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Copper(II) complex of a tridentate N-donor ligand with unexpected Cu–H interaction

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Abstract

The new pyridine–amine ligand, meophdpa (bis(dipyridylmethyl)-4-methoxyaniline) was synthesised and reacted with copper(II) perchlorate. The X-ray crystal structure of the resulting complex revealed a monomeric copper(II) site, with the copper bound to the three ligand nitrogens in a relatively unusual meridional fashion, as well as a chloride and a water molecule. The sixth coordination site was, unexpectedly, occupied by a phenyl ring hydrogen atom.

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The design and construction of supramolecular architectures has been a rapidly developing area in the past number of years [1]. Indeed, the last decade has witnessed a surge of interest in the discovery of simple building blocks capable of forming specific molecular arrays under certain chemical conditions [2]. For bio-inorganic model complexes, the design and synthesis of the ligand is perhaps the most important step in the modelling process. Control of the number and type of coordinating atoms is key to achieving metal complexes that mimics the coordination sphere and reactivity of metal-containing enzymes.

As part of our continuing research, we have previously reported upper and lower rim functionalised calix[4]arenes, capable of binding transition metal and alkali metal salts [3]. One such calix[4]arene contained picolyl groups [3a]. In extending this theme, we targeted the design of “pre-ligands”, capable of having two or three donor atoms present, with a view to attaching these to the lower rim of the calix[4]arene and thereby forming di- or tri-nuclear metal complexes. The compounds chosen as pre-ligands

were derivatives of bis(2-pyridylmethyl)amine (dpa) and are shown in Fig. 1. The related analogue of the ligands (R=H in Fig. 1, phdpa) has been previously reported by McKenzie et al. [4]. This paper reports the attempted synthesis of these pre-ligands and an X-ray crystallographically characterised copper(II) derivative containing one of them.

Ligands meophdpa¹ and hophdpa were, respectively, prepared by nucleophilic substitution of (2-chloromethyl)pyridine with 4-methoxyaniline or 4-aminophenol in a water–dichloromethane system, in a manner analogous to that previously described [4]. While the ligand meop-

¹ Meophdpa.HCl: %yield = 78.5%; Found: C, 60.79%, H, 6.24%, N, 11.10%; Calc. for C₁₉H₂₁Cl₂N₃O: C, 60.32%, H, 5.60%, N, 11.11%; δ_H (300 MHz, CDCl₃): 8.71 (d, 2H, *J* = 6.8 Hz, py-H6), 8.01 (t, 2H, *J* = 6.8 Hz, py-H4), 7.69 (d, 2H, *J* = 6.8 Hz, py-H3), 7.51 (t, 2H, *J* = 6.8 Hz, py-H5), 6.79–6.73 (m, 4H, Ph-H), 5.01 (s, 2H, CH₂), 3.99 (s, 3H, OMe); δ_H (300 MHz, d₆-DMSO): 8.93 (d, 2H, *J* = 6.8 Hz, py-H6), 8.24 (t, 2H, *J* = 6.8 Hz, py-H4), 7.81 (d, 2H, *J* = 6.8 Hz, py-H3), 7.68 (t, 2H, *J* = 6.8 Hz, py-H5), 6.72 (d, 2H, *J* = 6.8 Hz, *o*-Ph-H), 6.50 (d, 2H, *J* = 6.8 Hz, *m*-Ph-H), 5.05 (s, 2H, CH₂), 3.58 (s, 3H, OMe); δ_C (300 MHz, CDCl₃): 156.7, 153.6, 145.4, 141.3, 140.7, 124.0, 123.8, 116.6, 115.0, 56.4, 55.5; ESMS: *m/z* 306.4, (meophdpa + H); C₁₉H₁₉N₃O requires 305.37.

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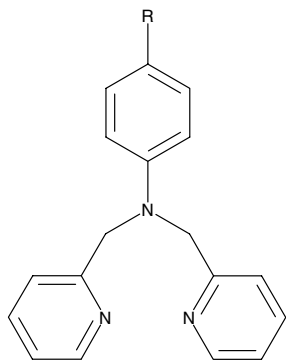


Fig. 1. Ligands chosen for synthesis; meophdpa, R=OMe; hophdpa, R=OH.

