obtained. In contrast we obtained crystals of $[Cu_2(Me–L^3–O)(H_2O)_2](ClO_4)_3$ by reacting the ligand Me–L^3–OH with $[Cu(H_2O)_6](ClO_4)_2$ in a mixture of water and methanol. A crystal structure determination supported the above formulation and showed that in the phenolate-bridged complex an additional water molecule is coordinated to each copper(II) ion, in a similar manner to the structurally characterized complexes $[Cu_2(F–L^4–O)(H_2O)_2](ClO_4)_3$ and $[Cu_2(CF_3–L^4–O)(H_2O)_2](ClO_4)_3$ where L^4 = 2,6-bis[bis(2-pyridylmethyl)aminomethyl]-4-R-phenol.[46] The quality of the structural refinement of $[Cu_2(Me–L^3–O)(H_2O)_2](ClO_4)_3$ was not good enough for publication due to disorder problems encountered with the perchlorate anions. Efforts in obtaining better quality single-crystals have also been unsuccessful. However, we accurately determined a pK_a value of 4.76(2) for the deprotonation of $[Cu_2(Me–L^3–O)(H_2O)_2](ClO_4)_3$ leading to $[Cu_2(Me–L^3–O)(OH)](ClO_4)_2$. The p$K_a$ value we determined is very close to the one obtained for the acid–base equilibrium between $[Cu_2(Me–L^4–O)(H_2O)_2](ClO_4)_3$ and $[Cu_2(Me–L^4–O)(OH)](ClO_4)_2$ (pK_a = 4.95).[46]

Treating complex **2** with an excess of chloride ions led to the formation of $[Cu_2(L^2–O)Cl_3]$ (**7**). It was also possible to regenerate **2** from **7** by adding water to a solution of **7** in acetonitrile, with both exchange reactions being readily monitored by UV-vis spectroscopy. Confirmation of the composition of **7** was obtained from a single-crystal X-ray structure determination. The asymmetric unit contains two crystallographically independent molecules of complex **7**. Both molecules have essentially identical coordination geometries, but the corresponding bond lengths and bond angles are different. A summary of the crystallographic data, bond lengths and angles for **7** can be found in Tables 1 and 2. An ORTEP[42] view of one of the crystallographically independent molecules of **7** is shown below in Fig. 5.

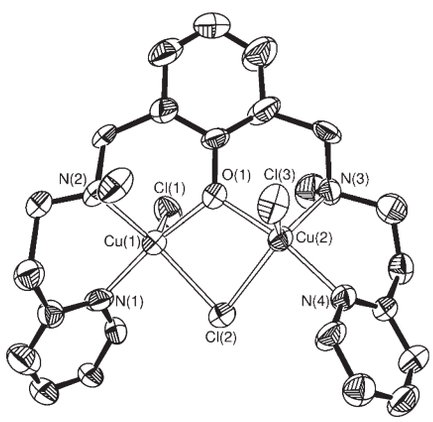


Fig. 5 ORTEP[42] representation (50% probability displacement ellipsoids) of **7**. Hydrogen atoms omitted for clarity.

Complex **7** is a dinuclear copper(II) complex of the same dinucleating ligand as in complex $[Cu_2(L^2–O)(OH)](ClO_4)_2$ (**2**).[40] The two copper(II) centres in complex **7** (Cu(1)···Cu(2) separation = 3.293(5) Å; for the other molecule 3.272(5) Å) are bridged by an endogenous phenolate and an exogenous chloride ion, with additional chloride coordination at each copper(II) centre. Both Cu(1) and Cu(2) are penta-coordinate being ligated by one pyridyl nitrogen, one aliphatic amine nitrogen, a phenolate oxygen and two chloride ions. The phenolate oxygen and a chloride ion bridge the copper(II) centres. The geometry about each copper(II) centre is best described as distorted trigonal bipyramidal/square pyramidal: τ[43] = 0.69 [Cu(1)] and τ = 0.41 [Cu(2)], the corresponding values for the other molecule are τ = 0.74 [Cu(1a)] and τ = 0.51 [Cu(2a)]. Cu(1) is displaced 0.09 Å and Cu(2) 0.11 Å out of the trigonal plane, towards the pyridyl nitrogen atom N(1) and N(4), respectively. The angles between the central phenolate ring and pyridyl rings are 18.4(8) and 42.1(7)° for the molecule shown in Fig. 5. The structural motif exhibited in complex **7** is rare; there are only three other structurally characterized copper(II) complexes of nitrogen donor-based ligands containing both a bridging phenolate anion and a chloride anion.[47–49]

