DOI: 10.1002/chem.200901720

Synthetic and Structural Studies on Copper 1*H*-[1,10]-Phenanthrolin-2-one Coordination Complexes: Isolation of a Novel Intermediate During 1,10-Phenanthroline Hydroxylation

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Abstract: The synthesis and crystal structure elucidation of a novel dinuclear heteroleptic copper(II) complex has led to an alternative mechanism in the formation of covalent hydrates. During further studies on the synthesis and properties of $[Cu_2(ophen)_2]$ (**1**), a dinuclear complex of copper(I) with 1*H*-[1,10]-phenanthrolin-2-one (Hophen), two intermediates/alternative products **2** and **3** were isolated. The dinuclear, antiferromagnetic complex $[Cu_2(ophen)_2(phen)_2]\cdot(NO_3)_2\cdot 9H_2O$ (**3**, phen = 1,10-phenanthroline) contains two five-coordinate copper(II) ions, both with trigonal-bipyramidal coordination, which are bridged together through deprotonated hydroxyl groups with a Cu–Cu non-bonding distance of 3.100 Å. Complex $[Cu(phen)_2(H_2O)]\cdot(NO_3)_2$ (**2**) is a polymorph of a previously reported material. The occurrence of **2** and **3** has led us to propose a variation to the Gillard mechanism for the formation of covalent hydrates in bidentate N-heterocycles in which the attacking nucleophile may be the deprotonated form of **2**, $[Cu(phen)_2(OH)]^-$, rather than free OH^-.

Keywords: copper · hydroxylation · nitrogen heterocycles · reaction mechanisms · structure elucidation

Introduction

Bidentate N-heterocycles such as 1,10-phenanthroline (phen) are important building blocks for the preparation of coordination compounds[1,2] and metallo–supramolecular assemblies.[3–7] These materials form reliable metal–ligand combinations that result in predictable 3D arrangements, and hence are an important aid in the rational design of materials with specific architectures and properties. To this end, recent reports of the synthesis of a novel chelating/bridging ligand, 1*H*-[1,10]-phenanthrolin-2-one (Hophen)[8,9] are particularly significant. This ligand tends to produce polynuclear clusters such as those observed in $[Cu_2(ophen)_2]$ (**1**),[8–10] $[Cd_3Cl(ophen)_5]\cdot 1.5H_2O\cdot 2CH_2Cl_2$,[11] $[Zn_4O(ophen)_4(OAc)_2]\cdot 4H_2O\cdot 2CH_2Cl_2$[12] and $[Ag_2(ophen)_2]$,[13] which offer even greater structural predictability and rigidity as building blocks in supramolecular chemistry. Hophen is important because the naked ligand is a purple-blue light emitter, and forms complexes with d^{10} metals[11,12] with photoluminescent properties in the blue/green region that are tuneable with metal type. Such complexes are promising as blue emitters in full-colour electroluminescent displays.

Hophen was first reported by Zhang et al.,[8–10] who unexpectedly generated the ligand in situ by reaction of a basic solution of copper(II) nitrate with phen under hydrothermal conditions to produce the neutral, dinuclear Cu(I) complex **1**. The pure ligand was isolated by demetallation with ammonium sulphide. Since this report of the stereospecific hydroxylation of phen (and bipy) in the presence of copper(II) ions, there has been considerable conjecture regarding an appropriate mechanism for the reaction because there are at least three possibilities: direct nucleophilic attack by free OH^- on the ligand; direct nucleophilic attack by metal-coordinated OH^- on the ligand; or an E2 elimination/addition, whereby OH^- attack generates a pyridyne intermediate fol-

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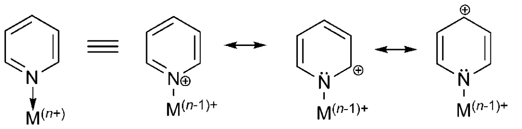
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901720.

lowed by water addition. This latter mechanism is comparable to the Dow Chemical hydrothermal process for the industrial preparation of phenol from chlorobenzene.[14]

