DOI: 10.1002/ejic.200700424

Pyrazole-Based Ligands for the [Copper–TEMPO]-Mediated Oxidation of Benzyl Alcohol to Benzaldehyde and Structures of the Cu Coordination Compounds

Jorge Salinas Uber,[a] Yorick Vogels,[a] Dave van den Helder,[a] Ilpo Mutikainen,[b] Urho Turpeinen,[b] Wen Tian Fu,[a] Olivier Roubeau,[c] Patrick Gamez,[a] and Jan Reedijk*[a]

Keywords: Copper(I) and copper(II) complexes / Catalysis / Oxidation / Luminescence / Bioinorganic chemistry

New pyrazole-based ligands have been designed, and the catalytic performances of their copper(II) complexes for the [copper/TEMPO]-mediated oxidation of benzyl alcohol to benzaldehyde have been examined. The pyridine-pyrazole ligands give efficient catalysts, while the use of naphthol-pyrazole ligands results in inactive catalytic systems. Single-crystals of four Cu coordination compounds obtained from pyridine-pyrazole ligands and a free ligand have been isolated and were characterized by X-ray diffraction. Thus, the solid-state structures of three copper(II) complexes are described, together with a copper(I) coordination chain, exhibiting luminescent properties.

Introduction

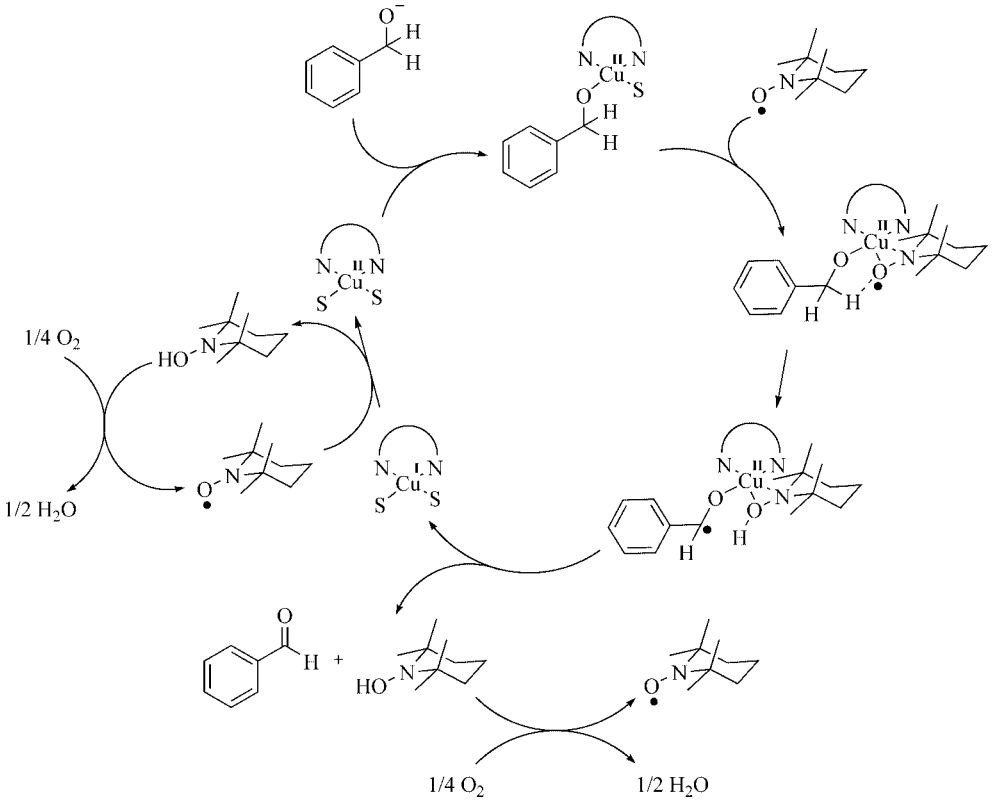
The selective production of aldehydes from primary alcohols is a very important chemical transformation of organic synthesis, since a wide variety of fine chemicals possess this carbonyl function.[1,2] Various effective methods have been developed to perform this oxidation reaction.[3,4] For example, the synthesis of aldehydes may commonly be achieved by heating the primary alcohol in an acidified solution of potassium dichromate, which is reduced to Cr^{3+} during the reaction,[5] or by the so-called "Swern oxidation" [$(CO)_2Cl_2$ + $(Me)_2SO$].[6] However, these oxidation procedures often involve the use of stoichiometric amounts of reagents, which leads to the formation of copious quantities of unfriendly waste for the environment. Hence, catalytic oxidations mediated by transition metal complexes represent a crucial and topical area of catalysis in term of green and sustainable chemistry.[7] Several efficient catalytic systems, including TEMPO-based ones have been reported;[8–16] nevertheless, severe limitations remain that are the chemo-, regio- and stereoselectivity of the catalytic oxidations. Recently, some of us have developed a bio-inspired copper-based catalyst able to selectively convert primary alcohols to the corresponding aldehydes in the presence of TEMPO as co-catalyst.[17,18] This catalytic system has been further developed by other research groups, showing its high potential and versatility for the production of a broad range of aldehydes.[19,20] In the present study, a number of related pyrazole-based ligands have been used for the [copper(II)/TEMPO]-catalysed oxidation of benzyl alcohol to benzaldehyde in order to obtain a better insight of its mechanism.

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, 2300 RA Leiden, The Netherlands
Fax: +31-715274671
E-mail: reedijk@chem.leidenuniv.nl
[b] Department of Chemistry, Laboratory of Inorganic Chemistry, P. O. Box 55 (A. I. Virtasenaukio 1), 00014 University of Helsinki, Helsinki, Finland
[c] Université Bordeaux 1, Centre de Recherche Paul Pascal – CNRS UPR 8641,
115 avenue du dr. A. Schweitzer, 33600 Pessac, France
Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

Results and Discussion

Preparation of the Ligands

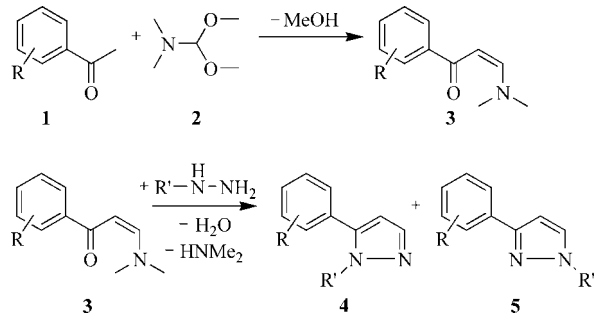
A few years ago, an effective catalytic system for the conversion of primary alcohols to the corresponding aldehydes, under mild conditions, has been reported.[17] This catalytic oxidation reaction involves a copper complex, and it has been shown that the use of aromatic N-donor ligands leads to efficient catalysts.[21] The proposed catalytic cycle of this reaction brings in copper(II) and copper(I) species (Scheme 1).[21] 2,2′-Bipyridine (and derivatives) has been shown to be a prime ligand for this reaction.[21] The pyrazole ring is known to stabilize Cu^{I} species. Thus, the use of mixed pyridine/pyrazole ligands is expected to generate active catalysts for the [Cu(ligand)-TEMPO]-mediated oxidation of primary alcohols, since both the Cu^{I} and Cu^{II} species may presumably be efficiently stabilised during the catalytic cycle. Therefore, a first series of new bidentate ligands have been designed and synthesized, which contain a pyridine unit connected to a less soft donor group, namely a pyrazole ring.



Scheme 1. Proposed catalytic cycle for the [copper/TEMPO]-catalyzed oxidation of benzyl alcohol to benzaldehyde.[21]

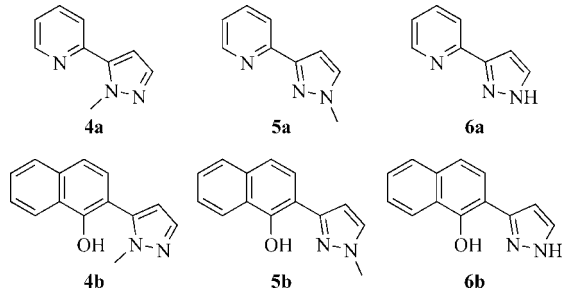
Moreover, the proposed catalytic cycle (Scheme 1)[21] of the [Cu(ligand)-TEMPO]-mediated oxidation is derived from the well-known mechanism of action of the copper enzyme galactose oxidase (GOase).[22] The active site of GOase contains a distorted square-pyramidal mononuclear copper(II) species, two of whose ligands are phenolic moieties (from tyrosinate side-chains).[22] A second series of pyrazole-based ligands possessing a naphthol group, have therefore been prepared to mimic the active site of GOase.