Magnetic characteristics

Due to the presence of the phenoxo-/hydroxo-bridge in **2** significant antiferromagnetic exchange coupling is present (−440 cm^{-1}).[41] Variable-temperature (80–300 K) magnetic susceptibility analyses for **4**–**7** were performed. Their magnetic properties are of interest owing to the presence of an invariant phenoxide bridge and variable exogenous bridges. At 300 K the μ_{eff}/Cu values (in μ_B) for this set of compounds are: 1.73 (**4**), 1.76 (**5**), 1.77 (**6**) and 1.25 (**7**). The corresponding values at 80 K are: 1.28, 1.33, 1.34 and 0.34,

Table 3 Magnetic data for endogenously phenoxo-bridged dicopper(II) complexes

Complex	$-2J$/cm^{-1}	ρ (%)	10^8R	Ref.
$[Cu_2(L^2–O)(OH)](ClO_4)_2$ (**2**)	−440			40
$[Cu_2(L^4–O)(\mu\text{-pyz})](ClO_4)_2\cdot H_2O$ (**4**)	−92	0.44	5.67	This work
$[Cu_2(L^4–O)(\mu\text{-OAc})](ClO_4)_2\cdot 2H_2O$ (**5**)	−86	0.40	11.60	This work
$[Cu_2(L^4–O)(\mu\text{-1,1-}N_3)](ClO_4)_2\cdot 2H_2O$ (**6**)	−88	0.53	20.20	This work
$[Cu_2(L^1–O)Cl_3]$ (**7**)	−374	0.91	7.05	This work
$[Cu_2(L–O)(OH)](PF_6)_2$	−600			7,48
$[Cu_2(L–O)Cl](BPh_4)_2\cdot$MeCOMe	−335			48
$[Cu_2(L–O)(\mu\text{-1,1-}N_3)](PF_6)_2$	−440			48,51

L–OH = 2,6-Bis[*N*-(2-pyridylethyl)aminomethyl]phenol.

respectively. Plots of $\chi_M T$ *vs*. T for two representative complexes **4** and **7** are shown in Fig. 6. The observed magnetic susceptibility data were fitted to the modified Bleaney–Bowers equation (1)[50] by allowing for the presence of monomeric impurity, where ρ is the mole-fraction of the non-coupled copper(II) impurity.

$$\chi_M = \frac{2N\beta^2 g^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-\rho)+\frac{N\beta^2 g^2\rho}{2kT}+2N_\alpha \quad (1)$$

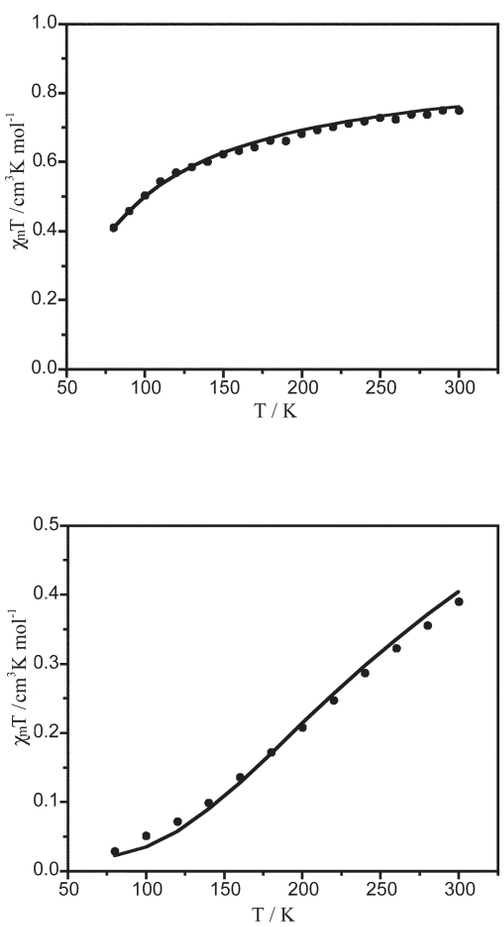


Fig. 6 $\chi_m T$ *vs*. temperature T plots for **4** and **7** (from top to bottom). Circles represent experimental data, the solid lines represent the fit.