Gillard[15] and Constable[16] have previously suggested that N coordination of pyridine-type ligands to metal ions is analogous to quaternisation by a proton (H^+) or an alkylating agent, allowing the positive charge from the metal centre to be delocalised over the pyridine ring, leaving the carbon atoms in the 2- and 4-position susceptible to nucleophilic attack (Scheme 1). In aqueous media this can result in hydroxylation of the heterocyclic ring and the formation of a covalent hydrate (CH, hydration across a −C=N− bond), which can then release a proton to form the conjugate pseudo-base (CB) or undergo an intramolecular shift to form the metal–hydroxy species (DH, IMS in Scheme 2). In subsequent steps, the covalent hydrate can be aromatised by oxidation (−2H), giving rise to the 2- (or 4-) substituted hydroxy-pyridine (HP in Scheme 2) in a reaction exactly analogous to the Chichibabin reaction in which sodamide ($NaNH_2$) aminates the 2-position of pyridine by direct reaction.[16]



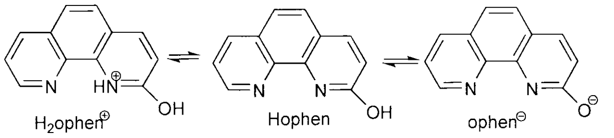
Scheme 1. A valence-bond representation of a coordinated pyridine (the donor covalent bond between N and M^{n+} can also be considered to form a shared covalent bond, effectively placing positive charge on the N atom). The positive charge is delocalised into the ring and the 2- and 4-positions develop electrophilic character, making them susceptible to nucleophilic attack.[10,16]

At the time of Gillard's publication,[15] an unambiguous mechanism could not be proposed owing to a lack of structural evidence. One suggestion was for a nucleophile such as OH^- to attach itself to the metal centre, and in the case of $[M(phen)_2]^{2+}$ to form a five-coordinate complex (similar to the DH, IMS structure in Scheme 2), rather than to bind to the N-heterocycle to form a covalent hydrate (CH).[16,17] It was not until several decades later when Zhang and co-workers[8–13] synthesised a range of d^{10} complexes with hydroxylated phen ligands (Hophen) that the Gillard mechanism was invoked as a viable rationalisation for the formation of such hydroxylated heterocycles.

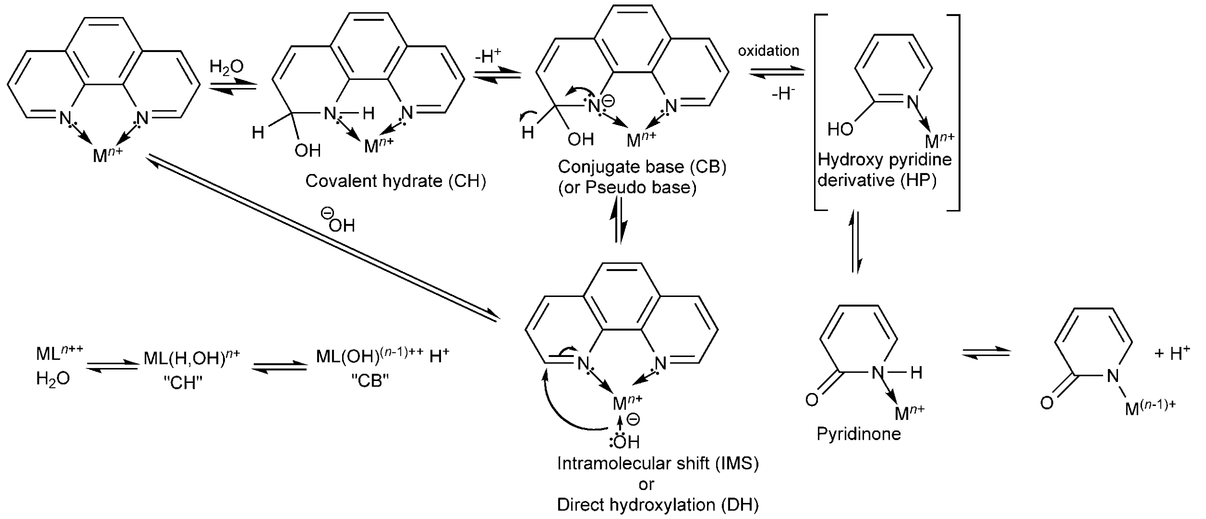
As part of our studies on the Cu phen/ophen system, we have isolated two further complexes in the series that have been characterised by X-ray structure determination, and which provide evidence for the role of a $Cu^{2+}-OH^-$ species as a possible intermediate in the reaction, thus clarifying the likely mechanism and supporting, at least in part, the original proposal of Gillard.[16]