The synthetic procedure for the preparation of the pyrazole-containing ligands is based on an earlier reported method.[23] The first step of the synthesis is the reaction of an acyl derivative (**1**) with *N*,*N*-dimethylformamide dimethyl acetal (**2**) (Scheme 2). The resulting propenone (**3**) is treated with a hydrazine derivative to generate the pyrazole ring, via a ring-closure step (Scheme 2).



Scheme 2. Synthetic pathway for the preparation of the pyrazole-based ligands.

Using this straightforward synthetic route, the pyrazole-pyridine and the pyrazole-naphthol ligands depicted in Scheme 3 have been prepared in good yields (see Experimental section).



Scheme 3. Ligands used for the [copper–TEMPO]-catalysed oxidation of benzyl alcohol.

These pyrazole derivatives have been tested as ligands in the [copper–TEMPO]-catalysed oxidation of benzyl alcohol. Furthermore, various copper coordination compounds, whose crystal structures are described below, have been obtained by reaction of copper(II) bromide and some of these ligands.

Description of the Structures

Crystal Structure of $[Cu_2(4a)_2Br_2]_n$ (7)

Reaction of one equivalent of copper(II) bromide with one equivalent of ligand **4a** in methanol yields colourless

plates of **7** after one day. **7** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP[24] view of compound **7** is depicted in Figure 1. Selected bond lengths and angles are given in Table 1, and details for the structure solution and refinement are summarized in Table S1 (see electronic supporting information). Compound **7** is constituted by tetracoordinate copper(I) ions exhibiting distorted tetrahedral coordination, with a τ_4 value of 0.85.[25] Each copper centre is coordinated by a pyrazole N atom and a pyridine N atom, belonging to two different ligands. These two ligands coordinate to a crystallographically related copper(I) ion, generating a dimer (Figure 1). The coordination sphere of the metal centre is completed by two bromide anions. The Cu–N and Cu–Br bond lengths, as well as the bond angles are within normal ranges for such Cu^I coordination geometry.[26,27] The $Cu_2(\mathbf{4a})_2Br_2$ dinuclear units are bridged by the bromine ions to form infinite one-dimensional chains (Figure S1). As evidenced in Figure S1, the crystal packing of **7** shows a two-dimensional arrangement of the chains along the *a* axis. Indeed, each 1D chain interacts with two adjacent chains by means of π–π contacts [the separation between the ring centroids amounts to 3.652(3) Å].

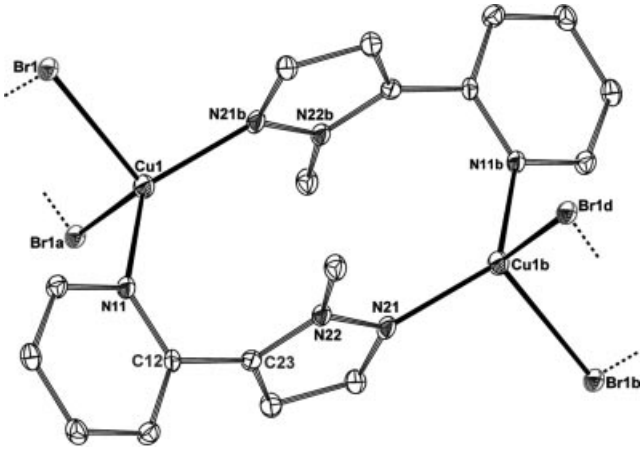
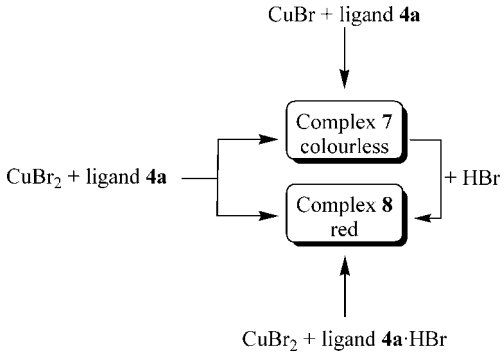


Figure 1. ORTEP drawing (30% probability level) of $[Cu_2(\mathbf{4a})_2Br_2]_n$ (**7**). Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **7**–**10**.

Compound **7**			
Cu1–Br1	2.590(1)	Cu1–Br1a	2.517(1)
Cu1–N11	2.075(5)	Cu1–N21b	2.032(4)
Br1–Cu1–Br1a	108.1(1)	Br1–Cu1–N11	102.6(1)
Br1–Cu1–N21b	99.7(1)	Br1a–Cu1–N11	103.6(1)
Br1a–Cu1–N21b	118.3(2)	N11–Cu1–N21b	122.5(2)
Compound **8**			
Cu1–Br1	2.372(1)	Cu1–Br2	2.394(1)
Cu1–Br3	2.371(1)	Cu1–N21	2.016(6)
Br1–Cu1–Br2	97.9(1)	Br1–Cu1–Br3	99.5(1)
Br1–Cu1–N21	138.4(2)	Br2–Cu1–Br3	134.6(1)
Br2–Cu1–N21	98.1(2)	Br3–Cu1–N21	96.1(2)
Compound **9**			
Cu1–Br1	2.345(1)	Cu1–Br2	2.354(2)
Cu1–N11	2.013(7)	Cu1–N21	2.003(7)
Br1–Cu1–Br2	100.2(1)	Br1–Cu1–N11	98.3(2)
Br1–Cu1–N21	146.7(2)	Br2–Cu1–N11	143.1(2)
Br2–Cu1–N21	99.8(2)	N11–Cu1–N21	80.9(3)
Cu2–Br3	2.385(1)	Cu2–Br4	2.416(2)
Cu2–Br3a	2.932(2)	Cu2–N31	2.098(7)
Cu2–N41	1.985(7)	Cu2–Cu2a	4.027(2)
Br3–Cu2–Br4	98.4(1)	Br4–Cu2–N41	96.1(2)
N41–Cu2–N31	79.2(3)	N31–Cu2–Br3	98.6(2)
Br3a–Cu2–Br4	132.0(1)	Br4–Cu2–N31	121.5(2)
N31–Cu2–Br3a	105.6(2)	Br3–Cu2–N41	164.1(2)
Compound **10**			
Cu1–Br1	2.444(1)	Cu1–N1	2.076(6)
Cu1–N7	1.995(7)	Cu1–N12	2.088(7)
Cu1–N18	1.997(7)		
Br1–Cu1–N1	123.3(2)	N1–Cu1–N12	114.8(3)
N12–Cu1–Br1	122.0(2)	N7–Cu1–N18	172.1(3)

Complex **7** can be obtained by reaction of one equivalent of copper(I) bromide with one equivalent of **4a** in acetonitrile (see Exp. Sect. and Scheme 4).



Scheme 4. Possible aerobic synthetic pathways for the preparation of complexes **7** and **8** (see Exp. Sect. for details).

As observed for other copper(I) complexes,[28,29] compound **7** possesses luminescence properties (see Figure S2). Indeed, under ambient conditions, solid **7** exhibits an intense blue-green emission centred at 490 nm, when excited at 365 nm.

Crystal Structure of [Cu(4aH)Br$_3$] (8)

Red block-shaped single-crystals start to grow up, after three weeks, in the previous solution (from which compound **7** had rapidly crystallized). X-ray diffraction analysis of these crystals reveal them to be the mononuclear compound [Cu(**4a**H)Br_3] (**8**) (Figure 2), in which the Cu atoms are divalent and the pyridine N atoms are protonated. Similarly to **7**, **8** crystallizes in the triclinic space group $P\bar{1}$. Selected bond lengths and angles are listed in Table 1, and crystallographic data for the structural analysis are given in Table S1. The copper(II) ion is tetracoordinate and adopts a highly distorted tetrahedral arrangement (τ_4 = 0.62),[25] as in previously observed for analogous $Cu^{II}Br_3N$ chromophores.[30,31] The Cu–Br as well as the Cu–N bond lengths are within normal ranges.[30] The coordination angles, ranging from 96.1(2) to 138.4(2)°, reflect the strong distortion, most likely due to the hydrogen bond involving the bromine atom Br1 (see Figure 3).