In this expression, N, g and k have their usual meaning; $2J$ is the energy difference between the singlet and triplet states; χ_M is the molar susceptibility per dimer. The values of g and temperature-independent paramagnetic susceptibility (N_α) were kept fixed at $g = 2.1$ [typical value for a tetragonal Cu(II)] and 60×10^{-6} cm^3 mol^{-1}, respectively, during the fitting procedure. To get a better control of g values the EPR spectra of **4–6** were recorded. In fact, in the polycrystalline state at 300 K each complex exhibits an almost isotropic signal. The g values are: 2.08 for **4**, 2.07 for **5**, 2.11 (g_{av} value from a weak axial spectrum). The best-fit parameters of J and ρ using eqn. (1) were obtained by a nonlinear least-squares fitting procedure. The quality of fit was estimated by the R index defined as $R = \sum(\chi_M^{expt} - \chi_M^{calc})^2/\sum(\chi_M^{expt})^2$. The parameters that were obtained are collected in Table 3.

There is an appreciable drop in the extent of antiferromagnetic coupling, comparing complexes **2** and **7** (Table 3). A similar trend was observed by Karlin and co-workers, for closely related systems (the geometry around the copper(II) centres, however, remained invariant).[48] Thus the extent of antiferromagnetic exchange coupling is much higher in **7** than that present in complexes **3–6**. Within the similar class of complexes **4–6**, temperature-dependent magnetic susceptibility studies reveal that (i) there is medium antiferromagnetic exchange coupling between pairs of copper(II) ions in each case and (ii) the magnitude of the antiferromagnetic exchange depends on the identity of the exogenous bridge (prz > azide > acetate). It is worth noting that the present work complements the ones of several authors who investigated the effect of exogenous bridges in the transmission of magnetic exchange between two copper(II) centres.[52]

The effective magnetic moments for **4–6** in MeCN solution (300 K) were determined by using the NMR method to examine whether or not the solid state structures of the complexes are retained in solution. The μ_{eff}/Cu values for **4** and **5** are in reasonable agreement with solid-state values. However, for **6** the solution-state value (1.55 μ_B) is slightly less than the solid-state value (1.77 μ_B). This behaviour could be due to a relaxed geometry in the solution state, allowing a better pathway for magnetic coupling.

Conclusions

Considering the large number of studies that have been performed on xylyl-bridged dicopper(I) complexes it is surprising that at present we do not have a detailed understanding of their reaction pathways when oxidized with dioxygen. Sorrell commented earlier that attempts to find a correlation between the physical properties of the complexes and their ability to support intramolecular ligand hydroxylation reactions have been unsuccessful.[17] Chelate ring sizes in the complexes seem to play an important role; for imine complexes such as $[Cu_2(H–BPB–H)S_2]^{2+}$ (Fig. 2) or for the amine complex $[Cu_2(R–XYL–H)]^{2+}$ (Fig. 1) a decrease in the chelate ring size from six to five completely suppressed the intramolecular ligand hydroxylation. In our work presented herein we also observed intramolecular ligand hydroxylation when dioxygen was reacted with the copper(I) complex of L^1 with only six-membered chelate rings present. Furthermore, intramolecular ligand hydroxylation was observed with the copper(I) complex of L^3, where two five-membered chelate rings were introduced additionally. Several other copper(I) complexes containing only five-membered chelate rings are known, which also show ligand hydroxylation reactions. Therefore, the occurrence of intramolecular ligand hydroxylation cannot be a result of chelate ring size alone. Based on the results/observations available it is more probable that the overall geometry, which the ligand enforces on the copper centres, plays an important role in determining the fate of the metal-bound "activated dioxygen adduct". If the ligand backbone allows the approach of the "activated oxygen adduct" close to the aromatic C–H bond to be activated then intramolecular ligand hydroxylation is observed. However, if the

steric demands of the ligand enforces a larger distance between the metal-bound "dioxygen adduct" and the aromatic ring then the hydroxylation reaction is suppressed and "normal" intermolecular oxidation reactions are observed.