Results and Discussion

Preparation of the dinuclear copper(I) complex **1** by using the method published by Zhang and co-workers[8] was generally successful, with blue-black, block-like crystals of $[Cu_2(ophen)_2]$ isolated from an emerald-green supernatant in 35–45% yield. However, this method was found to be extremely pH dependent, and a pH of 9 (slightly higher than initially reported) was required to ensure hydroxylation and deprotonation of the Hophen (Scheme 3). This observation is in accord with the expected weak-acid behaviour of Hophen, which contains the weakly acidic phenol group ($pK_a \approx 10$) and would have acid dissociation constants similar to the related model compound, 8-hydroxyquinoline with pK_a values of 4.85 (NH^+) and 9.95 (OH).[18]



Scheme 3. Deprotonation equilibria for Hophen.



Scheme 2. Equilibria demonstrating the formation of a covalent hydrate and its conjugate base. The conjugated base can either be oxidised to the hydroxypyridine (HP) species, or it may undergo an intramolecular shift of the hydroxyl group to form the metal hydroxy species, $ML(OH^-)^{n+}$ (IMS/DH).

Products **2** and **3** were isolated as light-green and emerald-green crystals in 20–25 and 3–5 % yield, respectively, from an emerald-green supernatant, and they may be intermediates in the Gillard mechanism.[15] The colour of these materials suggested that copper was present in the +1 state in **1** and the +2 state in **2** and **3**. FTIR spectra of **1** and **3** were similar, whereas that of **2** indicated the presence of coordinated water with a strong ν(H-O-H) band at 1428 cm^{-1}. The compositions of **2** and **3** were confirmed by single-crystal X-ray diffraction, which also provided unambiguous structural characterisation of each complex.

The structure of **2** had been previously determined by Nakai and Deguchi in 1975[19] and by Catalan et al. in 1995[20] with *R* factors of 11.8 (293 K) and 4.2 % (293 K), respectively. The structure was re-determined here with an *R* factor of 2.67 % (130 K). Structure **2** contains a five-coordinate mononuclear copper(II) cation in which the copper atom is coordinated to four nitrogen atoms from two phen ligands (Cu−N = 1.993–2.051 Å) and an oxygen atom from a water molecule (Cu−O = 2.054 Å), and is counter-balanced by two nitrate anions. Thus, the molecular unit of **2** has the composition $[Cu(phen)_2(H_2O)]\cdot(NO_3)_2$ (Figure 1 a).

This monoclinic complex exists as zig-zag ribbons of alternating copper cations that are held together by a network of hydrogen bonds and offset face-to-face (OFF) π–π interactions, which run along the *c* axis. The OFF interactions between the N1N2 phen rings are perfectly parallel, and each phen is engaged in OFF π–π interactions with two phen ligands from two neighbouring molecular units. The interplanar distances of the OFF interactions are 3.259 and 3.338 Å. The copper cations are also associated with the nitrate anions through hydrogen bonds (2.664–3.049 Å, Figure 2). Hydrogen bonds also occur between the methine CH of the phen rings and the coordinated water molecule.

Complex **2** is in fact a polymorph of the Nakai (CCDC code APENCU)[19] and Catalan (CCDC code APENCU01)[20] structures, although they possess very similar unit cell dimensions (Table 1). Complex **2** can transform to *I*2/*a* (an alternative space group setting) with similar dimensions to the earlier structures (*a* and *c* change as a result of this transformation, but *b* stays the same). However, that would require the earlier structures to be incorrectly reported as *C*2/*c* (*Cc*) when they should be *I*2/*a* (*Ia*). Also, the transformation does not affect the *a* axis, and in **2** the *b* dimension is 7.469 Å, whereas the corresponding values in the previously reported structures are 7.23 (APENCU) and 7.25 Å (APENCU01) and are, therefore, significantly different.