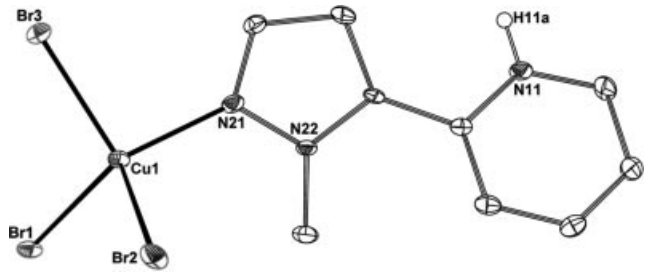


Figure 2. ORTEP drawing (30% probability level) of $[Cu(\mathbf{4a}H)_2Br_3]$ (**8**). Only the pyridinium hydrogen atom is shown.

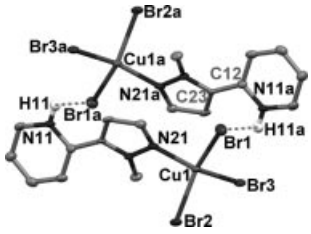


Figure 3. Representation of a dimer of complex **8**, assembled via double intermolecular hydrogen bonding interactions.

The crystal packing of **8** reveals interesting features (Figure 3 and S3). The bromide anion Br1 and the pyridinium hydrogen atom H11 are H-bonded to a neighbouring monocopper complex, producing a dimeric species resembling the dimer of **7** depicted in Figure 1. It thus appears that complex **8** is generated from the copper(I) complex **7** by addition of HBr, like reported by Haddad and Willett for the preparation of bis(dimethylaminopyridinium) tetrabromidocuprate(II).[32] HBr is most likely produced during the formation of complex **7** through decomposition of $CuBr_2$ to CuBr,[33] with concomitant oxidation of the solvent, i.e. methanol (see the section Catalytic Studies). The formal insertion of HBr between the atoms Cu1 and N11 of complex **7** under aerobic conditions (Figure 1) actually results in an increase of steric hindrance which prevents the generation of the 1D chains (observed in **7** and absent in **8**). In addition, the increased steric bulk owing to the additional bromine atom apparently forces the pyrazole ring to rotate around the C12–C23 bond (accordingly, the methyl groups are in opposite directions in Figure 1 and Figure 3).

The H-bonded dimer (Figure 3) is involved in multiple supramolecular interactions, generating a ladder-type framework (Figure S3). The pyrazole rings are π–π stacked with adjacent dimeric units [centroid-to-centroid distance of 3.647(4) Å]. Furthermore, the bromine atom Br3 is interacting with two pyridine rings, resulting in a π–anion–π motif [Figure S3, Br3···centroid A = 3.796(3) Å, Br3···centroid A' = 3.879(3) Å].[34]

To confirm the formation of **8** from **7**, via the addition of HBr under aerobic conditions (Scheme 4), the following experiment has been carried. As stated above, the reaction of $Cu^{I}Br$ with **4a** in acetonitrile produces complex **7**. The addition of HBr to this solution of **7** yields red crystals of **8** after one day, as confirmed by C, H, N, analyses and X-ray diffraction studies (see Exp. Sect.). Compound **8** can also be prepared by reaction of $Cu^{II}Br_2$ with the hydrobromic salt of **4a**, i.e **4a**·HBr (see Scheme 4 and Experimental Section).

Crystal Structure of $[Cu_3(5a)_3Br_6]$ (9)

Reaction of one equivalent of copper(II) bromide with one equivalent of ligand **5a** in methanol produces red needle-shaped single crystals of **9** after one day. **9** crystallizes in the triclinic space group $P\bar{1}$. The important bond parameters and crystallographic data for the structural analysis are listed in Table 1 and S1, respectively. An ORTEP[24] view of compound **9** is depicted in Figure 4. The crystal lattice of this compound is composed of two different copper(II) ions identified as Cu1 and Cu2 (Figure 4). The coordination geometry around Cu1 is intermediate between square-plane and tetrahedral, with τ_4 = 0.50.[25] The Cu–N and Cu–Br bond lengths can be considered as normal.[35,36] The coordination angles ranging from 96.1(2) to 146.7(2) reflect the strong distortion, most likely as a result of steric interactions between Br2 and the methyl substituent in the ligand (Figure S4). The geometry around the Cu2 atom is intermediate between the square-pyramid and the trigonal bipyramid (τ_5 = 0.53).[37] The Cu–N and Cu–Br bond lengths are in normal ranges for this type of $CuBr_3N_2$ chromophore.[38] Cu2 is doubly bridged by two bromide anions to a crystallographically equivalent copper(II) ion, namely Cu2a, giving rise to a dinuclear moiety with a Cu2···Cu2a separation of 4.027(2) Å (Figure 4).

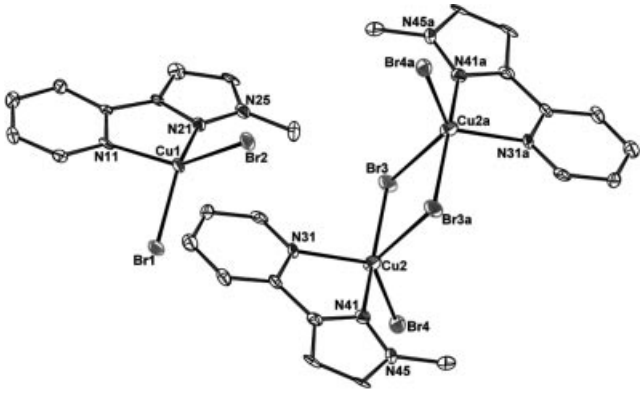


Figure 4. ORTEP drawing (30% probability level) of $[Cu_3(\mathbf{5a})_3Br_6]$ (**9**). Hydrogen atoms are omitted for clarity.

It has to be noted that, if the bromine atom Br3a, coordinated to Cu2 at a long distance of 2.932(2) Å, is omitted, the resulting tetracoordinate copper(II) centre (with τ_4 = 0.53)[25] resembles the Cu1 ion (Figure S5). It thus appears that **9** is constituted by three CuN_2Br_2 units, two of them bridged via bromide anions. The crystal packing of **9** along the *a* axis reveals supramolecular interactions (Figure S6). The mononuclear units are π–π stacked in pairs [Figure S6; centroid-to-centroid distance of 3.654(5) Å], whereas the dinuclear units form a 1D chain by means of π–π interactions [see Figure S6: centroid-to-centroid distance of 3.605(5) Å].

Crystal Structure of [Cu(6a)$_2$Br]Br·H$_2$O·CH$_3$CN (10)

Reaction of one equivalent of copper(II) bromide with one equivalent of ligand **6a** in acetonitrile yields green block-shaped single crystals of the mononuclear complex **10**. **10** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP[24] view of compound **10** is depicted in Figure 5. Selected bond lengths and angles are given in Table 1, and details for the structure solution and refinement are summarized in Table S1. The copper(II) ion is pentacoordinate by two ligands **6a** and one bromide anion (Figure 5). The coordination geometry is best described as slightly distorted trigonal-bipyramidal with a τ_5 value of 0.81.[37] The Cu–N and Cu–Br bond lengths are comparable to those of related $Cu^{II}N_4Br$ chromophores.[39,40] The lattice contains one water molecule and one acetonitrile of solvation as well as a bromide anion. The non-coordinating bromide ion and the water molecule are engaged in hydrogen bonding (Figure S7). Actually, the cationic part of **10**, namely [Cu(**6a**)$_2$-Br]$^+$, represents the building unit of a 1D supramolecular chain, assembled through π–π interactions [see Figure S7: centroid-to-centroid distances of 3.555(5) and 3.602(5) Å]. These chains are connected to two adjacent chains via H bonds between the bromine atom Br2, the water oxygen atom Ow, and the acidic pyrazolyl hydrogens H13A and H2A [see Figure S7: N13–H13A···Br2 3.286(7) Å, N2–H2A···Ow 2.801(9) Å].