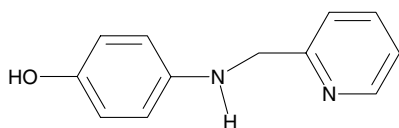


Fig. 2. Ligand obtained from reaction of 4-aminophenol with (2-chloromethyl)pyridine.

hdpda was obtained as a solid in good yield, the second synthesis of hophdpa only gave a monosubstituted aniline, hophmpa, as shown in Fig. 2. Complexation studies of this ligand will be reported elsewhere. The ligand meophdpa was isolated as the di-hydrochloride salt, as confirmed by the elemental analysis. No attempt to remove the HCl from the ligand was undertaken prior to complexation reactions. The ^1H NMR spectrum of meophdpa was obtained in both CDCl_3 and d_6 -DMSO. The spectra exhibited the same signal distribution with the exception of the phenyl protons, which appeared as a multiplet in the CDCl_3 but as two distinct doublets in the case of the d_6 -DMSO spectrum. This suggests that, in the DMSO solution, there was an interaction of the pyridyl nitrogens with the *ortho*-hydrogens of the phenyl ring (see Fig. 3). McKenzie et al. [4] report a similar pattern in the phdpa compound but make no comment on this possible interaction.

The reaction of the ligand, meophdpa.2HCl, with copper(II) perchlorate hexahydrate in methanol in a 2:1 ratio, resulted in the formation of a metal complex. [Caution! Although no problems were encountered in the preparation of the perchlorate salts, suitable care should be taken when handling such potentially hazardous compounds.] Elemental analysis for the complex² suggested the presence of a 1:1 metal–ligand complex, instead of the anticipated 1:2 stoichiometry generally observed for complexes of ligands of this general type [4,7,8]. The product was isolated as blue crystals from a suitable sample was selected for an X-ray structure determination.

² $[\text{Cu}(\text{meophdpa})\text{Cl}(\text{H}_2\text{O})_2](\text{ClO}_4)$: %yield = 91.5%; Found: C, 48.24%, H, 5.24% N, 9.10%; Calc. for $\text{C}_{19}\text{H}_{23}\text{Cl}_2\text{N}_3\text{O}_7$: C, 47.91%, H, 4.87% N, 8.82%.

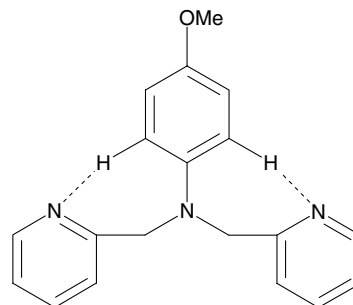


Fig. 3. Alternative structure of meophdpa showing potential interaction between pyridyl nitrogens and phenyl ring.

The crystal structure of $[\text{Cu}(\text{meophdpa})\text{Cl}(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{H}_2\text{O}$, **1**, is shown in Fig. 4 [5]. Selected bond lengths (Å) and angles ($^\circ$) are given in Table 1. The copper atom is bonded to the three nitrogens of the meophdpa ligand, a chloride and a water molecule in a distorted square-pyramidal arrangement. The water molecule is also hydrogen bonded to a second water molecule and that molecule is in turn hydrogen bonded to the perchlorate anion. Furthermore, the proton on C18 of the phenyl ring is located at a distance of 2.417 (Å) from the copper atom, which is less than the sum of the Van der Waals radii for these two atoms and hence must be considered as a reasonably strong interaction [6]. Thus, a pseudo-octahedral geometry is observed for the central metal. No other interactions about the copper are observed, which is interesting, since copper–chloride bridging might have been expected. However, the position of the phenyl ring precludes such bridging interactions on steric grounds.