Complex **3**, on the other hand, is new and exists as a heteroligand dinuclear copper(II) complex of formula $[Cu_2(ophen)_2(phen)_2]\cdot(NO_3)_2\cdot 9H_2O$ (Figure 1 b). The molecular unit contains two five-coordinate copper(II) ions, both with trigonal-bipyramidal coordination, which are bridged through deprotonated phenolic hydroxy groups on the ophen ligand. The latter, together with two nitrate anions, counter-balance the charge of the two copper(II) ions. Each copper(II) ion is coordinated by two N atoms from a phen ligand (Cu−N = 1.992–2.068 Å), two N atoms from an ophen ligand (Cu−N = 1.965–2.170 Å) and one oxygen (Cu−O = 1.976–1.980 Å) from a deprotonated phenolic hydroxy group on the neighbouring ophen ligand, hence forming an N=C−O$^-$ bridge between the two copper centres, which is support-

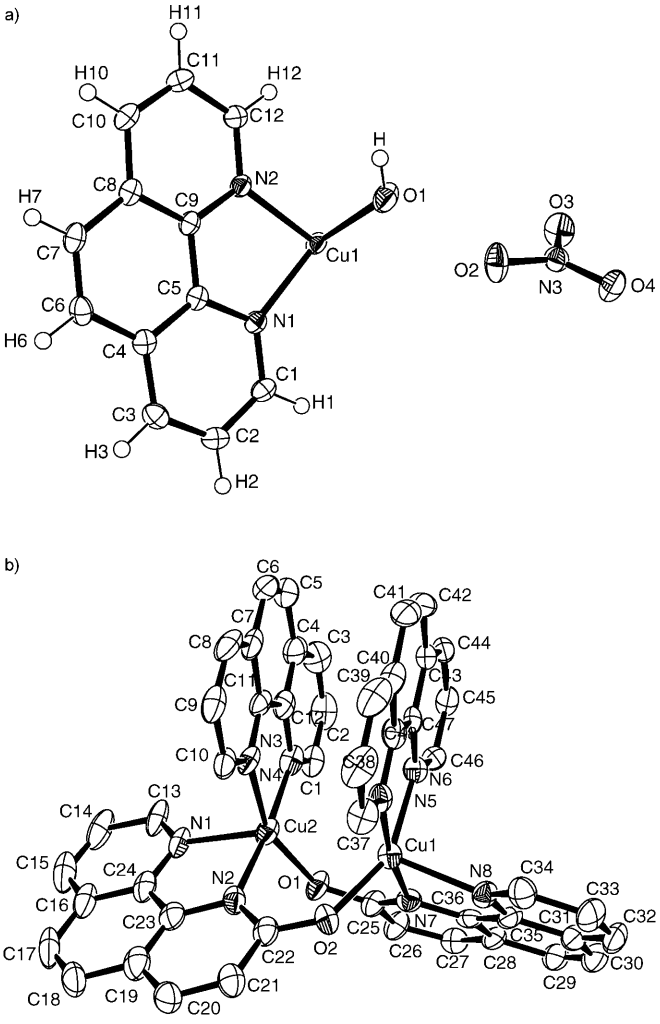


Figure 1. ORTEP diagrams of the asymmetric unit cell of a) **2** and b) **3** (after application of the SQUEEZE[21] routine to remove disordered water and nitrate anions).

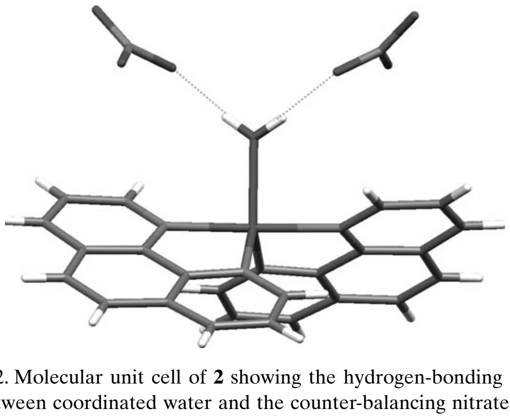


Figure 2. Molecular unit cell of **2** showing the hydrogen-bonding interaction between coordinated water and the counter-balancing nitrate anions.

Table 1. Summary of single-crystal XRD data for complexes **2** and **3**.

	2	APENCU[a]	**3**
formula	$C_{24}H_{18}CuN_6O_7$	$C_{24}H_{18}CuN_6O_7$	$C_{48}H_{39}Cu_2N_{10}O_{17}$
M_r	565.98	566.0	1154.97
crystal system	monoclinic	monoclinic	triclinic
space group	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	19.375(5)	22.58(2)	14.063(5)
b [Å]	7.469(5)	7.23(1)	14.257(5)
c [Å]	15.775(5)	16.59(2)	15.012(5)
α [°]	90.000(5)	90	114.293(5)
β [°]	100.782(5)	123.6(1)	95.803(5)
γ [°]	90.000(5)	90	111.651(5)
V [Å^3]	2242.5(18)	2256	2433.5(15)
Z	4	4	2
$R_1[F^2>2\sigma(F^2)]$	0.0267	0.118	0.0698
$wR[F^2]$	0.0776	–	0.1889
GOF	1.064	–	1.006

[a] As reported in reference [19].

ed by an OFF π–π interaction between the two coordinated phen groups (Figure 1b). The close proximity of the two magnetic centres, with a $Cu^{2+}-Cu^{2+}$ non-bonding distance of 3.100 Å, is short enough to suggest the possibility of an antiferromagnetic interaction.