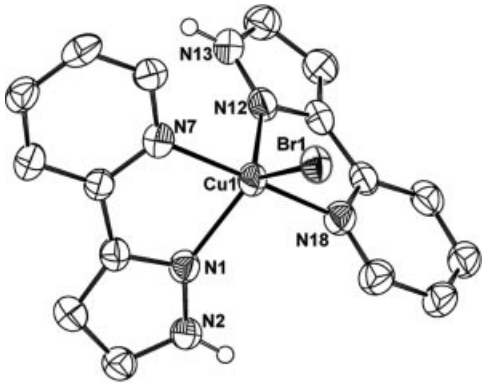


Figure 5. ORTEP drawing (30% probability level) of the cation [Cu(**6a**)$_2$Br]$^+$ of complex **10**. Only the N–H hydrogen atoms are shown for clarity.

Catalytic Studies

All the ligands prepared have been tested in the [copper/TEMPO]-mediated oxidation of a model substrate, i.e. benzyl alcohol. The initial catalytic oxidations of benzyl alcohol to benzaldehyde were performed applying the experimental conditions reported earlier,[17,21] namely 5 mol-% $CuBr_2$/TEMPO in acetonitrile/water (2:1) with potassium *tert*-butoxide as basic co-catalyst (required to deprotonate the alcoholic substrate).[17,21] For comparison, the conversions achieved with the [$CuBr_2$(2,2′-bipyridine)]/TEMPO system, reported in earlier studies,[17] have been included (Table 2, entry 1). Thus, the use of **4a** as ligand only leads to a conversion of 8% after a reaction time of 1 h (Table 2, entry 2). This poor catalytic activity (1.6 catalytic cycles) is most likely due to the observed precipitation of copper species (green precipitate). Indeed, the insolubility of the copper catalyst obviously retards the rate of the chemical transformation. However, a good conversion of 89% to the exclusive benzaldehyde is reached after 24 h. A more homogeneous reaction system is obtained when acetonitrile is used as the sole solvent (Table 2, entry 3). In that case, a conversion of 31% to benzaldehyde is achieved after 1 h. As no immediate precipitation is observed in the present experiment, this result suggests that the presence of an excess of water (Table 2, entry 2) probably leads to the formation of (multi)copper hydroxide species, which are poorly soluble in the reaction medium. The use of tetrabutylammonium hydroxide (a base exhibiting a higher solubility in acetonitrile than potassium *tert*-butoxide) as basic co-catalyst results in an efficient catalytic system, able to fully and selectively convert benzyl alcohol, after a reaction time of 24 h (Table 2, entry 4). The best catalytic activity is obtained when triethylamine is used as co-catalyst, since more than 2 catalytic cycles are completed after 5 min, and about 40% of benzaldehyde is produced after 1 h (Table 2, entry 5). Interestingly, colourless crystals, exhibiting luminescent properties, start to appear in the reaction mixture after a reaction time of about 15 min. X-ray diffraction studies on these crystals reveals that their solid-state structure corresponds to complex **7**. Surprisingly, this copper(I) complex **7** is very stable in the oxidative conditions of the reaction. Indeed, the reaction is performed in air in the presence of TEMPO, which is believed to play a role in the re-oxidation of the Cu^I species generated during the catalytic cycle (Scheme 1).[21,41] Thus, the lower catalytic activity achieved with this [copper/(pyrazole-pyridine)] system compared to the [copper/2,2′-bipyridine] one (Table 2, entry 1) may be justified by the gradual formation of **7** during the oxidation, resulting in a continuous decrease of active, homogeneous species in the reaction mixture. This high stability of **7** can be explained by the nature of the ligand **4a**. In fact, it has been lately established that a combination of hard/soft ligands appears to favour the stabilization of Cu^I species.[42] **4a** has been purposely designed to contain both a pyridine ring and a pyrazole ring. Therefore, such ditopic ligands apparently can efficiently stabilise copper(I) centres. Thus, the use of dihydrogen peroxide to promote the re-oxidation of the Cu^I ions to Cu^{II} does not lead to an enhancement of the catalytic activity (Table 2, entries 5 and 7). Actually, less active species appear to be formed in the presence of dihydrogen peroxide, because the conversions to benzaldehyde are significantly decreased (Table 2, entries 5 and 7). No improvement in conversion rate is observed when the reaction is performed at 50 °C (see Table 2, entries 5 and 6). On the contrary, the catalyst seems to be less effective (27% conversion after 1 h, whereas 39% conversion can be reached at room temperature), most likely as a result of its partial degradation at a higher temperature. Finally, in contrast to the published catalytic system,[21] the presence of non-coordinating anions, i.e. tetrafluoridoborate and

Table 2. Room temperature [copper(ligand)]-catalysed oxidation of benzyl alcohol.[a]

Entry	Ligand used	Cu(II) salt	Solvent	Basic co-catalyst	% Conv. after 5 min / 1 h / 24 h
1	**bipy**	$CuBr_2$	MeCN/H_2O	*t*BuOK	10 / 55 / 99
2	**4a**	$CuBr_2$	MeCN/H_2O	*t*BuOK	3 / 8 / 89
3	**4a**	$CuBr_2$	MeCN	*t*BuOK	5 / 31 / 97
4	**4a**	$CuBr_2$	MeCN	Bu_4NOH	8 / 20 / 99
5	**4a**	$CuBr_2$	MeCN	Et_3N	11 / 39 / 98
6	**4a**	$CuBr_2$	MeCN	Et_3N (50 °C)	7 / 27 / –
7	**4a**	$CuBr_2$	MeCN	Et_3N + H_2O_2	4 / 7 / 13
8	**4a**	$Cu(BF_4)_2$	MeCN/H_2O	*t*BuOK	3 / 7 / 25
9	**4a**	$Cu(BF_4)_2$	MeCN	*t*BuOK	6 / 14 / –
10	**4a**	$Cu(ClO_4)_2$	MeCN	Bu_4NOH	6 / 16 / –
11	**4a**	$Cu(ClO_4)_2$	MeCN	Et_3N	5 / 14 / –
12	**5a**	$CuBr_2$	MeCN/H_2O	*t*BuOK	10 / 29 / –
13	**5a**	$CuBr_2$	MeCN	Et_3N	11 / 23 / 30
14	**5a**	$CuBr_2$	MeCN/H_2O	*t*BuOK + H_2O_2	6 / 12 / –
15	**5a**	$CuBr_2$	MeCN	*t*BuOK + H_2O_2	9 / 14 / –
16	**6a**	$CuBr_2$	MeCN/H_2O	*t*BuOK	2 / 4 / 16
17	**6a**	$CuBr_2$	MeCN	Et_3N	5 / 31 / 33
18	**6a**	$Cu(BF_4)_2$	MeCN/H_2O	*t*BuOK	3 / 5 / 19
19	**6a**	$Cu(BF_4)_2$	MeCN	Et_3N	2 / 3 / –
20	**4b**[b]	$CuBr_2$	MeCN/H_2O	*t*BuOK	0 / 1 / –
21	**5b**	$CuBr_2$	MeCN/H_2O	*t*BuOK	0 / 2 / –
22	**6b**	$CuBr_2$	MeCN/H_2O	*t*BuOK	0 / <1 / –

[a] The catalytic oxidations of benzyl alcohol to benzaldehyde have been carried out using the procedure described in the Experimental Section. The ligand, copper(II) salt, solvent or solvent mixture, and basic co-catalyst used for each test reaction are mentioned in Table 2. [b] The use of 2 equiv. of *t*BuOK (instead of 1 equiv.) does not lead to a better catalytic activity (a conversion of 2% is achieved after a reaction time of 24 hours).

perchlorate, does not lead to an enhancement of the catalytic activity (see Table 2: entries 2 and 8, entries 3 and 9, entries 5 and 11, and entries 4 and 10). Presumably, coordinating anions, such as bromides, are required to complete the coordination sphere of the copper ion (see crystal structures of complexes **7** and **8**), giving rise to catalytically active species. Non-coordinating anions obviously leads to distinct coordination environments around the copper(II) centre, and actually to significantly less active species.