Experimental

Reagents and materials

Reagents and solvents used, unless stated otherwise, were of commercially available reagent grade quality. $[Cu(CH_3CN)_4]PF_6$ and $[Cu(CH_3CN)_4]ClO_4$ were synthesized according to literature procedures.[53]

Physical measurements

Elemental analyses were obtained either from the University of Erlangen-Nürnberg or the Facility for Ecological and Analytical Testing (FEAT) laboratory, Indian Institute of Technology, Kanpur. Solution electrical conductivity measurements were carried out with an Elico (Hyderabad, India) Type M-82 T conductivity bridge with a solute concentration of $\approx 1.0 \times 10^{-3}$ M. Spectroscopic data were obtained by using the following instruments: infrared, Bruker Vector 22; ^{1}H NMR, Bruker DXP 300 AVANCE (300 MHz, University of Erlangen-Nürnberg); UV-vis, Agilent 8453 diode-array. Variable-temperature solid-state magnetic susceptibility measurements were performed either by the Faraday technique using a local built magnetometer (at a fixed main field strength of ≈10 kG)[50] or a Quantum Design (Model MPMSXL-5) SQUID magnetic susceptometer operating at a magnetic field of 0.5 T. Solution state magnetic susceptibility measurements were done by the NMR technique of Evans[54] in MeCN with a PMX-60 JEOL (60 MHz, IIT Kanpur) NMR spectrometer. Susceptibilities were corrected by using appropriate diamagnetic corrections.[55]

Stopped-flow measurements at ambient and at low temperatures were performed as described previously.[10,56] Solutions of copper(I) complexes were prepared by mixing stoichiometric amounts of copper(I) salts with the appropriate ligand under argon in a glove box (Braun, Garching, Germany; water and dioxygen less than 1 ppm) and then transferred with gas-tight syringes to the instrument. A dioxygen saturated solution was prepared by bubbling dioxygen through the solvent for 20 min.

Ligand syntheses

α,α′-Bis[(2-pyridylethyl)aminomethyl]benzene (L^1). 2-(2-aminoethyl)pyridine 2.44 g (20 mmol) was added to a solution of isophthalaldehyde 1.34 g (10 mmol) in MeOH (110 cm^3) and the solution was stirred for 2 h at 60 °C. $NaBH_4$ 1.00 g (26 mmol) was added slowly to the solution and the cloudy solution was stirred overnight. By careful addition of 10 M HCl the excess $NaBH_4$ was destroyed and the solution was brought to a pH value of 2. After concentration of the solution *in vacuo*, aqueous 5 M NaOH was added to the residue until a pH value of 12 was reached. The aqueous solution was extracted with CH_2Cl_2 (4 × 30 cm^3 portions) and the organic fractions were combined and dried over anhydrous Na_2SO_4. Removal of the solvent yielded the crude product as a yellow oil which was chromatographed on silica gel (60 Å pore size, 70–230 mesh) with MeOH–Et_3N (50 : 1) as eluent (R_f = 0.37) yielding L^1 as a pale-yellow oil (6.2 g, 90%). δ_H (300 MHz; solvent $CDCl_3$; standard $SiMe_4$) 8.42 [2 H, d, Ar–*H*], 7.49–6.93 [10 H, m, Ar–*H*], 3.68 [4 H, s, ArCH_2NH–], 2.98 [8 H, m, –NHCH_2CH_2py]. δ_C (75 MHz; solvent $CDCl_3$; standard $SiMe_4$) 160.3, 149.5, 140.4, 128.9, 128.3, 127.5, 124.2, 121.4, 54.3, 49.1, 38.4.

α,α′-Bis[*N*-methyl-*N*-(2-pyridylethyl)amino]-*m*-xylene (L^2). L^2 was synthesized as described previously.[41]