This novel triclinic complex exists as layers of dinuclear copper cations separated by layers of disordered water molecules and disordered nitrate anions, which are held together by a network of hydrogen bonds and OFF π–π interactions, which run along the *c* axis. An intramolecular OFF interaction occurs between the N3N4 and N5N6 coordinated phen rings, which deviates from linearity by 6.65°, with a closest approach of 3.279 Å between N4 and N6 (Figure 1b). An intermolecular OFF interaction occurs between N1N2 ophen rings, between N5N6 phen rings and between N7N8 ophen rings. All interactions are perfectly parallel with interplanar distances of 3.551 Å, 3.361 Å and 3.282 Å, respectively. The copper cations are also associated with water molecules through hydrogen bonding (2.790–3.210 Å) between the O atoms on the ophen ligands and water, and between the methine CH groups of the N3N4 phen rings and the nitrate anions.

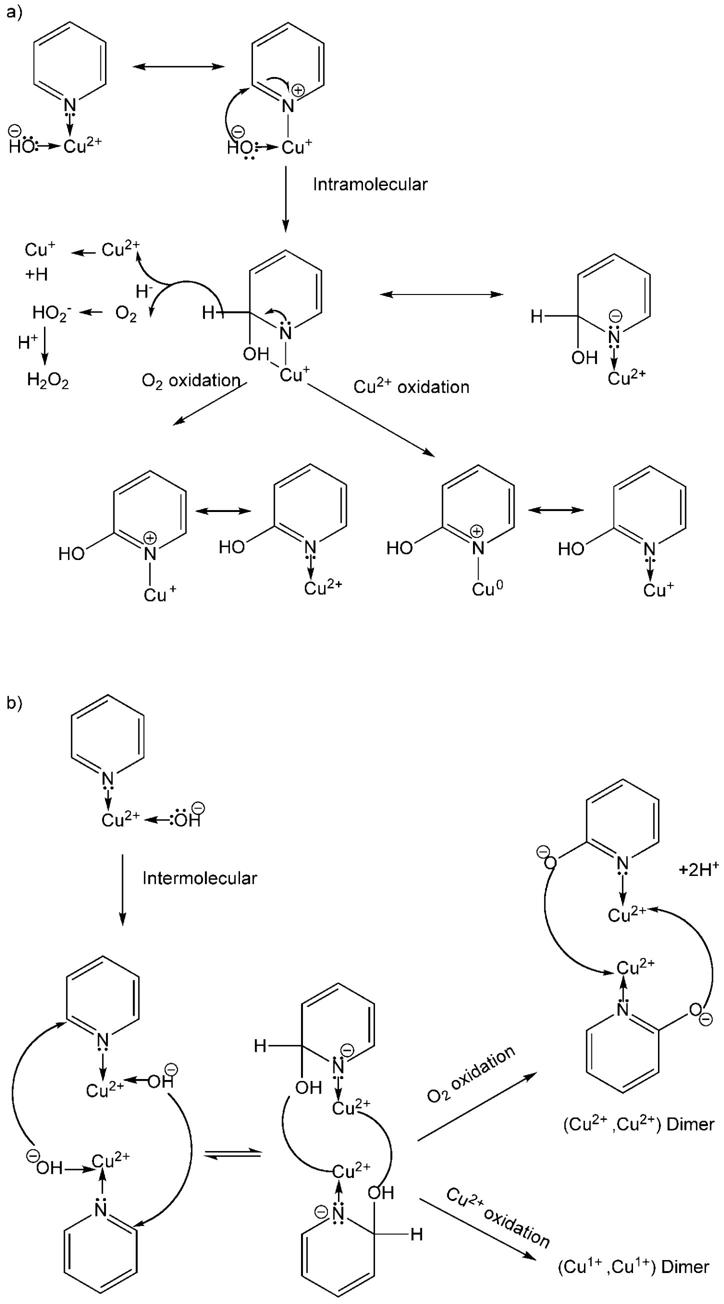
Magnetic measurements: Complex **3** was found to be paramagnetic with an isotropic *g* factor ($g=2.10$) indicating that the signal originates from the copper(II) centres. The effective magnetic moment was found to be 1.74 μ_B per Cu ion at ambient temperature, as expected for non-interacting spin-free Cu^{II} d^9 ions.[22] The complex obeys the Curie–Weiss law in the temperature range 80 to 310 K, but at lower temperatures spin pairing between the electrons on adjacent Cu^{II} ions occurs ($J=-44\ cm^{-1}$), giving rise to typical copper acetate antiferromagnetic behaviour ($J=-295\ cm^{-1}$)[23] for **3**. The lower exchange coupling for the present complex is consistent with the fact that the two Cu^{2+} centres are further apart (3.10 Å) than in the copper acetate-type derivatives (2.44–2.81 Å). In addition, in complex **3** the two Cu^{2+} centres are bridged by only two $N{=}CO^-$ groups supported by one OFF π–π interaction, whereas in copper acetate the two Cu^{2+} centres are bridged by four $O{=}C{-}O^-$, which provide a greater opportunity for superexchange coupling between the $Cu(d_{x^2-y^2})$ orbitals and the p π orbitals on the bridging moieties.[23]