The use of **5a** (regioisomer of **4a**) as ligand in the copper-catalysed oxidation of benzyl alcohol gives less efficient catalysts (Table 2, entries 12–15). In fact, in all cases, a white precipitate rapidly develops in the reaction mixture which shows luminescent properties. This feature suggests the presence of copper(I) species (similarly to ligand **4a**, see above). Due to the fact that, contrary to **4a**, **5a** is a chelating ligand, its coordination probably induces an even better stabilisation of copper(I) entities. This hypothesis is corroborated by the interruption of the catalytic activity after about 1 h (only a conversion of 30% is achieved after a reaction time of 24 h, Table 2, entry 13), while the initial conversions (after a reaction time of 5 min) are comparable to those obtained with **4a** (see for instance Table 2, entries 5 and 12). Moreover, the addition of dihydrogen peroxide in the reaction medium does not favour the re-oxidation of the Cu^{I} ions to Cu^{II} (Table 2, entries 14 and 15), once again indicative of very stable copper(I) species.

The use of **6a** as a ligand generates poorly active catalysts (Table 2, entries 16–19). A maximum conversion of only 33% has been reached in pure acetonitrile, with triethylamine as co-catalyst, after a reaction time of 24 h (Table 2, entry 17). This lack of activity can be justified by the presence of the acidic N-pyrazolyl proton in the ligand. Indeed, under basic conditions, pyrazoles can be deprotonated, and the resulting pyrazolato ligands are known to promote the formation of cluster species.[43] In the present case, the addition of the base (to initiate the catalytic reaction, see experimental section) immediately results in the development of a green precipitate, which may originate from the deprotonation of the pyrazole ring, followed by the formation of insoluble (hence inactive) copper clusters.

Finally, the use of the naphthol-containing compounds **4b**–**6b** (Scheme 3) as ligands does not result in active catalytic systems (Table 2, entries 20–22). This lack of reactivity is obviously due to the presence of the naphtholic donor group in the ligands. In all cases, a dark brown-reddish solution is obtained while a light orange colour is observed with the first series of ligands (compounds **4a**–**6a**). Thus, the different coordination environment around the copper ions has a dramatic effect on the catalytic competence of the corresponding complex. In previous investigations, a bidentate donor, namely 2,2′-bipyridine (see also Table 2, entry 1), has been reported as an efficient ligand for the [copper/TEMPO]-catalysed oxidation of primary alcohols.[21] In the present study, bidentate pyridine/pyrazole donors (ligands **4a**–**6a**) and pyridine/phenol donors (ligands **4b**–**6b**) have been designed and tested in this copper-mediated reaction. It clearly appears that the use of pyridine/phenol bidentate ligands is not beneficial for this reaction, which should be considered for the design of new catalysts for this reaction.

Conclusions

Two series of pyrazole-based bidentate ligands have been designed and used to coordinate copper ions. As expected and recently suggested by theoretical investigations,[42] the pyridine-pyrazole ligands are capable of stabilizing copper(I) species, so that an air-stable copper(I) coordination polymer could be isolated and characterized by X-ray diffraction. The copper complexes from these ligands show interesting catalytic behaviours. Indeed, high catalytic activities are observed at the beginning of the reaction, which start to significantly decrease after one hour reaction time. Actually, a colourless crystalline precipitate develops in the reaction medium after a reaction time of approximately 15 min. This luminescent solid material is ascribed to copper(I) species (in one case, the crystals obtained in the reaction mixture have been characterized by X-ray diffraction). Therefore, the amount of active species in solution decreases in time, resulting in the observed diminution of the catalytic activity. However, the total conversion of the substrate after a reaction time of 24 h suggests that the (very stable) copper(I) species are slowly re-oxidized by atmospheric oxygen, since the catalyst is not "dead". It appears that the use of naphthol-pyrazole ligands inhibits the catalytic abilities of the corresponding copper complexes, but more studies are required to appraise this ligand effect. For instance, the use of bis-pyrazole and pyridine-phenol ligands are now investigated to compare the catalytic activities of their copper(II) complexes with those reported in the previous[21] and present reports, and evaluate the influence of the phenol (naphthol) ring on the catalysis.

In summary, the results reported in this paper strongly indicate that the combination of well-chosen donors to design a bidentate ligand for this reaction would most likely lead to a very efficient copper catalyst. The mixed ligand should be able to stabilise both the Cu^{I} and Cu^{II} species occurring during the catalytic cycle, but also to allow an easy "switching" between the two oxidation states. Investigations are currently ongoing to find the right combination of donor groups.

Experimental Section

General Remarks: All chemicals were of reagent grade and were used as commercially obtained. Elemental analyses for C, H, and N were performed with a Perkin–Elmer 2400 analyzer. FTIR spectra were recorded with a Perkin–Elmer Paragon 1000 FTIR spectrophotometer, equipped with a Golden Gate ATR device, using the reflectance technique (4000–300 cm^{-1}). ^1H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) instrument. Chemical shifts are reported in δ (parts per million) relative to an internal standard of tetramethylsilane. ESI mass analyses were carried out on a Voyager Elite from PerSeptive Biosystems. The excitation and emission spectra were recorded with a Perkin–Elmer LS50B luminescence spectrometer. The intensity of the emission spectra was corrected for the sensitivity of the detector.

Syntheses of the Ligands: The preparation of the different ligands was based on an earlier published procedure.[44]

Synthesis of 3-(Dimethylamino)-1-(pyridin-2-yl)prop-2-en-1-one (3a):[45] 10 g (0.0825 mol) of 2-acetylpyridine (**1a**) were introduced in a round-bottomed flask. Then, 20 mL (17.9 g, 0.1504 mol) of *N*,*N*-dimethylformamide dimethyl acetal (**2**) were added, and the resulting reaction mixture was refluxed overnight. The dark brown solution obtained was evaporated to dryness. The resulting dark-brown crystalline material was washed with hexane (3 × 100 mL) and with diethyl ether (3 × 100 mL), yielding 10.6 g (yield 73%) of pure, bright yellow **3a**, as previously obtained by Balavoine et al.[45]

Synthesis of 3-(Dimethylamino)-1-(1-hydroxynaphthalen-2-yl)prop-2-en-1-one (3b):[46] **3b** was synthesized using the procedure described above for the preparation of **3a**, starting from 5 g (0.0269 mol) of 2-acetyl-1-naphthol. **3b** was obtained as a pure yellow powder,[46] with a yield of 75% (4.9 g).

Synthesis of 2-(1-Methyl-1*H*-pyrazol-5-yl)pyridine (4a) and 2-(1-Methyl-1*H*-pyrazol-3-yl)pyridine (5a): 3 g (0.0170 mol) of **3a** and 6 mL (0.1120 mol) of methylhydrazine were mixed in a 50 mL round-bottomed flask containing 10 mL of ethanol. The reaction mixture was heated at 60 °C and stirred for 30 min. After cooling to room temperature, 30 mL of distilled water were added, giving rise to the precipitation of a light yellow solid. This crude product containing both regioisomers, namely **4a** and **5a**, was purified by column chromatography (SiO_2, eluent ethyl acetate/hexane, 1:1 until the isolation of the first isomer **4a**; then an ethyl acetate/hexane mixture (8:2) was used as eluent to isolate pure **5a**). Yield 1.43 g of **4a** (53%) and 0.32 g of **5a** (17%).

Isomer 4a: $C_9H_9N_3$ (159.19): calcd. C 67.90, H 5.70, N 26.40; found C 68.20, H 5.32, N 25.95. ES(+)-MS: *m*/*z* = 160.04 [M + H^+], 181.99 [M + Na^+]. FT-IR (neat solid): $\tilde{\nu}$ = 2949, 1589, 1461, 1422, 1388, 1278, 1152, 996, 928, 765, 688, 648, 622, 403 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 3.99 (s, 3 H, CH_3), 6.35 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 4-H pz), 6.95 (dd, $^3J_{H,H}$ = 4.9, $^3J_{H,H}$ = 7.7 Hz, 1 H, 5-H py), 7.29 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 3-H pz), 7.32 (d, $^3J_{H,H}$ = 2.0 Hz, 1 H, 3-H py), 7.42 (dd, $^3J_{H,H}$ = 2.0, $^3J_{H,H}$ = 7.7 Hz, 1 H, 4-H py), 8.41 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, 6-H pz) ppm.