α,α′-Bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-*m*-xylene (L^3). A solution of Et_3N (0.475 g, 4.69 mmol) in dry MeOH (20 cm^3) was added dropwise to a solution of 2-pyridylethyl(2-pyridylmethyl)amine[57] (1.0 g, 4.69 mmol) in dry MeOH (40 cm^3) at 10 °C with magnetic stirring. A solution of α-α′-dibromo-*m*-xylene (0.62 g, 2.35 mmol) in dry MeOH (40 cm^3), over a period of 10 min was then added. The reaction mixture was stirred for a further 2.5 h and then was kept at ~30 °C overnight. The solvent was removed *in vacuo* to obtain the crude product as a brown–yellow semi-solid. The desired ligand was obtained by exhaustive extraction of the aqueous phase with $CHCl_3$ (a little water was also added at this stage) until the aqueous layer was colourless. The organic fractions were combined and then dried over anhydrous Na_2SO_4. Filtration and removal of the solvent yielded the crude product as a red–brown oil which was chromatographed on neutral aluminium oxide with ethyl acetate as eluent (R_f = 0.40) yielding L^3 as a yellow oil (0.9 g, 60%). δ_H (300 MHz; solvent $CDCl_3$; standard $SiMe_4$) 8.46 [4 H, d, py–*H*], 7.60–7.04 [16 H, m, Ar–*H*], 3.79 [4 H, s, pyCH_2N–], 3.69 [4 H, s, ArCH_2N–], 2.98 [8 H, m, pyCH_2CH_2N–]. δ_C (75 MHz; solvent $CDCl_3$; standard $SiMe_4$) 160.6, 160.2, 149.1, 148.7, 139.2, 136.2, 136.0, 129.2, 128.1, 127.4, 123.4, 122.7, 121.7, 121.0, 60.1, 58.5, 54.1, 36.0.

2,6-Bis[*N*-(2-pyridylethyl)-*N*-(2-pyridylmethyl)amino]-4-methylphenol (Me–L^3–OH). A solution of 2,6-bis(chloromethyl)-4-methylphenol[47] in MeOH (20 cm^3) was added dropwise to a vigorously stirred solution of 2-pyridylmethyl(2-pyridylethyl)-methylamine[57] (0.50 g, 2.44 mmol) and Et_3N (0.49 g, 4.88 mmol) in MeOH (40 cm^3) at 0 °C. The solution was then stirred at ~10 °C for 3 h and then stirred overnight at ~30 °C. Solvent was removed *in vacuo* and the ligand was extracted with $CHCl_3$. The organic layer was washed first with a saturated brine solution and then with distilled water and dried over anhydrous Na_2SO_4. Removal of the solvent *in vacuo* afforded Me–L^3–OH as a brown oil (0.67 g, 88%) that can be further purified by chromatography using basic alumina oxide with ethyl acetate as eluent (R_f = 0.50). δ_H (300 MHz; solvent $CDCl_3$; standard $SiMe_4$) 8.54 [2 H, d, $^3J_{HH}$ = 4.4 Hz, py–*H*], 8.48 [2 H, d, $^3J_{HH}$ = 4.4 Hz, py–*H*], 7.54–7.44 [4 H, m, py–*H*], 7.25–7.01 [8 H, m, py–*H*], 6.84 [2 H, s, Ar–*H*], 3.86 [4 H, s, pyCH_2N–], 3.76 [4 H, s, ArCH_2N–], 3.00 [8 H, s, pyCH_2CH_2N–], 2.16 [3 H, s, –CH_3]. δ_C (75 MHz; solvent $CDCl_3$; standard $SiMe_4$) 160.3, 159.2, 153.5, 149.1, 148.8, 136.4, 136.2, 129.2, 127.5, 123.4, 121.9, 121.1, 59.9, 54.7, 53.9, 35.6, 20.6.

Preparation of $[Cu_2(L^1–O)(OH)(ClO_4)]ClO_4$ (1). L^1 (0.173 g, 0.50 mmol) in MeOH (5 cm^3) was added dropwise under nitrogen to a suspension of $[Cu(CH_3CN)_4]ClO_4$ (0.327 g, 1.00 mmol) in MeOH (15 cm^3). The solution turned yellow in colour and was very sensitive towards oxidation by air. Exposure to air lead to the formation of a deep green solution. After removal of the solvent *in vacuo* a solid was obtained which was recrystallized by diffusion of Et_2O into a MeOH solution of complex **1** (0.26 g, 75%). Crystals of **1** suitable for a single-crystal X-ray structure determination were obtained in this manner. Found: C, 37.8; H, 3.7; N, 7.6. Calc. for $C_{22}H_{26}Cl_2Cu_2N_4O_{10}$: C, 37.5; H, 3.7; N, 7.9%.