Mechanistic considerations of the hydroxylation reaction: Hydrothermal reactions provide elevated temperature and pressure conditions, which allow the synthesis of compounds that cannot be achieved by using bench-type reactions. However, hydrothermal reactions tend to follow a non-equilibrium course and slight changes in pH, temperature, time and reactant ratios can have an extreme effect on the outcome of the reaction. Since the report of the formation of covalent hydrates of phen and bipy by Gillard,[15] there has been considerable emphasis on obtaining structural evidence to support this claim. Gillard proposed that the hydroxide ion attacks the 2- or 4-position of the coordinated pyridine to form a hydroxy-substituted 1,2- or 1,4-dihydropyridine. These hydroxy species are known as pseudo-bases, and it is suggested that the formation of these species provides an explanation for the observed pH dependence of a variety of reactions undergone by complexes of N-heterocycles.

Gillard suggested that with metal cations, pyridine-like ligands could form a 4- or 6-coordinate complex (depending on the metal centre), and in the presence of a nucleophile the 2- or 4-position on the pyridine ring could be attacked by the nucleophile (Scheme 1).[15] However, during the course of the mechanism of the reaction, the site of addition of the nucleophile to the metal–pyridine complex may initially be at the metal and not at the ligand[16] (see DH, IMS in Scheme 2). In other words, the hydroxide ligand directly coordinates to the metal ion instead of covalently attaching to the pyridine ring. It is of course very difficult to distinguish between these two processes on the basis of kinetic or simple spectroscopic data unless intermediates are isolated and structurally characterised. We appear to have isolated such intermediates in the reaction of phen with Cu^{2+} under mildly alkaline conditions.

The observation of significant yields of **2**, containing a $Cu^{2+}-OH^-$ moiety, is not surprising because this complex has been reported to form readily by reaction of copper(II) nitrate with phen in aqueous solution, even without pH adjustment.[19,20] Therefore, it appears that the first stage of the hydroxylation process may involve deprotonation of the coordinated water molecule on **2** to form a $Cu^{2+}-OH^-$ species (DH, IMS in Scheme 2). This step is then followed by either an intra- or intermolecular nucleophilic attack at the 2-position of a coordinated phen ligand to give the CB or CH depending on the pH, as illustrated in Scheme 2. We thus agree that covalent hydrates are formed during this reaction, but we propose that they may form through an alternative route to that favoured by Gillard[15] whereby, prior to nucleophilic attack on the carbon in the 2-position, a five-coordinate complex in which the hydroxide is coordinated to the metal centre is formed (see Scheme 4a for the intramolecular reaction and Scheme 4b for the intermolecular mechanism).