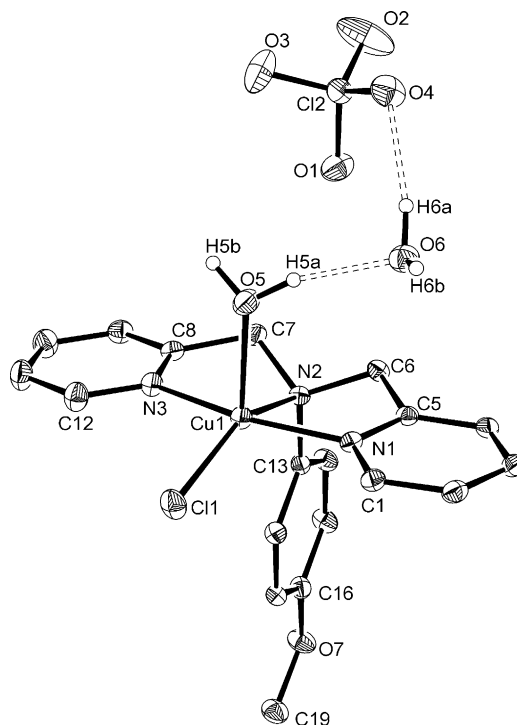


Fig. 4. X-ray crystal structure of $[\text{Cu}(\text{meophdpa})\text{Cl}(\text{H}_2\text{O})](\text{ClO}_4) \cdot \text{H}_2\text{O}$, **1**. Ellipsoids are represented at the 30% probability level.

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

Cu(1)–N(3)	1.989(2)	Cu(1)–N(1)	1.994(2)
Cu(1)–N(2)	2.078(2)	Cu(1)–O(5)	2.234(2)
Cu(1)–Cl(1)	2.2539(7)	Cl(2)–O(2)	1.395(3)
Cl(2)–O(1)	1.428(2)	Cl(2)–O(4)	1.433(2)
Cl(2)–O(3)	1.449(3)	O(7)–C(16)	1.360(3)
O(7)–C(19)	1.433(4)	N(2)–C(6)	1.490(3)
N(2)–C(7)	1.491(3)		
N(3)–Cu(1)–N(1)	163.83(9)	N(3)–Cu(1)–N(2)	82.01(9)
N(1)–Cu(1)–N(2)	81.94(9)	N(3)–Cu(1)–O(5)	93.84(9)
N(1)–Cu(1)–O(5)	88.45(8)	N(2)–Cu(1)–O(5)	105.30(9)
N(3)–Cu(1)–Cl(1)	96.99(7)	N(1)–Cu(1)–Cl(1)	97.91(7)
N(2)–Cu(1)–Cl(1)	150.04(6)	O(5)–Cu(1)–Cl(1)	104.64(7)
C(16)–O(7)–C(19)	116.9(2)	C(1)–N(1)–C(5)	119.3(2)
C(1)–N(1)–Cu(1)	126.01(18)	C(5)–N(1)–Cu(1)	114.62(17)
C(13)–N(2)–C(6)	111.7(2)	C(13)–N(2)–C(7)	111.7(2)
C(6)–N(2)–C(7)	112.8(2)	C(13)–N(2)–Cu(1)	109.67(15)
C(6)–N(2)–Cu(1)	105.93(15)	C(7)–N(2)–Cu(1)	104.62(15)
C(8)–N(3)–C(12)	119.3(2)	C(8)–N(3)–Cu(1)	114.44(18)
C(12)–N(3)–Cu(1)	126.19(19)	N(1)–C(1)–C(2)	121.8(3)

The three nitrogen atoms of the meophdpa ligand exhibit a meridional type of coordination at copper, whereas structures of complexes containing these ligand types show almost exclusively facial coordination of the ligands [4,8]. This coordination type observed here is unusual for structures of complexes containing bis(picoly)amine and N-substituted bis(picoly)amine, with only two previous examples reported for copper(II) complexes [7]. The structure of Cu(phdpa)Cl₂ [7b], which relates directly to that of **1**, consists of discrete copper(II) neutral complexes with the metal atom being five-coordinated to three nitrogens from the terdentate phdpa species and two chloride ions. One of the pyridine nitrogens therein is involved in an intramolecular hydrogen bond with one of the aniline protons, an interaction replaced by a H–Cu interaction in **1**. The pseudo-planar nature of the nitrogen donor atoms in **1** forces the phenyl ring attached to N(2) to be positioned in a manner that maintains the expected bond angle of 106.98° as found in ammonia. There are two water molecules present in the lattice; one of which is ligated to the copper and hydrogen bonded to the second water molecule, while this second water molecule is further hydrogen bonded to the perchlorate anion. The copper–O_{water} bond distance of 2.234(2) (Å), while being longer than that previously reported for [Cu₂(tpbd)(H₂O)₄](S₂O₆)₂ [7] at 2.170(5) (Å), where tpbd = *N,N,N',N'*-tetrakis(2-pyridylmethyl)benzene-1,4-diamine, can be rationalised in terms of the other bonding interactions in the structure.