Isomer 5a:[47] $C_9H_9N_3$ (159.19): calcd. C 67.90, H 5.70, N 26.40; found C 67.85, H 5.65, N 25.94. ES(+)-MS: *m*/*z* = 160.01 [M + H^+]. FT-IR (neat solid): $\tilde{\nu}$ = 2949, 1589, 1459, 1423, 1388, 1277, 1152, 996, 928, 764, 688, 648, 622, 402 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 3.97 (s, 3 H, CH_3), 6.85 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, 4-H pz), 7.28 (dd, $^3J_{H,H}$ = 4.8, $^3J_{H,H}$ = 7.8 Hz, 1 H, 5-H py), 7.40 (d, $^3J_{H,H}$ = 2.2 Hz, 1 H, 3-H pz), 7.54 (dd, $^3J_{H,H}$ = 7.8, $^3J_{H,H}$ = 7.9 Hz, 1 H, 4-H py), (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 3-H py), 8.61 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, 6-H pz) ppm.

Synthesis of 2-(1*H*-Pyrazol-3-yl)pyridine (6a): 3 g (0.0170 mol) of **3a** and 6 mL (0.1235 mol) of hydrazine monohydrate were mixed in a 50 mL round-bottomed flask containing 10 mL of ethanol. The reaction mixture was heated at 60 °C and stirred for 30 min at this temperature. After cooling to room temperature, 30 mL of distilled water were added, producing a light yellow precipitate. This solid was washed on a glass filter with hexane (2 × 200 mL) and diethyl ether (2 × 200 mL). After drying at 100 °C for 4 h, the pure ligand **6a** is obtained. Yield 0.74 g (30%). $C_8H_7N_3$ (145.16): calcd. C 66.19, H 4.86, N 28.95; found C 65.89, H 4.82, N 29.12. ES(+)-MS: *m*/*z* = 146.07 [M + H^+], 167.99 [M + Na^+]. FT-IR (neat solid): $\tilde{\nu}$ = 3122, 2896, 1590, 1503, 1454, 1417, 1356, 1191, 1000, 876, 758, 615, 403 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 6.84 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 4-H pz), 7.28 (dd, $^3J_{H,H}$ = 3.6, $^3J_{H,H}$ = 4.9 Hz, 1 H, 5-H py), 7.69 (d, $^3J_{H,H}$ = 1.9 Hz, 1 H, 3-H pz), 7.78 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, 4-H py), 8.69 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, 6-H py), 12.11 (s, 1 H, N–H) ppm.

Synthesis of 2-(1-Methyl-1*H*-pyrazol-5-yl)naphthalen-1-ol (4b) and 2-(1-Methyl-1*H*-pyrazol-3-yl)naphthalen-1-ol (5b): 3 g (0.0124 mol) of **3b** and 6 mL (0.1120 mol) of methylhydrazine were mixed in a 50 mL round-bottomed flask containing 10 mL of ethanol. The reaction mixture was heated at 60 °C, and stirred for 30 min at this temperature. After cooling to room temperature, 30 mL of distilled water were added, resulting in a light brown emulsion. This solution was extracted with dichloromethane (3 × 50 mL). The pooled organic phase was dried with magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The resulting brown viscous crude compound was purified by column chromatography (SiO_2, ethyl acetate/hexane, 1:1), yielding 1.6 g of **4b** (58%) and 0.78 g of **5b** (28%).

Isomer 4b:[48] $C_{14}H_{12}N_2O$ (224.26): calcd. C 74.98, H 5.39, N 12.49; found C 74.92, H 5.17, N 12.53. M.p. 85 °C. ES(+)-MS: *m*/*z* = 224.91 [M + H$^+$]. FT-IR (neat solid): $\tilde{\nu}$ = 2938, 1576, 1495, 1386, 1354, 1089, 805, 755, 745, 698, 659, 572, 486, 422 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 3.98 (s, 3 H, CH_3), 6.68 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, 4-H pz), 7.38 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 4-H naphthol), 7.43 (d, $^3J_{H,H}$ = 2.3 Hz, 1 H, 3-H pz), 7.45 (dd, $^3J_{H,H}$ = 4.8 Hz, 1 H, 6-H naphthol), 7.49 (dd, $^3J_{H,H}$ = 3.9 Hz, 1 H, 7-H naphthol), 7.65 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 3-H naphthol), 7.77 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, 5-H naphthol), 8.42 (d, $^3J_{H,H}$ = 3.9 Hz, 1 H, 8-H naphthol), 11.60 (br. s, 1 H, O–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 38.3, 101.9, 109.7, 118.5, 122.7, 123.6, 125.0, 125.3, 126.2, 127.2, 130.7, 133.8, 151.2, 151.4 ppm.

Single-crystals of **4b** were obtained, which were analysed by X-ray diffraction. An ORTEP view of ligand **4b** is depicted in Figure S8. The molecular structure is uneventful and as expected.

Isomer 5b:[48] $C_{14}H_{12}N_2O$ (224.26): calcd. C 74.98, H 5.39, N 12.49; found C 74.57, H 5.14, N 12.49. M.p. 142 °C. ES(+)-MS: *m*/*z* = 224.98 [M + H$^+$]. FT-IR (neat solid): $\tilde{\nu}$ = 2943, 1571, 1389, 1292, 1199, 1074, 809, 788, 739, 667, 570, 484, 436, 423 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 3.80 (s, 3 H, CH_3), 6.43 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, 4-H pz), 7.25 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, 4-H naphthol), 7.49 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, 3-H naphthol), 7.53–7.59 (m, 2 H, 6-H naphthol + 7-H naphthol), 7.61 (d, $^3J_{H,H}$ = 1.8 Hz, 1 H, 3-H pz), 7.84 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, 5-H naphthol), 8.33 (d, $^3J_{H,H}$ = 9.5 Hz, 1 H, 8-H naphthol), 11.72 (br. s, 1 H, O–H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 36.8, 106.8, 110.3, 119.8, 122.8, 125.1, 125.6, 127.1, 127.2, 127.4, 134.8, 138.7, 139.6, 150.4 ppm.

Synthesis of 2-(1*H*-Pyrazol-5-yl)naphthalen-1-ol (6b):[48] 2.76 g (0.0114 mol) of **3b** and 6 mL (0.1235 mol) of hydrazine monohydrate were mixed in a 50 mL round-bottomed flask containing 9 mL of ethanol. The reaction mixture was heated at 60 °C and stirred for 30 min at this temperature. After cooling to room temperature, 30 mL of distilled water were added, producing a light brown crystalline product. This solid was filtered off, and washed with hexane (2 × 200 mL). After drying at 100 °C for 4 h, the pure ligand **6b** was obtained. Yield 1.8 g (75%). $C_{13}H_{10}N_2O$ (210.23): calcd. C 74.27, H 4.79, N 13.33; found C 74.16, H 4.99, N 13.18. ES(+)-MS: *m*/*z* = 210.92 [M$^+$], 232.92 [M + Na$^+$]. FT-IR (neat solid): $\tilde{\nu}$ = 3303, 3054, 1636, 1579, 1505, 1389, 1283, 1077, 976, 878, 759, 720, 656, 571, 484, 420 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 6.80 (d, $^3J_{H,H}$ = 2.6 Hz, 1 H, 4-H pz), 7.41 (d, $^3J_{H,H}$ = 8.6 Hz, 1 H, 4-H naphthol), 7.46–7.53 (m, 2 H, 3-H naphthol + 6-H naphthol), 7.67–7.70 (m, 2 H, 7-H naphthol + 3-H pz), 7.78 (d, $^3J_{H,H}$ = 9.4 Hz, 1 H, 5-H naphthol), 8.43 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, 8-H naphthol), 10.2–10.8 (v br. s, 2 H, O–H + N–H) ppm.