Upon activation, the ring can be attacked by the nucleophile, which in our proposed mechanism is the OH^- of the Cu^{2+}–OH^- moiety. If this reacts through an intramolecular process attacking at the carbon in the 2-position of the phen ligand (Scheme 4a), it will produce the monomeric (CB or CH, Scheme 2) hydroxylated species. This can then be oxidised by either an external oxidant such as oxygen to give a Cu^{II} product, or undergo an internal electron transfer to give a Cu^{I} product. Dimerisation of the Cu^{II} intermediate yields **3**, whereas dimerisation and loss of one phen ligand gives **1**. Reaction through an intermolecular process proceeds in a similar fashion (Scheme 4b), but gives rise to a dimeric species containing two hydroxylated phen moieties. Again, oxidation by oxygen yields the Cu^{II} complex **3**, whereas oxidation by internal electron transfer leads to ligand (phen) release and the formation of the Cu^{I} complex **1**.



Scheme 4. Proposed mechanism illustrating a) intermolecular shift and b) intramolecular shift.

Conclusion

During studies of the reaction of phen with copper nitrate under mildly alkaline hydrothermal conditions several intermediate products were isolated. These included the expected, and previously reported, neutral Cu^{I} homodimer **1**,[8] together with the Cu^{II} complexes **2**[19,20] and a novel dinuclear heteroleptic copper(II) complex **3**. Complex **2** is a polymorph of a previously reported material, and following deprotonation of the coordinated water to produce a Cu^{2+}–OH^- species (DH, IMS, Scheme 2), may be a key intermediate in the production of **3** and **1** because it is always the primary species formed in an aqueous mixture of Cu^{2+} and phen under a variety of conditions.[19,20]

Thus, an alternative mechanism leading to the formation of covalent hydrates in the hydroxylation of N-heterocycles may be suggested, in which the nucleophile that attacks at the carbon in the 2-position of the phen ligand in the formation of **3** and **1** is not free OH^-, but rather the bound OH^- coordinated to Cu^{II} (the DH, IMS in Schemes 2, 4a and 4b). Nucleophilic attack is then accompanied by aerial oxidation to give the heteroligand Cu^{II} dimer **3**. The Cu^{I} dimer may be formed in a similar fashion, but through an internal electron transfer concomitant with ligand release to give the Cu^{I} product. Magnetic susceptibility studies on **3** confirmed that both Cu cations were in the +2 oxidation state (paramagnetic at $T > 80$ K), and exhibit antiferromagnetic behaviour (suggested by the short Cu–Cu non-bonding distance) at lower temperatures.

Experimental Section

1,10-phenanthroline monohydrate (phen) (99+%, $C_{12}H_8N_2{\cdot}H_2O$) was obtained from Aldrich Chemicals. Copper(II) nitrate trihydrate (Analar, $Cu(NO_3)_2{\cdot}3H_2O$) was obtained from BDH Laboratory Supplies. All chemicals were used as supplied without further purification.

Synthesis of 1 and the Cu^{II} intermediates 2 and 3: Complex **1** was synthesised according to the procedure described by Zhang,[8] with some modification. A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (0.12 g, 0.5 mmol), 1,10-phenanthroline (0.162 g, 0.9 mmol) and water (Milli-Q, 10 mL) was adjusted to pH 9 with NaOH solution (2 M). The blue suspension was then sealed in a Teflon-lined stainless-steel autoclave (20 mL), heated at 150 °C for 120 h under autogeneous pressure, and then allowed to cool slowly in the oven for 6 h. This synthesis was repeated several times. The expected dark-blue block-like crystals of **1** were isolated from an emerald-green supernatant on a number of occasions. However, in several cases only an emerald-green solution, similar in appearance to the supernatant from **1**, was obtained. This was stored in a sealed glass vial and allowed to crystallise at ambient temperature and a mixture of light-green crystals of **2** and emerald-green **3** formed after seven days (yield: 21 and 4%, respectively). The crystals were manually separated whilst viewing under an optical microscope. Analysis for **1**: IR (KBr): $\nu = 3415$(m), 1620(s), 1562(s),

Table 2. Significant bond lengths and bond angles for complexes **2** and **3**.