Preparation of $[Cu_2(L^3)(C_3H_6O)(ClO_4)]ClO_4$ (3). Under inert conditions $[Cu(CH_3CN)_4]ClO_4$ (0.327 g, 1.00 mmol) was added in small portions to a stirred solution of 0.264 g (0.5 mmol) L^3 in acetone (15 cm^3). Diffusion of Et_2O into this solution lead to the formation of yellow crystals suitable for a single-crystal X-ray structure determination.

Preparation of $[Cu_2(Me–L^3–O)(C_3H_3N_2)](ClO_4)_2·H_2O$ (4). A mixture of Me–L^3–OH (0.10 g, 0.179 mmol), NaOMe (0.0193 g, 0.358 mmol) and pyrazole (0.0122 g, 0.179 mmol) in MeCN (5 cm^3) was stirred at 0 °C for 0.5 h. A solution of $[Cu(H_2O)_6](ClO_4)_2$ (0.133 g, 0.358 mmol) in MeCN (5 cm^3) was then added dropwise. After 12 h the resulting greenish brown solution was filtered and allowed to evaporate slowly at room temperature. A deep brownish green microcrystalline product that deposited was filtered off, washed with a MeCN–Et_2O (1 : 4) mixture (5 cm^3) and recrystallized from a 2 : 1 (v/v) mixture of Et_2O–MeCN (15 cm^3) (0.1 g, 49%). Found: C, 47.6; H, 4.3; N, 11.6. Calc. for $C_{38}H_{42}Cl_2Cu_2N_8O_{10}$:

C, 47.1; H, 4.3; N, 11.6%. IR (KBr disc, selected peaks) $\bar{\nu}_{max}$/cm^{-1}: 3440br (OH); 1090 and 630 (ClO_4^-). Molar conductance, Λ_M (MeCN, 298 K) = 245 Ω^{-1} cm^2 mol^{-1} (expected value for a 1 : 2 electrolyte:[58] 220–300 Ω^{-1} cm^2 mol^{-1}). UV/vis (MeCN) λ_{max}/nm (ε/M^{-1} cm^{-1}): 660 (sh) (250), 470 (sh) (1000), 290 (sh) (9400) and 258 (19000). μ_{eff}/Cu (in MeCN, 298 K) 1.70 μ_B.

Preparation of $[Cu_2(Me–L^3–O)(O_2CMe)](ClO_4)_2·2H_2O$ (5). A mixture of Me–L^3–OH (0.10 g, 0.179 mmol) and Et_3N (0.018 g, 0.178 mmol) in MeCN (5 cm^3) was stirred at 0 °C for 20 min. $[Cu(H_2O)_6](ClO_4)_2$ (0.133 g, 0.358 mmol) was added and the mixture was stirred for 5 min resulting in a colour change from light brown to dark brown. A solution of $NaO_2CMe·3H_2O$ (0.024 g, 0.179 mmol) in MeOH (2 cm^3) under magnetic stirring was then added. During the addition the colour changed from deep brown to deep greenish brown. After 4 h of stirring the reaction mixture was filtered through a Celite pad and the filtrate kept for slow evaporation. The solid obtained was filtered off and recrystallized from a 1 : 2 (v/v) mixture (15 cm^3) of MeCN–Et_2O (0.112 g, 58%). Found: C, 45.4; H, 4.7; N, 8.8. Calc. for $C_{37}H_{44}Cl_2Cu_2N_6O_{13}$: C, 45.4; H, 4.5; N, 8.6%. IR (KBr disc, selected peaks) $\bar{\nu}_{max}$/cm^{-1}: 3436 (OH); 1570 and 1445 (OAc); 1084 and 626 (ClO_4^-). Molar conductance, Λ_M (MeCN, 298 K) = 260 Ω^{-1} cm^2 mol^{-1}. UV/vis (MeCN) λ_{max}/nm (ε/M^{-1} cm^{-1}): 680 (sh) (250), 450 (sh) (1250), 290 (sh) (9400) and 258 (sh) (19400). μ_{eff}/Cu (in MeCN, 298 K) 1.72 μ_B.