Preparation of the Coordination Compounds

Synthesis of [Cu_2(4a)$_2Br_2$]$_n$ (7): A solution of ligand **4a** (100 mg, 0.628 mmol) in methanol (10 mL) was added to a solution of copper(II) bromide (140 mg, 0.628 mmol) in methanol (10 mL). The resulting dark-green solution was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After one day, colourless crystals of **7** were collected (yield 146 mg, 77%). $C_{18}H_{18}Br_2Cu_2N_6$ (605.28): calcd. C 35.72, H 3.00, N 13.88; found C 35.20, H 2.93, N 13.72. IR (neat): $\tilde{\nu}$ = 3119, 3051, 1599, 1465, 1420, 1390, 1284, 1225, 1009, 940, 808, 786, 755, 700, 645, 542, 414 cm^{-1}. Unit cell parameters: *a* = 7.668(2) Å, *b* = 8.492(2) Å, *c* = 9.174(2) Å, α = 96.90(3)°, β = 114.06(3)°, γ = 107.49(3)° (see Table S1).

The same coordination compound (as evidenced by single-crystal X-ray analysis) was obtained from an acetonitrile solution of the reactants (using the same concentration), but after one week (instead of one day in methanol).

Complex **7** has also been isolated during the catalysis reactions, and characterized by X-ray diffraction analysis.

Complex **7** is insoluble in common solvents such as methanol, acetonitrile, THF, chloroform and dichloromethane. Consequently, NMR studies of the solution structure of the diamagnetic complex are not possible.

Complex **7** can also be prepared directly from CuBr and the ligand **4a**, using the following reaction conditions: a solution of ligand **4a** (25 mg, 0.157 mmol) in acetonitrile (5 mL) was added to a solution of copper(I) bromide (23 mg, 0.157 mmol) in acetonitrile (5 mL). The resulting light-green solution was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After two hours, colourless crystals of **7** started to grow. The crystals were collected after one day (yield 31 mg, 33%). $C_{18}H_{18}Br_2Cu_2N_6$ (605.28): calcd. C 35.72, H 3.00, N 13.88; found C 35.31, H 2.82, N 13.75. IR (neat): $\tilde{\nu}$ = 3119, 3054, 1560, 1464, 1418, 1392, 1284, 1225, 1010, 940, 808, 786, 755, 700, 645, 543, 414 cm^{-1}. The structure, corresponding to complex **7**, was confirmed by X-ray diffraction analysis. Unit cell parameters: *a* = 7.661(2) Å, *b* = 8.502(2) Å, *c* = 9.160(2) Å, α = 96.90(3)°, β = 114.12(3)°, γ = 107.39(3)°.

Synthesis of [Cu(4aH)Br$_3$] (8): Red crystals of **8** were obtained from the solution above. Since these few single-crystals were mixed with crystals of **7**, they were only characterised by X-ray diffraction (see Discussion). Unit cell parameters: *a* = 7.611(2) Å, *b* = 7.908(2) Å, *c* = 11.787(2) Å, α = 104.99(3)°, β = 100.48(3)°, γ = 94.75(3)° (see Table S1).

However, complex **8** could also be synthesized from $CuBr_2$ and **4a**·HBr according to the following procedure: 18 μL (0.157 mmol) of HBr_{aq} 48% were added to a solution of ligand **4a** (25 mg, 0.157 mmol) in 5 mL of acetonitrile. The solution was stirred for 10 min, and 35 mg (0.157 mmol) of $CuBr_2$ were subsequently added. The resulting dark-green solution was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After one day, red needle-shaped crystals were collected (yield 17 mg, 23%). $C_9H_{10}Br_3CuN_3$ (463.45): calcd. C 23.32, H 2.17, N 9.07; found C 23.10, H 2.63, N 9.12. IR (neat): $\tilde{\nu}$ = 2934, 2879, 1633, 1612, 1558, 1490, 1447, 1422, 1392, 1285, 1226, 1186, 1168, 1062, 1009, 914, 815, 764, 684, 640, 524, 469, 378 cm^{-1}. The structure, corresponding to complex **8**, was confirmed by X-ray diffraction analysis. Unit cell parameters: *a* = 7.598(2) Å, *b* = 7.892(2) Å, *c* = 11.785(2) Å, α = 105.12(3)°, β = 100.39(3)°, γ = 94.81(3)°.

Complex **8** could be obtained as well by addition of HBr to a solution of complex **7**. As for the preparation of complex **7** (from CuBr,

see above), a solution of one equivalent (25 mg, 0.157 mmol) of **4a** in 5 mL of acetonitrile was added to a solution of one equivalent of copper(I) bromide (23 mg, 0.157 mmol) in acetonitrile (5 mL). The resulting light-green solution was stirred for 15 min. Next, 18 μL (0.157 mmol) of HBr_{aq} 48% were added, which resulted in an immediate change of the colour of the reaction mixture to dark-green. The solution was filtered and the filtrate was left unperturbed for the slow evaporation of the solvent. After one day, red needle-shaped crystals were collected (yield 10 mg, 14%). $C_9H_{10}Br_3CuN_3$ (463.45): calcd. C 23.32, H 2.17, N 9.07; found C 23.15, H 2.25, N 8.93. IR (neat): $\tilde{\nu}$ = 2934, 2878, 1633, 1612, 1558, 1490, 1447, 1423, 1393, 1285, 1226, 1186, 1168, 1063, 1010, 914, 815, 764, 684, 640, 524, 470, 379 cm^{-1}. The structure, corresponding to complex **8**, was confirmed by X-ray diffraction analysis. Unit cell parameters: a = 7.605(2) Å, b = 7.911(2) Å, c = 11.792(2) Å, α = 104.96(3)°, β = 100.45(3)°, γ = 94.70(3)°.

Synthesis of $[Cu_3(5a)_3Br_6]$ (9): A solution of ligand **5a** (100 mg, 0.628 mmol) in acetonitrile (10 mL) was added to a solution of copper(II) bromide (140 mg, 0.628 mmol) in acetonitrile (10 mL). The resulting dark green-brown solution was filtered, and the filtrate was left unperturbed. After 10 min, red needle-shaped crystals of **9**, suitable for X-ray diffraction analysis, started to grow. After one day, the crystals were collected (yield 204 mg, 85%). $C_{27}H_{27}Br_6Cu_3N_9$ (1147.63): calcd. C 28.26, H 2.37, N 10.98; found C 28.29, H 1.95, N 11.19. IR (neat): $\tilde{\nu}$ = 3130, 1609, 1502, 1436, 1366, 1284, 1234, 1154, 1075, 1019, 896, 772, 719, 685, 643, 610, 417 cm^{-1}.

Complex **9** was also obtained (as evidenced by single-crystal X-ray analysis) from a methanolic solution of the reactants, exhibiting the same molar concentration.

Synthesis of $[Cu(6a)_2Br]Br\cdot H_2O\cdot CH_3CN$ (10): A solution of ligand **6a** (100 mg, 0.689 mmol) in acetonitrile (10 mL) was added to a solution of copper(II) bromide (154 mg, 0.689 mmol) in acetonitrile (10 mL). The resulting green solution was filtered, and the filtrate was left unperturbed for the slow evaporation of the solvent. After a few days, green block-shaped crystals of **10** were obtained (yield 142 mg, based on the ligand, 72%). $C_{18}H_{19}Br_2CuN_7O$ (572.74): calcd. C 37.75, H 3.34, N 17.12; found C 37.50, H 3.62, N 17.03. IR (neat): $\tilde{\nu}$ = 3301, 3113, 1610, 1454, 1442, 1432, 1375, 1290, 1187, 1090, 1060, 1016, 972, 768, 699, 642, 568, 487, 419 cm^{-1}.

Typical Catalytic Experiment: Benzyl alcohol (1.08 g, 10 mmol) was dissolved in 15 mL of acetonitrile. 112 mg (0.5 mmol) of copper(II) bromide were then added, followed by 0.5 mmol of ligand. Next, 78 mg (0.5 mmol) of TEMPO were added, resulting in a dark green solution. Finally, the oxidation reaction was initiated by the addition of 51 mg (0.5 mmol, 70 μL) of triethylamine, causing an instantaneous change of colour, from dark green to orange. The course of the reaction was monitored by gas chromatography (GC).