Fig. 5 illustrates the lattice hydrogen bonding between the water molecules and the perchlorate anions which afford supramolecular hydrogen bonded sheets in the array [9]. There are no interactions between adjacent copper atoms.

In summary, a new pyridine–amine ligand (meophdpa) has been synthesised and characterised. This ligand was reacted with copper(II) perchlorate and the resulting complex analysed. The X-ray crystal structure revealed that

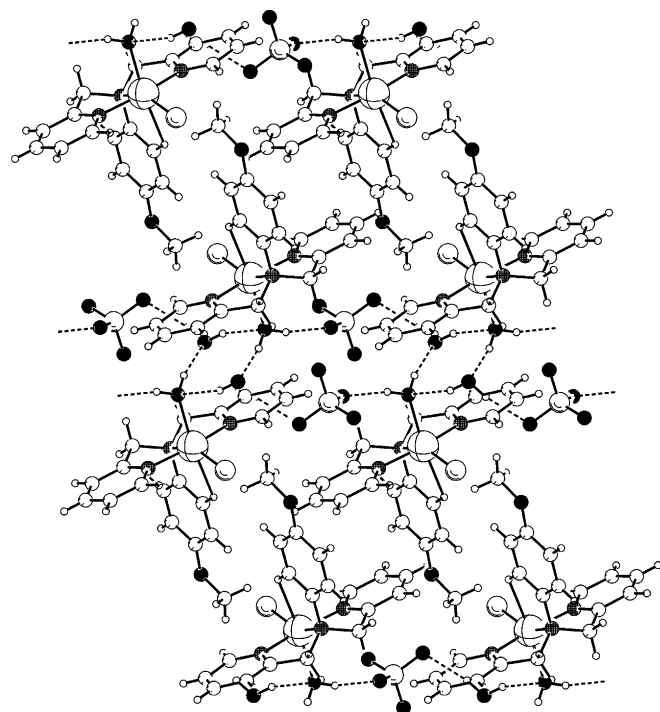


Fig. 5. Packing diagram for **1**, showing hydrogen-bonding interactions in the lattice.

the motif consists of a monomeric copper(II) site, with the copper bound to the three nitrogens of the ligand in a relatively unusual meridional fashion, as well as a chloride and a water molecule. The sixth coordination site is occupied by a Cu–H bond of the phenyl ring. The packing diagram of the structure reveals extensive hydrogen-bonding.

Appendix A. Supplementary data

Crystallographic data for the structural analysis on [Cu(meophdpa)Cl(H₂O)₂](ClO₄) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 286615. Copies of this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2005.11.008.

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- [5] Crystal data: $C_{19}H_{23}Cl_2CuN_3O_7$, $M = 539.84$, triclinic, $a = 8.9580(3)$, $b = 9.1280(3)$, $c = 13.8440(6)$ Å, $\alpha = 86.258(1)$, $\beta = 81.881(1)$, $\gamma = 86.341(2)$ °, $U = 1116.56(7)$ Å³, space group P-1 (No. 2), $Z = 2$, $\mu(Mo K\alpha) = 1.264$ mm⁻¹. Crystallographic measurements were made at 150(2) K on a Nonius kappaCCD diffractometer in the range $3.54 < \theta < 27.57^\circ$. The solution of the structure (SHELXS-86) [10] and refinement (SHELXL-97) [11] converged to a conventional [i.e. based on 4233F data with $F_o > 4(F_c)$] $R_1 = 0.0444$ and $wR_2 = 0.1090$. Goodness of fit = 1.064.
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