Preparation of $[Cu_2(Me–L^3–O)(N_3)](ClO_4)_2·2H_2O$ (6). This compound was prepared in the same way as **4** using NaN_3 (0.012 g, 0.179 mmol) as the bridging ligand; microcrystals of **6** were obtained and recrystallized from a 1 : 2 (v/v) mixture (15 cm^3) of MeCN–Et_2O (0.121 g, 64%). Found: C, 44.0; H, 4.5; N, 13.3. Calc. for $C_{35}H_{41}Cl_2Cu_2N_9O_{11}$: C, 43.7; H, 4.3; N, 13.1%. IR (KBr disc, selected peaks) $\bar{\nu}_{max}$/cm^{-1}: 3440 (OH); 2076 (N_3^-); 1090 and 630 (ClO_4^-). Molar conductance, Λ_M (MeCN, 298 K) = 290 Ω^{-1} cm^2 mol^{-1}. UV/vis (MeCN) λ_{max}/nm (ε/M^{-1} cm^{-1}): 660 (sh) (300), 500 (sh) (800), 390 (sh) (1560), 290 (sh) (8580) and 258 (17870). μ_{eff}/Cu (in MeCN, 298 K) 1.55 μ_B.

Preparation of $[Cu_2(L^2–O)Cl_3]$ (7). A solution of $[Et_4N]Cl·xH_2O$ (0.075 g, 0.402 mmol) in MeCN (5 cm^3) was added dropwise to a magnetically stirred MeCN (5 cm^3) solution of $[Cu_2(L^2–O)(OH)](ClO_4)_2$[40] (0.060 g, 0.082 mmol). During the progress of the reaction the colour of the solution changed from deep green to reddish-brown. After an additional stirring for 4 h the solution was concentrated *in vacuo* and Et_2O was slowly allowed to diffuse into the solution. Shiny red-brown crystals of **7** were obtained within two days (0.020 g, 40%), which were suitable for a single-crystal X-ray structure determination. Found: C, 45.8; H, 4.6; N, 8.7. Calc. for $C_{24}H_{29}Cl_3Cu_2N_4O$: C, 46.3; H, 4.7; N, 9.0%. Molar conductance, Λ_M (DMF, 298 K) = 30 Ω^{-1} cm^2 mol^{-1} (expected value for a 1 : 1 electrolyte:[58] 65–90 Ω^{-1} cm^2 mol^{-1}). UV/vis (DMF) λ_{max}/nm (ε/M^{-1} cm^{-1}): 980 (sh) (100), 805 (140), 460 (730) and 284 (sh) (2000).

Crystallography

Data collection and refinement details for 1, 3 and 7. Intensity data for **1** and **7** were collected on an Enraf Nonius CAD-4-Mach four-circle diffractometer (ω–2θ scan technique) (University of Erlangen-Nürnberg and IIT Kanpur, respectively) and for **3** on a Nonius Kappa CCD instrument using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data for **1, 3** and **7** were corrected for Lorentz-polarization effects. The structures were solved by direct methods for **1** and **3** and Patterson heavy-atom method for **7**. Complexes **1** and **7** were refined by full-matrix least-squares methods on F^2 using SHELXL-97[59] which was incorporated in the WINGX 1.61 collective crystallographic package.[60] All non-hydrogen atoms were refined with anisotropic thermal parameters. Problems during the refinement procedure for **7** were encountered; the problem was due to the poor diffracting nature of the crystals. All carbon atoms of the methylene groups of the *m*-xylyl spacers, *N*-methyl groups and one of the carbon atoms of the ethylene spacer on each arm of the ligand in one of the molecules of **7** (the molecule shown in Fig. 5 did not show any disorder) were disordered over two positions and were refined with isotropic displacement parameters. The positions of hydrogen atoms in **7** were calculated assuming ideal geometries of the atoms concerned, and their positions and thermal parameters were not refined. **3** was refined by full-matrix least-squares methods on F^2 using SHELXTL NT 6.12.[61] Absorption effects have been corrected on the basis of multiple scans using SADABS (T_{min} = 0.791, T_{max} = 1.000).[62] All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogen atoms are geometrically positioned with isotropic displacement parameters being 1.2 or 1.5 times U_{eq} of the preceding C atom.

CCDC reference numbers 211842 (**1**), 238967 (**3**) and 211448 (**7**).

See http://www.rsc.org/suppdata/dt/b4/b406329p/ for crystallographic data in CIF or other electronic format.

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