X-Ray Crystal Structure Determinations: Crystallographic data and refinement details are given in Tables S1 and S2. A crystal was selected for the X-ray measurements and mounted to the glass fiber using the oil drop method[49] and data were collected at 173 K (or 150 K for compound **10**) on a Nonius Kappa CCD diffractometer (Mo-K_α radiation, graphite monochromator, λ = 0.71073). The intensity data were corrected for Lorentz and polarization effects, and for absorption. The programs collect,[50] SHELXS-97,[51] SHELXL-97[52] were used for data reduction, structure solution and structure refinement, respectively. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms.

CCDC-643549 to -643552 (for **4b**–**9**) and -643309 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Crystallographic data for compounds **4b** and **7**–**10**, crystal structure of **4b**, crystal packing diagrams for **7**–**10**, excitation and luminescent spectra of **7**.

Acknowledgments

This work has been supported financially by the Graduate Research School Combination "Catalysis", a joint activity of the graduate research schools NIOK, HRSMC and PTN. Financial support from European Cooperation in the Field of Science and Technology (COST) Action D35/0011, Werkgroep Fundamenteel Materialen Onderzoek (WFMO) Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) – Foundation for the Chemical Sciences (Chemische Wetenschappen, CW), are gratefully acknowledged. Coordination by the FP6 Network of Excellence "Magmanet" (contract number 515767) is also kindly acknowledged. We would also like to thank Paul de Hoog for his help with the NMR studies.

[1] R. A. Sheldon, *J. Chem. Technol. Biotechnol.* **1997**, *68*, 381–388.
[2] R. A. Sheldon, *Chem. Tech.* **1991**, *21*, 566–576.
[3] G. Cainelli, G. Cardillo, in *Chromium Oxidations in Organic Chemistry*, Springer, Berlin, **1984**.
[4] W. S. Trahanovsky, in *Oxidation in Organic Chemistry*, Academic Press, New York, **1978**.
[5] E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, *20*, 399–402.
[6] A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165–185.
[7] R. A. Sheldon, I. Arends, G. J. Ten Brink, A. Dijksman, *Acc. Chem. Res.* **2002**, *35*, 774–781.
[8] P. Chaudhuri, M. Hess, J. Muller, K. Hildenbrand, E. Bill, T. Weyhermuller, K. Wieghardt, *J. Am. Chem. Soc.* **1999**, *121*, 9599–9610.
[9] P. Paraskevopoulou, N. Psaroudakis, S. Koinis, P. Stavropoulos, K. Mertis, *J. Mol. Catal. A* **2005**, *240*, 27–32.
[10] H. L. Wu, Q. H. Zhang, Y. Wang, *Adv. Synth. Catal.* **2005**, *347*, 1356–1360.
[11] M. J. Schultz, S. S. Hamilton, D. R. Jensen, M. S. Sigman, *J. Org. Chem.* **2005**, *70*, 3343–3352.
[12] E. Zueva, P. H. Walton, J. E. McGrady, *Dalton Trans.* **2006**, 159–167.
[13] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657–10666.
[14] W. Adam, C. R. Saha-Moller, P. A. Ganeshpure, *Chem. Rev.* **2001**, *101*, 3499–3548.
[15] A. E. J. de Nooy, A. C. Besemer, H. vanBekkum, *Synthesis* **1996**, 1153–1174.
[16] T. Inokuchi, S. Matsumoto, S. Torii, *J. Synth. Org. Chem. Jpn.* **1993**, *51*, 910–920.
[17] P. Gamez, I. W. C. E. Arends, J. Reedijk, R. A. Sheldon, *Chem. Commun.* **2003**, 2414–2415.
[18] R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071.
[19] D. Geisslmeier, W. G. Jary, H. Falk, *Monatsh. Chem.* **2005**, *136*, 1591–1599.
[20] N. Jiang, A. J. Ragauskas, *Org. Lett.* **2005**, *7*, 3689–3692.
[21] P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, *Adv. Synth. Catal.* **2004**, *346*, 805–811.
[22] P. Gamez, I. A. Koval, J. Reedijk, *Dalton Trans.* **2004**, 4079–4088.
[23] P. Gamez, J. von Harras, O. Roubeau, W. L. Driessen, J. Reedijk, *Inorg. Chim. Acta* **2001**, *324*, 27–34.

[24] A. L. Spek, *Platon, A Multipurpose Crystallographic Tool*, Utrecht University, The Netherlands, **2006**.
[25] L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955–964.
[26] J. C. Dyason, L. M. Engelhardt, P. C. Healy, C. Pakawatchai, A. H. White, *Inorg. Chem.* **1985**, *24*, 1950–1957.
[27] E. Bosch, C. L. Barnes, *J. Coord. Chem.* **2003**, *56*, 329–336.
[28] J. Wang, S. L. Zheng, S. Hu, Y. H. Zhang, M. L. Tong, *Inorg. Chem.* **2007**, *46*, 795–800.
[29] P. C. Ford, E. Cariati, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625–3647.
[30] A. Luque, J. Sertucha, L. Lezama, T. Rojo, P. Roman, *J. Chem. Soc. Dalton Trans.* **1997**, 847–854.
[31] M. M. Thackeray, L. R. Nassimbeni, *Acta Crystallogr., Sect. B* **1974**, *30*, 2469–2473.
[32] S. Haddad, R. D. Willett, *J. Chem. Crystallogr.* **2001**, *31*, 37–43.
[33] R. D. Willett, K. Halvorson, *Acta Crystallogr., Sect. B* **1988**, *44*, 2068–2071.
[34] T. J. Mooibroek, P. Gamez, *Inorg. Chim. Acta* **2007**, *360*, 381–404.
[35] A. M. Atria, R. F. Baggio, N. Espinosa, M. T. Garland, J. Manzur, Y. Moreno, E. Spodine, *Acta Crystallogr., Sect. C* **1994**, *50*, 1066–1069.
[36] M. B. Bushuev, V. P. Krivopalov, N. V. Semikolenova, E. V. Peresypkina, A. V. Virovets, L. A. Sheludyakova, L. G. Lavrenova, V. A. Zakharov, S. V. Larionov, *Russ. J. Coord. Chem.* **2006**, *32*, 199–207.
[37] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349–1356.
[38] M. T. Garland, D. Grandjean, *Acta Crystallogr., Sect. C* **1987**, *43*, 643–645.
[39] A. Morsali, A. Ramazani, M. Babaee, F. Jamali, F. Gouranlou, H. Arjmandfar, A. Yanovsky, *J. Coord. Chem.* **2003**, *56*, 455–461.
[40] C. M. Pask, K. D. Camm, N. J. Bullen, M. J. Carr, W. Clegg, C. A. Kilner, M. A. Halcrow, *Dalton Trans.* **2006**, 662–664.
[41] I. W. C. E. Arends, P. Gamez, R. A. Sheldon, *Adv. Inorg. Chem.* **2006**, *58*, 235–279.
[42] S. Sivasankar, N. Sadhukhan, J. K. Bera, A. G. Samuelson, *New J. Chem.* **2007**, *31*, 385–393.
[43] A. P. Sadimenko, S. S. Basson, *Coord. Chem. Rev.* **1996**, *147*, 247–297.
[44] L. D. Pachón, A. Golobic, B. Kozlevcar, P. Gamez, H. Kooijman, A. L. Spek, J. Reedijk, *Inorg. Chim. Acta* **2004**, *357*, 3697–3702.
[45] E. Bejan, H. A. Haddou, J. C. Daran, G. G. A. Balavoine, *Synthesis* **1996**, 1012–1015.
[46] Y. I. Lin, S. A. Lang, *J. Heterocycl. Chem.* **1977**, *14*, 345–347.
[47] W. R. Thiel, M. Angstl, T. Priermeier, *Chem. Ber.* **1994**, *127*, 2373–2379.
[48] J. Catalan, J. C. Delvalle, R. M. Claramunt, M. D. S. Maria, V. Bobosik, R. Mocelo, J. Elguero, *J. Org. Chem.* **1995**, *60*, 3427–3439.
[49] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615–619.
[50] Nonius, *COLLECT*, Nonius BV, Delft, The Netherlands, **2002**.
[51] G. M. Sheldrick, *SHELXS-97 Program for Crystal Structure Determination*, University of Göttingen, Germany, **1997**.
[52] G. M. Sheldrick, *SHELXL-97-2 Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received: April 18, 2007
Published Online: July 17, 2007