	2		**3**	
	[Å]	[°]	[Å]	[°]
Cu1–O1	2.052(3)	–	–	–
Cu1–O2	–	–	1.978(3)	–
Cu2–O1	–	–	1.977(3)	–
Cu1–N1	2.0586(16)	–	–	–
Cu1–N2	1.9962(17)	–	–	–
Cu2–N1	–	–	2.165(4)	–
Cu2–N2	–	–	1.968(4)	–
Cu2–N3	–	–	2.071(4)	–
Cu2–N4	–	–	1.992(4)	–
Cu1–N5	–	–	1.999(4)	–
Cu1–N6	–	–	2.068(4)	–
Cu1–N7	–	–	1.970(4)	–
Cu1–N8	–	–	2.168(4)	–
O1–C25	–	–	1.299(6)	–
O2–C22	–	–	1.292(6)	–
N1-Cu-O1	–	117.74(5)	–	–
N2-Cu-O1	–	89.32(4)	–	–
N1-Cu2-O1	–	–	–	100.90(14)
N2-Cu2-O1	–	–	–	94.85(16)
N3-Cu2-O1	–	–	–	156.42(15)
N4-Cu2-O1	–	–	–	91.08(16)
N5-Cu1-O2	–	–	–	90.30(15)
N6-Cu1-O2	–	–	–	153.99(15)
N7-Cu1-O2	–	–	–	97.77(16)
N8-Cu1-O2	–	–	–	104.08(15)
C25-O1-Cu2	–	–	–	133.9(3)
C22-O2-Cu1	–	–	–	135.3(3)
N1-Cu-N2 bite	–	81.95(6)	–	–
N1-Cu2-N2 bite	–	–	–	81.83(17)
N3-Cu2-N4 bite	–	–	–	81.32(16)
N5-Cu1-N6 bite	–	–	–	81.07(16)
N7-Cu1-N8 bite	–	–	–	81.44(16)
N1-Cu-N2′	–	98.70(6)	–	–
NI-Cu-N1′	–	124.53(9)	–	–
N2-Cu-N2′	–	178.63(8)	–	–
N1-Cu2-N4	–	–	–	95.19(17)
N2-Cu2-N3	–	–	–	93.91(16)
N2-Cu2-N4	–	–	–	173.77(17)
N5-Cu1-N7	–	–	–	171.73(16)
N5-Cu1-N8	–	–	–	94.89(16)

1512(s), 1485(s), 1384 s, 1128(m), 843(s), 731(m) cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{14}N_4O_2Cu$ ($M_r = 517.47$): C55.70, H 2.73, N 10.83; found: C 55.63, H 2.65, N 10.78. Analysis for **2**: IR (KBr): $\nu = 3407$(m), 1519(s), 1428(s), 1385(s), 862(s), 722(m) cm^{-1}. Analysis for **3**: IR (KBr): $\nu = 3413$(m), 1621(s), 1517(s), 1483(s), 1384(s), 847(m), 720(w) cm^{-1}.

Characterisation techniques: All products were analysed by FTIR and, where possible, by elemental analysis (insufficient material in the case of **2** and **3**) and single-crystal XRD. FTIR spectra were obtained on a Perkin–Elmer 1725X spectrometer by using KBr discs.

Crystal structure determination: Single-crystal data for complexes **2** and **3** was collected and integrated by using a Bruker Smart CCD area detector system at 130 K using $Mo_{K\alpha}$ radiation. The structures were solved by direct methods by using SHELXS-97[24] and were refined by using SHELXL-97.[24] A mixed strategy was used for the refinement of hydrogen atoms. Hydrogen atoms attached to carbon atoms were placed in calculated positions with a C–H bond length of 0.93 A, whereas hydrogen atoms attached to oxygen atoms were located from difference Fourier maps and were refined without constraint. Owing to the large amount of disordered water molecules and disordered nitrate anions, a SQUEEZE[21] routine had to be applied to **3** to obtain a satisfactory refinement. Molecular graphics were performed by using ZORTEP,[25] SHELXTL[26] and Mercury[27] programs. Selected crystal data for **2** and **3** are presented in Table 1 and Table 2.

CCDC-737244 (**2**) and 737245 (**3**) 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.

Magnetic measurements: Variable-temperature magnetic susceptibilities were measured on powdered 20 mg samples by using a Quantum Design MPMS5 SQUID magnetometer in a field of 1 T. Samples were contained in gel capsules that were held in the centre of a soda straw, and in turn were fixed to the end of the sample rod. The instrument was calibrated against the accurately known susceptibilities of a standard Pd pellet (Quantum Design) and that of $CuSO_4{\cdot}5H_2O$.

Acknowledgements

The authors wish to thank A/Prof. Helmut Huegel, RMIT for useful discussion.

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Received: June 23, 2009